

Non-Destructive Material Characterization Methods

EDITED BY AKIRA OTSUKI, SEIKO JOSE, MANASA MOHAN, SABU THOMAS



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Preface

Characterization plays an important role in scientific research and engineering. It is essential for understanding and predicting the properties and behavior of objectives/materials of interest. It is important for a graduate student to be a senior researcher as well as a field engineer. The researchers and engineers use various analytical tools during their work. Some of them are destructive and others are non-destructive in nature, with different objectives and expectations. Non-destructive characterization/testing has been gaining more attention due to the exponential complexity of modern heterogeneous materials and become diverse to adapt to more complex needs from the originally used for simple failure diagnostics commenced in the early 20th century. Thus this book aims to cover a comprehensive overview of the characterization methods of non-destructive materials written and edited by leading experts in their respective fields and showcase a full potential applicable and useful to the researchers and engineering in the field of not only materials science and engineering but also physics, chemistry, engineering, biological sciences, and many others.

The primary audience of the book is scientists, academics, and research scholars in the field of materials science. The book is also beneficial for faculty members, industries, and graduate students. The book can be used as a textbook for young researchers/students as well as engineers who are about to start working with one of those characterization methods. The book can be used as a handbook for experienced researchers/engineers for finding some practical tips and updated information in the relevant field, including sample preparation, measurement, and data analysis and interpretation.

The book starts with an introduction to the non-destructive material characterization. Then, the first part of the book discusses numerous microscopic and imaging techniques, that is, optical microscopy, polarized microscopy, atomic force microscopy, scanning electron microscopy, scanning probe microscopy, transmission electron microscopy, neutron imaging, infrared thermography, and ultrasonic scanning. These chapters provide a thorough explanation of the theory, method, and characterization using cutting-edge microscopic research. Neutrons and X-rays can be powerful probes for material characterization. Three chapters make up the

neutron-based characterization methods. In addition, a chapter describes the basics of stress analysis using neutrons and X-rays.

Further, a few chapters are assigned to spectroscopic analysis such as UV-Vis spectroscopy, X-ray fluorescence spectroscopy, hard X-ray photoelectron spectroscopy, mass spectrometry, atomic absorption spectrophotometry, dielectric spectroscopy, and Raman spectroscopy. A chapter has been dedicated to cloud-based non-destructive characterization, followed by another chapter on the complementary non-destructive characterization of complex electronic waste. In the final chapter, the leading editor narrates the future perspectives of non-destructive material characterization.

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CHAPTER 1

Introduction to non-destructive material characterizations

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1.1 Introduction

The science of non-destructive testing (NDT) covers a broad range of measurement and analysis techniques used in determining the current condition of structural materials or elements. It is often a quick and effective method, with the main benefit of being able to examine the material without causing damage or altering the composition or shape of the inspected object [1]. These methods or techniques rely on different phenomena covering a broad field that encompasses a wide range of testing methods and applications, as well as pre and postprocessing mathematics [2].

This chapter will briefly introduce conventional (Table 1.1) and non-conventional NDTs (Table 1.2) with their current status and how they help in the characterization, inspection, and maintaining a wide range of materials in their application in day-to-day life. Low-cost maintenance of material is always favorable in any industry to keep a balance on expenditure and maximize profit and at the same time safeguard the process and operation. Thus, choosing an appropriate testing method is important for smooth operation and keeping the safety of the workplace.

The methods discussed in this chapter are categorized based on the five major classifications:

- **Visual method** is the oldest and most widely used NDT method which is based on an inspection by the naked eye [94,95]. The method can be applied in casting, forgings, and welds, among others. Penetrant tests, on the other hand, detect material surface flaws based on the capillary rise principle where a penetrant or a liquid that glows

under UV illumination is applied to the material surface for defects [7,8]. The method is applicable to a wide range of materials including hairline and fatigue cracks on in-service components but is seen as inefficient for porous materials [8];

- **Radiographic testing method** employs the use of a radiation source from which the radiations strike the test specimen and are detected by a suitable radiation detector placed on the side opposite the source [96]. These radiations are absorbed in accordance with the thickness, physical density, and internal defects of the test specimen as they pass through it, and the detector system thus receives differential radiations from different parts of a defective specimen, which are recorded onto the detector [97];
- **Acoustic and vibrational methods** depend on exciting vibrations in a specimen by a local impact and then measuring some properties of the vibrations [86]. These methods are commonly applicable for materials exposed to plastic deformation, fractures of phase emissions [96]; and
- **Electrical and magnetic methods** detect flaws that are open-to-surface and just below the surface where the material property is measured as an electrical property variation in all electrical methods [86]. The methods included in this chapter are arranged based on the mechanism of their operation and their applications or the information generally obtained by using them for analysis. NDT has gained the interest of many scientists due to its high precision and sensitivity without destructing the structure and integrity of material [98]. This chapter aims to provide the readers with the mechanisms of existing and newly evolving NDT methods which could help and guide in choosing an appropriate method for their future studies and work.

1.2 Non-destructive material characterization methods beyond the conventional non-destructive testings

In addition to the traditional approaches outlined above, this section will introduce a modernized version of those procedures. These approaches follow the same/similar principles as traditional methods, but they use a much more refined mechanism, brought by technological improvements in the application of the techniques and processes. However, there is still limited commercial applicability for some methods.

Table 1.1 Conventional non-destructive testing methods.

Method	Mechanism	Application	References
<i>Visual methods</i>			
Magnifying glass	Magnifying glass makes objects appear larger due to convex lenses refracting or bending light rays bringing them to converge and in turn magnifying objects.	This method is relatively cheap and easy, which is generally used for first survey but just limited to observe any surface discontinuities.	[3,4]
Optical microscope	Microscopes enlarge an object view using the objective and oculus lenses. It follows the basic principle for magnifying glass where light plays with the lenses to produce an enlarged portion of material.	There are several types of microscopes that give several information regarding the material observed, defects are the commonly observed by this equipment but can also give information on topology, stress distribution and bonding defects, among others.	[5,6]
<i>Light penetrating method</i>			
Dye-penetrating method	A penetrant is applied and maintained on a material surface for 5 to 10 min for the liquid to penetrate any surface defect. After that time, a residue from the penetrant is left at the defects detected and a porous powder sprayed is sprayed on the surface to remove the residue.	The residue is analyzed by a flaw-detector operator where a red luminescent pattern is obtained which indicates any defects from the penetrant applied. This method allows the detection of invisible cracks and other flaws in several materials such as alloys, metals most especially in aerospace industry.	[7,8]

(Continued)

Table 1.1 (Continued)

Method	Mechanism	Application	References
<i>Radiometric methods</i>			
X-ray diffraction	The method uses x-ray beams to penetrate the material which excites the atoms in the structure forming coherent scattering which results in the diffraction of beams. The angle of diffraction under the principle of Bragg's Law can be used to determine the difference between atomic planes which is used to determine the composition and crystalline structure of a material.	X-ray diffraction (XRD) has been used for analyzing the atomic and molecular structure, crystal morphology, and electron density of predominantly crystalline or partially crystalline materials. Several studies use XRD in assessing micro-damages, residual stresses, dislocation density, and even intergranular stress corrosion cracking of different materials.	[6,9–12]
X-ray fluorescence (XRF)	The method utilizes ionizing radiation from either an x-ray tube or sealed radio isotope responsible for dislodging the outermost electron from the innermost shells of the atom that absorbed the radiation. The movement of electrons causes fluorescence radiation emission that is unique for each material, hence the elemental analysis of individual atoms is dependent on the energy of radiation emitted. Further, the intensity of the radiation emitted quantifies the amount of the specific elements present in the sample.	XRF is a technique for the qualitative and quantitative multielemental analysis of a sample. This method has a wide range of application from life sciences, environmental studies, mining, geology, and metallurgy to arts and archeology, among others. XRF is widely used for the characterization of geologic samples (such as presence of rare-earth elements) or material surfaces which can be used to determine and analyze the presence of different elements that could be attributed to the deterioration of several structures.	[13–22]

Infrared spectroscopy	As a spectrometry method, it probes molecular vibrations which corresponds to the energy difference between vibrational states of the IR Spectroscopy. The molecules absorb specific frequencies that are unique to their structure and are recorded by passing a radiation beam through a sample.	The technique is supposed to be complementary to other spectroscopic and microscopic techniques. It has been widely used in analytical chemistry for molecule analysis and has also been applied in corrosion detection for metal surfaces, dissolution property, degree of crystallinity, and lattice water content among others.	[23,24]
Raman spectroscopy	Raman Spectroscopy involves the two-photon inelastic scattering interaction of radiation (photon) with molecular vibrations in off-resonance which excites a molecule to an intermediate state resulting for a new photon to scatter from the virtual state and is accompanied by the relaxation of the molecule. This phenomenon results in a Raman spectrum which is used to quantify peaks characteristic of specific molecular vibrations.	Raman Spectroscopy provides information on molecular and chemical structure, phase and polymorphy, crystallinity and molecular interaction of a material from the bands produced in the process. The method is widely used in chemistry to materials engineering especially in its investigation for corroded surfaces to discriminate between polymorphs and to correlate color and chemical composition. The process is also used in archeology in its application identifying the phase characterization and identification of coating pigments.	[15,18,20,25–27]

(Continued)

Table 1.1 (Continued)

Method	Mechanism	Application	References
<i>Acoustic and vibration methods</i>			
Acoustic emission (AE)	AE uses elastic waves emitted from an emission source and is captured by piezoelectric sensors on the material surface. These waves are generated by internal sources appearing within the microstructure of material which detects damage accumulation of the material.	AE testing is highly sensitive to microcracks and has been used in image characterization of complex structures such as anisotropic alloys, steels, composites, rocks, ceramics, and other materials with structural components. The method also provided maximum amplitude, energy, rise time and duration which can provide information on how the material reacts with the signal aside from the damage progression profile it gives.	[28–31]
Ultrasonic testing (UT)	UT utilizes acoustic elastic waves which can be performed wither by pulse echo and through-transmission testing. Pulse echo uses echo signals to reflect the waves to the probe while the through-transmission testing uses an emitter to send ultrasound waves from one surface to the opposite side of the object, and a separate receiver to receive the sound energy; results are given in a line plot showing the intensity of the reflection where reduced amount of sound indicates imperfection of the material. This technique demands extreme testing conditions, as well as a complex system and operation.	UT provides measured signals for the determination of several parameters such as attenuation, fiber direction, and most commonly the distribution of damage in a material. This made the method to be widely used in medical and engineering fields specifically for monitoring crack growth, corrosion, flow rates, process control, and immediate inspection in production lines as well as monitoring and accident investigations in nuclear powers and interface quality investigation in bonded structures.	[32–36]

Electromagnetic methods

Eddy-current (EC)	EC testing is based on the principle of electromagnetic induction which consists of stimulating alternating current at a specific frequency through a coil and is placed in proximity to the component to be inspected in which eddy current is produced from the generation of varying magnetic field using an alternating current from the coil. As a result, the eddy current instrument plots changes in impedance amplitude and phase angle.	The amplitude and pattern of the eddy current and the resulting magnetic field will be interrupted or altered by changes in metal thickness or defects affects electron movement in the coil by varying the electrical impedance of the coil. Aside from defect detection, this method can also be used for characterization which includes peak point, frequency analysis, and statistical methods such as principal component analysis. Eddy current tests can be performed on any electrically conducting material which has applications including surface and subsurface crack sizing, thickness measurements for metallic plates and nonmetallic coatings on metal substrates, corrosion assessment, and electrical conductivity and magnetic permeability measurements are among them.	[37–40]

(Continued)

Table 1.1 (Continued)

Method	Mechanism	Application	References
Microwave testing	Microwave testing involves frequencies from 300 MHz to 300 GHz and can be performed by reflection and transmission mode. In reflection mode, the microwave signal is transmitted through the inspected material, and in turn, the internal structure reflections of the material are collected and processed in terms of magnitude and/or phase behavior. On the other hand, the transmission mode uses a probe to transmit the microwave signal from one side of the sample and another probe to receive the signal from its backside.	In microwave testing measurable parameters namely, dielectric constants, loss factors, reflection coefficients, and transmission coefficients can be correlated with suitable modeling and calibration techniques, also the amplitude and phase of the received signals can be affected by the variations of the thickness and/or electromagnetic properties at the damaged region which is helpful for damage detection. The technique has a wide range of applications such as for material characterization, estimation of mechanical properties, strain sensing, damage evaluation, measurement of the electromagnetic properties (i.e., permittivity and permeability), dimensional metrology (thickness measurement), cure state monitoring, optimal design of the experimental setups and quantitative analysis of the detection results.	[41–43]

Table 1.2 Nonconventional non-destructive material characterization methods.

Method	Mechanism	Application	References
<i>Visual method</i>			
Electronic imaging	Imaging with charge-coupled devices (CCD) captures images and transfers it to the memory system of the device to record the image as an electronic data. This is made possible by the interaction of photons within the photosensitive surface, storage of the liberated charge, and readout or the measurement of the stored charge. The employment of CCD components to monitor things and convert optical impulses into digital signals, which are subsequently delivered to video processing equipment for additional processing, display, and data extraction, is the most notable characteristic.	CCD camera generates high-quality images that are free of distortion and made of pixels. Surface stress may also be detected for very accurate deformation measurements, making it ideal for use in aerospace, automotive, marine, and high-tech materials manufacturing.	[44,45]
Video imagescope	The equipment uses video camera and TV monitor to view the sample where image may be magnified for precise viewing. The apparatus obtains a digital image of the object at a first location, electronically transmits the digital image to a second location remote from the first, views the digital image at the second location, transmits instructions to the first location, and performs an act on the object in response to the instructions.	Video Imagescope is used to detect surface or structural defects in all materials such as in aircraft structures, blades, and engines, among others; it is also a useful visual NDT in remote-visual inspection, which is generally unreachable.	[4,46]

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Table 1.2 (Continued)

Method	Mechanism	Application	References
Borescope	Borescopes are commonly called “endoscopes” or “endoprobes” these are optical instruments with built-in camera and light sources that displays the live image on the screen. In some cases, this tool contains improved optical systems and high-intensity light sources with magnification options, zoom settings, or accessories.	Similar to most visual NDT methods, borescopes detect surface deformation, however, this apparatus is widely used in the aerospace industry, especially in an aircraft engine. This technology allows for the inspection of engine parts for flaws such as nicks, dents, cracks,	[4,47]
Optical interferometry	Low coherence light from a broadband optical source is used in optical interferometry. This light is split into two beams that are supplied to the sample and reference arms of the interferometer by a beam splitter or fiber-optic coupler. While the sample arm has beam-delivery optics that aim the beam at the sample, the reference arm has a stationary mirror. A linear photodetector array records the interference of the two back-reflected or scattered beams, and it is then processed by a computer to determine the depth-resolved optical scattering characteristics of	Optical interferometry is commonly used for measuring microscopic deformation and electrochemical techniques for determining the corrosion current of metallic samples. This method works well in monitoring mechanochemical behavior, such as stress corrosion cracking, corrosion fatigue, and hydrogen embrittlement, of metallic electrodes in aqueous solutions.	[48–50]

	the sample. Interferometric images of the object are produced at a given time undergoing deformation, taken at a different time step. Fringe patterns are produced where each black fringe symbolizes the contour of the differential displacement. The fringe patterns were transformed into the spatial dependence of the differential displacement by using a variety of approaches to analyze the spatial dependence of the dark fringes. The differential displacement fields' wave properties were seen by repeating this process over several time increments.		
<i>Light penetrating method</i>			
Fluorescence penetrant inspection (FPI)	The fluorescent penetrant is distinguished by its capacity to emit visible radiation when stimulated by UV-A light and can be utilized on a wide range of materials. Due to the sensitivity of the fluorescent penetrant that is used, FPI operations use a dye that is much more sensitive to smaller flaws than penetrants used in conventional penetrating tests. FPI dye sharply contrasts with the dark background with its brilliant yellow glow caused by its reaction with ultraviolet radiation.	FPI is mostly used for metals with small, tight pores and flat surfaces due to its sensitivity to such small flaws. In fact, FDI is mostly used for detecting faults in nonporous materials that may affect the integrity or quality of a component.	[51–53]

(Continued)

Table 1.2 (Continued)

Method	Mechanism	Application	References
<i>Radiometric methods</i>			
<i>Computed radiography (CR)</i>	CR is a valuable imaging technology in which an image of an object probed with ionizing radiation, often X rays is captured on reusable storage phosphor plates. The resulting X-ray images had to be kept in large file cabinets, with separate, inefficient image retrieval techniques required. It was unable to exchange images. Aside from efficient storage and retrieval, one of the benefits of digital imaging is the ability to improve detail visibility through image processing.	Despite having first used in medical field, CR has been used to inspect an object's internal structure, such as a pipe or a welded component. In fact, x-ray images made directly on film are only common for NDT since the doses needed to make a useful image directly on film are much too high for medical imaging.	[54,55]
<i>Computed tomography (CT)</i>	A specimen is put on a rotational stage between the X-ray source and the detector produces a sequence of 2D radiographs in numerous directions. The images of the tested samples are shown with various gray level tones based on the properties of the material that make them up. These are then stitched together to create a comprehensive 3D depiction of the interior of the sample.	CT is a rapid 3D-imaging of the interior of a sample in real-time and is commonly used in material science such as in weld and crack inspections on metal parts to soldering inspection in electronics and contaminant identification in food industry.	[56–58]

<i>Direct radiography</i>	The image is often captured straight onto a flat panel detector, which has a phosphor screen that converts the X-ray image into a visible light image. In an a-Si photodiode layer, light generates a digital output signal, which is then read out by thin film transistors.	In comparison to computed radiography, digital radiography enhances productivity by producing higher image quality instantly and giving up to three times more dosage efficiency. This allows the method to be one of the sought-after methods for NDT.	[55,59]
<i>Positive material identification (PMI)</i>	The elemental analyzer uses energy-dispersive X-ray fluorescence technology and an X-ray tube to produce a complete report in 5 to 10 s. The equipment used is commonly used to ensure that materials provided in the industry meet the required standards and requirements.	The PMI is used for quality control and safety compliance in a variety of sectors, including oil and gas, power generation, chemical, pharmaceutical, nuclear, aerospace, and metal fabrication, and is a vital aspect of both production and asset integrity management It can accurately measure elements such as Cr, Ni, Mo, Ti, Cb, Ta, W, Co, V	[60,61]
<i>Neutron radiography (NR)</i>	NR follows a similar principle to x-ray where a penetrating radiation is used to obtain a visual image of the internal form of an object. The method is based on the mitigation of a collimated neutron beam through the sample where neutron can either be absorbed, scattered, or <i>undisturbedly</i> pass through the sample where the intensity of neutron flux is detected by a two-dimensional imaging system.	The imaging system records the sample's transmitted neutrons and creates an image of the sample's internal structure where the lower-density areas correspond to parts of the object that are more effective at attenuating the direct neutron beam. This method is widely adopted in industrial, medical, materials science, nuclear, in explosive inspections.	[62–66]

(Continued)

Table 1.2 (Continued)

Method	Mechanism	Application	References
<i>Prompt gamma-ray activation analysis (PGAA)</i>	The prompt gamma activation analysis (PGAA) is a rapid non-destructive radio-analytical technique that is based on the detection of gamma rays, emitted by the atomic nucleus after neutron capture where de-excitation of these nuclei results in the emission of prompt gamma rays, which may be measured to provide multielement analysis of the sample.	The technique is a multielemental analysis of almost every element in the periodic table can be identified from light to heavy elements. The method has wide range of application from elemental composition of bulk materials for the detection of drugs, toxic agents, fissile materials, explosives, and chemical warfare agents; further, this testing is very useful for performing trace element analysis on boron, cadmium, samarium, and gadolinium, which have isotopes with sufficient neutron absorption cross sections.	[22,67–70]
<i>Positron beam</i>	Positron annihilation is a process in which positive and negative electrons collide and merge, releasing γ photons in the process which penetrates the sample and obtains state information inside the material. The unique sensitivity of the method to radiation-induced defects provides information that cannot be obtained in a non-destructive manner using any other technique.	The method gives the installation location of sensors, shielding between sensors, and the calculation method of sensor events influence the detection results as well as information on positron spectroscopy and positron yield. This method is currently used in the field of material microstructure as well as to explain the nature, localization, and thermal stability of the defects that cause dimensional (swelling) and mechanical property stability under neutron irradiation.	[71–73]

Scanning electron microscopy (SEM)	The equipment uses electron waves, some of which can be stopped and maintained in the sample by scattering with the atoms in the sample, while others can be severely deflected and escape the sample surface as backscattered particles; excited electrons may collect enough energy from the particle-specimen interaction to escape into space as secondary electrons. Electromagnetic lenses guide the electron beam and focus it on a specific place on the sample. The beam over the sample produces the image, and the visual output is synchronized with the beam's raster. The strength of the signal is determined by the quantity of secondary electrons or backscattered electrons found.	Electron microscopy is commonly used to image, enabling the acquisition of high-resolution images from small sample regions, typically in the range of several micrometers. Using the different electron waves in the machine, a wide array of applications can be detected from the material such as the topography from the secondary electrons, the chemistry imaging in the backscattered electrons, the chemical analysis from the x-rays and the crystallography from the diffracted electrons.	[74–77]
Acoustic and vibration methods			
Atomic force microscopy (AFM)	A very sharp probe is used in AFM to scan across a surface of interest and measure the topography of the surface. The interactions between the probe and the surface are used to create a very high-resolution image of the sample, potentially to the	The high-spatial-resolution image produced by AFM measures the topology, surface forces and interaction mechanisms of various material systems at the nanoscale.	[78–81]

(Continued)

Table 1.2 (Continued)

Method	Mechanism	Application	References
	subnanometer scale, depending on the method and sharpness of the probe tip. Depending on the oscillation state of the cantilever, these imaging modes can be divided into contact or tapping modes. In the contact method, the probe can be moved along two directions inside the horizontal plane by a piezoelectric quartz which is connected to the cantilever. Depending on the topography of the surface, the quartz keeps the probe in touch with the surface sample, causing a displacement along the vertical axis. A laser beam reflected from the top of the cantilever surface to a photoelectric cell is used to measure the deflection. The cell's output signal enables the construction of a first image known to be derivative image. On the other hand, in the tapping method, a larger oscillation amplitude typically in the range of several to 200 nm is used during which the tip-sample interactions move from locations far from the sample surface with no tip-sample interaction covering the attractive and repulsive regimes in the force-distance curve.		

Phased array ultrasonic test (PAUT)	Ultrasonic testing probes with phased arrays are made up of numerous piezoelectric crystals that broadcast and receive data at different periods. Time delays are added to the elements to induce constructive interference in the wavefronts, focusing on an ultrasonic beam. This interference allows the energy to be focused on the test specimen at any depth and angle.	UT methods are ideal for detecting flaws in weld and rivets quality, however, PAUT detects cracks, voids, and pits commonly caused by corrosion. Moreso, it can determine the thickness of materials and coatings, as well as changes in material properties and interfaces, such as adhesive mapping.	[82,83]
Ultrasonic corrosion mapping	Ultrasonic Corrosion Mapping is a nonintrusive approach that uses ultrasonic techniques to map material thickness where the data is recorded on a computer and can be color coded to illustrate changes in thickness readings.	The software can produce high-quality corrosion or erosion maps where colors are quantified to indicate thickness. This method is frequently used in the oil and gas industry to detect and characterize corrosion in pipes and vessels in real time.	[84,85]

Electromagnetic methods

Alternating current field measurement	A remote uniform current is introduced into an area of the component under test which results to the flow of alternating current in the surface of the material. When a crack occurs, the electromagnetic field is disrupted, and the return signal is instantly translated using advanced mathematical procedures, alerting operators to the presence of defect or deformation.	The method can detect and sizing fatigue cracks which are commonly inspected in fillet welds and offshore drilling units, highway bridges and rail components, among others. However, this method is only applicable for surface-breaking defects and subsurface flaws in some nonmagnetic materials.	[86–88]

(Continued)

Table 1.2 (Continued)

Method	Mechanism	Application	References
Eddy sonic harmonic test	The method is based on a multifrequency analysis of harmonics and phases, with a database of reference parts including good and faulty components created during calibration. It can monitor many channels at several frequencies in real time and simultaneously.	This technique can detect the separation between layers of laminated structures, disbands in adhesive-bonded systems, impact damage, and exfoliation corrosion. Further applications for this method have been used for fairings, cowl and wing trailing edges, rudder, flaps, ailerons, elevators, and other large structures which are made up of composites and honeycomb materials.	[4,89,90]
Terahertz imaging	Terahertz Imaging uses THz radiation which has general short wavelengths (3.0 mm to 3.0 μ m) and produces images with higher spatial resolution while not posing health risk of X-ray. It follows the same principle with microwave testing where the electromagnetic wave interacts with the test object through transmission or reflection. The frequency dependency of parameter allows for the spectrum information about the evaluated structure to be retrieved. The primary benefits of this technology include noncontact, nonionizing examination, reasonably high resolution up to submillimeter order, and the availability of volumetric information on the depth/	Many common production materials, including plastics and polymer compounds, glass fiber reinforced composite materials (GFR), wood, paper, and cardboard, dry and wet paint layers or other coatings can be penetrated by terahertz radiation at low absorption rates and good penetration depths. The small terahertz wavelengths, which range from a few millimeters to several tens of micrometers, provide an ideal foundation for imaging techniques with image resolutions comparable to typical, relevant defect sizes in components made from the materials mentioned. The information detected using this type of imaging greatly depends on geometry and	[91–93]

position of the defect, such as the existence of a delamination between which layers. Terahertz imaging can usually be separated into two different approaches: time domain and continuous wave imaging. While continuous wave imaging proves to be the least complex and relatively more affordable option, it may be more suitable for some industrial applications where the temporal information is not required. Time domain imaging uses femtosecond pulsed lasers and specially designed transducers to have the precision to acquire the shape of the wave front.

electromagnetic properties such as permittivity, permeability, and electric conductivity of examined structure.

1.3 Conclusions

In this chapter, different NDT methods were presented as both conventional and nonconventional methods for material characterization. As a scientist or an engineer, characterization plays a crucial role in the determination of the behavior and/or status of the material that could affect the processes involved. With NDT, samples can be kept in their form and shape without alteration and are more favored especially dealing with fragile materials. Although the methods presented and reviewed were limited to the most common methods, combining several methods in studies has been promising to increase the applicability of one method. Choosing the right method is crucial to obtain the most useful information for analysis or study. Remote Inspection has also made a promising entry in the industry which involves the analysis of materials in isolation. These trends and developments in NDT could unlock more possibilities in materials characterization and application.

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CHAPTER 2

Optical microscope: interferometric and non- interferometric optical microscopy techniques

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2.1 Introduction

In non-destructive material measurements, quantitative optical microscopes are considered among the simplest and most accurate methods to characterize the tested samples without damaging them [1]. The light optical microscope is a kind of microscope that uses visible light (400–700 nm). and a group of lenses to perform qualitative characterization for tested objects [2]. There are numerous variations in the design of optical microscopes for specialized tasks. These designs include stereo microscope, phase-contrast microscope, confocal microscope, interferometric microscope, and petrographic microscope [2–4]. All these designs gave optical microscopes unique features compared to other microscopes. These features can be summarized as follows; investigate opaque objects and produce their 3D view, show a large distance work, provide high contrast and resolution imaging, generate sharp images without overlapping from the intensity of the background, and eliminate glare or out-of-focus light in tested objects whose thickness transcends the focus plane [4].

The importance of quantitative optical microscopes is especially prominent in some particular fields such as the investigation of the optical and structural features of polymeric and fibrous materials [5], biomedical imaging [6,7], metrology [8], plasma physics [9], and other fields [3]. Many authors have used the optical microscope and their designs to investigate the morphology of different polymeric materials. Egerton and Murphy

used optical microscopy and confocal optical microscopy to investigate fibers generated via colloidal systems with micrometrical attributes [2,4]. Sokkar et al., used an optical microscope to track the craze propagation velocity in polypropylene (PP) and isotactic polypropylene (iPP) fibers and calculate the areal craze density inside them [10,11]. Also, they utilized the optical microscope to reconstruct the 3D visualization of polyethylene terephthalate (PET) treated with TiO₂ nanoparticles to detect its morphology and the distribution of TiO₂ nanoparticles along the axis of the fiber [12]. Raslan et al., present a photo-elastic method based on an optical microscope system for obtaining direct birefringence of iPP fiber [13].

Generally, quantitative optical microscopes can be classified into two main types, namely, interferometric and non-interferometric microscopes [14,15]. Both interferometric and non-interferometric techniques are widely used in commercial microscopes to retrieve the phase structure. In the medical field, the optical microscope, whether interferometric or non-interferometric plays an indispensable role in diagnosing diseases in which the refractive index of a normal biological cell differs from the refractive index of an abnormal cell [6]. Industrially, these microscopes and these techniques are used to obtain significant information about manufactured samples which, helps to improve their properties and increase their lifetime [16,17]. This information includes a refractive index, opto-mechanical features, birefringence, opto-thermal features, dispersion, and so on [18]. Due to the importance of optical microscopes, an understanding of their optical setups and their applications is essential for designing polymeric and fibrous materials with high performance. Applications in this chapter are focused on polymeric and fibrous materials.

The used fibers in this chapter are extruded and prepared using Fiber Extrusion Technology single screw extruder machine with different spinning conditions [19]. In this process, many controllable zones are used for achieving the gradual melting of the polymer [19]. To investigate the obtained fibers using the optical microscope and their modified designs, a filament of fiber is fixed on a glass slide and then transferred to the bed of the microscope stage. To achieve high accuracy in measurements via these techniques, some practical tips should be taken into consideration. These tips include immersing the fiber in a liquid with a refractive index close to the refractive index of the fiber to reduce refraction inside the fiber, and aligning the tested fiber in the center of the glass slide without any lax.

2.2 Optical interferometry techniques

The optical interferometry techniques are accurate non-destructive methods for investigating the physical features of polymeric and fibrous materials [17,20]. According to the number of interfering beams, the optical interferometry techniques are divided into two categories: two-beam interferometers and multiple-beam interferometers [20]. Examples of two-beam interferometers include the digital holographic interferometer (DHI) [21,22], the Mach–Zehnder interferometer, the Michelson interferometer [23], the Pluta interference microscope [24], the Phase-shifting interferometer, and others [25]. On the other side, Fizeau and fringes of equal chromatic order (FECO) systems are considered the most common and accurate multiple-beam interferometers [20,26,27]. The optical setups of these techniques are based on splitting one light source into two beams (two-beam interferometer) or many beams (multiple-beam interferometer) that propagate in different optical paths and interfere with them at the surface of the imaging sensor [21]. Many authors have used these techniques to investigate the optical and structural features of polymeric and fibrous materials [3,18,28–31]. Principles, optical setups, and analysis methods for some optical interferometry techniques will be discussed in the following subsections.

2.2.1 Digital holographic interferometry technique

The DHI technique is considered one of the most remarkable and accurate experimental methods to capture and reconstruct both the amplitude and phase of the optical wave field [32,33]. This technique is distinguished from other interferometric techniques due to its ability to overcome the manual focusing issue by performing numerical focusing for the object wave field [22]. Generally, the DHI technique includes two essential steps, namely, capture and reconstruction [21,22].

2.2.1.1 Capturing a digital hologram and demodulating the phase at the recording plane

In the capturing process, an optical setup based on Mach–Zehnder interferometer is utilized to capture digital holograms as shown in Fig. 2.1. To capture a digital hologram for the tested sample via this optical setup, the beam splitter (BS_1) is utilized to split the amplitude of the coming wave into two waves. One of them is the object wave, which is passed through the tested sample in the microscope stage and the other wave is the

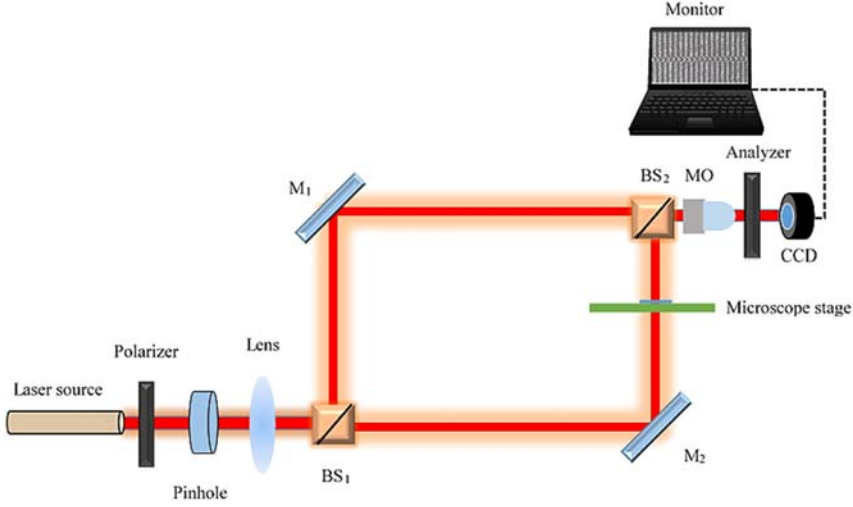


Figure 2.1 Schematic diagram illustrates the optical system of the DHI technique in which, M_1 & M_2 are two identical mirrors, MO is the microscope objective, and BS_1 & BS_2 are two identical beam splitters [21].

reference. Both reference and object waves have interfered at the surface of the imaging sensor (CCD) producing a digital hologram [21]. Mathematically, the intensity profile of the generating digital hologram or any two-beam microinterferogram ($h(x, y)$) can be expressed as [22,32];

$$h(x, y) = \rho(x, y) + \xi(x, y)e^{i2\pi f_o x} + \xi^*(x, y)e^{-i2\pi f_o x} \quad \text{in which,} \quad (2.1)$$

$$\xi(x, y) = \frac{\beta(x, y)e^{i\Delta\varphi(x, y)}}{2} \quad \& \quad \xi^*(x, y) = \frac{\beta(x, y)e^{-i\Delta\varphi(x, y)}}{2}$$

Here, $\rho(x, y)$ presents the incoherent part, $\beta(x, y)$ refers to the amplitude, f_o is the spatial frequency, and $\Delta\varphi(x, y)$ is phase that has the key information about the tested sample.

To analyze the captured hologram and demodulate the phase object, the spatial carrier frequency algorithm can be used [34]. According to this algorithm, the complex amplitude and phase map at the recording plane can be obtained by the following steps [34,35];

- Implementing a two-dimensional Fourier transform (2D FFT) on the captured hologram in Eq. (2.1) to generate its spectrum as given in the following equation;

$$h(f_x, f_y) = \rho(f_x, f_y) + \xi(f_x - f_o, f_y) + \xi^*(f_x + f_o, f_y) \quad (2.2)$$

- Applying an adaptive filter to the obtained spectrum to remove the unwanted components (the first and third terms in Eq. (2.2)) as described in the following equation;

$$h(f_x, f_y) = \xi(f_x - f_o, f_y) \quad (2.3)$$

- Shifting the rest spectrum component in Eq. (2.3) to the origin point of the frequency coordinates and executing 2D IFFT, the complex amplitude at the recording plane $\xi(x, y)$ will be obtained.
- Finally, the phase at the recording plane $\Delta\varphi(x, y)$ can be demodulated as

$$\Delta\varphi(x, y) = \arctan\left(\frac{\Im[\xi(x, y)]}{\Re[\xi(x, y)]}\right) \quad (2.4)$$

where $\Im$ and $\Re$ are the imaginary and real parts of $\xi(x, y)$, respectively.

2.2.1.2 Numerical reconstruction of the object wave field at the object plane

In this step, the complex amplitude at the recording plane $\xi(x, y)$ is numerically propagated at a defined distance (d) to produce the complex amplitude at the object plane $\xi_{ob}(x, y)$ using the convolutional approach as described in the following equation [22];

$$\xi_{ob}(x, y) = F^{-1} \left\{ F \{ \xi(x, y) \} \cdot \exp \left[\frac{i2\pi d}{\lambda} \sqrt{1 - \lambda^2 |f_o|^2} \right] \right\} \quad (2.5)$$

in which, λ is the wavelength of used light, F & F^{-1} refer to the implementation of the Fourier transform and its inverse, respectively. Here, the demodulated phase at the object plane can be expressed as follows;

$$\Delta\varphi_{ob}(x, y) = \arctan\left(\frac{\Im[\xi_{ob}(x, y)]}{\Re[\xi_{ob}(x, y)]}\right) \quad (2.6)$$

The demodulated phase in Eq. (2.6) is a wrapped phase and needs to be unwrapped to get actual phase values [34]. Depending on the demodulated phase in Eq. (2.6), many physical features such as refractive indices ($n^{\parallel}$ & $n^{\perp}$) at parallel ($\parallel$) and perpendicular ($\perp$) polarization directions, isotropic refractive index (n_{iso}), polarizabilities ($\mu^{\parallel}$ & $\mu^{\perp}$), birefringence (Δn), optical molecular orientation ($P(\theta)$), density (D), degree of volume crystallinity ($\chi(\%)$), electric polarizabilities of one molecule ($\tau^{\parallel}$ & $\tau^{\perp}$), optical stress coefficient, (ς_{stress}), number of chains between cross-links per unit

volume (κ), and the average work per chain (ϖ) can be calculated as given in the following equations [29,36–38]:

$$n^{\parallel} = \frac{\Delta\varphi^{\parallel}\lambda}{2\pi t} + n_L \& n^{\perp} = \frac{\Delta\varphi^{\perp}\lambda}{2\pi t} + n_L \quad (2.7)$$

$$n_{iso} = \frac{n^{\parallel} + 2n^{\perp}}{3} \quad (2.8)$$

$$\mu^{\parallel} = \frac{(n^{\parallel 2} - 1)}{(n^{\parallel 2} + 2)} \& \mu^{\perp} = \frac{(n^{\perp 2} - 1)}{(n^{\perp 2} + 2)} \quad (2.9)$$

$$\Delta n = n^{\parallel} - n^{\perp} \quad (2.10)$$

$$P(\theta) = \frac{\Delta n}{\Delta n_{\max}} \quad (2.11)$$

$$D \left[\frac{\left(\frac{n^{\parallel} + n^{\perp}}{2} - 1 \right)}{\left(\frac{n^{\parallel} + n^{\perp}}{2} + 2 \right)} \right]^{-1} = \omega \quad (2.12)$$

$$\chi(\%) = 100 \frac{D - D_a}{D_c - D_a} \quad (2.13)$$

$$\tau^{\parallel} = \frac{3M\Theta}{N_A D} \left(\frac{(n^{\parallel 2} - 1)}{(n^{\parallel 2} + 2)} \right) \& \tau^{\perp} = \frac{3M\Theta}{N_A D} \left(\frac{(n^{\perp 2} - 1)}{(n^{\perp 2} + 2)} \right) \quad (2.14)$$

$$\varsigma_{stress} = \frac{3\pi}{45KT} \left[\frac{\left(\frac{(n^{\parallel} + n^{\perp})}{2} + 2 \right)^2}{\left(\frac{(n^{\parallel} + n^{\perp})}{2} \right)} \right] (\tau^{\parallel} - \tau^{\perp}) \quad (2.15)$$

$$S = \kappa KT \left(DR - \frac{1}{DR^2} \right) \quad (2.16)$$

$$\varpi = \frac{3}{2} KT \left[\frac{1}{3} (DR^2 - DR^{-1}) + (DR^{-1} - 1) \right] \quad (2.17)$$

In the above equations, t is the thickness of the tested sample, n_L refers to the refractive index of immersion liquid, $\Delta n_{\max}$ refers to the maximum value of birefringence, ω is a constant associated with polymer materials. For example, ω values for nylon 66, PET, and polyethylene (PE) are 529, 4.047, and 2.944, respectively. D_c & D_a are the densities of the completely crystalline and completely amorphous polymers, respectively, Θ is the free space permittivity, N_A is Avogadro's number, M is the molecular weight of the monomer unit, K is Boltzmann's constant, T is absolute temperature, S is the value of applied stress, and DR is the value of draw ratio.

Many authors have used the DHI technique to calculate the refractive index, birefringence, and optical molecular orientation of fibrous materials according to the demodulated phase map [5,21,31,33]. For example, Fig. 2.2A shows a recoded digital hologram of isotactic iPP fiber with a wavelength equal to 632 nm and immersion liquid of a refractive index equal to 1.501 at the parallel polarization direction. According to Eq. (2.4), the demodulated phase map of iPP fiber at the recording plane is shown in Fig. 2.2B. The phase map at the fiber plane is constructed using Eq. (2.6) at a propagation distance equal to -0.052 mm and the result is given in Fig. 2.2C. From the constructed phase map shown in Fig. 2.2C, the optical and structural properties of iPP fiber can be calculated using Eqs. (2.7)–(2.17).

2.2.2 Pluta interference microscope

The Pluta interference microscope has the same fundamentals as the Nomarski microscope, with some modifications [20,24,39]. This microscope has three operating systems namely: differential mode, fringe field mode, and uniform field mode [20,24]. The fringe field mode of the Pluta microscope is considered the most remarkable operating system to investigate the optical and structural features of polymeric and fibrous materials [10,40]. This mode has two positions; the non-duplicated position which directly produces the birefringence of anisotropic materials, and duplicated position which is used to determine the refractive indices of anisotropic materials at different polarization states and then calculate their birefringence [10,20,39]. The optical setup of the Pluta interference microscope is shown in Fig. 2.3.

In the non-duplicated position, only one birefringent prism (W1) that is located after the objective microscope is utilized to obtain the birefringence (non-duplicated) position [24]. Here, the birefringent prism (W1)

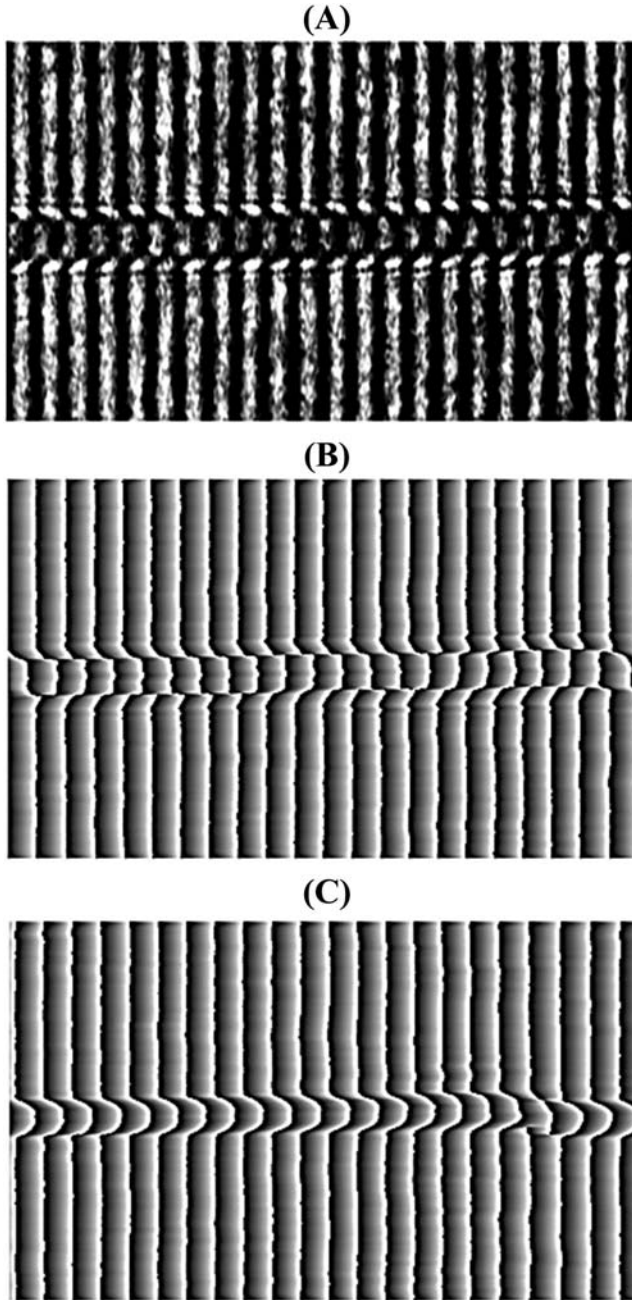


Figure 2.2 (A) Recoded digital hologram of isotactic polypropylene (iPP) fiber with a wavelength equal to 632 nm and immersion liquid of a refractive index equal to 1.501 at the parallel polarization direction. (B) The demodulated phase map of iPP fiber at the recording plane. (C) The demodulated phase map of iPP fiber at the fiber plane.

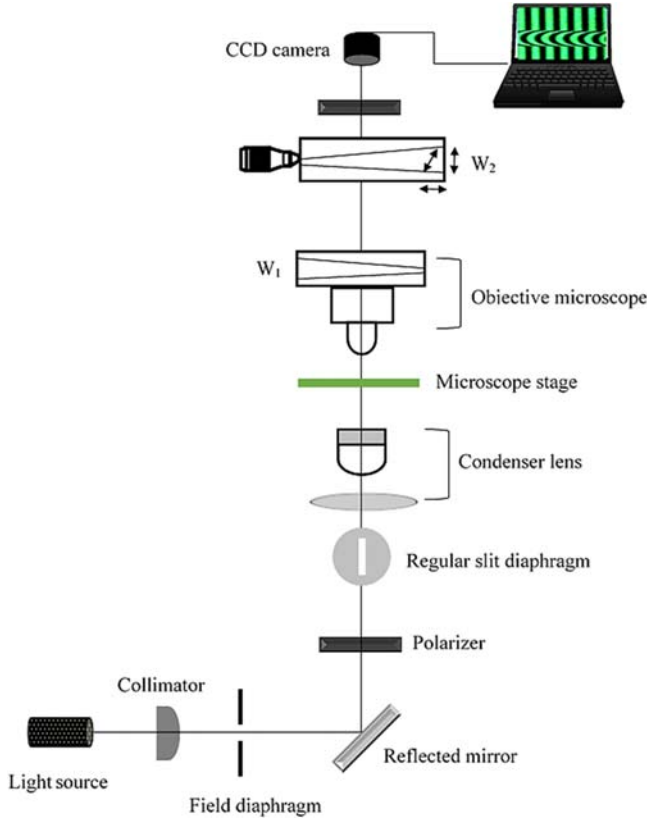


Figure 2.3 Schematic diagram illustrates the optical system of the Pluta interference microscope [24].

divides the incident light wave into two waves, namely, extraordinary and ordinary, and introduces a sufficient phase shift between the splitter light waves [24,39]. In this position, the birefringence of tested polymeric or fibrous materials (Δn) can be calculated by the following equation [17];

$$\Delta n = \frac{\Delta\varphi(x, y)\lambda}{2\pi t} \quad (2.18)$$

Here, $\Delta\varphi(x, y)$ presents the demodulated unwrapped phase of a tested sample from the recoded non-duplicated microinterferogram. As an example of the non-duplicated position, Fig. 2.4A shows a recoded non-duplicated microinterferogram of PP fiber at a wavelength equal to 546 nm. As mentioned above, $\Delta\varphi(x, y)$ can be extracted using the spatial carrier frequency

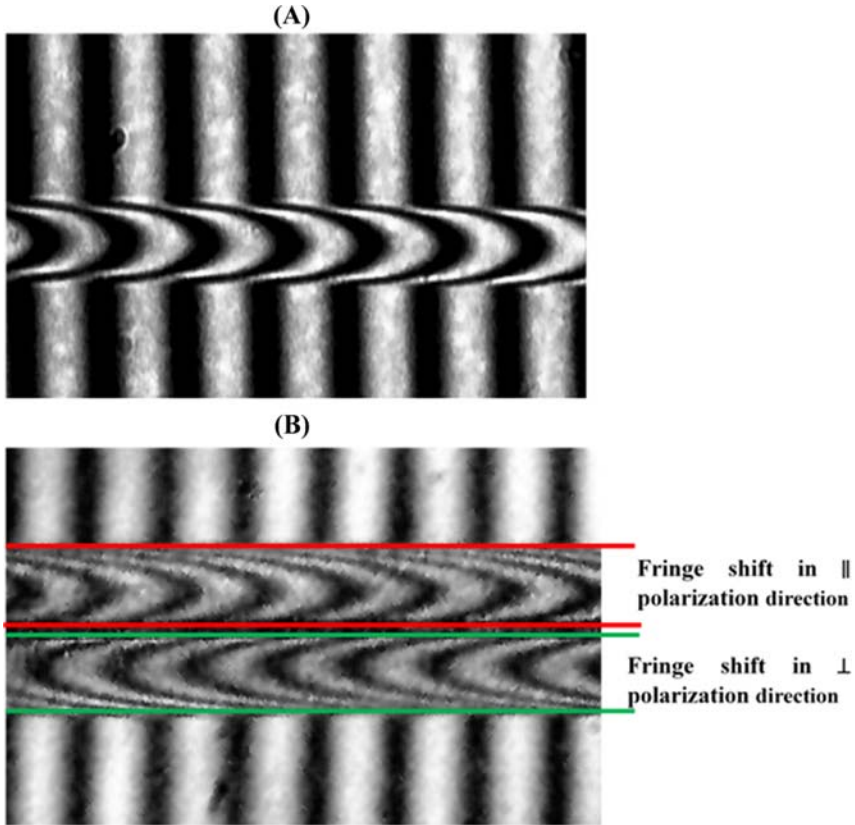


Figure 2.4 (A & B) Recoded non-duplicated and duplicated microinterferograms of polypropylene (PP) fiber at wavelength equal to 546 nm, respectively.

algorithm (see Eq. (2.4)). From the extracted map, the birefringence (Δn) and the optical molecular orientation ($P(\theta)$) can be calculated using Eqs. 2.11 and 2.18.

On the other side, two birefringent prisms (W1 & W2) are used to generate the duplicated position of the Pluta microscope. In this position, the prism (W2) is designed to have a refraction angle larger than the refraction angle of (W1) which helps to maximize the shearing effect [20,24,39]. As an example of duplicated position, Fig. 2.4B shows a recoded duplicated microinterferogram of PP fiber at a wavelength equal to 546 nm. In the same way, the phase map of the PP fiber in this duplicated microinterferogram can be demodulated via the spatial carrier frequency algorithm. In this figure, the refractive indices ($n^{\parallel}$ & $n^{\perp}$) at the

parallel ($\parallel$) and the perpendicular ($\perp$) polarization directions of the tested sample can be calculated simultaneously from a single-shot microinterferogram using Eq. (2.7).

2.2.3 Phase shifting interferometry technique

Phase-shifting interferometry (PSI) is a sequence-shots technique that is considered among the highest sensitivity and accurate non-destructive methods to investigate many physical quantities of polymer and fibrous materials by demodulating the phase map [17,25,36,41,42]. The PSI technique has the ability for measuring the deviation in the wavefront to the order of $\lambda/200$ [15,42]. This technique is based on analyzing the pixel-by-pixel intensity of several microinterferograms (at least three microinterferograms) as the phase difference changes [43,44]. The demodulated phase map via the PSI technique has high resolution and provides full field investigation. Experimentally, piezo-electric transducer unit can be added to the optical setup of the optical interferometry techniques, (such as DHI, Mach–Zehnder interferometer, Michelson interferometer) to conduct the phase shift between the recorded microinterferograms [44,45]. Over the past few decades, various PSI algorithms (for example, three-shot phase shifting algorithm, four-shot phase shifting algorithm, and Hariharan 5-shot phase shifting algorithm) have been proposed for extracting the phase map [42,44–46]. In the following subsections, the strategies of these algorithms will be discussed.

2.2.3.1 Three-shot phase shifting algorithm

In this algorithm, three microinterferograms with phase shifts 0, $2\pi/3$, and $4\pi/3$, respectively, are required to demodulate the phase object. Mathematically, the intensities of these phase-shifted microinterferograms can be expressed as [44,45];

$$\begin{aligned} h_1(x, y) &= \rho(x, y) + \beta(x, y)\cos[2\pi f_o x + \Delta\varphi(x, y)] \\ h_2(x, y) &= \rho(x, y) + \beta(x, y)\cos\left[2\pi f_o x + \Delta\varphi(x, y) + \frac{2\pi}{3}\right] \\ h_3(x, y) &= \rho(x, y) + \beta(x, y)\cos\left[2\pi f_o x + \Delta\varphi(x, y) + \frac{4\pi}{3}\right] \end{aligned} \quad (2.19)$$

From Eq. (2.19), the phase object can be calculated using the following relation [45];

$$\Delta\varphi(x, y) = \arctan \left[\frac{\sqrt{3}(h_2(x, y) - h_3(x, y))}{2h_1(x, y) - h_2(x, y) - h_3(x, y)} \right] \quad (2.20)$$

2.2.3.2 Four-shot phase shifting algorithm

In the four-shot phase shifting algorithm, the phase object can be calculated by capturing four microinterferograms with phase shifts 0, $\pi/2$, π , and $3\pi/2$, respectively. Here, the intensities of four phase-shifted microinterferograms can be given as [17,36,41,42];

$$\begin{aligned} h_1(x, y) &= \rho(x, y) + \beta(x, y)\cos[2\pi f_0 x + \Delta\varphi(x, y)] \\ h_2(x, y) &= \rho(x, y) + \beta(x, y)\cos\left[2\pi f_0 x + \Delta\varphi(x, y) + \frac{\pi}{2}\right] \\ h_3(x, y) &= \rho(x, y) + \beta(x, y)\cos[2\pi f_0 x + \Delta\varphi(x, y) + \pi] \\ h_4(x, y) &= \rho(x, y) + \beta(x, y)\cos\left[2\pi f_0 x + \Delta\varphi(x, y) + \frac{3\pi}{2}\right] \end{aligned} \quad (2.21)$$

According to Eq. (2.21), the phase object can be calculated from the intensities of the four phase-shifted microinterferograms using the following relation [42]:

$$\Delta\varphi(x, y) = \arctan \left[\frac{h_4(x, y) - h_2(x, y)}{h_1(x, y) - h_3(x, y)} \right] \quad (2.22)$$

2.2.3.3 Hariharan 5-shot phase shifting algorithm

In this algorithm, five microinterferograms with a linear phase shift ϑ between shots are required to demodulate the phase object. Mathematically, the intensities of these phase-shifted microinterferograms can be expressed as [46]:

$$\begin{aligned} h_1(x, y) &= \rho(x, y) + \beta(x, y)\cos[2\pi f_0 x + \Delta\varphi(x, y) - 2\vartheta] \\ h_2(x, y) &= \rho(x, y) + \beta(x, y)\cos[2\pi f_0 x + \Delta\varphi(x, y) - \vartheta] \\ h_3(x, y) &= \rho(x, y) + \beta(x, y)\cos[2\pi f_0 x + \Delta\varphi(x, y)] \\ h_4(x, y) &= \rho(x, y) + \beta(x, y)\cos[2\pi f_0 x + \Delta\varphi(x, y) + \vartheta] \\ h_5(x, y) &= \rho(x, y) + \beta(x, y)\cos[2\pi f_0 x + \Delta\varphi(x, y) + 2\vartheta] \end{aligned} \quad (2.23)$$

Using Eq. (2.23), the phase object can be calculated using the following relation [46]:

$$\Delta\varphi(x, y) = \arctan \left[\frac{2(h_2(x, y) - h_4(x, y))}{2h_3(x, y) - (h_1(x, y) + h_5(x, y))} \right] \quad (2.24)$$

The demodulated phase objects in Eqs (2.20), (2.22), and (2.24) are wrapped and need to be unwrapped to get the actual phase values. As an application for the four-shot phase shifting algorithm, Fig. 2.5A shows four stimulated microinterferograms for an object with phase shift 0 , $\pi/2$, π , and $3\pi/2$, and their corresponding cross sections, respectively. The phase map of this object can be extracted using Eq. (2.22) as given in Fig. 2.5B. The unwrapped phase object for the wrapped phase maps in B

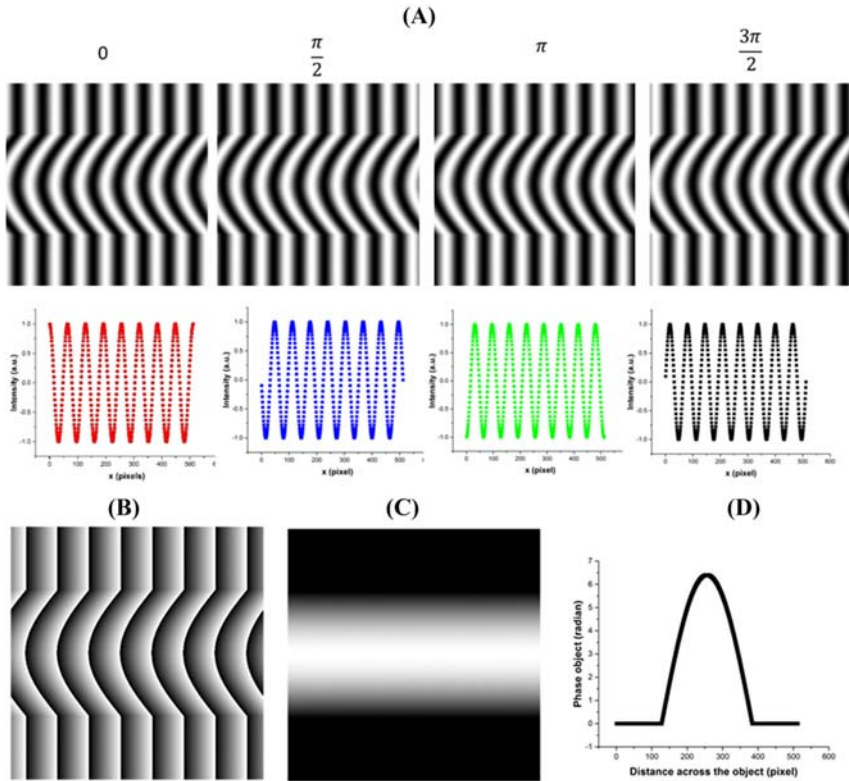


Figure 2.5 (A) Stimulated microinterferograms for an object with phase shifts 0 , $\pi/2$, π , and $3\pi/2$, and their corresponding cross sections, respectively. (B) The wrapped phase object. (C) The unwrapped phase object. (D) The phase distribution values of the tested object at a constant line.

Table 2.1 Comparison between the demodulation phase object via the spatial carrier frequency technique and the phase shifting interferometry (PSI) techniques.

	Demodulation of the phase object via the spatial carrier frequency technique	Demodulation of the phase object via Phase shifting interferometry (PSI) techniques
Field of analysis	Frequency field	Spatial field
Optical system	Simple	Complex
Number of microinterferograms required	Single microinterferogram	$\geq$ three microinterferograms
Computational complexity	High	Low
Suitability of Performing dynamic investigation	Suitable	Not suitable
Memory requirements	Medium	Low

is estimated as shown in Fig. 2.5C. From the unwrapped, the phase distribution values can be calculated at a constant line as given in Fig. 2.5D. From the calculated phase distribution values in Fig. 2.5D, the optical and structural properties of the tested object can be calculated using Eqs (2.7)–(2.17).

Table 2.1 shows a comparison between the demodulation phase object via the spatial carrier frequency technique and the PSI techniques [34].

2.2.4 Multiple-beam Fizeou fringes technique

The history of optical multiple-beam interferometry begins in 1836 with Airy, where he formulated a primary mathematical expression for describing the distribution of intensity for fringes generated via two parallel—plane plates [47]. In 1862, Fizeau conducted the first experimental interferometer for creating multiple-beam microinterferogram [48]. In multiple- beam interferometers, the Fizeau fringe technique has been regarded as a non-destructive and accurate method for characterizing polymeric and fibrous materials because of its high resolution [28,49,50]. Investigation of the local variations of the refractive indices ($n^{\parallel}$ & $n^{\perp}$) and birefringence (Δn) of polymeric and fibrous materials is considered the most prominent application for the multiple- beam Fizeau fringe technique [28]. Creating multiple-beam microinterferogram via the Fizeau system can be done on reflection (dark sharp fringes on a bright background) and in transmission (bright sharp fringes on a dark background)

[20]. The optical setup of multiple-beam Fizeau fringes in the transmission is given in Fig. 2.6A.

In this optical system, a multiple-beam microinterferogram can be created by inserting the tested sample into a wedge interferometer. This wedge comprises two optical flats that are coated with partially transmitting highly reflecting silver and attached to a designed jig [20]. Here, parallel sharp bright fringes perpendicular to the axis of the tested object can be obtained by adjusting the thickness of the gap for the wedge and the

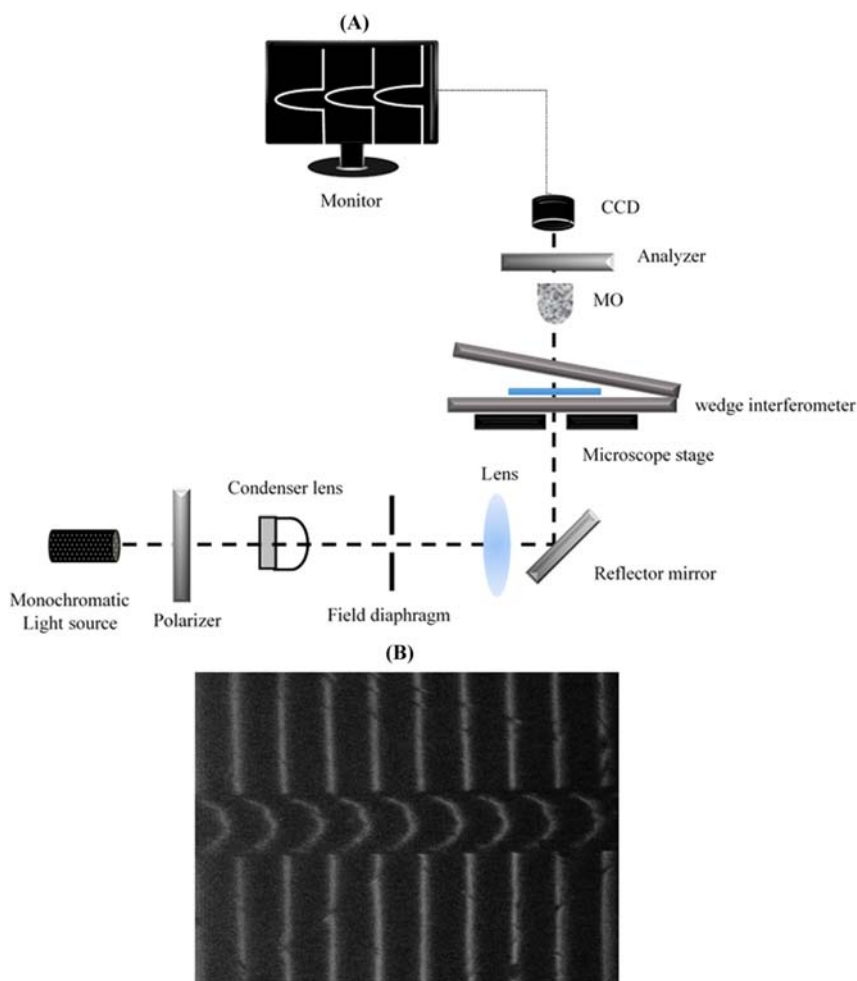


Figure 2.6 (A) Optical setup of multiple-beam Fizeau fringes in transmission, and (B) Recoded multiple-beam Fizeau microinterferogram of polypropylene (PP) fiber at a wavelength equal to 546 nm for light vibrating parallel to the fiber axis, respectively.

angle of the wedge [51]. As an example, Fig. 2.6B shows the recoded multiple-beam Fizeau microinterferogram of PP fiber in transmission at a wavelength equal to 546 nm for light vibrating parallel to the fiber axis.

Mathematically, the intensity profile of the creating multiple-beam Fizeau microinterferogram ($h(x, y)$) can be described as [51];

$$h(x, y) = \frac{\Lambda}{\Psi - \Omega \cos \Delta \varphi(x, y)} \quad (2.25)$$

in which Λ , Ψ , and Ω are constants relying on the transmittance and the reflectance of the wedge interferometer. The intensity profile in Eq. (2.25) can be rewritten as;

$$h(x, y) = \frac{1}{\rho(x, y) + \xi(x, y)e^{i2\pi f_o x} + \xi^*(x, y)e^{-i2\pi f_o x}} \quad (2.26)$$

To simplify the analysis process for the multiple-beam Fizeau microinterferogram and reduce the error during phase object demodulation, the inverse microinterferogram principle is utilized as described in the following equation [51]:

$$h_{inv}(x, y) = \frac{1}{h(x, y)} = \rho(x, y) + \xi(x, y)e^{i2\pi f_o x} + \xi^*(x, y)e^{-i2\pi f_o x} \quad (2.27)$$

Now, Eq. (2.27) becomes similar to the intensity profile of the two-beam microinterferograms and the phase object can be directly extracted by the spatial carrier frequency technique as described in Eq. (2.4). According to the extracted phase map from multiple-beam Fizeau microinterferogram, the variations of the refractive indices ($n^{\parallel}$ & $n^{\perp}$) for the tested object can be calculated as given in the following relations [28,51]:

$$n^{\parallel} = \frac{\Delta \varphi^{\parallel} \lambda}{4\pi t} + n_L \& n^{\perp} = \frac{\Delta \varphi^{\perp} \lambda}{4\pi t} + n_L \quad (2.28)$$

The other optical and structural properties can be calculated depending on the values of the refractive indices, as indicated earlier in Eqs. (2.8–2.17).

2.2.5 Fringes of equal chromatic order technique

The FECO technique is a type of non-destructive multiple-beam interferometers [52]. It has many applications in the fields of thin film and polymer characterizations [26,52–54]. Compared to the multiple-beam Fizeau fringe technique, the FECO system has a unique property, which

is its ability to investigate the dispersion parameters of the tested sample from a one-shot microinterferogram [54]. The optical setup of the FECO fringe system is nearly similar to the optical setup of the Fizeau fringe system in Fig. 2.6A. The main differences between these two systems are that in the Fizeau fringe system, a monochromatic light source (single wavelength) is used to produce the microinterferogram while in the FECO fringe system, a white-light source (various wavelengths) is used to produce the microinterferogram. Also, the FECO fringe system includes a spectrometer to analyze white light into its wavelengths in the visible spectrum (400–700 nm).

According to the optical system of FECO, their microinterferograms are generated by illuminating the wedge of the interferometer that includes the tested sample, using a parallel beam of white-light source (halogen lamp). A prism will direct the outward pattern from the wedge to the spectrometer for analyzing the white light into its wavelengths [26]. Here, each fringe in the formed FECO microinterferogram has a specific wavelength and optical path difference [53]. Then, it is possible to conduct an accurate single shot dispersion study for the tested samples using this optical system.

2.3 Optical non-interferometric techniques

On a different note, various non-destructive optical non-interferometric techniques are used to characterize the polymeric materials depending on the extracted phase object [1,14,55,56]. The primary non-interferometric experiments are based on measuring the deflection angle of a laser beam across the tested object core [57]. Here, the numerical Abel inversion formula can be utilized to calculate the refractive index by finding the inversion of the deflection angle [57].

Generally, the optical non-interferometric techniques can be classified into two main categories (wavefront sensing and phase retrieval) according to the way of the phase demodulation [15]. In the wavefront sensing category, the Shack–Hartmann wavefront is considered the most widely used and accurate technique to demodulate the phase map of the tested object and hence its physical properties [15,58]. In this technique, phase demodulation can be performed by estimating the aberration of the wavefront that is equal to the difference between the distorted wavefront (real optical system) and the reference wavefront (ideal optical system) [58,59].

Phase retrieval is another common and accurate non-interferometric technique that extracts phase objects [60]. It is based on considering the phase estimation from intensity/ amplitude as a mathematical problem and its solution is called phase retrieval [61]. Generally, phase retrieval techniques are divided into two main classes: iterative methods and deterministic methods [15,60,61].

In the iterative methods, the Gerchberg–Saxton (GS) algorithm is considered the first iterative phase retrieval method [60]. In this method, the phase object can be estimated from the far-field diffraction pattern of the tested object and its intensity image [61]. However, the GS method has high performance in many fields (such as X-ray diffraction imaging, quantitative phase microscopy, and adaptive optics). It has some limitations that relate to the iterative algorithm itself [15]. In other means, a large number of iterations are required for getting an actual solution. To overcome the limitations of the GS algorithm, Fienup proposed another iterative algorithm so-called hybrid input-output (HIO) [62,63]. In this algorithm, some improvements are implemented on the GS algorithm to forbid the iterative method from producing stuck at the local minima [63]. The major drawback of the HIO algorithms is that they need a large number of analyses and skills to estimate the phase objects [15].

In contrast, the deterministic phase retrieval method utilizes the principles of propagation to demodulate the phase object directly [64,65]. The first algorithm for the deterministic phase retrieval method was demonstrated by Teague in 1982 [64]. He utilized the Helmholtz equation that describes the energy conservation for propagation for deriving a second-order elliptic partial differential equation (PDE) under the paraxial approximation [64]. This PDE outlines the relationship between the phase of the optical field and the variation of intensity [65]. Teague named this equation the transport of intensity equation (TIE). To find the solution for this equation and demodulate the phase of the optical field, various approaches have been proposed [15]. These approaches include iterative Fourier transforms, the multi-grid method, Green's functions, and the Zernike polynomial method [1,14,15]. The use of these approaches mainly depended on the nature of the tested sample and the experimental setup [1,14,56].

Recently, the TIE technique has been considered among the most accurate and successful non-destructive optical non-interferometric

methods to characterize polymeric and fibrous samples [1,14,55,56]. So, the principles, optical setups, and analysis methods for the TIE technique will be discussed in the following subsection.

2.3.1 Transport of intensity equation technique

The TIE is an adaptive tool for optical microscopy that demodulates the phase objects of transparent phase materials. As previously mentioned, the TIE is a PDE that outlines the link between the axial variation of intensity and the phase of the optical field. Mathematically, the general formula of the TIE can be expressed as [65],

$$\vec{\nabla}_{\perp} \cdot [h(x, y; z) \vec{\nabla}_{\perp} \varphi(x, y; z)] = -k \frac{\partial h(x, y; z)}{\partial z} \quad (2.29)$$

here, $k = \frac{2\pi}{\lambda}$ is the wave number of the free space propagation, $\vec{\nabla}_{\perp}$ is 2D transverse gradient (Hamiltonian) operator in $x - y$ plane, and $\frac{\partial h(x, y; z)}{\partial z}$ is the axial intensity variation. Experimentally, the term $\frac{\partial h(x, y; z)}{\partial z}$ can be estimated by finding the difference between two defocused intensities ($h_1(x, \Delta z) & h_2(x, -\Delta z)$) that separate by propagation distance (Δz). Deterministically, the phase object $\Delta\varphi(x, y)$ can be directly demodulated by finding the solving of Eq. (2.29) as given in the following equation [1,14,56];

$$\Delta\varphi(x, y) = F^{-1} \left[\frac{1}{f_x^2 + f_y^2} F \left(\frac{2\pi}{\lambda h_o(x, y)} \frac{\partial h(x, y; z)}{2\Delta z} \right) \right] \quad (2.30)$$

where the h_o the intensity of the recorded micrograph at the focus plane, and $f_x^2 & f_y^2$ are frequencies in the Fourier field. The demodulated phase map in Eq. (2.30) is directly unwrapped.

Experimentally, the parameters of Eq. (2.30) can be estimated via a simple optical system for the TIE technique as shown in Fig. 2.7A. In this optical system, parallel temporally and spatially partially coherent beam illuminate the tested object. Here, the focus intensity image $h_o(x, y)$ can be recorded at the focus plane of the CCD camera ($\Delta z = 0$) and two defocused intensities ($h_1(x, \Delta z) & h_2(x, -\Delta z)$) can be recorded by displacing the microscope stand at different propagation distances. In this experiment, the propagation direction of the parallel light beam is perpendicular to the detector plane.

According to the demodulated phase in Eq. (2.30), the refractive indices ($n^{\parallel} & n^{\perp}$) for the tested object can be determined using the relations

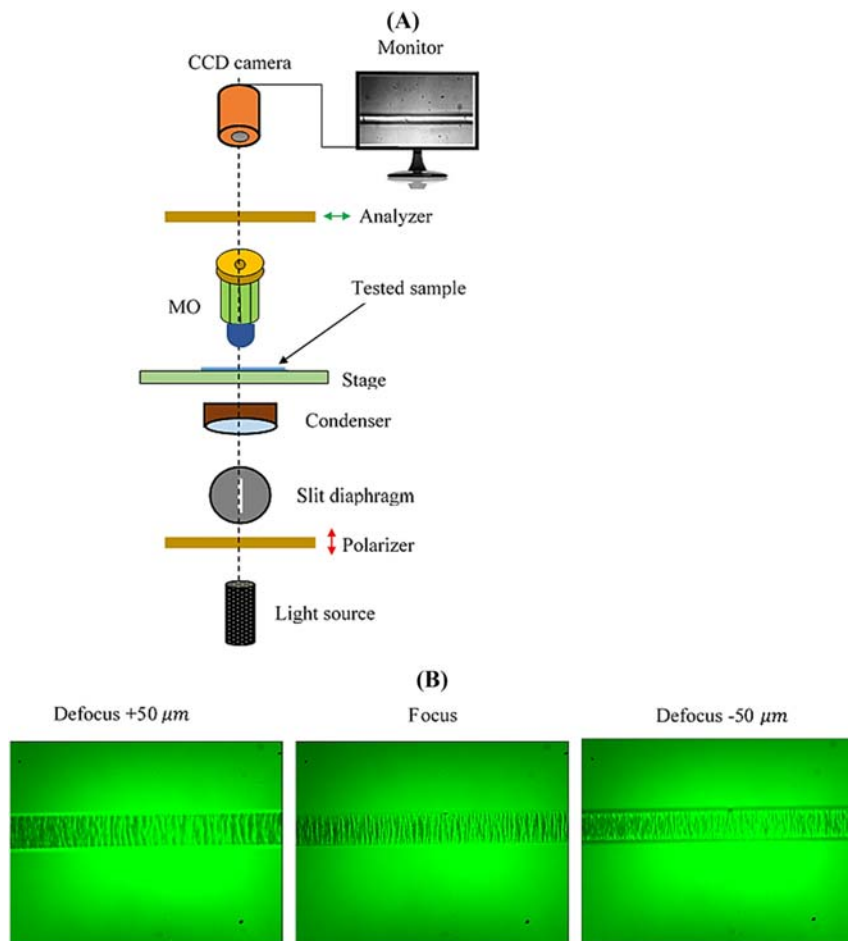


Figure 2.7 (A) Optical system of TIE technique and (B) Recoded intensity images of crazed PP fiber at propagation distances +50, 0, $-50\ \mu\text{m}$ in parallel polarization direction.

in Eq. (2.7). The other optical and structural properties can be calculated depending on the values of the refractive indices, as indicated earlier in Eqs. (2.8–2.17). As an example for investigating optical and structural properties of fibrous materials via the TIE technique, Fig. 2.7B shows recoded intensity images of crazed PP fiber at propagation distances +50, 0, $-50\ \mu\text{m}$ in parallel polarization directions. The significant differences between the interferometric techniques and non-interferometric techniques (TIE) can be summarized as given in Table 2.2 [14].

Table 2.2 General comparison between Interferometric techniques and Non-interferometric techniques (TIE) [15].

	Interferometric techniques	Non-interferometric techniques (TIE)
Optical setup	Complicated	Simple
Stable measurement environment	Not stable	Stable
Phase unwrapping	Need phase unwrapping	Does not need phase unwrapping
Reference beam	Need reference beam	Does not need reference beam
Coherent beams	Temporally/spatially complete coherent beams	Temporally/spatially partially coherent beams
Calculation	Simple	Simple

2.4 Summary and future perspectives

This chapter aims to throw light on non-destructive material characterization methods using the optical microscope and their modified designs. A general introduction with a review of the previous works and applications of the optical microscope and their modified designs for investigating polymeric fibers is illustrated. Section 2.2 dealt with optical interferometry techniques, where the theoretical considerations and the optical setups of the DHI technique, Pluta interference microscope, PSI, multiple-beam Fizeou fringes, and FECO techniques are described. Moreover, the phase demodulation methods for these techniques are presented. Section 2.3 dealt with optical non-interferometric techniques, where the concepts and applications of the TIE are illustrated. Given the importance of optical microscopes and their modified designs, future studies are needed to link these optical systems with artificial intelligence and machine learning techniques in order to increase the accuracy of their results and facilitate the interpretation of their obtained results.

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CHAPTER 3

Polarized microscopy

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3.1 Introduction: basic principles and instrumentation

Optical microscopy is a powerful means for visual observations of various types of materials. Basically, this technique consists of a light source and a lens system. Despite its low resolution with respect to electronic microscopy, optical microscopy can show great advantages over other techniques. Indeed, beyond providing unique information on the crystalline structure and optical properties, optical microscopy allows the observation of heat-sensitive samples and their reuse for further analytical examinations. This is particularly useful when samples are available only in a limited amount, such as in forensics. Compared with electronic microscopies, sample preparation for optical microscopy has the advantage to preserve the chemical composition and the morphology of samples, leading to very few artifacts. Because of the deep knowledge of light-matter interactions and of their visual results, possible artifacts produced by optical microscopy may be easily recognized by experienced researchers. Electronic microscopy needs more complex sample preparation and severe conditions that may destroy the original structure of delicate samples and result in misrepresentation. Especially for biological samples, that generally require careful handling, optical microscopy is a valid alternative to other damaging techniques.

The effective use of a polarized microscope needs the knowledge of basic concepts related to the wave's propagation and interaction of light with matter. These issues are just mentioned here to describe the phenomenon of birefringence but can be deepened in Refs. [1–4]. It is well known that, because of the slower light propagation in media other than air, any solid is able to refract light. The degree of deviation of the refracted ray through a medium, under specific conditions of temperature and pressure, is expressed by the refractive index, that is the ratio between the speed of light in vacuum (which is maximum) and the speed of light in that medium. As a consequence, the refractive index of a material is

inversely proportional to the velocity of light through the material. In addition, birefringent solids may split visible light into two polarized rays, with different rates and directions. Therefore, the two rays emerging from birefringent solids show a phase difference. Because of the phenomenon of double refraction, birefringent solids appear bright under a polarized light microscope. This latter is essentially an optical microscope endowed with two polarizers, ordinarily called polars, between which a solid is placed. The first polarizer is positioned in the light path before the specimen, whereas the second one, referred to as the analyzer, is positioned between the objective and the observation or camera tube. Within the observation tube is mounted a Bertrand-Amici lens whose insertion produces the shift of the focus from the plane of the specimen to an upper plane, corresponding to the plane of interference figures formed in the objective rear focal plane. A polarized light microscope also contains a slot positioned between the specimen and the analyzer. The slot allows the insertion of compensators and retardation plates, which are used to enhance optical path differences in the specimen seen under crossed polarizers. The utility of the Bertrand-Amici lens and retardation plates will appear evident herein later. The polarizing microscope allows various optical measurements and applications, although it is also frequently used for detailed qualitative observations of birefringent solids. Such materials belong to asymmetric crystallographic systems, whereas solids of the monometric system packed in a cubic lattice do not show birefringence. Only solids of the monometric system, therefore, cannot be distinguished from the dark background under a polarizing microscope with crossed polars. Birefringence may be defined as the property of asymmetric systems to divide incident light into two rays with different wavelengths and propagation rates due to optical anisotropy, that is birefringence is connected to the variation of the refractive index of substances with the spatial direction. It is worth noting that the refraction index, even for isotropic substances, does also depend on the temperature and wavelength of the incident light. Therefore, the common assumption of negligibility of “dispersion” (wavelength dependency of the refractive index causes a wavelength dependency of the refraction angle at the interface between two media) is not universally valid. Substances that are able to repetitively switch the birefringence sign from positive to negative and vice versa by temperature changes are also known [5]. The two rays emerging from a birefringent material are assumed to be orthogonally polarized [6], and their directions can be obtained by considering the spherical (for an

ordinary ray) or elliptical (for an extraordinary ray) wave surfaces originated by each point of the material surface, as described in basic books on optics. Although, theoretically, the two decomposed refracted rays are polarized in two normal planes, the two polarization directions are, in general, not detectable when the incident light is not polarized. This nondetectability has been explained by the incoherence of nonpolarized incident light (two waves are considered incoherent when the phase difference between them is not constant and, indeed, natural light is constituted of a beam of waves with variable phase differences), that produces incoherence also in the two refracted rays so that their supposed polarization would not be appreciable. Indeed, the incoherence of refracted waves from a birefringent crystal allows only the observation of the splitting of the rays, but not the difference in polarization states. Therefore, before entering the sample under a polarizing microscope, light is first linearly polarized. To evidence birefringence in all its aspects, and to detect also optical parameters and other general information, substances are usually located between two crossed linear polarizers before being observed through the microscope; such observations allow to detect birefringent objects, for instance, spherulites developing in a dark liquid phase, and to draw information on their formation and constitution [7]. In an ordinary wave, the electric vectors along the propagation direction are not parallel one to another at all points of the wave, so that also the oscillation planes formed by the propagation axis and each electric vector are not parallel. The electric field of a linearly polarized wave oscillates instead in a specific plane, determined by the orientation of the polarizer. A polarizer, in other words, is able to select only a vibration direction of the electric field associated with a wave. Hence, before reaching an observer through the eyepiece, the light emerging from a sample is polarized again by means of a second polarizer. The polarizer and the analyzer are usually positioned in such a way that their polarization directions are perpendicular. Fig. 3.1 shows the effect of two polarizers on ordinary light.

Nonpolarized light can be considered constituted of several vibration planes of electrical vectors; these planes are randomly oriented around the propagation direction of light. A polarizer is able to transmit only oscillations with a specific orientation of the electric field. If a polarized wave emerging from a polarizer enters an analyzer, only the electrical component parallel to the polarization plane of the analyzer will be transmitted. Therefore, when the two polarizers show orthogonal polarization directions, no light will reach the eyes of an observer located in O. The light

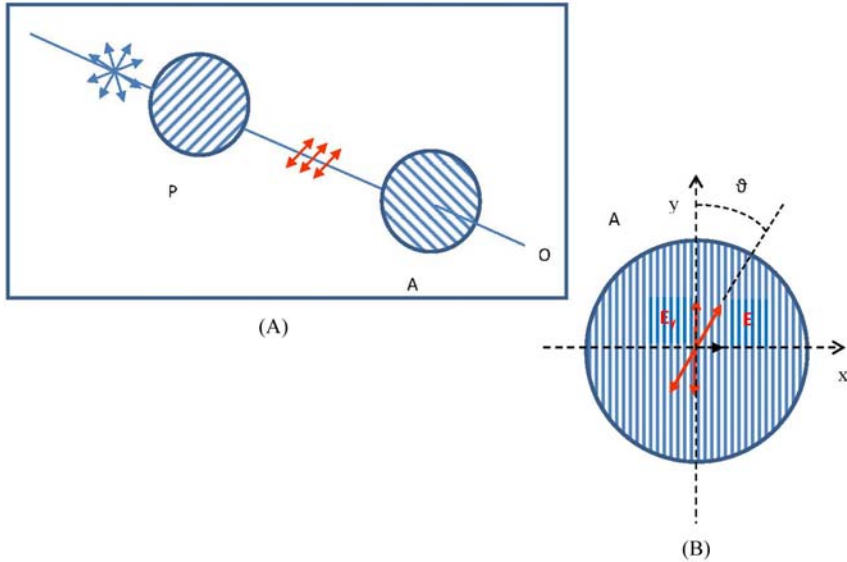


Figure 3.1 Influence on ordinary light of two combined linear polarizers. (A) The polarization direction of light conveyed by the polarizer (red arrows) is inclined with respect to the polarization direction of the analyzer. (B) The analyzer can transmit only the component $E_y = E \cos \vartheta$ of the electric vector E of polarized light.

intensity will be instead maximum when two parallel polarization directions are selected (in this case, according to the Malus law, the intensity of the transmitted light is halved, since 50% of nonpolarized light is transmitted through the first polarizer, whereas the analyzer cannot absorb any components of the polarized light). When the polarization directions of the two polarizers P and A form a generic angle ϑ , as shown in Fig. 3.1B, only the component $E_y = E \cos \vartheta$ will propagate through the analyzer up to the observation point. When no sample is placed onto a plate of a microscope with crossed polarizers, no light will reach the eyepieces, since the analyzer cannot transmit waves oscillating in a plane perpendicular to its own polarization plane. Through a microscope with crossed polarizers are, indeed, observable only substances able to change the polarization state of light, such as birefringent solids and liquid crystals. Optical isotropy is characteristic of common liquids and amorphous materials in the absence of secondary magnetic, electrical, or mechanical fields and is due to the ability to transmit light at the same rate in all spatial directions; as a result, isotropic substances cannot be visible between crossed polarizers. Indeed, an incident polarized wave will be deviated by an isotropic sample

according to Snell's law and the vibration plane of the electric field of the emerging wave (which will have an unaltered direction) will not undergo any rotational change. If the waves emerging from the sample preserve the polarization direction determined by the first polarizer, the crossed analyzer will completely hinder further light propagation and an observer cannot see more than a dark optical field through the eyepiece of the microscope. As seen before, anisotropic substances are able to split an incident ray into two polarized waves oscillating in two perpendicular planes. The two waves, of which at least one (the extraordinary ray) does not follow the ordinary refraction laws, propagate through the sample with different rates and emerge, with a phase shift, at two different positions. In other words, birefringence is due to a direction-dependence of the refractive index: the refractive index n_0 corresponding to the ordinary ray is constant, whereas that of an extraordinary ray n_e varies between n_0 and a maximum or minimum value; n_0 and the maximum or minimum refractive index are achievable, respectively, when the propagation of the incident light is parallel or perpendicular to a particular direction, known as the optical axis. Crystals with two optical axes are referred to as biaxial and split incident light in two extraordinary rays. By rotating a biaxial crystal, each ray rotates around the middle point between the two emerging rays. The surface which gives, for monochromatic light, the value of the refractive index of a crystal for different spatial directions, is referred to as the optical indicatrix. Considering the center of the indicatrix as the center of the crystal, the length of a segment from the center to the indicatrix surface gives the refractive index of the crystal for that direction. For an isotropic crystal, the optical indicatrix is a sphere, for a uniaxial crystal the optical indicatrix is a biaxial ellipsoid of rotation with the rotational axis coincident with the optical axis. For a biaxial crystal the optical indicatrix is a triaxial ellipsoid. The two principal refractive indexes of a uniaxial crystal express, respectively, the velocity of the ordinary ray and the velocity of the extraordinary ray when traveling normally to the optical axis (see Fig. 3.2). Uniaxial crystals have two principal refractive indexes and may show positive ($n_\gamma > n_0$) or negative ($n_0 > n_\gamma$) birefringence. Therefore, all the sections of the indicatrix associated with a uniaxial crystal orthogonal to the optical axis, are circles. The circle normal to the optical axis and containing the center of the ellipsoid is referred to as a circular section. Each elliptical section of the indicatrix containing the optical axis is defined as a principal section. It is worth observing that it is not possible to transform a positive indicatrix into a negative one

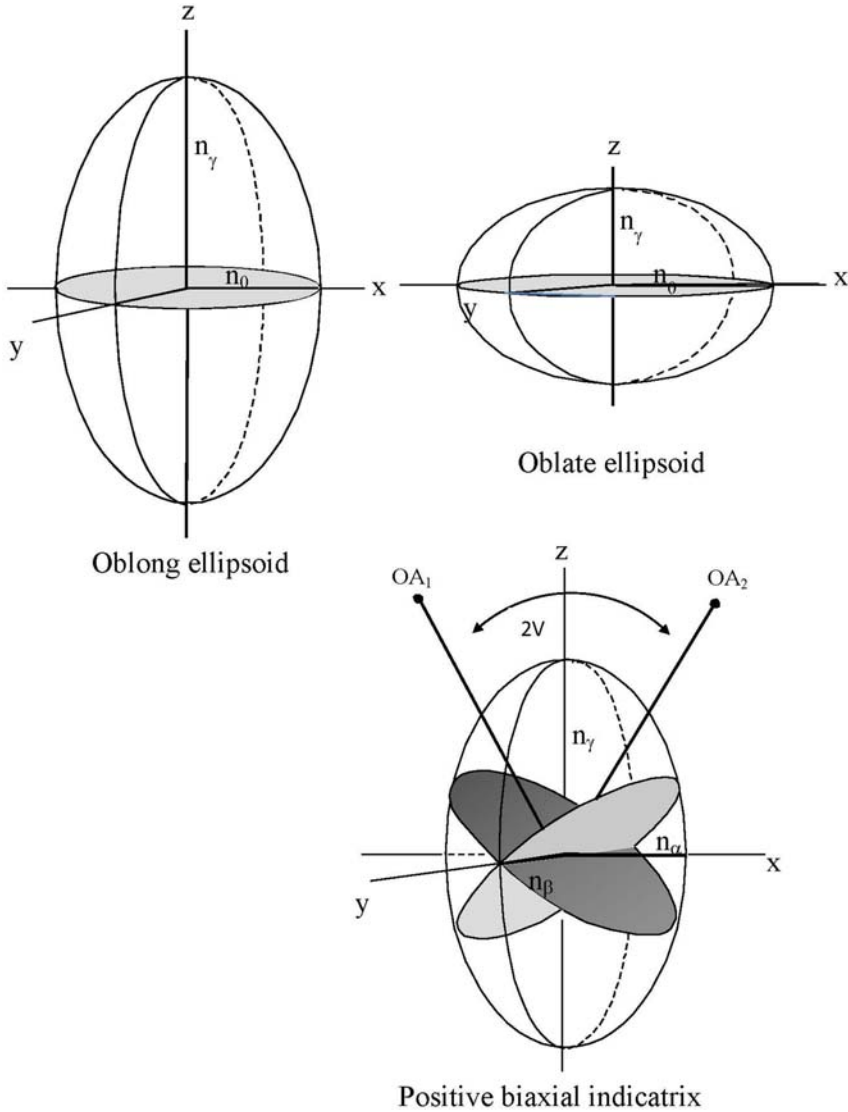


Figure 3.2 Optical indicatrices of crystals. Top: indicatrix of a positive (*left*) and negative (*right*) uniaxial crystal. Bottom: indicatrix of a positive biaxial crystal. Negative biaxial indicatrices have n_β closer to n_γ than to n_α .

(and vice versa) by a 90-degree rotation since this operation only changes the direction of the optical axis from z to x leading the circular sections perpendicular to x . The difference between the refractive indexes of a principal section is the characteristic birefringence of a certain substance.

All other nonprincipal sections will show a birefringence, given by the difference between the two refractive indexes along the axes of the ellipse, lower than the characteristic birefringence of the principal section. If the optical axis coincides with the major axis of the ellipsoid, the birefringence is referred to as positive, whereas if the optical axis has the direction of the minor axis of the indicatrix, the birefringence is conventionally negative. For a biaxial crystal, the optical indicatrix has three unequal orthogonal axes and two optical axes symmetrically found with respect to one of the three Cartesian axes. Therefore, the optical properties of a biaxial crystal are described by three main refractive indexes. A triaxial ellipsoid, as that drawn in Fig. 3.2, shows only two circular sections, with a radius n_β ($n_\alpha < n_\beta < n_\gamma$), which intersect along the y axis. This means that the refractive index changes with the direction also in two families of elliptical sections, each normal to one of the two indicatrix axes. Each optical axis of a biaxial crystal forms an acute angle V with one of the axes of the scalene indicatrix so that only two circular sections are passing for the center of the indicatrix. Each circular section is orthogonal to one of the optical axes. Only these two circular sections of a biaxial crystal behave as isotropic when viewed perpendicularly. All other sections of a triaxial optical indicatrix are ellipses and, therefore, show birefringence. A biaxial crystal is positive when n_β is closer to n_α than to n_γ , that is $n_\beta - n_\alpha < n_\gamma - n_\beta$, so that the bisectrix of the $2V$ angle in the associated triaxial indicatrix is the z axis, as shown in Fig. 3.2. In a negative indicatrix n_β is closer to n_γ than to n_α , that is $n_\beta - n_\alpha > n_\gamma - n_\beta$, so that the bisectrix of the $2V$ angle is the x axis. For simplicity, we will consider for further theoretical discussions mainly uniaxial crystals, yet conclusions may be extended to biaxial crystals. It is worth pointing out that to observe the maximum birefringence of a crystal placed between crossed polarizers, the crystal has to be oriented so that the circular section of the crystal indicatrix is perpendicular to the stage of the microscope, that is the surface of the crystal hit by light has to correspond to one of the principal sections of the indicatrix. This also entails that the optical axis of the crystal lies on the plane of the stage. As a consequence, a crystal will never result birefringent if it is placed on the microscope plate with a contact surface perpendicular to the optical axis. Relatively to optical properties, uniaxial crystals (like those of the tetragonal, hexagonal, and trigonal systems) split polarized light into an ordinary and an extraordinary ray, whereas biaxial crystals (orthorhombic, monoclinic, or triclinic structures) split light in two extraordinary rays, none of which follows the Snell's

law. Since optical properties depend on the crystalline array, polarized microscopy allows not only the identification of solids with different chemical structures but also to distinction between polymorphs of a certain material. For instance, cinnabar, consisting of uniaxial crystals of trigonal α HgS, shows a strong positive birefringence ($n_0 = 2.58$, $n_\gamma = 2.82$, $n_\gamma - n_0 = 0.24$, yellow light of Na = 5893 Å). The black β form of HgS, on the contrary, belongs to the monometric system and is nonbirefringent. Polymorphism is a very common phenomenon amongst solids. For macromolecules, it may concern not only the crystalline packing but also the chain conformation [8]. The α form of HgS is also optically active, because of the presence of helices in its crystalline structure [9–11]. Optical activity or circular birefringence is due to the capability of a chiral structure (i.e., a structure existing as mirror images that cannot be superimposed upon each other) to propagate at different rates the two circular components with opposite handedness of a linearly polarized wave. As quartz, α HgS exists as dextro-rotatory and laevorotatory enantiomorphs associated with helices with different handedness. In organic substances, chirality is mainly caused by the presence of asymmetric carbon atoms, that is carbon linked to four different groups of atoms and, contrary to chirality due to helical structures, is preserved in the liquid state. The simplest application of polarized microscopy is the determination of the melting point of a solid as the temperature at which birefringence disappears and the entire microscope field becomes dark. This kind of measurement needs the presence of a hot stage and very low heating rates for accurate estimations. Another common application is the distinction between amorphous and crystalline substances. For instance, a simple observation under crossed polars allows distinguishing coal from mineral particles [12]. A popular application in polymer science is the determination of the linear growth rate of spherulites, defined as the increase of the radius of a spherulite in a unit of time at a constant temperature. Differently from the true growth rate of spherulites (that is the increase of the mass of spherulites with time), the linear growth rate of spherulites measured during the short time before impingement remains constant and can be advantageously calculated as the slope of the line interpolating the length of a radius as a function of crystallization time. An important parameter is also the size of spherulites in completely crystallized samples since it affects the overall growth rate and the mechanical resistance of materials [13]. In principle, these simple measures are applicable to any birefringent material. Examples of negative uniaxial solids are trigonal MgCO_3 ($n_0 = 1.700$,

$n_\gamma = 1.509, n_\gamma - n_0 = -0.191$), trigonal CaCO_3 ($n_0 = 1.6585; n_\gamma = 1.4864, n_\gamma - n_0 = -0.1721$) and hexagonal Fe_2O_3 ($n_0 = 3.22; n_\gamma = 2.94; n_\gamma - n_0 = -0.28$). Most solids are however biaxial, and their birefringence usually does not achieve the highest values associated with uniaxial solids. Briefly, a uniaxial crystal possesses one optical axis and shows the same value of the refractive index along each propagation direction parallel to the optical axis, (it is worth repeating that all the sections of a uniaxial optical indicatrix perpendicular to the optical axis are circles) whereas biaxial crystals have two optical axes and only the circular sections of their indicatrix show the same value of the refractive index when observed normally (with the exception of two circular sections, all sections of a scalene ellipsoid are, indeed, ellipses and, therefore, birefringent). Although strictly interconnected to light polarization, birefringence is a different, and somehow more complex, phenomenon.

The main optical components of a polarizing microscope do not differ from those of a classical optical microscope, well described in Chapter 3. The main differences consist in the presence of two polarizers (usually Polaroid filters or Nicol prisms), one positioned between the light source and the rotating circular stage and the other between the objective and the eyepieces. The insertion of a Bertrand-Amici lens mounted in the microscope tube allows observations of interference figures originated by colonoscopic (i.e., convergent) polarized light. Finally, the insertion of oriented sections of appropriate birefringent substances (referred to as compensators and wave plates) between the specimen and the analyzer allows the determination of the birefringent sign. This chapter is mainly described optical polarized microscopes of the transmission type, which are suitable for transparent substances that, at least as thin sections, allow light to pass through. However, a polarized microscope working in reflection can be successfully used for metallurgic applications and ceramics characterization [13–17]. Notwithstanding the current massive use of X-Ray diffraction for easier identification of materials, optical techniques add additional information on the crystal growth process [18,19] and are often indispensable, for instance, in fibers identification and self-assembled peptides and amino acids structures [20].

3.2 Sample preparation

The observation with transmitted light requires very thin samples sandwiched between glass slides. The exact preparation depends on the nature

of the sample. For linear polymers, the procedure is very simple. A small piece of material is placed onto a microscope slide and a cover glass is put on it. Then the polymer is melted, and a small pressure is applied onto the cover object until the desired thickness is achieved.

Sample preparation is more complex for minerals. “Grain mounts” consists of grounded crystals placed on a slide, embedded in refractive index oil, and overlapped with a cover glass. Grain mounts is an old procedure now replaced by the most common preparation of thin sections of rocks. This preparation requires many stages of cutting and polishing, prior to the final cutting with a diamond saw to achieve a 30- μm thickness.

The preparation of biological specimens is even more delicate, because of the easier deformability of tissues and cell components. Rapid *in vivo* observations are made with samples immersed in water into a small cavity of a glass slide. Prolonged observations need the incorporation of the dried specimen into paraffin, and the cutting of a thin slice from the paraffin. To increase the contrast, biological samples may need to be colored.

Sample preparation for optical observation, and the optical observation itself, generally preserve the physical structure and the chemical composition of the original sample. Therefore, the sample might be recovered (physically or by an appropriate solvent) from the glass slide after optical examination and used for other kinds of chemical or physical analyses. This is very important when only a small amount of a sample is available, for instance in the field of forensic investigations, or when the source of the sample is not terrestrial or scarce and in all cases of hard accessibility.

3.3 Observations under crossed polarizers: interference colors

When observed between crossed polarizers, each section of a transparent and colorless birefringent material shows an artificial color. These colors, referred to as interference colors, are due to the delay of the slow wave with respect to the fast wave. The delay is due to two causes. The first is the negative interference between rays with equal intensity, equal amplitude, and a phase difference of $\lambda/2$; the second is the fact that different rates v_1 and v_2 produce a different time elapse for the two rays to emerge from a section of thickness d , with a delay $\Delta t = d/v_2 - d/v_1$. Therefore, the pathway difference $c\Delta t$ in the vacuum will be $c\Delta t = c(d/v_2 - d/v_1) = d(n_2 - n_1)$, where $n_2 - n_1$ is the difference between the

refractive index of the two refracted rays for a certain section. As a consequence, the two waves emerging from the analyzer will show a difference R in the total pathway:

$$R = \Delta S + \lambda/2 = d(n_2 - n_1) + \lambda/2 \quad (3.1)$$

Eq. (3.1), referred to as the delay equation, expresses the fact that if for a visible wavelength λ results $R = n\lambda$, with n integer, (i.e., $\Delta S = n\lambda - \lambda/2 = (2n - 1)\lambda/2$), the wavelength will be reinforced because of full positive interference between the two refracted rays. Whereas if $R = (2k + 1)\lambda/2$, with k integer, (i.e., $\Delta S = k\lambda$), there will be full negative interference between the two refracted rays and the wavelength λ will be eliminated originating the complementary color. Since the delay R depends also by the birefringence value $n_2 - n_1$ and by the thickness, each section of a birefringent solid will show an own color variable with varying thickness. For equal thickness, the color of the section with maximum birefringence corresponds to maximum interference that, therefore, provides an estimation of the birefringence power of a solid. By rotating the stage R does not change, hence the interference color remains the same (in the last paragraph we will deal with pleochroic substances, whose true color varies with rotating the stage). However, its intensity changes because of the variation of the angle α between each vibration plane of the refracted rays and the vibration plane of the wave produced by the polarizers (or, equivalently, by the analyzer). The extinction will occur four times during a 360-degree rotation correspondently to the coincidence of the vibration planes of the refracted rays with those of the two polarizers.

The first radiation which could negatively interfere is that with the higher frequency in the visible spectrum, corresponding to a wavelength of 380 nm. However, waves with $\lambda < 200$ nm cannot produce ΔS value of 380 nm (i.e., negative interference) and are not even sufficient to achieve a value of $R = 380$ nm for full positive interference in the visible. As a consequence, the solid will appear dark or light gray depending on the birefringent power. For $200 \text{ nm} < \lambda < 350 \text{ nm}$ the value of ΔS is still inferior to 380 nm, however partial positive interference of the refracted rays is possible and the solid will appear matt white. For $\Delta S = 380$ nm, $R = 380 + 190 = 570$ nm and therefore the wavelength 380 nm will be eliminated and the close violet radiations ($\lambda \sim 433$ nm) weakened whereas the yellow ones ($\lambda \sim 650 = 3/2 \cdot 433$ nm) will be strengthened. Yellow, hence, is the first interference color. With increasing of ΔS up to 520 nm,

which corresponds to $R = 520 + 260 = 780$ nm, the radiations following violet will be progressively eliminated whereas the radiations following yellow will be strengthened. Each radiation will be subtracted not only when $\Delta S = \lambda$ but also when $\Delta S = k\lambda$. Therefore, each color will appear more than one time in correspondence of $k = 1, 2, 3 \dots$. For instance, yellow will appear not only for $\Delta S = 380$ nm but also for $\Delta S = k \cdot 380$ nm as the yellow of order k . Colors are therefore referred to as colors of 1°, 2°, 3° ... order. The transition from k to the $k + 1$ order occurs for $\Delta S = k \cdot 550$ nm, that is from 0 to 550 nm substances will show colors of the first order, from 550 to 1100 nm colors of the second order, and so on.

If the thickness of a birefringent lamina of a crystal is known, the interference color of the lamina allows determining the value of the birefringence by using the Michel—Levy Table of Interference Colors (Fig. 3.3). Beyond the sequence of interference colors, in this table are reported the lines of equations $\Delta S = d(n_2 - n_1)$ with slope $n_2 - n_1$ in the plane of axes ΔS and d . Observing the colors of different sections of a same mineral with a standard thickness of 30 μm and estimating the maximum birefringence value (i.e., considering only the highest color of maximum interference), is often possible to identify the mineral, or at least recognize a limited number of probable chemical formulae by using appropriate tables listing optical and physical characteristics of crystals. A section of a mineral with randomly oriented crystals will show also colors

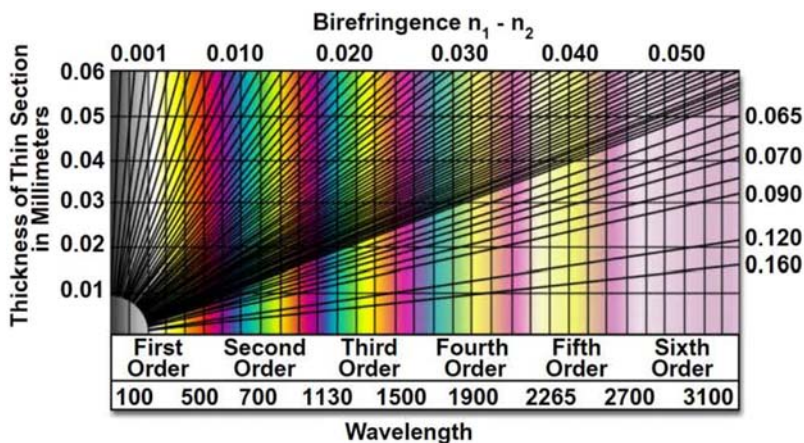


Figure 3.3 Michel—Levy interference colors chart (see text for explanation). Reproduced courtesy of Nikon MicroscopyU.

lower than that of maximum interference. The identification is feasible also when crystals are randomly oriented in sections of a rock if only the color of maximum interference is considered. For instance, a section of cordierite 30 μm thickness shows a first-order interference color, whereas the highly birefringent olivine shows third order interference colors. The colors of maximum interference of crystals are at the intersection between the oblique lines giving the birefringence values and the horizontal line corresponding to a typical petrographic thickness of 30 μm . From the intersection points, the oblique lines lead to the maximum birefringence values. If the obtained birefringence value is not characteristic of a particular crystal, the measurement of other optical properties such as habit and shape, cleavage, relief, optical sign, type of extinction, etc. allows the correct identification. Nowadays, the Michel–levy chart of interference colors is used not only for the identification of minerals, but also of fibers, polymers, drugs, food, additives, and any kind of birefringent substance in a wide field of applications, ranging from aerospace to forensic investigations.

Fig. 3.4 shows the interference colors of a precipitate of N-ethyl-L-glutamine (also called L-theanine). Different artificial colors arise because of different thicknesses or orientations of crystals. Few materials show

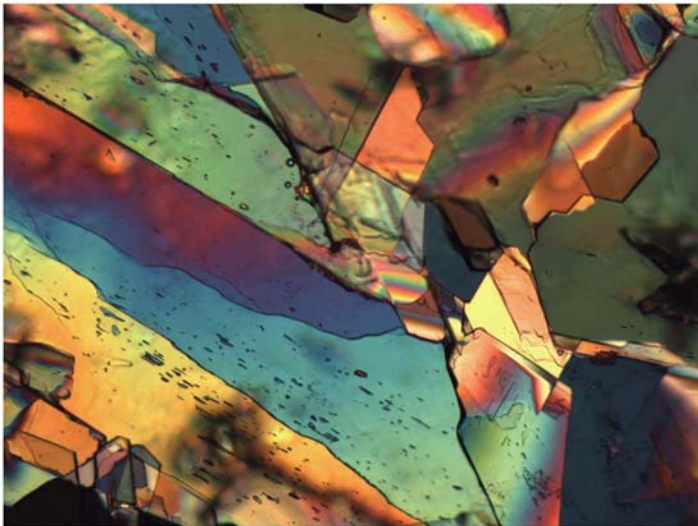


Figure 3.4 Optical micrograph of an aggregate of crystals of L-theanine, illuminated with white light, under crossed polarizers. Different thicknesses and orientations of crystals originate different interference colors.

interference colors that do not concord with the Newton sequence. For instance, chlorates (phyllosilicate minerals with a low birefringence) often show anomalous interference colors as blue, purple, or brown instead of first order gray. Since this type of anomaly is relatively rare, anomalous colors can also be used as diagnostic properties for materials identifications.

Solid substances show often a spherulitic structure, where spherulites mostly consist of minute crystals growing from a common center in all directions [21]. When crystals are doubly refracting and their optical axes form with the respective longitudinal axes a constant and radially uniform angle, spherulites show *quaquaversus* polarization. Since the optical axis has all spatial directions, spherulites originate light polarized in every direction, which can be mistaken for circularly polarized light [22]. In such spherulites, a dark cross, referred to as the Maltese cross, divides four birefringent sectors. Fig. 3.5 shows a Maltese cross within a spherulite of poly(3-hydroxybutyrate) (PHB). When the optical axis is longitudinal or transversal with respect to the geometrical axis of each radial crystal, the dark cross coincides with the vibrations planes of the polarizer and analyzer. Otherwise, the two arms of the Maltese cross will form an acute angle α with the polarization directions. The extinction is referred to as

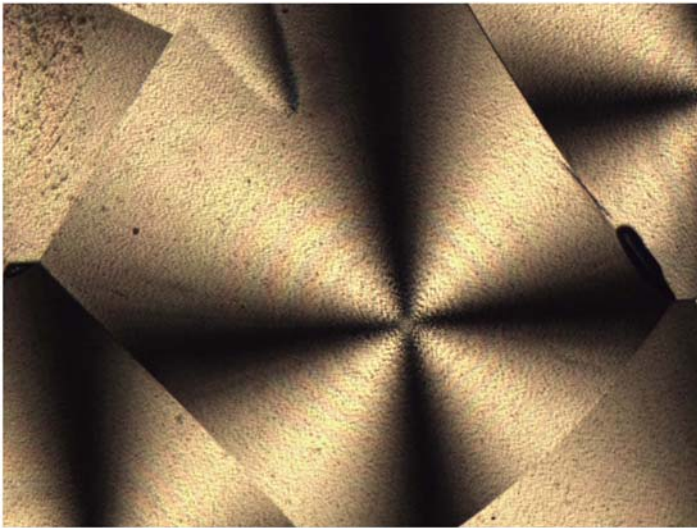
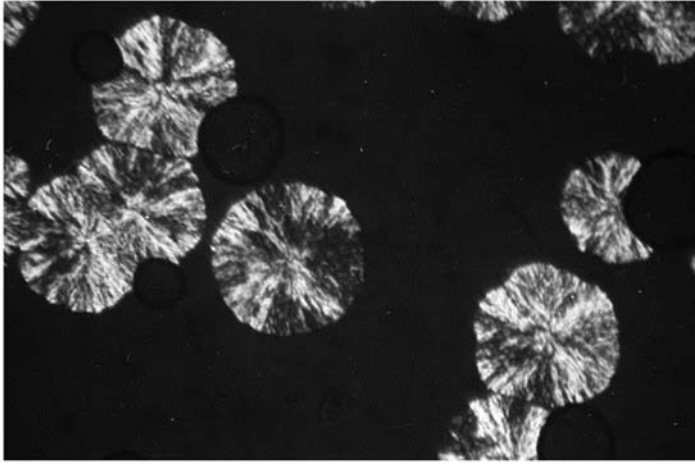
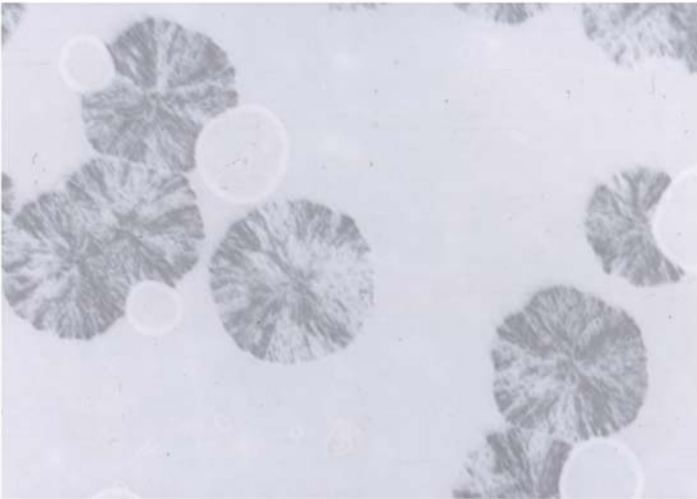


Figure 3.5 A crystallized sample of PHB showing the Maltese cross within spherulites. The extinction is parallel, as the arms of the Maltese cross are parallel and perpendicular to the polarization directions.

parallel in the former case and inclined in the latter case. Tetragonal, hexagonal (including trigonal), and orthorhombic solids will have parallel or symmetric extinction, whereas monoclinic and triclinic crystals have inclined extinction. The extinction angle can depend upon wavelength and, therefore, should be measured with monochromatic light. If radial crystals within spherulites are differently oriented from a crystallographic point of view, so that the optical axis forms with the geometrical axis of each crystal at a variable angle, radial uniformity is broken: crystals will have different birefringence powers and a Maltese cross will not be visible. The absence or the scarce visibility of a dark cross indicates that spherulites are mixed: although the orientation of the term of crystallographic axes is constant along each radial direction, it can differ from one radial direction to another. The higher the number of fibrils with different orientations of the optical axis, the lower the spherulite birefringence. In conclusion, mixed spherulites are weakly birefringent and do not show a definite Maltese cross under a polarizing microscope. Fig. 3.6 illustrates mixed spherulites of polyoxymethylene (POM) growing at 123°C from (PHB)/POM liquid blend. It is worth noting that the term mixed has nothing to do with the presence of different polymorphic phases, but refers to the random orientation of the optical axes amongst radial crystals. Because of their poor birefringence, polymers show interference colors of the first order, from dark to light gray. However, in highly oriented films and fibers higher colors may arise, since the physical properties of polymers are considerably affected by molecular orientation. Orientation produces birefringence in amorphous polymers, which is maximum for 100% extension of random coil chains, and enhancement of birefringence in crystalline polymers. Nylon 6 fibers, for instance, are yellow in the center and, because of their perfect cylindrical shape [23], show the borders thin longitudinal strings of different colors (see Fig. 3.7). Red strings in fibers separate colors of a different order and their number indicate the order of the central color. Only a red color between the central part and each edge of fiber, for instance, entails that the central yellow color is of the second order. However, in practice, it is very difficult to resolve the colored strings at the edge of a fiber. Sometimes, it is possible to distinguish the interference fringes on a cone shaped end of a fiber, where they will appear as hyperbolas, or on a wedge, where fringes appear as equally spaced ellipses for uniform radial birefringence distribution [24]. The correct order of the central color is obtained by cutting the edge at a sufficiently low angle to ensure complete resolution of the fringes. The cone



(A)



(B)

Figure 3.6 Micrograph (A) and its negative (B) showing POM spherulites developing from a liquid mixture of PHB/POM 40/60. Domains of PHB, which modify the shape of growing spherulites, are also visible. Crossed polars.

and wedge methods, however, need a rather large fiber since an accurate cone or wedge at the end of filaments with a small diameter may be difficult, or even impossible, to cut. [Fig. 3.8](#) shows the interference colors at the wedge cut end of a nylon 6 fiber (diameter 0.4 mm).

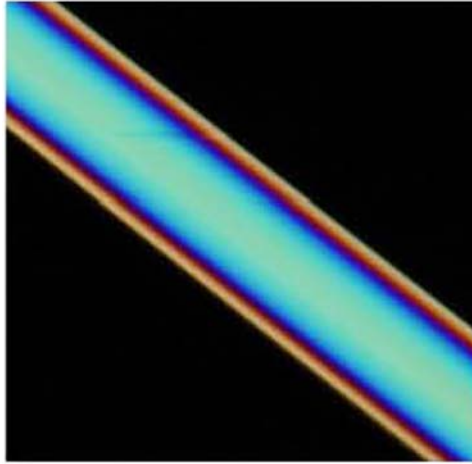


Figure 3.7 Interference colors in a nylon 6 fiber. Because of the cylindrical shape of the fiber, the “thickness” decrease from the central axis to the borders, giving rise to colored longitudinal strips. *Published with permission from Nikon MicroscopyU.*

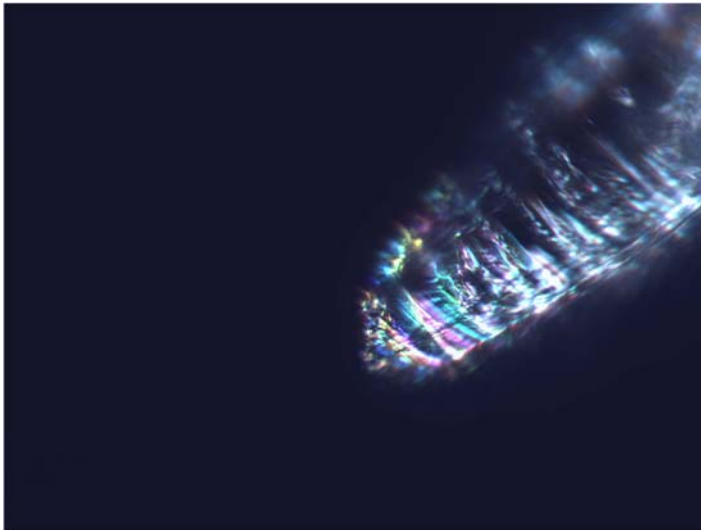


Figure 3.8 Micrograph of a wedge cut nylon 6 fiber, showing transversal interference colors at the end.

3.4 Crystallographic orientations and extinction positions

Crystallographic directions in solids may be revealed by cleavage, twin planes, and crystal faces. Because of the relationship between crystallographic

and optical directions in crystal systems, polarizing microscopy provides useful crystallographic information for birefringent solids. Readers not familiar with the subject can benefit from Ref. [25]. Crystallographic axes are three intersecting lines such that if one plane of the system makes intercepts a , b and c on them, any other plane of the system will make intercepts na , nb , nc with n integer. If the three crystallographic axes are orthogonal to each other, the crystal belongs to a monometric system if $a = b = c$, to a dimetric system if two of the three intercepts are equal, and to a trimetric system if the three intercepts are all different. The hexagonal system has three nonorthogonal axes forming equal angles with each other and three equal intercepts. In the monoclinic system, two axes are orthogonal to the third, in the diclinic system two axes are orthogonal to each other, in the triclinic system all axis is inclined. As already stated, substances that crystallize in the symmetric cubic lattice do not show birefringence at all. Therefore, if all sections of a true solid are indistinguishable from the dark background at crossed polarizers, it means that the solid belongs to the cubic crystallographic system. A birefringent section of a crystal will appear extinct four times for a 360-degree rotation of the stage. Extinction occurs when the polarization direction is parallel (or normal) to one of the optical directions (i.e., the vibration directions of the two birefracted rays, respectively in the plane determined by the optical axis and the incident direction, and the orthogonal plane). The birefringence will reach a maximum for positions at 45 degrees with respect to each extinction position. Because of the different relationship between crystallographic and optical directions in different crystal systems, polarizing microscopy provides useful crystallographic information also for birefringent solids. Tetragonal and orthorhombic systems are characterized by three axes at 90 degrees to each other. The hexagonal system shows three axes at 120 degrees to each other and an axis at 90 degrees to the plane of the other three axes. For uniaxial crystals the crystallographic axis c coincides with the optical axis of the indicatrix and, hence, the optical directions coincide with crystallographic directions. Therefore, sections of uniaxial materials (tetragonal and hexagonal systems) showing crystallographic directions relative to the c axis or to the perpendicular (001) plane, will show parallel extinction illustrated in Fig. 3.9A. A parallel extinction for a section of mineral showing parallel cleavages (indicating a crystallographic direction) is hence sufficient to classify the mineral in the dimetric group. Briefly, we can say that both principal and inclined sections of uniaxial minerals show parallel extinction characteristics of the dimetric group.

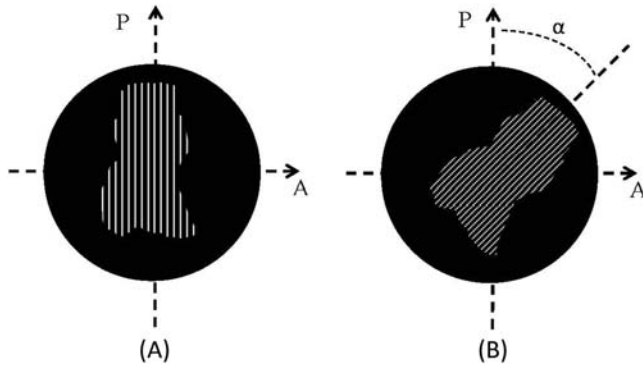


Figure 3.9 Parallel (A) and inclined (B) extinction of a mineral with cleavage lines, identifying crystallographic directions.

The extinction type of biaxial minerals depends on the relative orientation of the optical indicatrix within each specific crystalline lattice of the trimetric group. For the orthorhombic system, the three crystallographic axes have to coincide with the three axes of the optical indicatrix. Sections of minerals of such a system parallel to one of the crystallographic axes and showing crystallographic directions relative to one of the axes, will show parallel extinction. Sections of an orthorhombic crystal oblique with respect to the three crystallographic axes, showing cleavage lines relative to one of the axes, will show inclined extinctions since none of the two birefracted rays is polarized along the direction of the cleavages. The angle between the parallel cleavage planes and the polarization direction of light is the extinction angle, shown in Fig. 3.9B. When the section of an orthorhombic crystal parallel to one of the crystallographic axes shows a double set of cleavage planes parallel to one of the two remaining crystallographic axes, the extinction will be symmetric relative to the two cleavage systems. In this case, the axis of the optical indicatrix, corresponding to the crystallographic axis parallel to the section, coincides with the bisectrix of the opposite angles formed by the two types of cleavage planes.

For a mineral of the monoclinic system, only the crystallographic axis *b* coincides with one of the axes of the optical indicatrix. If the section under the microscope is parallel to the such axis, then it will show parallel extinction. All oblique sections showing crystallographic directions will be characterized by an inclined extinction. The maximum extinction angle may be an identifying characteristic of monoclinic minerals, such as pyroxenes.

For minerals of the triclinic system, none of the three crystallographic axes can coincide with one of the axes of the optical indicatrix and, as a consequence, every section of these minerals will show an inclined extinction.

3.5 Compensators and retardation plates

Compensators and retardation plates consist of birefringent materials (usually mica, quartz, calcite, and gypsum) with a known orientation producing a likewise known retardation between the birefracted rays. A Berek compensator is cut perpendicularly to its optic axis as a parallel plate and mounted between two glass layers. The plate is able to rotate around its long axis, so as to tilt its optic axis away from the direction of the incoming light. A tilted plate appears anisotropic and retardation is created. The larger the tilt, the larger the retardation [26]. Compensators have a variable optical path length, whereas retardation plates have a fixed optical path. The three most common retardation plates produce optical path length differences of an entire wavelength ($\cong 550$ nm), one-half wavelength ($\cong 270$ nm), or a quarter wavelength ($\cong 143$ nm). These accessories allow the measurement of the birefringence and the identification of the planes of the polarized light with the higher and the lower refractive index propagating within an anisotropic substance. The use of compensators and retardation plates, which are positioned on the optical path of the waves birefracted by material, is based on Eq. (3.1). As already seen, the interference colors of a material change with changing $\Delta S = d(n_1 - n_2)$. Therefore, the use of one of these equipment will change the retardation between the waves emerging from the analyzer, causing a change in the interference color of a material. Compensators are usually laminae rotating around an axis lying in the plane of the lamina itself, or wedges with variable thickness. By rotating the lamina or by moving the wedge, the optical path difference ΔS changes because of the change of the lamina orientation or thickness. In both cases, the motion of such compensators will originate all colors of the Michel–Levy chart between the dark gray and the color of maximum birefringence (usually corresponding to a 90-degree rotation) or the colors between the minimum and the maximum thickness. Retardation plates originate one color, which is subtractive or additive with respect to the interference color of the specimen. For the measure of the birefringence of a material, compensators and plates are oriented such that the vibration directions of the birefracted rays are at 45 degrees from the polarization direction of light. When no

birefringent specimen is on the stage, the interference color of the compensator, or retardation plate, is observed at the maximum intensity. The vibration direction of the slow wave is indicated by an arrow incised on the rectangular frame containing the retardation plate and is usually parallel to the short side γ of the frame. The interference color of a specimen is conveniently appreciated, in absence of compensators and plates, at 45 degrees with respect to the extinction positions. Then a compensator or a retardation plate is inserted, and the variation of the interference color of the specimen, or the change of colors with the change of the thickness or birefringence of the retardation material, is observed. According to this geometrical arrangement, the polarization directions of the specimen and those of the compensator or plate are coincident. If the slow axis of the specimen has the same direction of γ , then the colors increase towards high orders. This circumstance is referred to as “additive” since the total optical path is given by the sum of the optical paths of the sample and that of the compensator (or plate). Vice versa, if the slow axis of the specimen is normal to that of the compensator or plate (i.e., coincides with the fast wave of the compensator), subtractive colors appear and the total optical path will be given by the difference between the optical path of the sample and that of the compensator or plate. Once identified the subtraction direction, the compensator is moved or the plate is rotated in such a direction until extinction is achieved. At extinction, the optical path of the compensator or plate, which is known, is equal to that of the specimen. Knowing the thickness of the specimen, from appropriate tables it is possible to derive its birefringence. Moreover, a qualitative test due to Brewster [22] allows for determining the birefringence sign of elongated sections of minerals and fibers. This test required a parallel extinction, however, it is still valid for small extinction angles. The elongated structure is oriented according to the extinction position, which should be normal or parallel to the polarization plane of the incident light. From the extinction position, the specimen is rotated at 45 degrees such that the elongation direction is parallel to the γ direction of the plate. If the interference color of the sample rises relative to the interference color of the retardation plate, then the slow wave in the sample vibrates parallel to the slow wave of the retardation plate, vice versa, if the color goes down, the fast wave vibrates parallel to the γ direction of the retardation plate. Fig. 3.10 [27] illustrates the Brewster test for an elongated structure weakly birefringent, showing a first-order gray interference color in absence of a λ plate. In this case, the two complementary interference

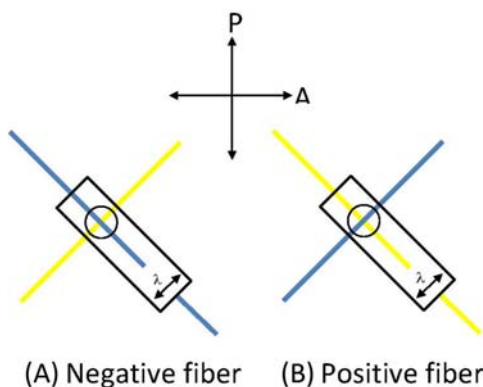


Figure 3.10 Scheme of the Brewster test for determination of the birefringence sign of a fiber. When a fiber is parallel to the long side of the frame of the retardation plate: (A) a fiber with a negative birefringence sign appears blue; (B) a fiber with a positive birefringence sign appears yellow. Reproduced from M. Raimo, *An optical test to unveil twisting of birefringent crystals in spherulites*, *R. Soc. Open. Sci.* 6(1) (2019) 181215. <https://doi.org/10.1098/rsos.181215>.

colors are the first-order yellow and the second-order blue, positioned respectively on the left and right side of the interference color of the λ plate (magenta). When the longer side of the frame of the λ plate is parallel to a fiber in the NW–SE direction, the sign is negative if the fiber is blue (Fig. 3.10A), positive if the fiber is yellow (Fig. 3.10B). By rotating the fiber at 90 degrees, the two interference colors are exchanged. Due to its low sensitivity, the $\lambda/4$ plate can be used only to determine the elongation sign of substances having a birefringence value sufficiently high to determine detectable optical path differences. Further use of a $\lambda/4$ plate aims to transform linearly polarized light into circularly polarized light and vice versa. $\lambda/4$ plates are often used to amplify the brightness and contrast of images of samples with low birefringence. For instance, through circularly polarized light microscopy it is possible to classify hematite crystals within iron ore into granular, lamellar, or lobular [28]. Since spherulites consist of elongated crystals, the Brewster test can be applied to determine the birefringence sign of spherulites, according to the colors of the two orthogonal sets of luminous sectors; these are separated by a Maltese cross having the interference color of the λ plate alone. Fig. 3.11 shows, for instance, two spherulites with oblate and oblong optical indicatrices respectively, which have, hence, opposite birefringence signs. Arrows indicate the polarization directions of the light behind (P) and forward (A) the specimen. Conventionally, the birefringence of spherulites is positive

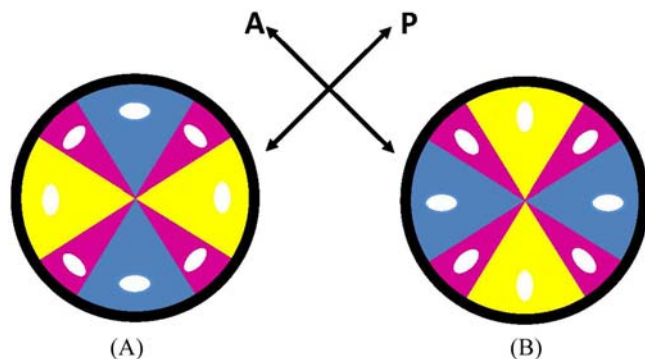


Figure 3.11 Evaluation of the birefringence sign of spherulites using a λ plate. Two spherulites with oblate and oblong optical indicatrices show opposite birefringence sign.

if the value of the refractive index measured along the radial direction is higher than the value of the tangential refractive index. On the contrary, a spherulite is defined as negative. The exact sign of each spherulite depends on the precise direction of the optical axis: assuming that the optical axis is the major axis of the ellipses, the birefringent sign is negative if the optical axis is tangential as in the spherulite on the left side of Fig. 3.11, positive if the optical axis is radial as in the spherulite on the right. This entails that the macromolecules, whose axes are parallel to one of the crystallographic axis [29], are oriented tangentially within the left spherulite and radially within the right spherulite. The opposite is true if the optical axis is instead the minor axis of the indicatrices. In polymers, the orientation of the optical indicatrix depends on the chain direction within crystals forming spherulites, therefore the birefringence sign depends ultimately on the chain orientation. However, it is worth specifying that to infer the chain direction in a radial crystal of a polymer spherulite, the birefringence sign of the spherulite must be compared to that of stretched fibers of the same polymer. In strained fibers, chain axes are mainly parallel to the elongation direction, and therefore spherulites should show the same optical sign as stretched polymer fibers if polymer chains are radially oriented, and the opposite optical sign if the chain axes are tangential within spherulites. Generally, from the discordance of optical signs between fibers and spherulites, it is assumed that chains are tangentially oriented [30]. According to Bunn and Alcock [31], when the radii of spherulites are directions of crystal growth, the crystals grow much faster in directions normal to the molecular axes than they do parallel to

the molecular axes; it is evidently much easier for a molecule to add on to the edge of a sheet of molecules than to start a new layer. In the case of polythene, we can scarcely imagine crystal growth (in the sense of accretion) taking place along the molecular axes. Growth would instead occur entirely at right angles to the molecular axes: we must imagine, in the formation of a spherulite, crystals growing outwards in all directions from a point, and growing by the continual side-by-side accretion of portions of very long-chain molecules. If spherulites of a certain polymer show the same sign of oriented fibers, indicating that the chain axes in the spherulites are radially oriented, the apparent discrepancy between the expected and true sign of birefringence may be explained by a different growth mechanism of spherulites: the spiral growth [32–35]. Indeed, if a 360-degree rotation of the plate of the microscope preserves throughout a Maltese cross in a polymer spherulite, the center of the Maltese cross is the nucleation point of radial isomorphous crystals with the same radial crystallographic orientation or the nucleation point of a unique thin crystal growing as a spiral. With very few exceptions, the macromolecular axis coincides with the crystallographic *c* axis in polymer solids. As a consequence, the optical axis of the growing crystals in polymer spherulites is normal to the crystallographic *c* axis and has radial or tangential directions according to the type of formation mechanism. The side-by-side accretion of macromolecules leads to a radially oriented chain in a spiral spherulite and to a tangentially oriented chain in radial spherulites so that the birefringence sign of the two types of spherulites will be opposite. A birefringent spherulite could be ideally generated by a 360-degree rotation around the microscope axis of a unique, real or hypothetical, thin crystal. Rod-shaped polymer crystals have the chain axis normal or parallel to the elongation direction if the arms of the Maltese cross coincide with the polarization directions of the microscope. If a spherulite is constituted of radial crystals, each of these crystals could reproduce by the fast rotation of the whole spherulite. In spiral spherulites, the crystal whose fast rotation could reproduce the circular appearance has no real existence, but it can be ideally replaced by a succession of separate crystallites along a radial direction. Optical properties and appearance of spherulites depend not only on the crystal structure and orientation but also on the growth mechanism. The optical differences between radial and spiral spherulites are ultimately due to the fact that radial spherulites are actually formed by elongated crystals, whereas along radial directions of spiral spherulites, there are sequences of separate portions of a wound crystal. Because of

this main difference between radial and spiral spherulites, often banding appears in spiral spherulites, whereas lines appear in radial spherulites when optical contact between close crystals is imperfect [22]. Therefore, the formation mechanism of a spherulite can be often inferred from its optical characteristics. The recognition of spirally grown spherulites, often indistinguishable from banded spherulites, explains why a same isomorph of a polymer can form both positive and negative spherulites. Indeed, although the polymer chain axes are still parallel to the growth front, the spiral wound of the growing crystal around the center of the spherulite leads to an almost radial arrangement of chains in the spherulite.

Retardation equipment can be also used for the evaluation of characteristic extinction angles. Once determined the angle between the lines of cleavage and one of the extinction directions for an unidentified mineral is, it is not known if the vibration plane in the extinction direction corresponds to the wave with the higher or the lower refractive index. This information is fundamental for the identification of several minerals, such as pyroxenes and amphiboles, and can be obtained using a retardation plane. The stage is rotated 45 degrees from the extinction position, such that the vibration direction of the ray with the higher refractive index is parallel or orthogonal to the γ direction of the plate. If the interference color increases, then the measured angle is the diagnostic angle $\epsilon\hat{\gamma}$ between the crystallographic direction ϵ and the vibration direction of the wave with the maximum refractive index. Otherwise, the color is subtractive and the measured angle is the angle complementary to $\hat{\gamma}$.

3.6 Conoscopic observations

Previous paragraphs involve orthoscopic observations, that is observations with parallel light. When the condensator for orthoscopic methods is replaced by a convergent lens, an objective of large numerical aperture and magnification ($40\times$ and $50\times$) is used and a Bertrand-Amici lens is inserted below the eyepiece, under crossed polars interference figures appear that allow distinguish uniaxial from biaxial substances and to establish the birefringent sign and optical axis dispersion. Observation under convergent (i.e., conic) light allows, moreover, the determination of the chirality of asymmetric substances.

The interference figures obtained in linearly polarized light are characterized by one or more extinction bars, which are referred to as isogyres, and colored curves referred to as isochromes. For instance, Fig. 3.12

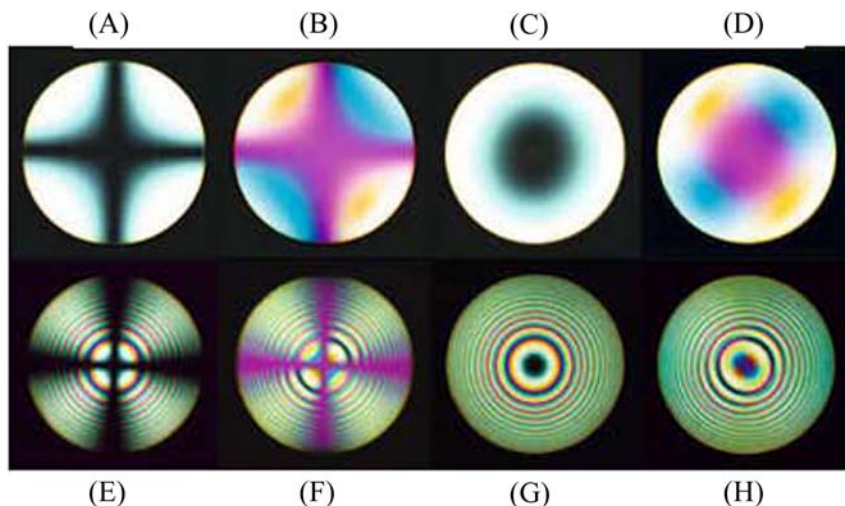


Figure 3.12 Conoscopic micrographs of positive quartz (*top row*) and negative calcite (*bottom row*) in linearly (A, B, E, F) and circularly (C, D, G, H) polarized white light. The use of a λ plate (B, D, F, H) allows determining the birefringence sign. *Published with permission from Carl Zeiss.*

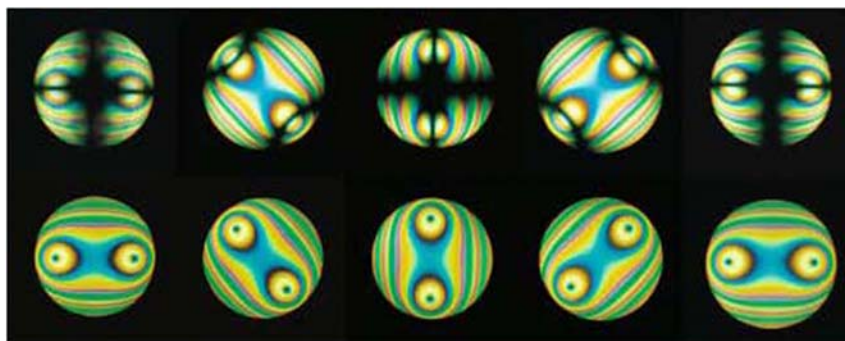


Figure 3.13 Conoscopic micrographs of a biaxial crystal of muscovite in linearly (*top row*) and circularly (*bottom row*) polarized white light. The crystal is consecutively rotated of 45 degrees, from 0 to 180 degrees. *Reproduced courtesy of Carl Zeiss.*

shows conoscopic images of birefringent uniaxial quartz and calcite. [Fig. 3.13](#) shows micrographs of biaxial muscovite.

As in orthoscopic observations, also in conoscopic observations extinction corresponds to vibration directions of the birefracted waves parallel or normal to the vibration direction of the incident light. Isochromatic curves arise from waves with the same retardation producing the same

interference color. Generally, the form and position of both isogyres and isochromes change by rotating the mineral section or the grain on the stage. In uniaxial figures, the isogyres form a dark cross that remains visible by rotating the stage. By rotating biaxial figures, instead, the dark cross splits into two branches of hyperbola, as shown in [Fig. 3.13](#).

Uniaxial solids can be identified by the typical interference figure of sections or grains with the optical axis orthogonal to the stage. These sections are recognizable in orthoscopic view since they are always extinct. Under conoscopic light, the correspondent interference figure consists of two orthogonal isogyres intersecting at the center of the section, referred to as melatope, and of a series of concentric rings with colors following the Michel–Levy chart (see [Fig. 3.12E](#)). The characteristic of this interference figure is the absolute invariability under rotation of the stage. Isochromes in these figures arise from the intersection of nappes of the conical light with a plane higher than that of the mineral section: each nappe cuts the section with a certain angle and, therefore, covers a definite optical path encountering a definite birefringence. The values of these two quantities determine the delay ΔS between the birefracted rays associated with each conical nappe. The retardation is a function of the aperture of the conical nappes and of the maximum birefringence of the mineral. As explained above, birefracted waves emerging from the analyzer originate interference colors. For sections with equal thickness but different composition, conical nappes with equal aperture originate different interference colors associated with two values of the retardation ΔS . The higher the maximum birefringence of a mineral section, the higher the retardation values. A highly birefringent mineral will show a high number of isochromatic curves, whereas a substance with low birefringence will show only gray and first-order white isochromes. Since the vibration planes of the ordinary and extraordinary rays are respectively tangential and radial with respect to the circular isochromes, the polarization directions of the polarizer and the analyzer are extinct, originating the isogyres. Sections with inclined optical axis have interference figures with a noncentral melatope, asymmetric isogyres, and ovaloid isochromes. The birefringence sign of a uniaxial substance can be determined by overlapping a λ plate to the interference figure of a section perpendicular to the optical axis. Indeed, the isogyres will acquire the interference color of the retardation plate, whereas the interference colors of the isochromes will increase or decrease according to the additive or subtractive position of the optical indicatrices of the section and the plate. Depending on the sectors

(I and III or II and IV) of the interference figure that acquire higher colors, it is possible to establish the birefringent sign (Fig. 3.12B, D, F, and H). As for elongated weakly birefringent crystals and fibers, white isochromes of low birefringence minerals will assume a yellow color in the II and IV quadrants and a blue color in the I and III quadrant if the refractive index is higher in the radial direction (positive birefringence), blue color in the II and IV quadrant and yellow color in the I and III quadrant if the refractive index is higher in the tangential direction (negative birefringence).

The interference figures of biaxial minerals are more complex. The simple figure (see Fig. 3.13) is obtained from the birefringent section normal to the bisectrix of the angle $2V$ between the optical axes. Rotating this section such that the plane of the optical axes overlaps with one of the polarization planes of the polars, the interference figure shows two isogyres of different thicknesses and ovoidal isochromes which change in elliptical with increasing the interference colors. The isogyres still form a dark cross positioned at the center of the figure. By rotating this figure of 45 degrees, the two isogyres transform in two branches of hyperbola, whose vertexes (melatopes) correspond to the exit points of the two optical axes. Therefore, the distance between these points provides a measure of the angle $2V$ between the optical axes when appropriate references with known $2V$ angles are used for comparison. Sections different from that orthogonal to the plane of optical axes will show not centered crossed isogyres in the extinction position and a likewise not centered hyperbola at 45 degrees. In particular, a section normal to an optical axis shows only a bar-shaped isogyre in the extinction position and one branch of hyperbola at 45 degrees. As for uniaxial interference figures, also for biaxial figures, it is possible to ascertain the birefringence sign. For a section normal to an optical axis, it is sufficient to orient the axis of the dark branch of hyperbola at 45 degrees relatively to the polarization directions and to observe the different changes of colors in the two regions separates by the isogyre (see Fig. 3.14A and B). As usual, opposite changes of colors will be indicative of opposite birefringence signs. For a section normal to the plane of the optical axes of the biaxial indicatrix, the change of colors concerns the region between the two isogyres and the regions between each isogyres and the contour of the interference figure (Fig. 3.14C and D). The laser conoscopic pattern of optically active crystals allows distinguishing between enantiomorphs when a $\lambda/4$ a plate of the known sign is used [36]. To enlarge the interference figures, which under monochromatic He-Ne laser ($\lambda = 632.8$ nm) show only gray-white colors, the

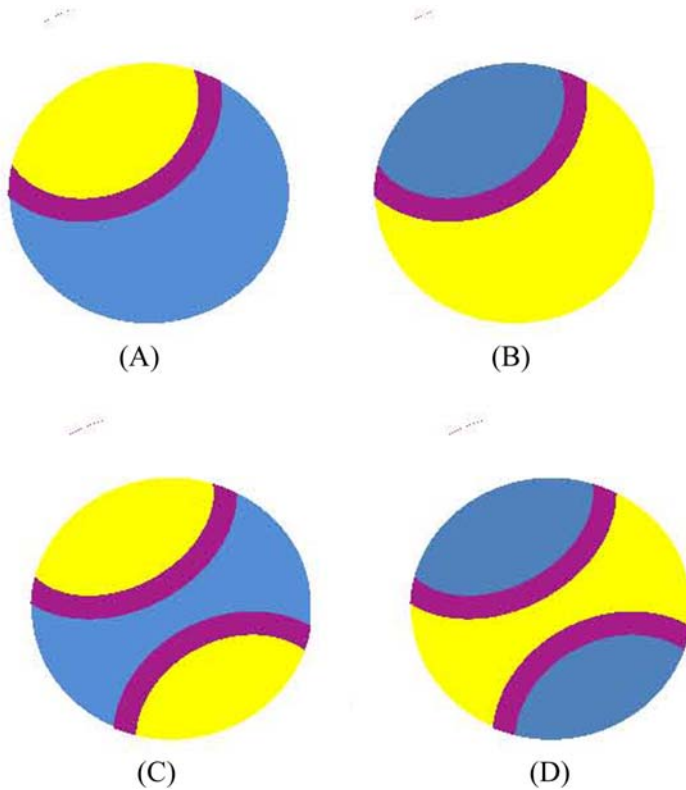


Figure 3.14 λ plate test to determine the sign of biaxial sections. (A and B) Conoscopic images of a section normal to an optical axis (A positive and B negative birefringence). (C and D) Images of a section orthogonal to the plane of the optical axes (C positive and D negative birefringence).

objective and the eyepiece of the microscope are replaced by a screen. The $\lambda/4$ plate transforms linearly polarized light into circularly polarized light with the electric vector rotating in the clockwise or counterclockwise direction. Sections of the optically active substance with the optical axis in the direction of the laser beam (i.e., with the optical axis normal to the plane of the section) observed with a $\lambda/4$ plate at 45 degrees between crossed polars, project on the screen a spiral pattern with isogyres visible only at the circular border, such that spiral isochromes are well visible in the central part of the interference figure. Depending on the spiral direction (clockwise or counterclockwise) and on the opposite quadrants (I and III or II and IV) which contain the beginnings of the spirals, it can be established if the crystal has the same or the opposite sign of the used $\lambda/4$ plate.

3.7 Observations with one polarizer: pleochroism, relief, Becke line

Although the polarizing microscope is mainly used at crossed polarizers, observations with one polarizer allow obtaining useful pieces of optical information, for instance pleochroism for birefringent colored materials and relief for both isotropic and anisotropic materials. Pleochroism indicates the change of the true color of a birefringent section of a substance with the variation of the relative directions of the polarization plane of the incident white light and the polarization planes of the birefracted waves. Since the absorption coefficients of the birefracted rays of a pleochroic substance vary with the wavelength and, moreover, the spectrums of the two rays are different, each of the two waves emerging from the material will have a color whose intensity ($I_0 \sin \varphi$ and $I_0 \cos \varphi$, respectively) will also vary with the angle φ between the polarization plane of the incident light and the polarization planes of the birefracted rays. The angle φ can be changed by rotating the polarizer or equivalently the microscope stage. To detect pleochroism, it is therefore needed to rotate the stage and see if there are changes in colors. The color of each wave will occur two times in a 360-degree rotation, when the polarization planes of the polarizer and of one of the refracted waves are parallel, whereas the average colors will appear four times in a complete rotation. Since each birefringent section has its own refractive indexes, different sections show different colors. The colors relative to the principal refractive indexes are referred to as primary colors. The uniaxial substance shows only two primary colors, whereas biaxial crystals show three primary colors. Only one or two colors are variable, respectively, in a section of a uniaxial or biaxial crystal. Although pleochroism may be very useful in the identification of minerals, it cannot be seen in all sections of a mineral. For instance, pseudo-hexagonal lamellae of biotite do not show pleochroism, which is instead evident (generally from brown to ocher) in perpendicular rectangular sections, where also cleavage planes are visible.

A substance shows a positive or negative relief, appearing on a higher or lower plane of the embedding material when it has a refractive index (or an average refractive index for birefringent substances) higher or lower than that of the surrounding. Relief is highlighted by the so-called Becke line, that is a bright thin halo at the interface between two different media. Focusing a plane higher (generally lowering the stage) than the common focus between two substances, the Becke line enters into the

substance with the higher refractive index. Vice versa, focusing a plane lower than the common focal plane, that is raising the stage, the Becke line will shift toward the substance with the lower refractive index. Fig. 3.15 shows a sample of isotactic polypropylene (iPP) containing a Kevlar fiber and crystallizing from the melt at a prefixed temperature. Two spherulitic layers are distinguishable [37]. Spherulites of one plane show a Becke line on the liquid side, spherulites on the upper plane show an inner Becke line. The presence of the Becke line is due to the imperfect orthogonality of the light that therefore incises vertical surfaces between different media, producing total reflection and refraction phenomena which, in turn, originate a higher illumination on one side of the interface.

The Becke line provides also a useful test for comparison of the unknown refractive index of a substance with that of a liquid. Particles of the samples are mounted in a liquid and viewed under a microscope with polarized light. If the refractive index of the substance is higher than that of the liquid, liquids with progressively higher indexes are chosen until the Becke line vanished. Vice versa, if the refractive index of the sample is lower than that of the first liquid. When the refractive indexes of the solid and the liquid are equal, the solid is not more distinguishable. The index

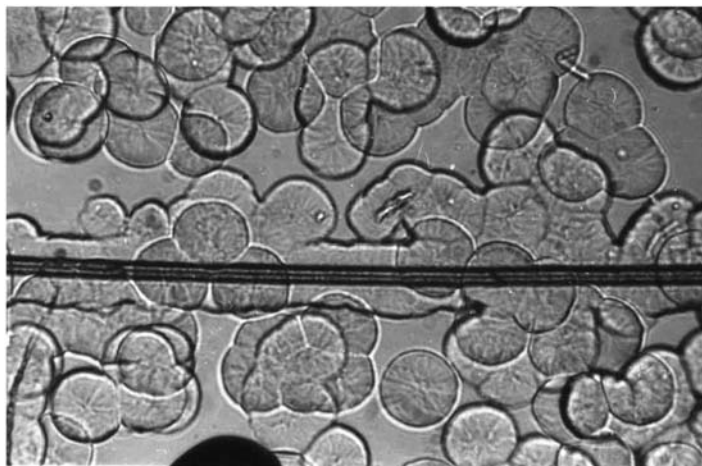


Figure 3.15 Micrograph (parallel polarizers) of a sample of iPP during crystallization at 123°C in the presence of a kevlar fiber, showing layered spherulites and transcrystallinity embedded in liquid iPP. The bottom and upper layer of spherulites show, respectively, an inside and outside Becke line.

of such a liquid, if unknown, can be measured with a refractometer. This method is easy for nonbirefringent samples, that is for monometric solids and amorphous materials, whereas the measurement of the average refractive indexes of uniaxial and biaxial substances requires the preparation and examination of numerous sections of a solid. For anisotropic materials it is convenient to measure the birefringent power; in the past, this measurement has been carried out by using a universal or Fedorow stage. Such a stage, which unfortunately is nowadays out of production, allows orienting a birefringent lamina in all possible directions by means of a complex system of graduated rings. The orientation corresponding to the higher color in the Newton series is associated with the maximum birefringence power, whose value is obtainable from the Michel–Levy chart. With its capability to rotate a lamina around four or five differently oriented axes, the universal stage is also useful to determine the extinction positions, that is the polarization directions of the birefracted rays and, hence, the angle $2V$ between the optical axes of biaxial crystals. Moreover, endowing the Fedorow stage with a device for temperature control, refractive indices can be rapidly determined by exploiting both temperature and wavelength variations to match the index of a mineral grain and a liquid with a minimal change of index liquids [38].

3.8 Summary and future perspectives

This chapter deals with the fundamentals of optical polarizing microscopy and its main applications. The concepts herein expressed help in designing and arrangement of optical measurements, aiming at the identification and characterization of a broad kind of samples in various fields. However, compared with electronic microscopies, traditional optical microscopy has a low-resolution power (usually two distinct points are hardly or not distinguishable at all when their distance is lower than 400 nm), due to diffraction. Recently superresolution optical microscopy has been developed that overcomes the limits imposed by diffraction, allowing special resolution up to 20 nm in biological samples or even less depending on the samples [39]. For instance, single-molecule localization microscopy, which includes stochastic optical reconstruction microscopy and photoactivated localization microscopy, extracts the positions of fluorophores by single-molecule localization [40]. Most of the superresolution techniques entail scanning-based data acquisition followed by reconstruction of a supersolution image and apply only to fluorescent samples. These techniques are

very useful for biological and biomedical applications, especially for in vivo observations. Many efforts in the development of white light superresolution microscopy with a broad range of applicability are in progress. For instance, new objectives referred to as SMAL (Super-Resolution Microscope Amplifier Lens, based on microspheres of diameter 15–250 μm) are claimed to achieve a resolution of 100 nm and lower, depending on the samples [41]. Holographic—Single Scatterer Localization Microscopy, or H-SSLoM, has been shown to apply also to nonfluorescent samples provided that they are able to scatter light [42]. In Ref. [42], Spatial Light Modulator, which represents an interesting optical device for microscopy, has been used to control the illumination pattern so that its results are composed of points randomly placed on the sample plane. Images produced by the only lightened points are then processed to obtain a dot density map for scattering centers localization.

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CHAPTER 4

Atomic force microscopy

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4.1 Introduction and principle of atomic force microscopy

Recent advances in nanotechnology have prompted many industrial processes to handle nanosized materials, such as nanoparticles, in order to benefit from their superior properties [1]. When handling nanoscale materials, it is of utmost importance to characterize them with molecular-scale resolution with regard to geometry and surface properties in order to control the quality of products produced [2].

The development of a series of scanning probe microscopes (SPMs), followed by the invention of the scanning tunneling microscope (STM) in 1982 [3], is regarded as an important cornerstone of progress in nanoscience and nanotechnology. The appearance of STM provided unprecedented access to single atoms on surfaces of conducting and semi-conducting materials. Atomic force microscopy (AFM), invented as an adaptation of SPM by Binnig et al. in 1986 [4], extended atomic level imaging to nonconducting surfaces by introducing the optical lever method and combining it with stylus probes and feedback control incorporated from the STM.

AFM has become a powerful tool for exploring surface structures and properties in various scientific and engineering research areas [5]. The widespread adoption of AFM can be attributed to the great advantages of AFM over other imaging techniques, which can be summarized in the following three points. First, the AFM can be operated in various environmental conditions, including liquids and gases, without vacuum or any conductive coatings. This versatility gives AFM measurements non-destructive nature, which is highly beneficial in various research fields. Second, the AFM enables in situ measurements. Not only surface morphology, but other surface properties such as stiffness, adhesiveness, viscosity, chemical structure, hydrophobicity/hydrophilicity, conductivity, and surface potential with nanometer resolutions can also be directly evaluated during scanning over a surface. In addition to surface imaging,

interaction forces between the probe and surface are also available in situ. Third, AFM surface observations and interaction force measurements with high resolution is relatively easy to obtain.

This chapter provides an overview of the principles of AFM and various advances in AFM applications for surface characterization and force measurements. In this section, the principles of AFM imaging and force measurements are described in detail. In [Section 4.2](#), the basics of surface imaging and characterization will be provided with examples of observations and current advances. In [Section 4.3](#), a variety of practical examples of force measurements in various systems will be introduced.

4.1.1 Principle of atomic force microscopy and imaging

The basic composition of a typical AFM instrument is illustrated in [Figure 4.1](#). The main elements which compose an AFM system include; the probe, laser, photodetector, piezoelectric scanner, and controller. The probe has a very sharp tip, the typical radius of which is 2–20 nm, attached to the end of a microfabricated cantilever, usually made either of Si or Si_3N_4 . The spring constant of commercial probes ranges typically from 0.01 to 50 N/m. Based on the locations of the incident beam at the detector, a laser beam is reflected from the rear of the cantilever to detect vertical deflections and lateral distortions of the cantilever with a four-segment photodiode detector. In response to the applied voltages, the probe is scanned over the sample surface by expanding or contracting the piezoelectric scanner. Commercial AFMs have a system either moves the probe attached to the scanner over the sample (in which case the sample remains stationary) or moves the sample on the scanner under the probe (the probe is stationary). In typical imaging, the signals from the photodetector are evaluated by a controller to adjust the z -displacement of the piezo scanner to keep the feedback control parameter constant (that is, the sample or probe moves upward and downward). Mapping the resultant z -piezo motions in the x and y directions yields images of the sample surface.

Conventionally two different modes are employed to obtain surface topographic images. One is contact mode, in which the probe scans over a sample surface whilst constantly in contact with the surface. The feedback loop adjusts the z -position of the piezo scanner to maintain a constant degree of deflection of the cantilever during the scan. The other is the dynamic mode, also known as the tapping mode. During scanning in

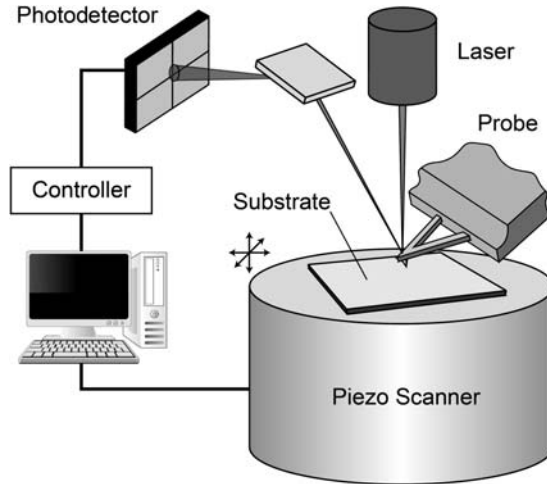


Figure 4.1 Schematic drawing of the atomic force microscope.

dynamic mode, the cantilever oscillates at a frequency near the resonance frequency. The feedback mechanism adjusts the z -position of the piezo scanner to maintain a consistent amplitude when the amplitude of the oscillation varies owing to the distance between the probe and the sample. The dynamic mode is more commonly used nowadays because it allows observations with less damage to the sample and the probe, which is particularly beneficial for observations of soft surfaces.

4.1.2 Principle of interaction force measurement

One of the most distinguishing characteristics of AFM is its ability to quantify interaction forces between surfaces in addition to surface imaging. The interaction forces between two opposed surfaces in air and liquid provide a crucial foundation for analyzing and managing particle behavior in a variety of engineering processes [6].

In order to measure the interaction forces, the probe or flat substrate is moved vertically (z -direction) to change the distance between the probe and the substrate. In most commercial AFMs, one measurement cycle consists of approaching the probe to the substrate, bringing them into contact, and retreating the probe from the substrate. During the cycle, the interaction forces acting between the probe tip and the substrate make the probe cantilever deflect vertically. The photodetector output voltage detects this deflection as a function of sample or probe displacement. A positive deflection usually represents a repulsive force. For the force

indicated in Fig. 4.2A, a repulsive force between the surfaces is observed for large surface separations, and the surfaces come into contact due to an attraction acting at a shorter range, shown by point A in the figure. If the attraction is strong, the surfaces often collide abruptly due to cantilever instability, which happens when the slope of the interaction force over the separation distance exceeds the cantilever spring constant. This is referred to as “jump-in.” When the surfaces come into contact, the change in cantilever deflection equals the change in displacement, resulting in a linear area known as the “constant compliance region.” Because the cantilever deflection is calculated by dividing the photodiode voltage by the slope of the constant compliance region, this region is critical for force measurement. An adhesion force may be noticed between the surfaces as they are separated. When the adhesion force appears between the surfaces, the cantilever normally experiences a jump-to-zero interaction

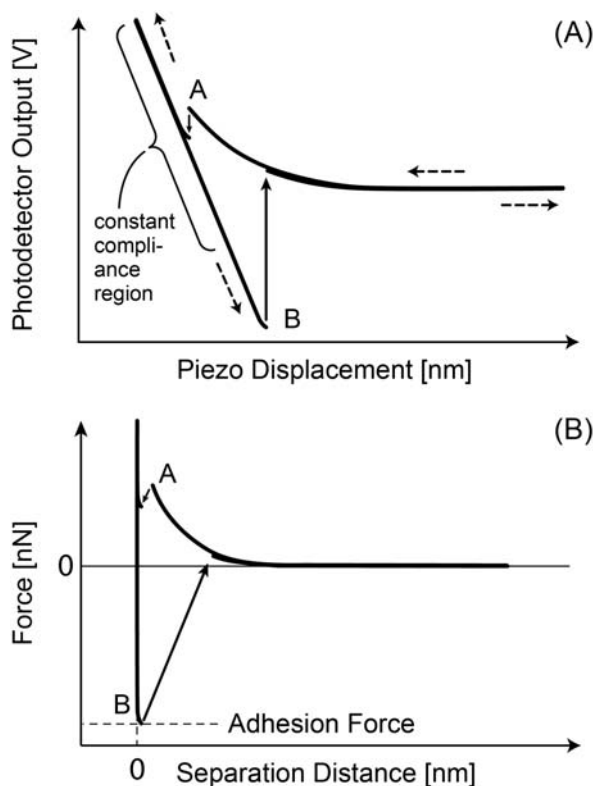


Figure 4.2 Schematic drawings of typical force data obtained in AFM measurements. (A) The raw data, (B) the force-separation distance curve converted from (A).

during retraction, as shown in the figure by point B. The reverse effect of the jump-in effect is known as “jump-out.”

The AFM basically lacks a device or method for directly measuring the separation distance between interacting surfaces. As a result, the force versus distance relationship must be determined using the AFM’s photodiode voltage vs. piezo displacement curve [7]. Using the constant compliance region, the separation distance can be determined by adding the cantilever deflection to the piezo displacement at each point. The force value is then calculated by multiplying the cantilever deflection by the cantilever’s spring constant, as illustrated in Fig. 4.2B.

It should be noted that this approach cannot ensure that the zero distance obtained is zero. A certain distance offset should be assumed if there is an adsorbed layer of any molecule on the surface and the molecules are not excluded from the surfaces when they come into contact. As a result, in AFM force measurements, the distance acquired using this approach should be regarded as the relative distance from the point of closest contact.

4.2 Surface characterization using atomic force microscopy

As previously mentioned, the images can be obtained in situ in both gaseous and liquid environments without the need for any conductive coatings and vacuum by AFM, unlike electron microscopy. As AFM has now become a very universal observation technique due to this advantage, “AFM imaging” has been the subject of many studies. On a yearly basis, more than 1000 AFM imaging-related studies get published nowadays*, including many review articles to show the progress and perspective in this field. Thus, providing comprehensive imaging examples that cover every field of AFM application is almost impossible. This chapter, therefore, provides the basics of surface imaging and characterization by AFM, with examples of observations mainly in biochemistry and polymer chemistry. These fields particularly take complete advantage of the non-destructive nature of AFM, enabling observation in the liquid phase and realizing the visualization of soft materials up to a molecular scale.

*Based on a search on Web of Science.

4.2.1 Height image and topographic characterization

Height imaging by AFM is used not only to observe the morphology of flat surfaces but also to evaluate the size and the shape of materials by depositing them onto a flat surface, as a handy technique for characterization. On the other hand, when the size of the samples to be observed is small enough to be comparable to the size of the probe tip, as in the case of nanomaterials, the accuracy of the image width of the surface feature decreases significantly. This is because the geometry and the width of the AFM tip broaden the image for the x and y dimensions [8]. In this case, the true images should be reconstructed by a deconvolution of the obtained images, which is usually performed by using image processing software. Alternatively, the image size in the vertical (z) dimension is sometimes used when the material is not deformable. In any case, however, the size evaluation by AFM imaging should be conducted carefully.

One of the most significant quantitative characteristics that may be derived from height images is surface roughness. AFM excels in measuring surface roughness at the nanoscale, with a resolution much beyond that of conventional stylus-based and optical approaches. The root mean square (RMS) roughness is commonly employed in AFM imaging to indicate the amount of surface roughness. The RMS roughness is calculated by the standard deviation of the z -values (heights of the sample) for the sample area. While surface roughness itself is a particularly important parameter to evaluate the morphological feature of the surfaces, it has also been related to functional properties of materials, such as adhesion [9], friction, [10] and optical [11] properties. A change in the roughness values often provides important information about the properties of the molecules present on the surfaces such as the conformational changes taking place as a result of environmental conditions [12].

After its invention, AFM was swiftly recognized as having important potential applications in biochemistry because of its ability to capture images of materials in situ in a liquid environment without coating, staining, or freezing samples. Thus, there have been early accomplishments of direct imaging on biomolecules such as soluble proteins [13] and DNA–protein complexes [14]. Despite the inherent difficulty to obtain stable images of soft, deformable samples, direct imaging of cells also became already a reality in the mid-1990s as shown in Fig. 4.3A [15]. Then, detailed submolecular analysis using advanced AFM has been developed for small materials such as proteins and DNAs, as described later.

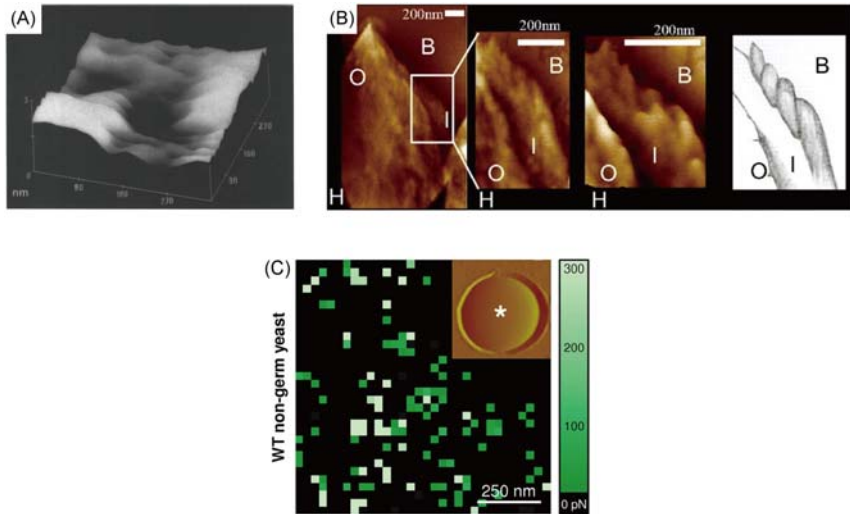


Figure 4.3 High-resolution AFM imaging of biomaterials. (A) Image of lamellipodium surface of an MDCK-F cell. (B) Image of an inner peptidoglycan surface of *Bacillus subtilis* showing helical arrangement of the cross striations. (C) Adhesion force mapping on yeast cells for detecting Als3 protein using AFM tips terminated with an anti-Als3 antibody. Adapted with permission from H. Oberleithner, E. Brinckmann, G. Giebisch, J. Geibel, *Visualizing life on biomembranes by atomic force microscopy*, *Kidney Int.* 48 (1995) 923–929, Copyright (1995), with permission from Elsevier; E.J. Hayhurst, L. Kailas, J.K. Hobbs, S.J. Foster, *Cell wall peptidoglycan architecture in *Bacillus subtilis**, *Proc. Natl. Acad. Sci. USA* 105 (2008) 14603–14608, Copyright (2008) National Academy of Sciences, USA; A. Beaussart, D. Alsteens, S. El-Kirat-Chatel, P.N. Lipke, S. Kuchariková, P. Van Dijck, et al., *Single-molecule imaging and functional analysis of als adhesins and mannans during *Candida albicans* morphogenesis*, *ACS Nano* 6 (2012) 10950–10964, Copyright (2012) American Chemical Society.

On the other hand, for cells, for their relatively large size, the enhanced resolution of the conventional AFM allows more detailed subcellular analysis. Improved stability and resolution of imaging have brought novel structural information such as pore-like structures at the epithelial cell surface [16] and the architecture of the peptidoglycan on the bacterial cell wall [17]. AFM may also be used to assess the local characteristics of cellular surfaces by measuring the interaction force between the cell surface and an AFM tip that has been modified with different molecules. The Als3 protein in yeast cells is a recent example of a molecular mapping investigation [18]. AFM tips ended with an anti-Als3 antibody were employed in this case to identify the presence of Als3 on cell surfaces with nanometer-order resolution.

Another distinguishing aspect of AFM imaging in biochemistry is the constant development of improved AFM equipment integrated with other microscopes or instruments. Integration of AFM and confocal laser scanning microscopy [19], for example, which are especially appropriate technologies for imaging biological systems, have effectively given a revolutionary way of simultaneous high-resolution structural and fluorescence imaging for cells and membranes.

Another example of AFM imaging integrated with other characterization methods frequently used in biochemistry is AFM-Raman spectroscopy. In particular, tip-enhanced Raman spectroscopy (TERS) is a quite powerful chemical imaging tool [20], which achieves a very high spatial resolution (4 nm). In TERS, a laser is irradiated to a sharp metal or metal-coated AFM tip. By laser irradiation at the apex of the tip, a local electromagnetic field is enhanced at the tip, causing intense Raman scattering. This enables surface-enhanced Raman spectroscopy simultaneously with surface imaging. As TERS is a label-free, real-time, and high-resolution method, many biological materials are extensively studied utilizing this method, including DNA [21], proteins [22], and amyloid fibrils [23].

Using AFM in polymer chemistry has resulted in the retrieval of direct pictures of polymer chains as single molecules. The first high-resolution direct measurements of individual polymer chains were made using polyethylene chains in cold-extruded microfibrils in 1991 [24]. The surface texture pattern with repeat distances along the chain corresponding to the separation between the CH₂ groups of 0.25 nm indicated extended chain conformation of the polyethylene molecules. The first example of capturing single polymer chains with molecular resolution would be the visualization of *Escherichia coli* RNA polymerase complexes with DNA fragments deposited on mica [25]. Often, biomolecules such as DNAs and peptides were used to visualize individual chains in the early stage of single-chain observations, probably because the molecular length and conformation control is easier than those of synthetic polymers. Single-chain observation for synthetic polymers subsequently progressed, including a random conformation of poly (2-vinyl pyridine) (P2VP) chain (Fig. 4.4A) [26] and branching topology in polyacrylates (Fig. 4.4B) [27]. The structural features of macromolecular chains have been successfully evaluated using AFM observation, including the chain helicity of phenyl isocyanides and cholesteric liquid crystals [28], topologies of knotted polymers [29], and unimolecular micelles of block copolymers [30].

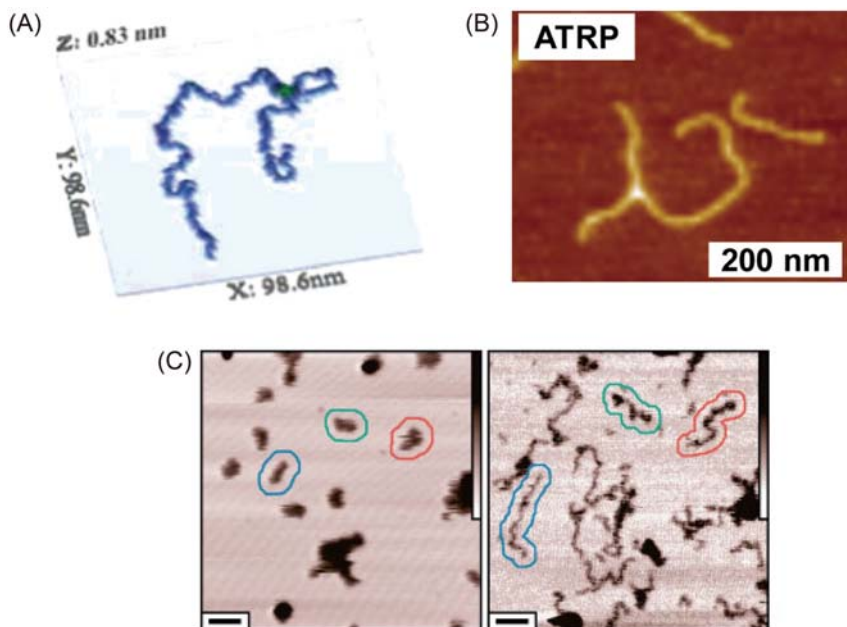


Figure 4.4 Imaging of individual macromolecules by AFM. (A) 3D image of single P2VP molecule adsorbed on mica. (B) Molecular image of a poly(*n*-butyl acrylate) brush made from a poly(2-(2-bromopropionyloxy)ethyl acrylate) backbone. (C) Images of P2VP molecules on mica compacted by exposure to ethanol vapor (left) and extended in water vapor (right). Adapted with permission from Y. Roiter, S. Minko, *AFM Single molecule experiments at the solid – liquid interface: in situ conformation of adsorbed flexible polyelectrolyte chains*, *J. Am. Chem. Soc.* 127 (2005) 15688–15689, Copyright (2005) American Chemical Society; S.Y. Yu-Su, F.C. Sun, S.S. Sheiko, D. Konkolewicz, H.-I. Lee, K. Matyjaszewski, *Molecular imaging and analysis of branching topology in polyacrylates by atomic force microscopy*, *Macromolecules* 44 (2011) 5928–5936, Copyright (2011) American Chemical Society; M.O. Gallyamov, A.R. Khokhlov, M. Möller, *Real-time imaging of the coil-globule transition of single adsorbed poly(2-vinylpyridine) molecules*, *Macromol. Rapid Commun.* 26 (2005) 456–460, Copyright (2005) Wiley.

AFM has also helped in observing molecular-scale processes of polymers reacting or interacting on substrates. The vapor-divided coil–globule transition of adsorbed poly(2-vinyl pyridine) molecules on mica when exposed to vapors of ethanol or water was envisaged in real time (Fig. 4.4C) [31]. Then, many processes such as adsorption-induced degradation of brush-like polymers [32] and cis-to-trans reversion of ABA-type triblock copolymer [33] on substrates have been successfully characterized.

One of the integrated methods with other instruments frequently used in polymer chemistry is AFM-IR [34]. In AFM-IR, a pulsed tunable IR laser is irradiated to the samples to be imaged. The irradiated laser induces photothermal heating to the sample when its wavelength corresponds to an absorption band of the sample. It causes a local material expansion, which excites oscillations of the AFM cantilever at its resonance frequency. Fourier transformation of the oscillation amplitudes against the laser wavenumber gives IR absorption characteristics of the sample material [35]. This feature of AFM-IR is quite useful to understand the chemical distribution of polymer blends consisting of multiple components, by mapping absorption intensity for specific wavelengths [36]. This technique was also successfully applied to identify additives such as antioxidants and lubricants in a polymer film [37].

4.2.2 Imaging modes for the characterization of surface properties

Except for the topological images, AFM can visualize the distribution of various properties of the sample surfaces utilizing its feedback principle. Thus far, a number of imaging modes have been developed based on the two previously mentioned primary imaging modes, namely, contact mode and dynamic mode. Some typical imaging methods are described here.

Phase imaging is probably the most extensively used imaging mode. This mode allows one to evaluate the viscoelastic properties of the material surfaces, which are not clearly detected in the height images in most cases, as shown in Fig. 4.5 [38]. During scanning using the dynamic mode, the alterations in the oscillation phase between the signal driving the probe and the actually observed signal are monitored in phase imaging. The phase shifts can be correlated to the differences in the surface properties such as elasticity and adhesion. Thus, by mapping the degree of the shifts over the surfaces, information about the variations in the surface viscoelastic properties can be obtained, which is complementary to the information derived from the height image. While phase imaging is generally used to characterize the viscoelastic properties of the sample material on flat surfaces, it has also been applied to detect the chemical heterogeneity of microparticles of size < 10 nm [39,40].

Lateral force microscopy (LFM), also known as friction force microscopy, allows the relative strength of the lateral (frictional) force between the tip and the sample surface to be imaged. The contact mode may capture LFM and height pictures at the same time. Because of the frictional

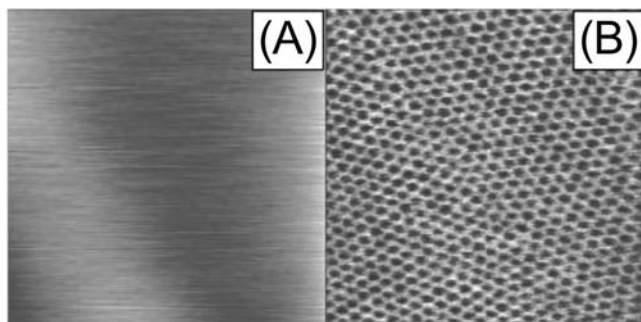


Figure 4.5 AFM height image (A) and corresponding phase image (B) of a hydrogenated poly(butadiene-*b*-ethyleneoxide) film on a silicon wafer prepared by spin coating. Reprinted with permission from G. Reiter, G. Castelein, J.-U. Sommer, A. Röttele, T. Thurn-Albrecht, *Direct visualization of random crystallization and melting in arrays of nanometer-size polymer crystals*, *Phys. Rev. Lett.* 87 (2001) 226101, Copyright (2011) American Physical Society.

force between them, the cantilever twists while scanning the tip over a sample surface. The lateral displacement of the laser on the photodetector may be used to determine the degree of cantilever twisting. The distribution of the relative intensity of the friction over the surface is provided by the mapping of the lateral output signals. LFM has been used to investigate the frictional properties of various materials such as polymers [41], metal oxides [42], and carbon materials [43].

Lieber et al. [44] created a method known as chemical force microscopy (CFM) to detect and map the spatial distribution of chemical functional groups on surfaces, therefore expanding the usefulness of LFM. These authors modified the tips and samples with a self-assembled monolayer of COOH and CH₃ groups and conducted the LFM mapping of the sample. The obtained images indicated the patterns of these groups arising from the differences in the adhesion force between CH₃/CH₃, CH₃/COOH, and COOH/COOH groups on the tip and the sample, and were correlated directly with the frictional force. The CFM technique has now been developed so as to detect the distribution of various molecules on the surfaces at a spatial resolution down to 10 nm [45].

Electrostatic force microscopy (EFM) and Kelvin probe force microscopy (KPFM) are also important characterization techniques, allowing mapping of the electrostatic properties of solid surfaces by applying a voltage between an AFM tip and a sample. EFM applies a voltage to the oscillating cantilever. During the scan of the sample surface, the

electrostatic forces cause a change in the oscillation amplitude and phase, which can be related to electrical properties such as the surface potential and/or the charge. In KPFM, both AC and DC voltage is applied to the cantilever, inducing an oscillating electrostatic force between a tip and a sample. The DC voltage is feedback controlled to minimize the deflection oscillation of the probe. The voltage equals the local contact potential difference between the tip and sample, which enables the mapping of the surface potential. Both techniques are powerful tools to investigate the local electrostatic properties of various device materials including semiconductors [46,47], organic materials [48,49], and solar cells [50], achieving nanoscale mapping of their surface potential. Although these methods are used in the air, they are also utilized to the characterization of biomolecules [51,52].

4.2.3 Recent advances in atomic force microscopy imaging

As has been mentioned previously, AFM is now used as a universal technology in different fields of science. Currently, the evolution of AFM has two main directions: higher resolution with a subatomic-level resolution to detect atoms and bonds between them and higher speed to enable the observation of molecular motion.

For improved resolution, advances in the frequency modulation (FM) technique, a type of noncontact imaging mode originally invented in 1991 [53], are important for achieving subatomic resolution. In the FM mode, the cantilever oscillates at or near its natural resonant frequency during scanning. Because of the interaction force between the cantilever tip and sample, the shift in resonant frequency Δf is directly detected. An FM demodulator is utilized to detect the Δf , and feedback is then employed to keep the cantilever oscillating at its resonant frequency and constant amplitude to accurately maintain the distance between the tip and sample throughout scanning.

Initially, subatomic resolution imaging by FM-AFM was performed under an ultrahigh vacuum. In the vacuum, a Q factor of a cantilever resonance becomes extremely high compared to air, resulting in a high force resolution. Furthermore, the vacuum-like condition enables experiments under well-controlled atomically clean conditions. A visualization of sub-molecular structures was first achieved for small organic molecules using a specially customized probe known as qPlus sensor with etched W wires bonded to the tip of a quartz tuning fork and passivation of the tip apex

modifying it with an inert CO molecule to avoid unintentional manipulation. The images of a pentacene molecule, including the atomic and bond images inside it, were first captured in 2009 [54]. Since then, many studies have contributed to applying this bond imaging technique to visualize

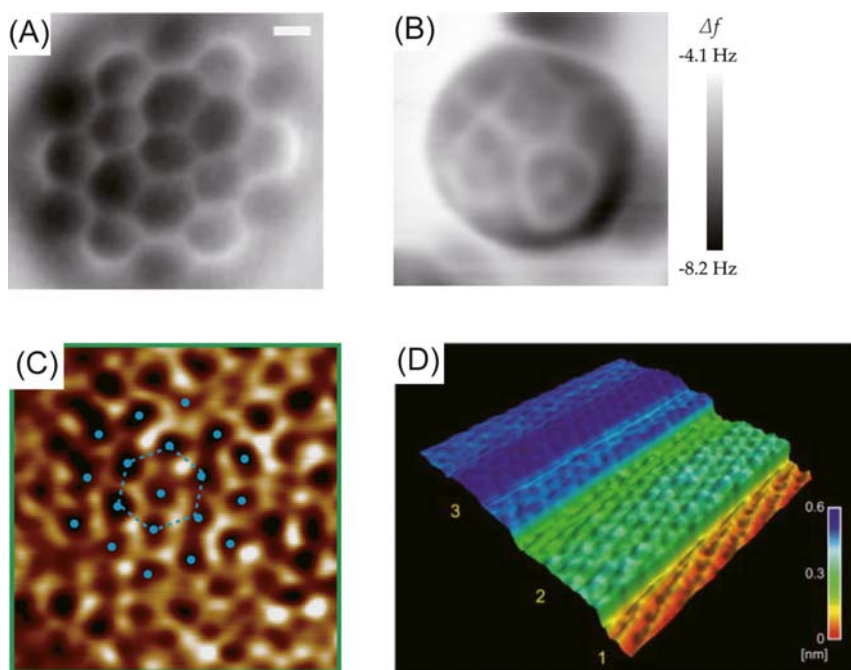


Figure 4.6 Subatomic resolution imaging by FM-AFM. (A) Image of a polycyclic aromatic hydrocarbon with chemical bond resolution acquired with a CO-modified tip and ball and stick model of the molecule. (B) Δf image of C60 molecule. (C) Image of pillar[5]arene monolayer film. The dot features indicate that the hexagonal voids displayed high regularity. (D) Image of the DPPC bilayer in phosphate buffer solution. The images for three different terraces are shown. *Reproduced with permission from X.-Y. Wang, M. Richter, Y. He, J. Björk, A. Riss, R. Rajesh, M. Garnica, F. Hennersdorf, J.J. Weigand, A. Narita, R. Berger, X. Feng, W. Auwärter, J.V. Barth, C.-A. Palma, K. Müllen, Exploration of pyrazine-embedded antiaromatic polycyclic hydrocarbons generated by solution and on-surface azomethine ylide homocoupling, Nat. Commun. 8 (2017) 1948; C. Moreno, O. Stetsovych, T.K. Shimizu, O. Custance, Imaging three-dimensional surface objects with submolecular resolution by atomic force microscopy, Nano Lett. 15 (2015) 2257–2262, Copyright (2015) American Chemical Society; T. Ogoshi, S. Takashima, N. Inada, H. Asakawa, T. Fukuma, Y. Shoji, et al., Ring shape-dependent self-sorting of pillar[n]arenes assembled on a surface, Commun. Chem. 1 (2018) 92; T. Fukuma, M.J. Higgins, S.P. Jarvis, Direct imaging of individual intrinsic hydration layers on lipid bilayers at ångstrom resolution, Biophys. J. 92 (2007) 3603–3609, Copyright (2007) Elsevier.*

several molecular systems on surfaces. The imaging of aromatic compounds [55] and polycyclic aromatic hydrocarbons (Fig. 4.6A) [56,57] with the possibility of discriminating bond order is only a small part of many research examples. Even intermolecular bonding between adsorbed molecules on a substrate can be detected [58], which is still under intense controversy on their interpretation. Using a modified technique, the complex 3D organic structures of the C60 molecule with intramolecular resolution have been visualized as shown in Fig. 4.6B [59]. These state-of-the-art investigations have led our understanding of molecular structures to a new level. Currently, the application of FM-AFM is being extended to quantify interatomic interactions, manipulate molecules and reactions, and determine molecular characteristics.

Despite the rapid development of FM-AFM imaging under ultrahigh vacuum, applications of FM-AFM in the liquid phase were limited in its early stages. The main challenge in realizing atomic resolution in the liquid phase is the low Q factor of a cantilever in liquids, which causes a low force sensitivity and leads to inaccurate and unstable oscillation of the cantilever. The atomic resolution image in the liquid phase was first obtained in 2005 for the surface of muscovite mica in water [62] by overcoming these negative factors. The technological innovation was based on three points as follows: (1) a relatively stiff cantilever to suppress thermal vibration and prevent tip adhesion to the sampling surface, (2) a cantilever with an extremely small oscillation amplitude to improve sensitivity to a short-range interaction force between tip and sample, and (3) the development of an ultra-low noise cantilever deflection sensor.

These technological improvements have opened new opportunities for various atomic-scale imaging in liquids using FM-AFM. The imaging of various inorganic surfaces such as calcite [63] and graphite [64], and surfaces covered with self-assembled monolayers [65] revealed the detailed structures of liquid molecules at a solid-liquid interface. Moreover, the subnanometer-scale imaging of various organic molecules (Fig. 4.6C) [60,66] and their self-assemblies [67] confirmed how the arrangement of such molecules occurs on a solid substrate. Such high-spatial-resolution imaging in liquids has considerable attention in bioscience-related research. Examples of imaging for biomolecules in liquids include secondary structures of proteins such as α -helices [68] and β -strands [69], lipid complexes with water (Fig. 4.6D) [61], and phosphate groups of DNAs [70].

The imaging speed of conventional AFM is slow, and the observed images are not clear in most cases if the scanning speed is increased. Therefore, it has been extremely impossible to make observations of molecular motions such as structural changes of biomolecules in real-time until the invention of high-speed AFM (HS-AFM) [71]. The HS-AFM noticeably reduced the time required to obtain an image by increasing the scanning speed several hundred times to realize real-time observations of molecular motions. HS-AFM is based on conventional tapping-mode AFM. The most important points to achieve high-speed scanning without reducing image clarity are speeding up the feedback process during scanning and minimizing feedback errors to maintain a constant interaction force between the probe and sample. For this purpose, high-speed scanners, high-speed amplitude measuring instruments, and microcantilevers with high resonance frequency have been developed [71]. This allows the HS-AFM to acquire images at 1–20 frames per second, thus making it possible to observe molecular motion in detail, similar to moving images.

HS-AFM is now primarily used to observe the motion of biomolecules. In particular, studies that capture the dynamic behavior of myosin V molecules moving on actin wires [72] as shown in Figure 4.7 has significantly impacted biomolecular research. Following these studies, motions of many other vital proteins and related biological systems have been obtained including molecular motors [73], molecular chaperones [74], channels [75], and transporters [76], membrane-associated proteins [77] and protein-DNA complexes [78]. These studies have visualized not only previously speculated molecular behaviors but also previously unnoticed behaviors, thus providing considerable insight into the functional mechanisms of these molecules.

4.3 Measurements of interaction forces by atomic force microscopy

As mentioned in Section 4.1.2, one of the most distinguishing characteristics of AFM is it can be utilized to evaluate interaction forces between surfaces. The introduction of the surface force apparatus (SFA) permitted the direct measurement of interaction forces between macroscopic solid surfaces in the air [79] and liquids [80] with molecular-level precision, which was the first significant advance in understanding surface forces in detail. However, despite the greater accuracy of the SFA, the surfaces used are practically restricted to mica and silica by instrumental

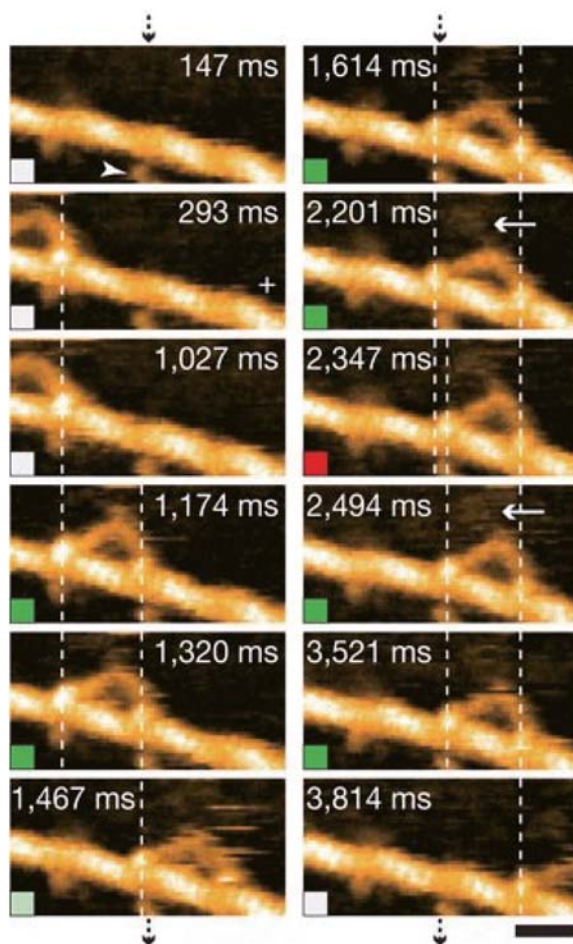


Figure 4.7 HS-AFM images of the processive movement of a myosin V molecule on an actin wire in $1\ \mu\text{M}$ ATP. Arrowhead and arrows show streptavidin molecule and coiled-coil tail of the myosin V, respectively. Adapted from N. Kodera, D. Yamamoto, R. Ishikawa, T. Ando, *Video imaging of walking myosin V by high-speed atomic force microscopy*, *Nature* 468 (2010) 72–76, Copyright 2010 Springer Nature.

requirements. In contrast, various materials can be used for AFM, overcoming the SFA limitations. As a result of the use of AFM to force measurements following SFA, the potential of force measurements has been extended to new study domains.

The use of the colloid probe (colloidal probe) technique [7,81] allows the quantitative measurement of forces between macroscopic surfaces, such as a particle and a flat surface. A spherical particle with a typical

diameter of 3–40 μm is attached to the end of a probe tip for the colloid probe (Fig. 4.8). Using a micro-positioning device, such as a micromanipulator, the particle is bonded with epoxy glue or hot-melt epoxy resin while being seen with an optical microscope or CCD camera. Currently, various colloid probes can be obtained commercially. When using a colloid probe, the force values are frequently divided by the radius of the probe particle since this value, according to the Derjaguin approximation, is proportional to the interaction potential between parallel surfaces.

4.3.1 Force measurements in gas phase

4.3.1.1 Capillary force

When particles are handled in air, the behavior, such as flowability, depends critically on the relative humidity because the formation of liquid bridges between particles leads to strong adhesion. A number of force measurements of capillary forces have been conducted using either a probe tip or a colloid probe against a flat plate or a particle. The fundamental force-distance profiles of the capillary force have been observed on separating the colloid probe and the plate [82,83]. The obtained forces were found to agree well with the theoretical capillary model under constant volume conditions, as shown in Fig. 4.9. The dependency of adhesion forces on the relative humidity is somewhat complicated as there has been some discrepancy in the data published thus far. Adhesion forces have been reported to increase monotonically [84,85] or in a step-like fashion [82] with increasing humidity in some cases, while in other cases

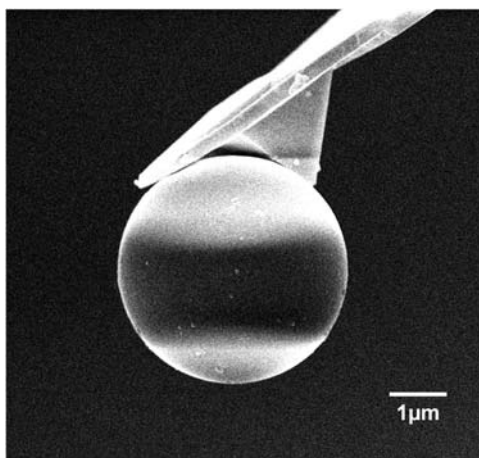


Figure 4.8 Scanning electron microscope image of a colloid probe.

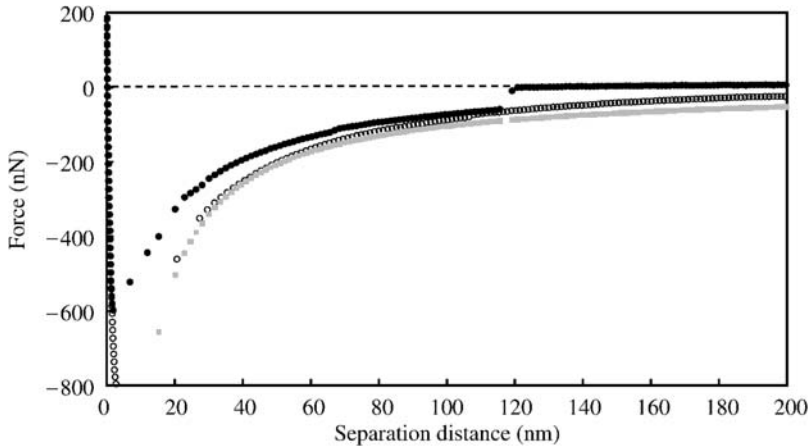


Figure 4.9 Approaching (closed circle) and retracting (open circle) force curves between a glass sphere and a glass surface in air at a relative humidity of 30%. The dashed line and solid gray squares show the van der Waals force and fit the constant volume capillary force model, respectively. Adapted with permission from S. Biggs, R.G. Cain, R.R. Dagastine, N.W. Page, *Direct measurements of the adhesion between a glass particle and a glass surface in a humid atmosphere*, *J. Adhes. Sci. Technol.* 16 (2002) 869–885. Copyright (2002) Taylor & Francis Ltd.

the adhesion had a maximum at a certain value of humidity [86,87]. Moreover, the adhesion between hydrophobic surfaces is less dependent on humidity [87]. These discrepancies are likely due to multiple factors including roughness, deformability, hydrophilicity, geometrical shape, dissolved species, and the size of the surfaces employed [88], but the detailed contribution of these variables to the overall capillary force is not yet completely understood.

4.3.1.2 Electrostatic force

The electrostatic force is the main source of the adhesive force in the gaseous state along with the van der Waals force and the liquid bridge (capillary force). Thus, the estimation of the electrostatic force is critical for particle handling. Although an electrostatic force has been measured using a normal probe [89], a tip with an applied voltage has been already used from the early stage of AFM force measurement [90], which then evolved into KPFM and EFM techniques introduced in the previous section. The direct measurement was subsequently expanded and modified to account for the cantilever shape [91] and relative humidity [92].

The colloid probe method has been employed in studies of electrostatic charging of single particles. Both model spherical particles [93,94] and particles used in applications such as printer toner particles [95] have been used. The particles are initially charged by various methods, such as simple contact with the surface [93], application of electric fields, [94] and charging with the beam in a scanning electron microscope [95]. Fitting the adhesion force between the particles and sample plates to theoretical models has allowed the charge density on particles to be estimated. Bunker et al. have utilized a similar method to analyze dynamic changes in the charge state of pharmaceutical particles [96].

4.3.2 Force measurements in liquid phase

Because particle dispersions in various liquids are employed in several industrial processes, analyzing, and managing particle dispersions is critical. The interaction forces between the surfaces (surface forces) of particles in dispersion, which depend intimately on the characteristics of the liquid, the surfaces, solutes, and so on, determine the behavior of particles in liquids. Evaluations of interaction forces in liquids are thus essential in many sectors of science and engineering in order to understand how particulate matter (including fluids such as emulsions and air bubbles) behaves in diverse systems. Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [97,98], introduced in the 1940s, provides the theoretical basis for surface forces between charged particles in aqueous solutions and is still used as a standard theory today. Developments in direct force measurements with SFA and AFM have not only provided an experimental confirmation of the DLVO theory but also found many forces outside the DLVO paradigm, often referred to as non-DLVO forces.

4.3.2.1 DLVO force

The total interaction force between two similar surfaces is defined by the DLVO theory as the sum of van der Waals attraction and electrostatic double-layer repulsion. Force measurements with the SFA and AFM between charged surfaces in aqueous electrolyte solutions confirmed that the observed forces agreed with the DLVO theory (Fig. 4.10), indicating that the DLVO theory can properly represent actual contact forces.

DLVO forces between many different types of surfaces have been measured using AFM. Gold [99], alumina [100], titania [101], zirconia [102], zinc, and lead sulfide [103] are among the metals and compounds that have been used. Polystyrene [104] and Teflon [105] were also used

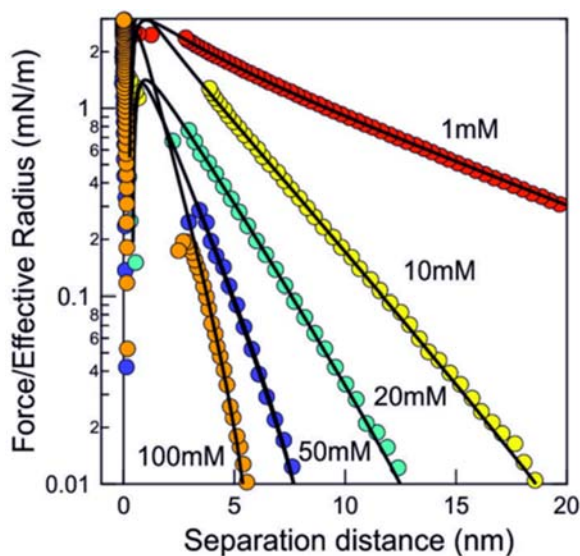


Figure 4.10 Force curves between latex particles at different KCl concentrations and pH 4 measured using AFM. The solid lines represent the theoretical data calculated from DLVO theory for each concentration. Adapted with permission from F.J.M. Ruiz-Cabello, M. Moazzami-Gudarzi, M. Elzbieciak-Wodka, P. Maroni, *Forces between different latex particles in aqueous electrolyte solutions measured with the colloidal probe technique*. *Microsc. Res. Tech.* 80 (2017) 144–152. Copyright (2017) Wiley.

to quantify the forces between polymer particles. Not only have measurements been taken between identical surfaces, but also between dissimilar surfaces [100,103].

4.3.2.2 Non-DLVO force

Although the force curves between charged surfaces in aqueous solutions recorded by SFA and AFM follow the DLVO theory well at surface separations of a few nanometers or less, the forces at shorter distances frequently diverge from the theory. This discrepancy is generated by the DLVO theory's assumption that liquids are a continuum. At these small distances, the physical attributes and granularity of trapped liquid molecules appear. The hydration force, which has a range of around 1–5 nm, is frequently measured instead of the expected van der Waals attraction between charged surfaces in aqueous electrolyte solutions, as shown in Fig. 4.11. The hydration force [106] is the energy necessary to remove hydration water (primary hydration) and hydrated ions (secondary hydration) from surfaces when they come into contact. For a 1:1 electrolyte,

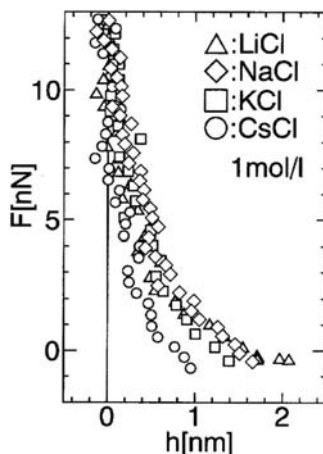


Figure 4.11 Forces measured between an AFM tip and a mica surface in 1 M electrolyte solutions of various monovalent cations. Adapted from K. Higashitani, K. Ishimura, *Evaluation of interaction forces between surfaces in electrolyte solutions by atomic force microscope*, *J. Chem. Eng. Jpn.* 30 (1997) 52–58.

the repulsive force is frequently represented empirically by an exponential function with a characteristic decay length in the region of 0.6–1.1 nm. More extensive SFA measurements revealed that the hydration force is not always monotonically repulsive, but rather oscillates at separations of less than 1.5 nm between molecularly flat mica surfaces [107]. The mean periodicity of the oscillatory force was found to be about equivalent to the diameter of the water molecule in this case.

The electrolyte species inevitably influence the properties of hydration forces. The range of the hydration force measured between mica surfaces increased following the hydration enthalpy of the cations (Fig. 4.11) in the order of $\text{Li}^+ \sim \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ [106]. This tendency was also observed between silica surfaces by AFM measurements [108]. Although the hydration force is a very short-range force, it significantly affects the stability of dispersions. The rapid coagulation rate of silica particles in high-concentration salt solutions was found to be reduced by the orders of magnitude when the particle size is less than 300 nm [109], which is attributable to the existence of the hydration force.

While hydration repulsion is a force that exists between hydrophilic surfaces, there is also an additional force that exists between hydrophobic surfaces. The strong attractive attraction between hydrophobic particles in aqueous liquids was empirically predicted due to their rapid aggregation.

The first direct force measurement, made in 1982 [110], demonstrated that the force is stronger than the van der Waals force. Numerous research has been conducted since then to understand the nature of hydrophobic attraction, which may reach hundreds of nanometers (an example of force data is presented in Fig. 4.12A). Because of its long-term nature, the origin of hydrophobic attraction is debatable.

The bridging of nanobubbles is recognized as the main cause of the long-range nature of the force. Nanobubbles can stably attach to surfaces that are highly hydrophobic and robust, such as surfaces hydrophobized by the chemisorption of hydrocarbons. The existence of stable nanobubbles on surfaces in contact with an aqueous solution was experimentally confirmed by AFM observations [111] (Fig. 4.12B) concerning the hydrophobic attraction [112]. In addition to nanobubbles, long-range electrostatic attractions can be the origin of hydrophobic attraction. When hydrophobic surfaces are prepared by the physical adsorption of surfactants or amphiphiles, they tend to form aggregates on the surface [114]. These aggregates can form when the surfaces approach each other [115]. The domains of these aggregates create patches with

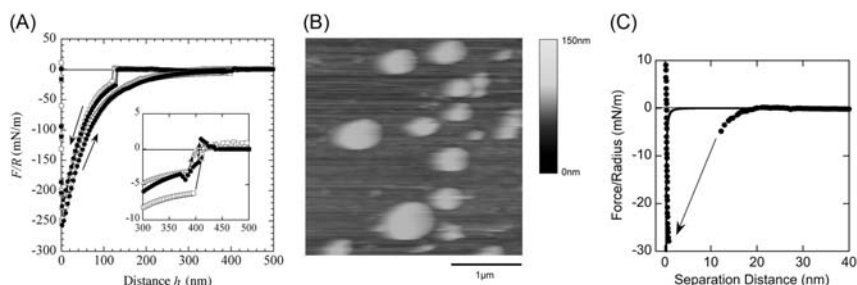


Figure 4.12 (A) Typical approaching and retracting force curves between the silica surfaces hydrophobized with octadecyltrichlorosilane (OTS) measured in water, (B) a tapping-mode AFM image ($2 \times 2 \mu\text{m}^2$) in water of the silica surface hydrophobized with OTS and (C) a typical approaching force curve in 1 mM NaNO_3 solution after the nanobubbles were completely removed. The solid line in (A) and (C) represents the calculated van der Waals attraction. Adapted from N. Ishida, T. Inoue, M. Miyahara, K. Higashitani, Nano bubbles on a hydrophobic surface in water observed by tapping-mode atomic force microscopy, *Langmuir* 16 (2000) 6377–6380, Copyright (2000) American Chemical Society; N. Ishida, M. Sakamoto, M. Miyahara, K. Higashitani, Attraction between hydrophobic surfaces with and without gas phase, *Langmuir* 16 (2000) 5681–5687, Copyright (2000) American Chemical Society; N. Ishida, Y. Kusaka, H. Ushijima, Hydrophobic Attraction between silanated silica surfaces in the absence of bridging bubbles, *Langmuir* 28 (2012) 13952–13959, Copyright (2012) American Chemical Society.

different charge properties, resulting in a long-range electrostatic attractive force.

Recent research has revealed that even in the absence of nanobubbles or electrostatic attraction, there is still a hydrophobic attraction between highly hydrophobic surfaces [113], albeit it is somewhat short-ranged (Fig. 4.12C). Because the forces created by bubbles or charge domains are not always thought to be those produced by surface hydrophobicity, this sort of attraction might be considered the “pure” component of the force [116]. So far, it appears that such “pure” hydrophobic attractions have a range of less than 10–15 nm, independent of the hydrophobic surface type [115]. On the contrary, the hydrophobic forces measured between fluorocarbon oil droplets [117] have a range of less than 5 nm, which is shorter than that for solids. This difference implies that the nature of the pure hydrophobic force could also vary depending on the system.

4.3.2.3 Force with polymers

Polymers are commonly employed in many industrial processes as dispersants and flocculants. The interactions of polymers with particle surfaces are critical to surface forces because adsorbed and bulk polymers affect the force in different ways depending on the polymer type and concentration, as shown schematically in Fig. 4.13.

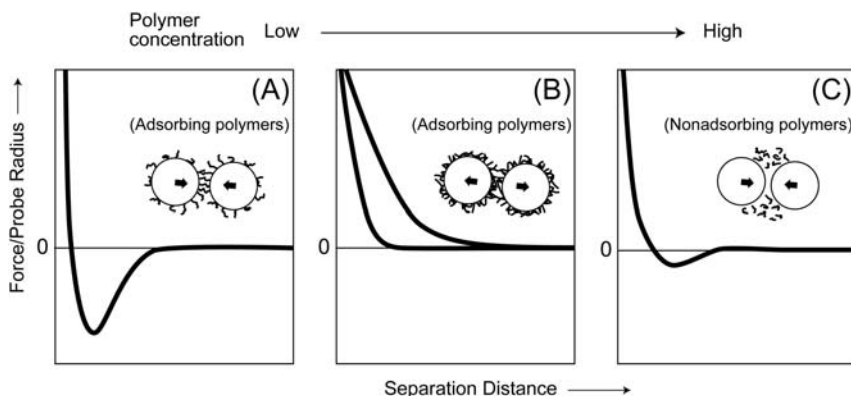


Figure 4.13 Schematic drawing of the change in the interaction forces between surfaces depending on the polymer concentration. An attractive bridging force (A) changes to a repulsive steric force (B) in adsorbing polymer solutions as the concentration increases. The depletion force (C) acts in a solution of a nonadsorbing polymer at a high concentration.

When adsorbing polymers are introduced to particle dispersion, the dispersion aggregates at low polymer concentrations. In this case, the polymer molecules are bridged across particle surfaces due to the limited surface coverage of the polymers, resulting in an attractive long-range force as detected using AFM [102,118].

At higher concentrations, the adsorbing polymers covered a greater fraction of the available surface. As the adsorbed polymer's surface coverage grows sufficiently high, the positive attraction is then replaced by a repulsive interaction caused by overlapping polymer molecules on opposing surfaces and the unfavorable entropy of constraining polymer chains between the surfaces. This repulsive force is referred to as steric repulsion. AFM has mostly been used to detect steric repulsion between silica surfaces in block copolymer solutions [119,120].

Particles frequently flocculate in nonadsorbing polymer solutions at high polymer concentrations. To explain flocculation, Asakura and Oosawa proposed a proposal an attractive force known as the depletion force in 1954 [121]. When solid surfaces are immersed in a high-concentration solution of a nonadsorbing polymer, the polymer molecules are barred from the area between the surfaces when the distance between them is smaller than the effective diameter of the polymer. The difference in osmotic pressure between the surfaces relative to the bulk solution results in an attractive force due to the lower polymer concentration between the surfaces. The depletion force was experimentally demonstrated between stearylized silica surfaces in polydimethylsiloxane solutions in cyclohexane for the first time [122]. Then, depletion forces have been observed not only in polymer solutions but solutions containing various micelles [123] and solid nanoparticles [124]. These results indicate that the depletion phenomenon is common in solutions containing nonadsorbing particulate matter at high concentrations.

4.3.2.4 Fluid interfaces

Many industrial processes, such as froth flotation, include particle interactions with fluid interfaces such as air bubbles and oil droplets. Because of AFM's adaptability, it is ~~now~~ able to detect the interactions between a particle and a bubble or oil droplet. AFM measurements between a particle and a bubble or oil droplet may be easily done in a liquid cell utilizing the colloid probe method by attaching a bubble or oil droplet to a hydrophobic plate. However, this approach has not been as extensively utilized as the measurement of the solid-solid interactions because fluid surface

deformations make interpreting the observed forces challenging. The colloid probe can also penetrate the bubble or oil droplet if it is hydrophobic.

Several investigations, nevertheless, have advanced our knowledge of the interaction force between particles and fluid surfaces. Between a hydrophilic silica particle and an air bubble, a monotonic repulsive force was discovered [125]. The repulsive force produced by the negative charge of the water–gas interface and the repulsive van der Waals force, fit well with the DLVO theory. Fluid interactions with hydrophobic surfaces are more difficult to study because the attraction between a particle and the fluid interface frequently results in the particle being swallowed in the fluid. Nevertheless, by fitting the repulsive force before the jump to the DLVO theory, the separation distance between the surfaces shortly before the particle jumping in and getting swallowed in the bubble was calculated [126]. Before rupturing, the thickness of the water layer between the particle and bubble surfaces was calculated to be 10–15 nm, which is quite near to the range of the hydrophobic attraction indicated in the preceding section. A particle's interaction with an oil droplet is comparable to that of a particle with a bubble. Negatively charged oil surfaces created a repulsive interaction between a silica particle and a decane droplet [127]. The decay length of the repulsive force corresponded nicely to the Debye length.

The forces between two fluid interfaces, bubble–bubble and oil–oil, were also successfully measured and analyzed. By attaching a small bubble or an oil droplet on the top of a specially microfabricated cantilever, the interaction forces were measured with another bubble/oil droplet placed on a hydrophobic plate [128–130] as shown in Fig. 4.14. The separation distance of the surfaces and bubble deformations were obtained by calculations using a mathematical model that combines the surface forces, hydrodynamic forces, and surface deformations. One of the important findings provided by the series of measurements between the bubbles and oil droplets is that the DLVO theory well describes their coalescence; no additional force was found between them. This was a surprising result, considering that a hydrophobic force was expected between the highly hydrophobic bubbles and oils based on experiments on solid hydrophobic surfaces. Instead, hydrodynamic forces were influential, deforming the surfaces and inducing water drainage while thinning the water film between the surfaces.

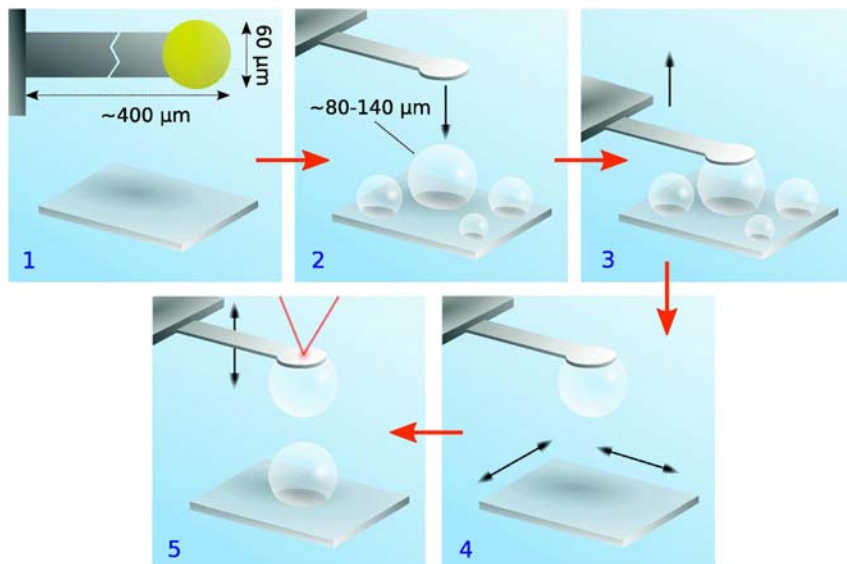


Figure 4.14 Schematic drawing showing how to attach a bubble or drop to a probe and to measure interactions using the AFM. *Reprinted with permission from R.F. Tabor, F. Grieser, R.R. Dagastine, D.Y.C. Chan, Measurement and analysis of forces in bubble and droplet systems using AFM, J. Colloid Interface Sci., 371 (2012) 1–14. Copyright (2012) Elsevier.*

4.3.2.5 Hydrodynamic force

In addition to the comparatively “static” interactions discussed thus far, the hydrodynamic force between solid surfaces is crucial in engineering, particularly in processes like stirring, separation, and transportation. AFM investigations on hydrodynamic force appear to have mostly focused on the boundary slip of Newtonian liquids over a solid wall. When a liquid flows over a solid surface, the liquid close to the solid is considered to have the same velocity as the solid (that is, the liquid is stationary relative to the solid) in classical fluid mechanics, which is known as the nonslip boundary condition. However, under specific conditions, microscale and nanoscale liquid boundary slips over a solid surface have been found. The degree of boundary slip is characterized by the distance behind the interface at which the liquid velocity extrapolates to zero, defined as the slip length.

The first measurement of boundary slip in aqueous solutions using AFM was conducted between a gold-coated silica colloid probe and mica with partially hydrophobized aqueous sucrose solutions [131].

By analyzing the obtained hydrodynamic drag force, the slip was found to occur with a varying slip length of up to ~ 20 nm. The slip length depends on the liquid viscosity and shear rate. As a result of numerous studies conducted following this study, the slip for liquids on lyophobic surfaces is now generally accepted, although the slip length seems to have a broad range of up to about 100 nm [132], depending on the experimental conditions. On the contrary, no definite slip is observed on completely wet and smooth surfaces [133], although surface roughness could induce slip [134]. Nanobubbles attached to a hydrophobic surface can also cause huge slips [135].

This technique has also been utilized to investigate the rheological properties of the behavior of solutions such as aqueous electrolyte solutions [136] and polymer solutions [137], confined between two surfaces. By measuring the hydrodynamic force upon approach and withdrawal of the surfaces, the change in viscosity of the solution can be evaluated against the shear rate, by which the local viscosity of fluids in the gap region can be estimated [137].

Recently, the effect of the flow of bulk solutions on the forces acting between a colloid probe and a flat surface has been investigated by making a flow through the fluid cell of the AFM with a peristaltic pump [138]. The magnitude of the repulsive forces in the solutions with NaCl and MgCl_2 was found to decrease with increasing the flow rate and ionic strength, which is attributable to the shrink of the electrostatic double layers by the flow.

4.3.2.6 Friction force

Both normal and frictional forces between particles are critical in the flow of liquids with relatively large particle concentrations. Frictional forces are also crucial in new technologies like chemical mechanical planarization and microelectromechanical systems. Understanding frictional phenomena at the molecular level has become an important issue in a variety of technologies.

The friction measurement by AFM can be conducted using the same principle as LFM described previously. When a probe is scanned over a surface with a constant applied load, cantilever twisting is detected by the photodiode output in the lateral direction. From the twist magnitude, the lateral force can be measured as a function of the applied load. The colloidal probe technique can be readily applied to friction measurements [139].

The friction between silica surfaces in aqueous electrolyte solutions has been investigated extensively. The ions adsorbed on the surfaces provide better lubrication between silica surfaces than pure water. In addition, the degree of lubrication has been found to follow the order of hydration enthalpy of cations ($\text{Li}^+ > \text{Na}^+ > \text{Cs}^+$) [140], as shown in Fig. 4.15. This effect is attributed to the lateral mobility of water molecules in the hydration shell of the adsorbed cations.

The adsorption of the surfactant also reduces friction. The friction between the silica surfaces in a cationic surfactant solution decreased with increasing concentration and became constant at concentrations higher than the CMC [141]. A layer of weak polyelectrolyte [142] and hydrophilic polymer [143] adsorbed on silica also reduced the friction between the surfaces, implying that various forms of hydrated layers play an important role in friction reduction.

Currently, the friction studies have been expanded to the research on surface “superlubricity,” where the friction coefficient is the surface extremely low (typically less than 0.01). By using the colloid probe method, superlubricity has been found in various systems, such as silica

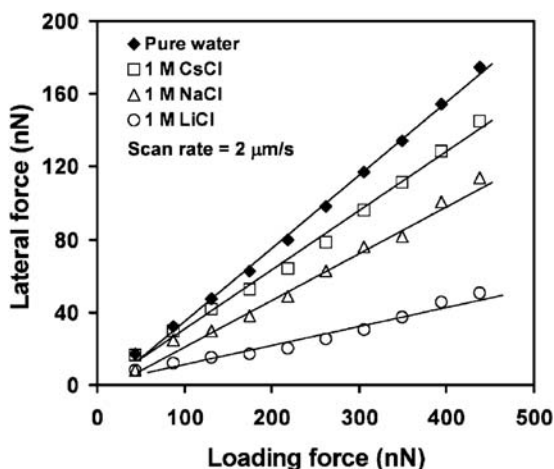


Figure 4.15 Dependence of friction force on the loading force between a silica particle and a silica substrate in pure water and CsCl, NaCl, or LiCl solutions of 1 M. Adapted with permission from B.C. Donose, I.U. Vakarelski, K. Higashitani, *Silica surfaces lubrication by hydrated cations adsorption from electrolyte solutions*, *Langmuir* 21 (2005) 1834–1839. Copyright (2005) American Chemical Society.

surfaces adsorbed by surfactant micelles [144], titanium alloy-polymer interfaces bearing liposomes, [145] and silica-graphite interfaces in ionic liquid under electric potential [146].

4.4 Summary and future outlook

In this chapter, an overview of how AFM has been employed for evaluating surface properties and measuring interaction forces across various fields of science and engineering has been provided. The studies introduced clearly show that AFM is undoubtedly one of the best tools to gain a direct understanding of how micro- and nanoscopic substances behave on a surface or interact with each other down to the molecular-scale level in various environments.

As mentioned in Section 4.2, the evolution of AFM imaging has achieved a subnanometer resolution with FM-AFM and enabled real-time video-like imaging of molecules with HS-AFM. Further demands for both higher resolution and speeds will drive research into the compatibility of the two techniques, as currently the imaging speed of FM-AFM is usually lower and HS-AFM has some more room to achieve higher spatial resolution. Finding proper operating conditions, selecting a more effective excitation method for probes, and constructing faster and more stable feedback control could be key to obtaining ideal systems.

Attempts to combine AFM with other characterization methods will continue in the future, depending on the demands of the characterization. Among various methods, quartz crystal microbalance and surface plasmon resonance might be fascinating techniques to be combined with AFM, as both methods can evaluate quite precisely various properties of molecules on flat surfaces.

For interaction forces, understanding the origin of non-DLVO forces from a molecular perspective is one of the most important issues to be addressed in the near future. In particular, the molecular mechanisms of hydrophobic attraction and hydration forces remain unclear and further research progress is strongly expected. Understanding the interactions in nonaqueous solvents, which are also much less well understood than those in water, is also critical considering their industrial importance.

The application of the colloid probe method to interactions between nanoparticles is a challenging issue. Because the size and/or the shape of the particle affect the behavior of the particles, the force data measured between real nanoparticles are desirable to analyze their behavior of them

in detail. As nanoparticles are too small to be attached under optical observation, alternative methods to attach a nanosized particle on the tip of an AFM stably and effectively are certainly necessary.

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CHAPTER 5

Non-destructive imaging of buried interfaces using decelerated electron-beam in scanning electron microscopy

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5.1 Introduction

Recent development in nanoelectronic devices relies on three-dimensional layer stacking requires precise evaluation of their interfaces to minimize the formation of any defects and pinholes [1]. In nanoelectronics, three-dimensional sequential integration (3DSI) [2] and through silicon via [3] have been developed recently allowing the integration of over 100 layers vertically with at least submicrometric interfacial smoothness. Similarly, spintronic memories and sensors have been widely used and developed [4,5], which require atomic smoothness. These devices are typically based on a magnetic tunnel junction (MTJ), of which transport properties are governed by several factors such as barrier thickness and interfacial roughness [6,7]. To understand the difference in these device performances, microanalytic techniques are highly required to be linked to these transport properties [8].

Nowadays, numerous analytic techniques are available as listed in Fig. 5.1 [9], which can be categorized into four major techniques: microscopy, spectroscopy, scattering and reflection, and electrical measurements. The most common method to investigate the interfaces of multilayered junctions and devices is cross-sectional transmission electron microscopy (TEM) and chemical spectroscopy associated as listed as follows: Although atomic information can be resolved, TEM involves a time-consuming and destructive preparation process via mechanical polishing or focused ion beam (FIB) methods for electron transparency (typical sample thickness of <80 nm [10]). Namely, a high-energy Ga-ion beam in FIB can cause

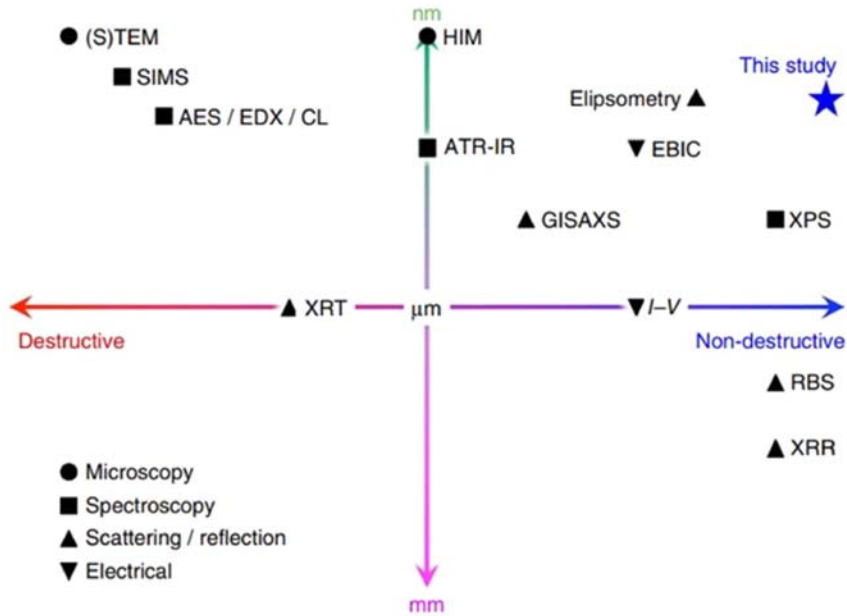


Figure 5.1 Major techniques for evaluating a buried junction with respect to their resolution and destructiveness [9].

substantial damage to a sample [11], especially a formation of a nonmagnetic region in a ferromagnet. Additionally, the observable area is usually less than a micrometer, which makes it difficult to extract adequate information from a sample to correlate with macroscopic transport properties. To avoid such issues, plan-view imaging can be employed for in-plane characterization with atomic resolution but this is not suitable for multi-layered samples.

The other two techniques offer macroscopically (and mesoscopically) averaged properties of a device and their imaging resolution depends on the probe diameter. Optical beams and electrical currents have been commonly used as a probe for ellipsometry [12] and electrical transport [current-voltage (I - V)] measurements between macro- and mesoscopic scales [13]. An X-ray can also be employed as a probe, of which diameter is controlled typically measures between μm and mm by the slits used, allowing us to measure interfacial roughness by X-ray reflectivity [14] and chemical compositions by X-ray photoelectron spectroscopy [15] and grazing incidence small angle X-ray scattering [16]. Similarly, backscattered electrons (BSE) can be used for electron backscatter diffraction

patterns for grain mapping [17]. By further reducing the probe diameter with α -ray and electron-beam, micrometric measurements can be achieved, such as Rutherford backscattering spectroscopy [18] and electron-beam induced current [19], respectively. By controlling the probing depth for imaging and measurement with Ar-ion milling for instance, the vertical profile can be obtained with infrared light and helium ion for attenuated total reflectance [20] and helium ion microscopy [21], respectively. By reducing the sample dimensions below the penetration depth of a probe, 3D imaging can be achieved, for example, x-ray tomography [22]. These imaging and measurements techniques can also be combined with associated spectroscopic characterization, such as Auger electron spectroscopy [23], cathodoluminescence (CL) [24], energy dispersive X-ray spectroscopy (EDX) [24] and secondary ion mass spectrometry [25].

To overcome such difficulty and limitation, a more efficient analytic technique needs to be developed to fulfill the demand. This chapter describes a recently-demonstrated non-destructive technique using controlled electron-beam in scanning electron microscopy (SEM) with JEOL in 2016 [9]. The in-plane resolution of this imaging technique was confirmed to be down to the nanometric scale by varying the thickness of a capping layer overdispersed subnanometre-thick heavy metal islands [26] (see Section 5.4.1). This technique was first used in metallic spin-valve junctions to evaluate the interfacial contaminations as shown in Section 5.4.2. The non-destructive method was then combined with X-ray dispersive spectroscopy (EDX) [27] to identify the cause of the magnetoresistance reduction and subsequently to improve the device yield as discussed in Section 5.4.3. It was also applied to nanoparticles to reveal their synthesis process [28] in Section 5.4.4. In situ imaging was also achieved under transport measurements, revealing inhomogeneous current distributions at a spintronic junction, as described in Section 5.4.5. These results confirm this non-destructive imaging technique can be greatly useful for the analysis of buried interfaces correlating with the corresponding chemical compositions and electrical transport properties.

5.2 Principles

5.2.1 Scanning electron microscope

The primary beam of electrons in an SEM originates in the electron gun. Most modern SEMs use a Schottky-type emitter due to their high

brightness, coherence, and emitter lifetime. The tip of the emitter consists of a tungsten needle which has a tip size of about a micron and zirconia (ZrO_2) reservoir further down the needle. The zirconia coats the tip of the needle and lowers the work function of the tungsten. The sharpness of the tip creates a small source size to be demagnified later and helps to improve the coherence of the liberated electrons. As the name suggests, the gun operates by way of Schottky emission; the tip is held at a negative bias with respect to a nearby anode creating an electric field along the axis of the tip. The field lowers the energy barrier for the thermionic emission of electrons from the heated tip and leads to higher beam currents which are required for analytical SEM methods.

After the electron gun is the accelerator stack which consists of a number of biased plates which accelerate the electrons toward the sample. Typically, primary beam energies are in the range of 1–30 keV. Since the interaction cross-section of different electron interactions within a sample is based upon the incident energy, an operator can choose the accelerating voltage to affect both resolution and the excitation of different detectable signals within the microscope.

Focusing of the electrons is achieved with simple magnetic lenses, albeit with optimized pole piece geometries. At the top of the column condenser lenses and apertures are used to form the primary electrons into small probes. This is where probe size and current density are determined [29], both of which affect point resolution, signal-to-noise, and sample damage. The objective lens is located at the bottom of the column and its pole piece (and magnetic field) protrudes into the sample chamber [30]. The function of the objective lens is to focus the probe of primary electrons onto the surface of the sample. The sample is usually translated such as to have a short working distance from the end of the objective lens pole piece (typically <5 mm for high-resolution imaging).

The microscope column also contains a number of electrostatic and magnetic coils for translating and correcting the primary electron-beam. To maximize the signal and reduce aberrations the electrons are made to pass through the optic axis of the objective lens. Inhomogeneities in the magnetic fields influencing the electrons can cause the electron probe to stretch (ellipsoidal cross-section) and can blur/stretch the image. Stigmator coils are used to correct this [31]. Finally, scan coils are used to raster the beam along the surface of the sample. These coils are normally placed in pairs such that the translation of the beam does not result in an associated tilt of the beam.

The scanning action of the electron beam is the key principle on which the SEM is based. As the beam moves across the sample, the signals captured by the various detectors are correlated to the position of the electron beam, as shown schematically in Fig. 5.2. In this way the signals become sensitive to position and an image is formed- thus making an SEM a serial imaging technique- as opposed to an optical microscope or TEM which forms their images in parallel. A consequence of this scanning action is that the optical conditions of the primary electrons remain the same and it is the scan size that determines the magnification of the sample. The scan speed then determines the integration time of the detected signals.

With regard to SEM specimens, care must be taken in their preparation if one is to extract the most information from them. Specifically, the electron-beam can cause charging of the surface of the sample which will obscure most of the information from the surface. For this reason, SEM specimens must be conductive down the specimen stage/holder which provides an effective ground for the electrons. Since not all materials are electrically conductive, thin coatings are usually employed to prevent charging while still conforming to the surface topography of the sample.

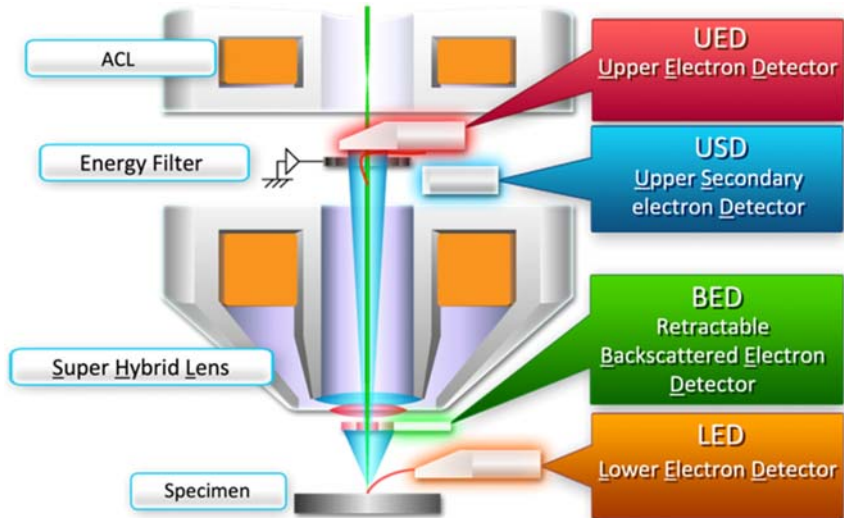


Figure 5.2 Schematic diagram of SEM. ACL represents an aperture angle control lens, which automatically optimizes the aperture angle of the objective lens over the whole probe current range. When a probe current increases, ACL suppresses the spread of incident electrons to maintain the smallest probe diameter. The large variations of probe currents are also controlled by ACL to enable smooth SEM operation.

The most common coating methods are the thermal evaporation of carbon and sputtering of the metals such as gold or platinum. This consideration is crucial to both biological samples and those relevant to materials science where ceramic and thick semiconducting substrates are commonplace. The conductivity of the sample to the SEM stage can be leveraged to electrically bias the SEM specimen, a factor that will be crucial to the imaging techniques described in this section.

The versatility of electron microscopy is due largely to the number of detectable signals that are generated by the specimen due to the fluence of the primary electron-beam. The most common signals detected using SEM include secondary electrons (SE), BSE, and characteristic X-rays used for EDX and wavelength dispersive spectroscopy. However, other signals include Auger electrons, transmitted and diffracted electrons, fluorescence X-rays, and CL photons. It should be noted that for a given primary beam energy, the signals originate from different depths within the sample. Each has its own interaction cross-section and lateral distribution in the plane of the sample. For example, SE signals are used to generate images that are very sensitive to surface topography, while BSE signals typically yield information about the difference in materials within the sample (atomic number contrast). Therefore, careful selection of accelerating voltage can optimize the imaging conditions to yield the desired information.

The relatively large sample chamber of most modern SEMs allows multiple detectors to be mounted in order to make use of the abovementioned signals. The large sample chamber also allows other devices to be mounted around the sample, thus enabling both *in situ* and correlative microscopy (both of which are growing in popularity). These techniques allow electron imaging while specimens are subjected to varying conditions of heat, gas, mechanical stress, voltage, current application, etc.

As mentioned the most common SEM signals used for nanoelectronics are secondary and BSE. These electrons can be detected by in-chamber detectors or through-the-lens (TTL) detectors. In-chamber detectors are usually Everhart-Thornley (ET) detectors which consist of a biased Faraday cage in front of the scintillator, light guide, and photomultiplier device. The bias is applied to attract low energy (<50 eV) SEs onto the scintillator. BSE have kinetic energies up to the primary beam energy and are not influenced by the bias. Thus, BSE signals with line-of-sight to the detector are always detected. Thus, the bias can be changed to influence the contribution of SEs to the image. ET detectors offer large collection

efficiencies and are ubiquitous in modern SEMs. TTL detectors are located above the objective lens pole piece and receive electrons that escape from the specimen close to the optic axis of the microscope. BSEs with line-of-sight to the detector and SEs which are captured by the magnetic field of the objective lens travel up the column to the detectors. TTL detectors have lower collection efficiencies than in-chamber detectors but allow for very low working distances between the objective lens and the specimen. This is the reason why TTL detectors are used for imaging with high spatial resolution. A biased mesh in front of TTL detectors enables tunable sensitivity to both SE and BSE signals.

5.2.2 Controlled electron-beam imaging

A new imaging technique for the interfacial study has been developed with a nanometric resolution non-destructively. This method controls the penetration depth of the electron beam introduced in SEM and the generation of the resulting BSEs by controlling the energy of the beam via the acceleration voltage and an applied bias voltage on the specimen stage. A field-emission SEM (JEOL, JSM-7800F Prime) has been used for mapping the changes in BSE generation at buried interfaces, corresponding to a wide range of resistance due to the presence of defects and contaminations. In order to maintain nanometric in-plane resolution, the incident electron-beam is accelerated at $(V_{\text{spec}} + V_{\text{acc}})$ keV, where the voltage applied for the specimen is $-V_{\text{spec}}$ and the effective landing voltage on the specimen are V_{acc} . Note that the electron beam is decelerated only in the vicinity of the specimen (“gentle beam” mode), allowing the penetration depth of the beam to meet the vertical position of a buried interface under investigation. This beam introduction generates the resulting BSEs and SEs near the buried interface. BSEs and SEs are used for non-destructive imaging in combination with an energy filter placed beneath the upper electron detector (UED) and the upper secondary electron detector (USD) (see Fig. 5.2). Two additional detectors, a retractable backscattered electron detector and a lower electron detector are also installed just above the sample space in SEM. Normally, UED with an energy filter is used for the collection of reflected electrons from the specimen with their energies above 10 keV under the V_{spec} application, and USD is employed for those below 1 keV. These detectors can cover the energy range between +500 V and −2 keV coincidentally. In parallel, the initial beam acceleration of $(V_{\text{spec}} + V_{\text{acc}})$ can be controlled typically between 2 and 30 keV.

By definition, SEs are electrons that escape the sample with < 50 eV and BSEs are any with > 50 eV up to the primary beam energy. Accordingly, BSEs are expected to undergo fewer interactions within the sample, probing electronic conditions deep into the specimen with maintaining good contrast corresponding to the atomic numbers of the specimen. On the other hand, SEs undergo many more interactions and/or are generated within the penetration depth of 5–20 nm of the specimen, producing contrast sensitive to surface morphology and conditions. SEs are also known to be strongly affected by the magnetic field generated by the immersion lens, while BSEs are not. Accordingly, the use of BSEs with energy filters can provide information on a buried interface in a specimen to be collected by an appropriately placed detector [32].

5.3 Electron flight simulation

Monte Carlo simulations are used for the investigation of phenomena with statistically relevant data using powerful single particle models, which calibrate the depth information received. Among many programs available, Monte Carlo simulation of electron trajectory in solids (CASINO) [33] is the program of choice as CASINO has been specifically designed to simulate the electron-beam flight in SEM, especially at low electron-beam energies below 5 keV [34]. CASINO uses an empirical model for elastic scattering with the Mott cross-section formula. It requires approximating the frequency of scattering events [35] to simulate electron travel within a specimen. This frequency is dependent upon the mean free path, λ_{el} . CASINO uses the Joy and Luo model for inelastic scattering [36]. Their semiempirical model modifies Bethe's original model [37] to include the reduction of averaged loss in electron energy per scattering event once the electron energy reaches < 10 keV. Here, the interaction volume is a predictor of the actual resolution of SEM. Assuming smooth surfaces and interfaces, the energy and angle of the incident electron-beam energy and the composition [atomic number(s), Z] and thickness of the specimen are key parameters. About 2000 electron paths with their scattering cross-section are then calculated. The interaction volume decreases as Z increases as shown in Fig. 5.3 due to an increase in the Coulomb force with increasing Z . This increases the number of scattering events with a higher angle deflection, deviating the electrons from their original paths more quickly and accordingly influencing the SE/BSE ratio at the same probe current.

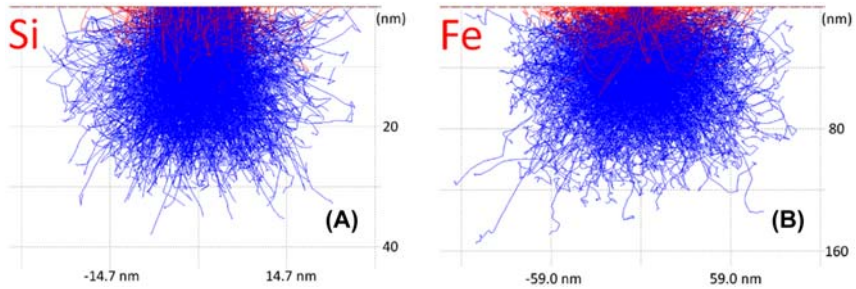


Figure 5.3 Effect of Z , (A) 14 (Silicon) and (B) 26 (Iron), on the maximum penetration depth of BSEs (red) and spent electrons (blue), simulated in CASINO [27].

The angle of incidence, θ , also influences the electron flight as deduced from the scattering equations [27]. With increasing θ , the penetration depth decreases, which makes the interaction volume to be less symmetric. The most probable change in θ after an elastic scattering event is estimated to be ~ 4 degrees. As θ increases, scattering tends to happen either laterally or penetratively. Here, asymmetry in the electron flight is induced even at such small θ . θ can also reduce the electron penetration. Kanaya and Okayama assumed the maximum penetration depth to be proportional to a factor of $\cos\theta$ [38].

The interaction volume can reduce the in-plane resolution in SEM imaging while offering significant (sub)surface information. It is hence important to consider the influence of electron-beam energy, Z and θ , which can significantly affect an SEM image. This becomes even more critical in heterogeneous specimens, for example, multilayers and junctions, because interaction products from subsurface layers are overlaid on an SEM image. To image a buried interface under investigation in such a specimen, SEM images taken at controlled electron-beam energy focusing above and below the interface can be subtracted as detailed in the following section.

5.4 Non-destructive imaging

5.4.1 Resolution

In order to determine the in-plane resolution of the non-destructive imaging technique, nanoparticles were embedded under an overlayer with three different thicknesses. The samples were deposited by a high vacuum sputtering system (PlasmaQuest, HiTUS) with the following three

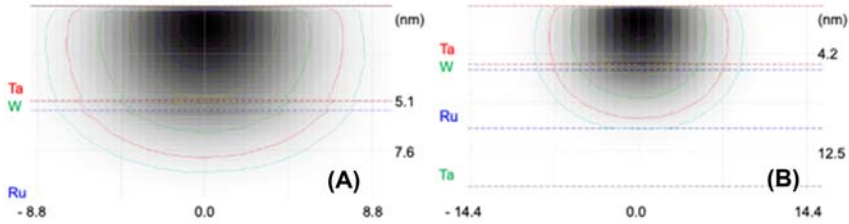


Figure 5.4 CASINO simulations on the sample consisting of Si substrate (SiO_2)/Ta (5)/Ru (5)/W (0.5)/Ta (5) (thickness in nm), revealing different electron penetration calculated at $V_{\text{acc}} =$ (A) 0.9 and (B) 1.1 keV. The electron beam is introduced vertically from the surface of the sample, followed by the Ta layer (red), the W insertion (amber), Ru (blue), the Ta seed layer (green), and the Si substrate (purple) [26].

structures; (1) Si substrate (SiO_2)/Ta (5)/Ru (5)/W (0.5)/Ta (5), (2) Si substrate (SiO_2)/Ta (5)/Ru (5)/W (0.5)/Ta (10), and (3) Si substrate (SiO_2)/Ta (5)/Pt (0.5)/Ta (60) (thickness in nm). Pt and W were chosen to form nanoscale islands with different diameters [39], which were then buried under a Ta capping layer with different thicknesses between 5 and 60 nm. For the three samples, CASINO simulations were first performed to estimate V_{acc} to be sensitive to the top and bottom of the W nanometric islands. As shown in Fig. 5.4, electron-beam was calculated to penetrate down to the top surface of W at 0.9 keV and further down to the bottom of W at 1.1 keV for the case of the 5-nm-thick Ta capping layer. By subtracting these data, the buried W nanoislands dispersed should be able to be imaged, leading to the assessment of the in-plane resolution of the non-destructive imaging.

The samples with 0.5 nm thick W islands were then observed at $V_{\text{acc}} = 0.9$ and 1.1 keV according to the CASINO simulations. As seen in Fig. 5.5A and B, it was difficult to identify the W islands clearly in the SEM images taken at these V_{acc} . Accordingly, these images were subtracted to highlight the differences. To align the two SEM images, a carbon-contaminated area induced by initial imaging and/or some minor features on the surface was used for image subtraction using a MATLAB[®] program [27]. The resulting subtracted image is shown in Fig. 5.5C. The white contrast as circled represents W islands due to more BSEs generated than the surrounding regions. These nanoislands show their diameters to be approximately $(24\text{--}39) \times (75\text{--}110) \text{ nm}^2$. Here, ImageJ was used to measure the diameter of the islands on a series of similarly subtracted SEM images. These islands were used to determine the in-plane resolution of the non-destructive imaging. Approximately 50 islands were acquired for each SEM image

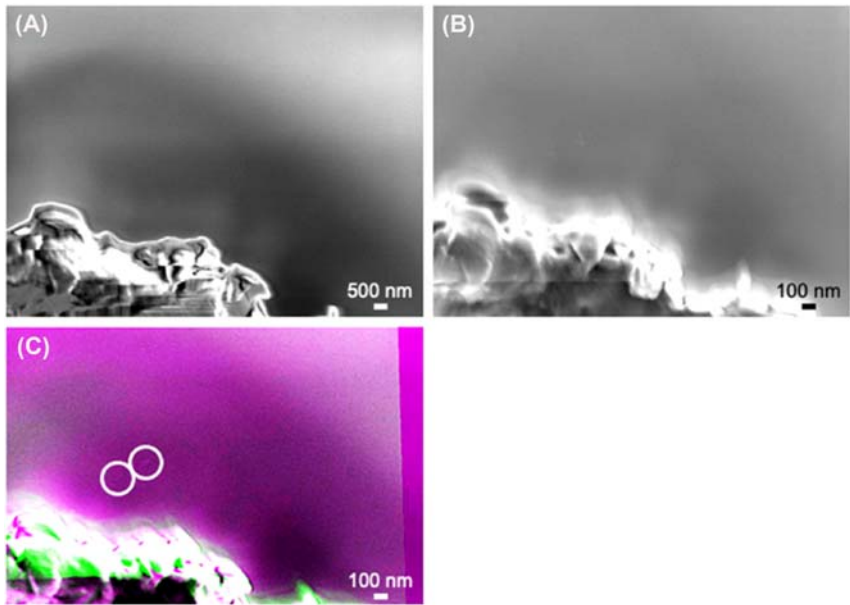


Figure 5.5 SEM images of Si substrate (SiO_2)/Ta (5)/Ru (5)/W (0.5)/Ta (5) (thickness in nm) with the $40,000\times$ magnification taken at V_{acc} = (A) 0.9 and (B) 1.1 keV. (C) Subtracted image between (A) and (B), showing the depth profile from magenta (below the Ru/W interface) to green (above the W/Ta interface). Circles highlight the white contrast corresponding to the presence of W nanoislands [26].

Table 5.1 List of minimum feature size of W and Pt nanoislands measured.

Ta capping layer thickness (nm)	Minimum feature size (nm)
5	2–3.9
10	8.4
60	12.2

subtracted, revealing the minimum island diameter to be 2–3.9 nm. Similarly, the other two samples with thicker Ta capping layers were characterized to obtain the minimum island diameter, representing their in-plane resolution as listed in Table 5.1.

From Table 5.1, we can achieve the in-plane resolution of 2 nm for non-destructive imaging. Generally, the resolution can be further increased by reducing the thickness of an overlayer above the buried interface of interest. Additional crucial factors for the improvement of resolution are the precise focus and contrast of SEM images. The contrast is predominantly

controlled by the differences in the atomic numbers between elements used in the layers above and below the buried interface in the first approximation. By optimizing these parameters for non-destructive imaging, the in-plane resolution can be improved further.

5.4.2 Lateral spin valves

As an example of nanoelectronic devices, lateral spin-valve devices, consisting of a single buried interface sandwiched by two different materials, were employed to test non-destructive imaging. The devices were fabricated by conventional lift-off processes using electron-beam lithography (JEOL, JBX-6300FS) [9]. Two $\text{Ni}_{0.8}\text{Fe}_{0.2}$ nanowires (30 nm thick and 200 nm wide) were first deposited on a thermally oxidized Si substrate by a high vacuum sputtering system (Leybold, UNIVEX 350) forming different shapes at their ends (square and sharp) to induce a difference in their magnetization-reversal fields. After the lift-off, a Cu nanowire (70 nm thick and 200 nm wide) were patterned to bridge these $\text{Ni}_{0.8}\text{Fe}_{0.2}$ nanowires in the same manner after Ar-ion milling for 10 s at 50 W to remove contaminations and oxides formed on the $\text{Ni}_{0.8}\text{Fe}_{0.2}$ surface. Electrical contacts attached to these wires were finally prepared by lift-off with photolithography (EGV, Mask Aligner) after depositing Cr (10 nm)/Au (150 nm) layers by an electron-beam evaporator. The device was characterized by the conventional four-probe method, confirming giant magnetoresistive behavior.

Based on the estimation of V_{acc} using CASINO simulations, SEM images were taken at two distinctive V_{acc} of 1 and 5 keV as shown in Fig. 5.6A and B, respectively. V_{acc} of 1 keV allows the electrons to penetrate only into the surface Cu layer well above the interface, showing a conventional SEM

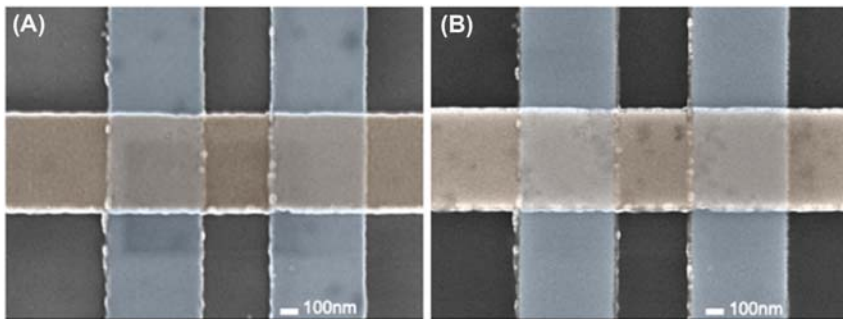


Figure 5.6 SEM images taken by UED at V_{acc} = (A) 1 and (B) 5 keV. False blue and amber colors are overlaid on the $\text{Ni}_{0.8}\text{Fe}_{0.2}$ and Cu nanowires [9].

image sensitive to the surface morphology (see Fig. 5.6A). On the other hand, V_{acc} of 5 keV lets the electrons penetrate through the Cu top layer to the buried $Ni_{0.8}Fe_{0.2}/Cu$ interface (see Fig. 5.6B). Fig. 5.6B shows gray regions at the corners of the $Ni_{0.8}Fe_{0.2}/Cu$ interfaces, which generate fewer BSEs than the rest of the interface. This means the resist used for the fabrication of the Cu nanowire is partially left even after the Ar-ion milling. By applying longer milling time, the fabrication process can be optimized with increasing the effective junction area in similar spin valves [40]. This clearly indicates that the effective landing energy at the sample surface, which is proportional to V_{acc} , is the controlling parameter to determine the non-destructive imaging depth.

5.4.3 Magnetic tunnel junctions

Using a multilayer, more than two buried interfaces with different top and bottom materials (asymmetric junction) were imaged non-destructively. A MTJ, consisting of MgO(001) substrate//Cr (80)/Pd (5)/Co₂Fe_{0.4}Mn_{0.6}Si (5)/MgO (2)/Co_{0.5}Fe_{0.5} (5)/IrMn₃ (10)/Ru (7) (thickness in nm), was deposited by ultrahigh vacuum (UHV) sputtering [41]. The multilayer was then patterned into a series of MTJ pillars with dimensions between 10×10 and $50 \times 50 \mu m^2$ using both photolithography and Ar-ion milling similar to the process used in Section 5.4.2. The milled regions were filled with Al-O and finally, a top electrode of Au (80 nm) was deposited. MTJs were electronically characterized using the four-probe method, categorizing them into two distinctive tunneling magnetoresistances (TMR) ratios; low ($<20\%$) and high ($>80\%$) at room temperature.

After the estimation of V_{acc} by CASINO simulations, SEM imaging was performed on MTJs with both high and low TMR ratios to reveal the origin of the reduction in the TMR ratios [41]. Fig. 5.7A and D show SEM images of the MTJs with low and high TMR ratios, respectively. The subtracted images highlight two features: Both MTJs had no obvious features at the Co₂Fe_{0.4}Mn_{0.6}Si/MgO/Co_{0.5}Fe_{0.5} interfaces but only the low TMR junction showed a broader edge. This means that the interfacial layers are not the cause of the reduction in the TMR ratios but the edges may change the magnetic transport properties.

To identify the origin of the edge features, EDX was employed as shown in Fig. 5.7, where mapping of B carbon and C aluminum is from the low TMR MTJ and their counterparts E and F is from the high TMR MTJ. EDX mapping shows that there is an apparent discrepancy in

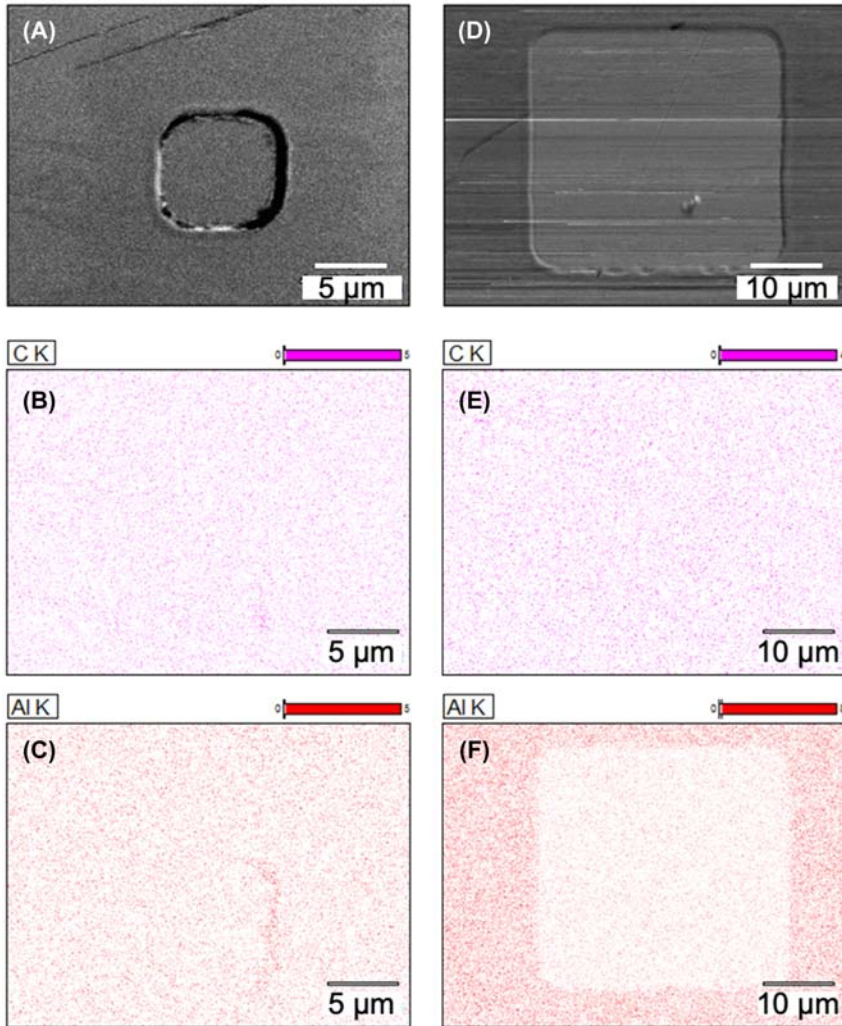


Figure 5.7 SEM images of junctions with (A) low and (B) high TMR ratios are taken at $V_{acc} = 10.5$ keV. The corresponding elemental maps of (B) C and (C) Al for the low TMR junction, and those of (E) C and (F) Al for the high TMR junction [41].

the distribution of both C and Al. MTJs with low TMR ratios show large concentrations of C and Al in areas at the edge of the pillar. This concludes that during the Al-O sputtering to isolate the pillar from the bottom and top electrodes, Al reacted with C from the remaining resist, forming aluminum carbide at the edge of the MTJ pillars. Al-C provides a conductive path for an electrical current perpendicular to the pillar, drastically reducing the TMR ratios. By feeding this finding back to the Al

deposition process to reduce the sputtering energy, the yield to fabricate MTJs with high TMR ratios on a wafer was improved by 15% [41].

Additionally, the non-destructive imaging was used to analyze symmetric $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.2}$ -based MTJs similarly fabricated [27], consisting of Si substrate (SiO_2)/Ta (5)/Ru (10)/Ta (5)/ $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.2}$ (10)/MgO (2)/ $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.2}$ (2)/Ta (3)/Ru (5)/Ti (20)/Au (280) (thickness in nm). The patterned pillars were annealed at 500°C for 1 hours for crystallization. Using the non-destructive imaging, the quality of the bottom $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.2}$ /MgO and top MgO/ $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.2}$ interfaces were then evaluated independently without destroying the devices.

Again, CASINO simulations were first performed to estimate appropriate V_{acc} to obtain information from the buried MgO barrier interfaces. V_{acc} was selected to be between 16.6 and 16.4 keV as well as 16.4 and 16.2 keV for the analysis of the bottom and top MgO interfaces, respectively. Similar to the above asymmetric junctions, MTJs for imaging were grouped into two with distinctive TMR ratios above 60% and below 1.8% at room temperature. Fig. 5.8 shows the resultant subtracted SEM images of the abovementioned pairs of V_{acc} . Fig. 5.8A and C show the

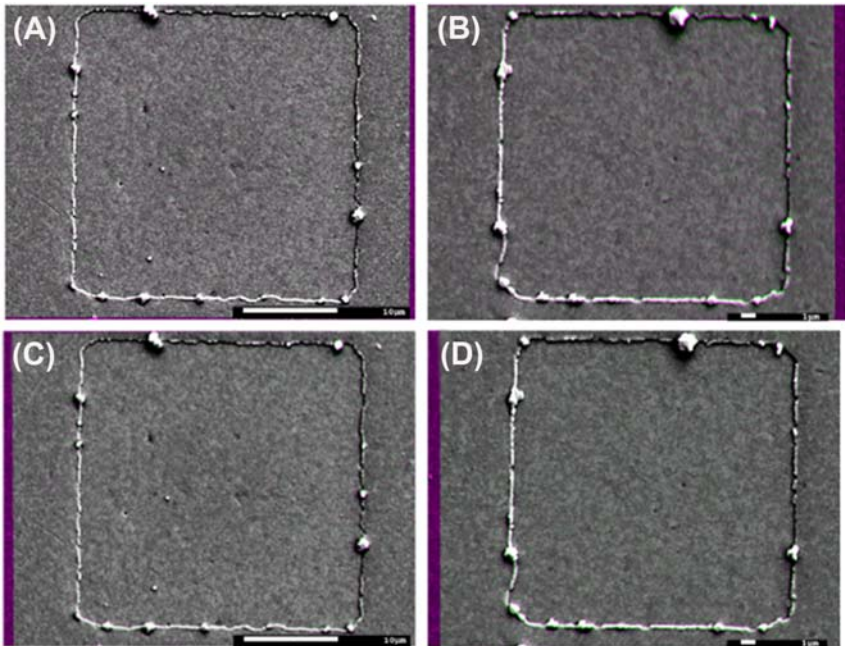


Figure 5.8 Subtracted SEM images focused on the bottom $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.2}$ /MgO interfaces for MTJs with (A) high and (B) low TMR ratios as well as on the top MgO/ $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.2}$ interfaces for those with (C) high and (D) low TMR ratios [27].

bottom and top MgO interfaces for a high TMR MTJ, respectively. Fig. 5.6B and D, on the other hand, show those for a low TMR MTJ. Black dots in the middle of MTJ pillars correspond to possible pinholes and the white particles represent contaminants possibly with a high cross-section of electron scattering. Here, the high TMR MTJs are found to contain a higher density of contaminants than the low TMR MTJs, whilst maintaining a similar density of pinhole features. These images suggest that some contaminants may be introduced during the annealing at 500° C, either through intermixing or phase segregation, at the $\text{Co}_{0.2}\text{Fe}_{0.6}\text{B}_{0.2}/\text{MgO}$ interfaces and their grain boundaries. These highly scattering contaminants seem to be linked to the increase in the TMR ratio, suggesting the precise optimization of the process can further increase the TMR ratios. This demonstrates the significant advantage of non-destructive imaging for quality assurance as well as process optimization and improvement for MTJs, which are the fundamental building block of magnetic random access memory and magnetic sensors.

5.4.4 Nanoparticles

Non-destructive imaging was also applied for the investigation of the synthesis process for nanoparticles, revealing different interfacial areas buried by almost a micron-thick particle and the resulting nanoparticle shape depending on the conditions [28]. For example, prominently elongated arm-like features were obtained for $\text{Cu}(\text{COOCH}_3)_2$ with methanol synthesized on thermally oxidized Si substrates by X-ray radiolysis under a series of pH between 7 and 9. Due to the size of the particles, a larger V_{acc} , 18–20 keV, for imaging is needed for non-destructive imaging. Fig. 5.9A shows a subtracted SEM image, indicating an almost white contrast at the interfaces between the nanoparticles and the substrate for the Y-shaped particles. This confirms that their interfaces are uniformly formed with high adhesion, which generates a sufficient number of BSEs for imaging. Some minor distributions in color can also be seen, which indicates the presence of some minor voids at the interfaces.

A similar interfacial configuration is achieved by increasing synthesizing pH to 9 as shown in Fig. 5.9B, also confirming the formation of a uniform interface. Here, each arm of the Y-shaped particles becomes more granular than that synthesized under pH = 8, which suggests the two Y-shaped nanoparticles are connected by overlapping them. For the higher pH = 9, the growth along the facets becomes asymmetric, forming

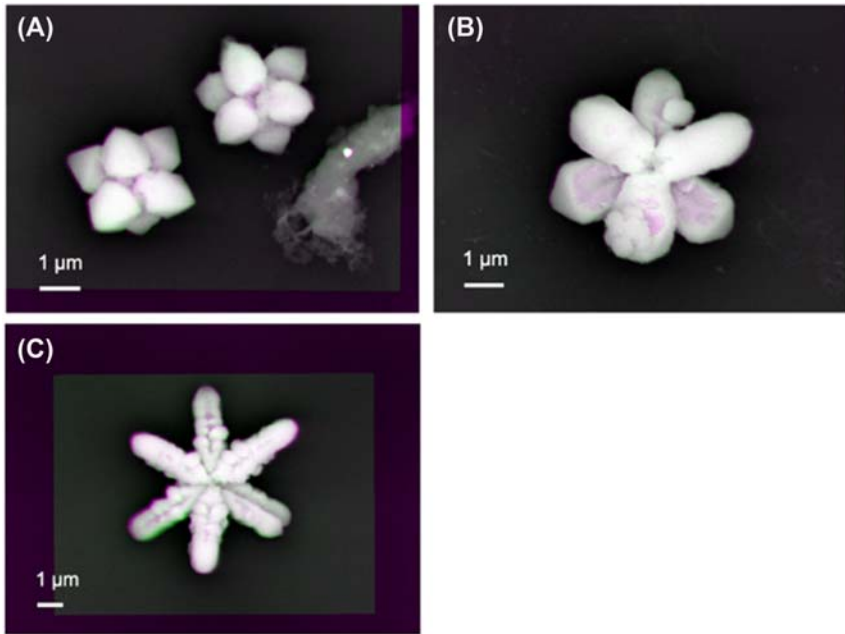


Figure 5.9 SEM images of the interfaces between the nanoparticles and the substrate after subtracting two images taken at V_{acc} of 18 and 20 keV for those synthesized at pH = (A) 7, (B) 8, and (C) 9 [28].

wire-like arms as shown in Fig. 5.9C. It should be noted that all the Y-shaped nanoparticles show stronger adhesion to the substrate than the inverse Y-shaped one, confirming they overlapped after the Y-shape formation. These images suggest that initially formed triangular seed crystals grow along their preferred three-facet directions to achieve a Y-shaped nanoparticle. Their arm shape and length depending on the substrate and pH during synthesis, which controls the mobility of the atoms for growth. By rotating the Y-shaped nanoparticles by 60 degrees, two of them can form a hexagonal structure by overlapping each other [42]. Such a detailed mechanism of synthesis can only be revealed by non-destructive imaging.

5.4.5 In situ imaging

To correlate the quality of buried interfaces with their electron transport properties, an in situ setup was developed in SEM in collaboration with JEOL UK (see Fig. 5.10). The in situ imaging can be used for the precise determination of current distributions in a buried interface. A device was

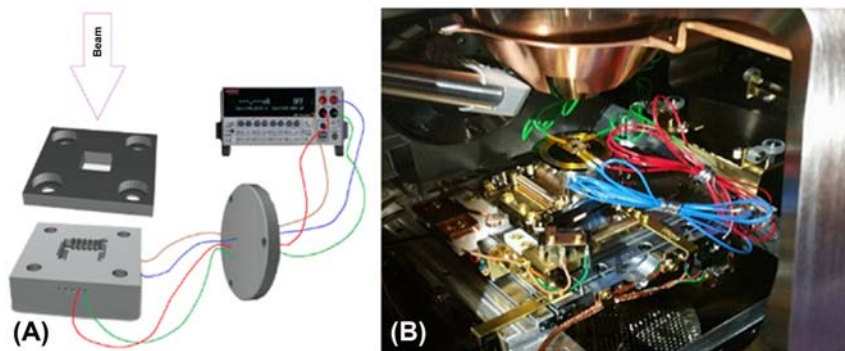


Figure 5.10 In situ non-destructive imaging setup for four-probe measurements; (A) schematic diagram and (B) photograph [27].

wire-bonded to a standard 20-pin chip carrier for electrical connections, which was held on a reusable holder 3D printed. The connections were taken through a custom-made flange to an external current source and a voltage meter (Keithley, Source Meter 2400) to perform a conventional four-probe measurement. These connections also act to ground the sample, which significantly reduces electrical charges to be built up on the specimen surface during SEM imaging. This in situ imaging allows us to observe active interfaces buried in a device during the device's operation, which can determine the effective junction area contributing to electrical transport.

A Fe/GaAs(001) lateral spin-valve device was employed for in situ non-destructive imaging. An epitaxial Fe film was grown on a GaAs(001) substrate by UHV molecular beam epitaxy using the optimized process as reported previously [43]. The Fe/GaAs sample was patterned into a lateral spin-valve using the lift-off process with electron-beam lithography as described in Section 5.4.2. The width of the Fe wires was designed to be 1, 4, and 20 μm for the injector, the first detector, and the second detector, respectively. The GaAs mesa underneath was designed to be 2 μm thick.

The Fe/GaAs spin-valve was imaged under the introduction of spin-polarized electrons from Fe into GaAs under elevated currents from 0.25 to 400 μA . As shown in Fig. 5.11, the left spin injector is shown as bright color, unambiguously confirming that the corresponding Fe/GaAs interface is activated by a large number of electrons as compared with the other interfaces. Even so, some minor distributions are seen in the contrast of the injector interface, namely, three dark dots with a diameter of

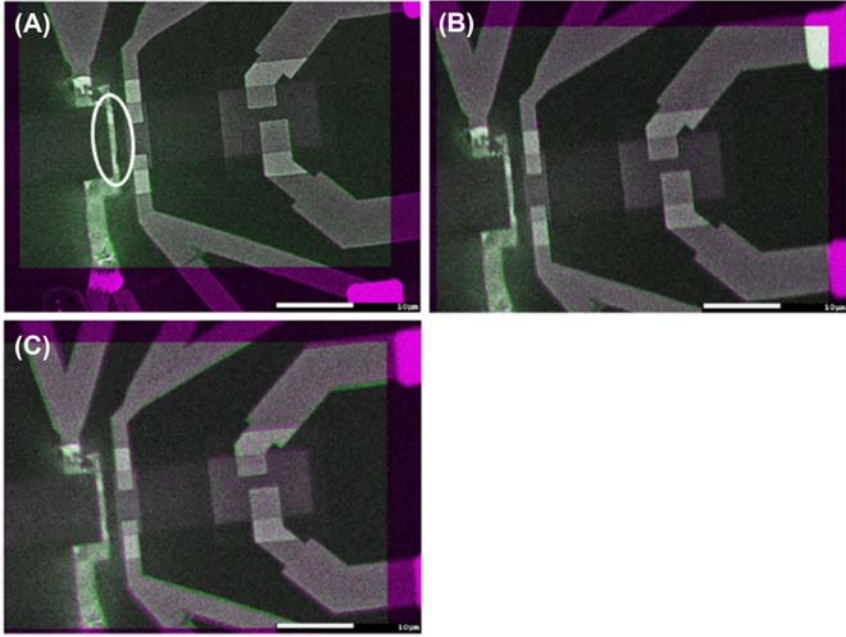


Figure 5.11 In situ SEM images of the Fe/GaAs lateral spin-valve under the current applications of (A) 0.25, (B) 200, and (C) 400 μA after subtracting two images taken at V_{acc} of 2.5 and 3.0 keV [27].

$\sim 1 \mu\text{m}$ within the $4\text{-}\mu\text{m}$ -wide injector as circled in Fig. 5.11A. These dark dots generate fewer BSEs than the remaining injector, that is, nonactive for spin-polarized electron transport in the spin-valve. This image indicates that the current injection is not uniformly distributed across the entire interface under the current application of 0.25 μA . With increasing the current to 200 μA , only one dark dot remains in the center of the injector as shown in Fig. 5.11B. A further increase in the current to 400 μA removes the dots as shown in Fig. 5.11C, confirming an almost uniform current distribution. This demonstrates that the in situ non-destructive imaging can visualize electron charge distributions and the corresponding effective junction area active for transport under different conditions for operation [44].

5.5 Summary

New non-destructive imaging has been developed by combining electron flight simulations and controlled electron-beam acceleration in SEM.

Such imaging can be very powerful for the analysis of buried interfaces with the in-plane resolution of ~ 2 nm in a broad range of nanoelectronic devices and beyond. By subtracting SEM images focusing above and below the interface under investigation, interfacial quality can be assessed, including the presence of contaminations, defects, and voids. The cause of these interfacial features can be identified by chemical analysis and can be fed back to fabrication processes to improve the processes for optimization. In situ imaging further allows us to correlate interfacial images with the corresponding electron transport properties, achieving the precise determination of active interfacial area under device operation. Therefore, this new imaging technique is ideal for fundamental studies in materials science and quality assurance for industrial production.

Acknowledgments

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CHAPTER 6

Scanning probe microscope

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6.1 Introduction

The Scanning probe microscope (SPM) is a versatile instrument that has evolved from its invention in the early 1980s. In today's research laboratory, the availability of advanced techniques is critical to solving the complex problems that scientists and engineers face [1–4]. The demands of today's research laboratories require the use of advanced techniques that are capable of solving complex problems and addressing pressing questions related to adhesion, bonding, contamination and surface cleanliness, corrosion, surface morphology, surface roughness, and topography, failure analysis and process monitoring [5–10]. The research laboratory is also required to respond quickly and efficiently to new requests. This requires a set of tools that are easy to use and provide accurate results in a timely manner. One needs a microscope that can provide high-resolution, quality images and quantitative data for analysis [11–16]. Rarely few analytical instruments effectively span such a wide range of applications. The rapid rise of scanning probe microscopy provides a truly marvelous tool that provides useful information about many topics. The ability to perform measurements with an SPM is one of the most powerful analytical techniques available today. Sample preparation technique elaborately reported by Seidel et al. [17] so we crossed sample preparation here. The SPM is a microscope that uses a probe tip to scan over the surface of a sample and measure the electrical, mechanical, or chemical properties of the material. SPM is mainly used to measure the electrical and mechanical properties of materials [18–22].

The SPM is a microscope that uses a probe tip to scan across the surface of a sample, generating an image by measuring small changes in light intensity as the probe interacts with different features on the surface. This measures the interaction forces between a probe tip and sample surface as shown in Fig. 6.1 [23–27]. These forces are measured on a scale of pico-Newtons (10^{-12} N) to nano-Newtons (10^{-9} N). The probe tip is placed

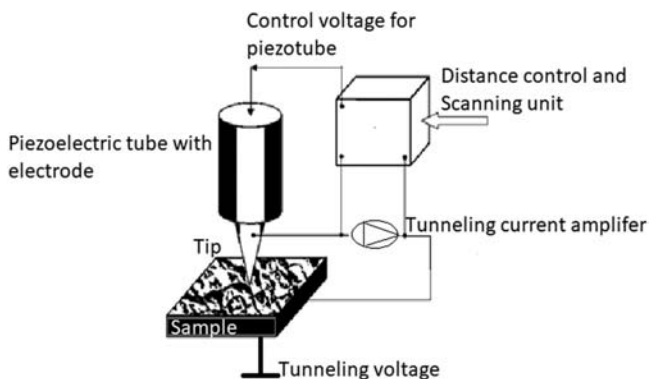


Figure 6.1 Working principle of scanning probe microscope.

in close proximity to the sample surface, typically within 10 nm (a nanometer is one billionth of a meter), but can be as far away as several hundred nanometers. In addition, SPM can be used to investigate the mechanical properties of materials at the atomic scale. The most common types of SPM are Scanning tunneling microscopy (STM), atomic force microscope (AFM), and XPS [16,28–35].

This article will provide an overview of the current state-of-the-art in scanning probe microscopy, Sample tip selection and illustrate how this technology can be used to answer a wide range of important questions related to science.

6.2 Working principles of scanning probe microscopes

The working principle of SPMs is using a probe, which is a tip made of either metal or glass, to measure the forces between it and the sample. SPMs are based on the fact that when a tip is brought into contact with a surface, it will respond by deforming in accordance with the properties of the material underneath. This deformation can be measured to yield information about the morphological properties of that material. SPMs are used for high-resolution imaging of surfaces and interfaces at the atomic scale. They use fine probes that can be moved in three dimensions to scan the surface, allowing for very large areas to be imaged quickly. However, their resolution is limited by the size of their probe tips. The probe consists of one or more tiny tips that can be moved across the surface at high speeds in order to collect data.

moves across a surface, it's constantly changing its resonance frequency. This means that each microscopic bump in the surface causes it to vibrate at a different frequency than before. By measuring these changes in frequency, we can map out the topography of the sample [2,31,36,37].

The laser can be used to measure distance by bouncing light off of a surface and measuring the time it takes for the light to reflect back. This is known as time-of-flight technology. A beam of light is sent from the microscope's objective lens, which focuses it onto a point on the sample. The cantilever used is similar to the one used in an AFM, which uses the tip to measure surface topography. This method allows scientists to study the location and size of atoms within materials. The AFM can also be used to detect defects in materials and investigate how they affect the material's properties. The cantilever in AFM is made from a unique material called a piezoelectric polymer. This type of material generates an electric field when it's stressed or bent, and vice versa [38,39]. The cantilever has a very sharp tip that can measure the smallest movements of a surface. The length of the cantilever is typically about 0.5 cm, but it can be as long as 3 cm [11,40,41].

6.2.1 Scanning probe microscope practical tip

The SPM technique is based on scanning a very sharp tip on the sample surface, which would provide critical information about its morphology. The SPM technique may be used to measure the shape and elevation of features that form the outer boundary of an object. The tip acts as a microscope lens, focusing light onto the sample surface and directing it back through an objective lens onto a detector. The tip is typically a single atom or molecule at the end of a cantilever beam.

The tip is scanned over the sample surface at different heights and the resulting signals are used to reconstruct an image. Which would provide critical information about its morphology as shown in Fig. 6.3 [42]. The tip typically consists of a hard material such as diamond or silicon carbide and is coated with an ultra-thin layer of metal such as gold to make it electrically conductive. It is a powerful technique that can be used to characterize materials at the nanoscale. It is widely used in material science and industrial applications, including semiconductor manufacturing, micro-electromechanical systems (MEMS) and other MEMS, surface chemistry, biotechnology, and medical diagnostics. The tip would be scanned very slowly, making it possible to obtain different kinds of information about the sample surface.

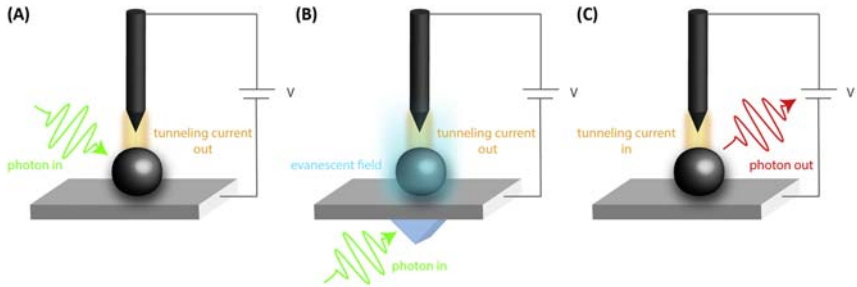


Figure 6.3 (A) Shows photon in (B). shows evanescence effect (C). tunneling current [42].

6.2.2 Scanning probe microscope piezoelectric effect

The piezoelectric scanner in SPM is designed to bend, expand, and contract in a controlled, predictable manner. The piezoelectric scanner is made up of two main parts: a ceramic plate and a piezoelectric element. The ceramic plate acts as the base of the scanner, while the piezoelectric element serves as its tip. This process is accomplished through the use of a piezoelectric material, which generates electricity when it's subjected to stress. If you take two pieces of quartz crystal and apply pressure to them, they will bend. This principle is what made it possible for an SPM to operate.

This is accomplished by attaching a piezoelectric crystal to the tip of a cantilever. The scanner is comprised of a thin, flexible membrane that is placed between two rigid electrodes as shown in Fig. 6.4. When an electric current is applied to the electrodes, they expand and contract due to the electrostrictive effect. The device contains a small amount of piezoelectric material—a composite that changes shape when an electric current is applied. When the material is heated, it expands; when it cools, it contracts. When the piezoelectric material is heated, it expands and pushes against one side of the membrane. When it cools, it contracts and pulls on the other side. This back-and-forth motion causes a vibration in the cantilever that moves back and forth across a surface like an inkjet printer head does when it scans an image onto paper. When the scanner is placed in the magnetic field, it experiences a torque that causes it to bend. This bending motion is proportional to the strength of the magnetic field and can be used as an output signal. This expansion causes the flexible membrane to bend, which in turn moves the cantilever. The amount of force applied to the cantilever is determined by how much current is applied between the electrodes. The piezoelectric material is mounted on the end of a cantilever that is attached to the scanner. The piezoelectric material causes the

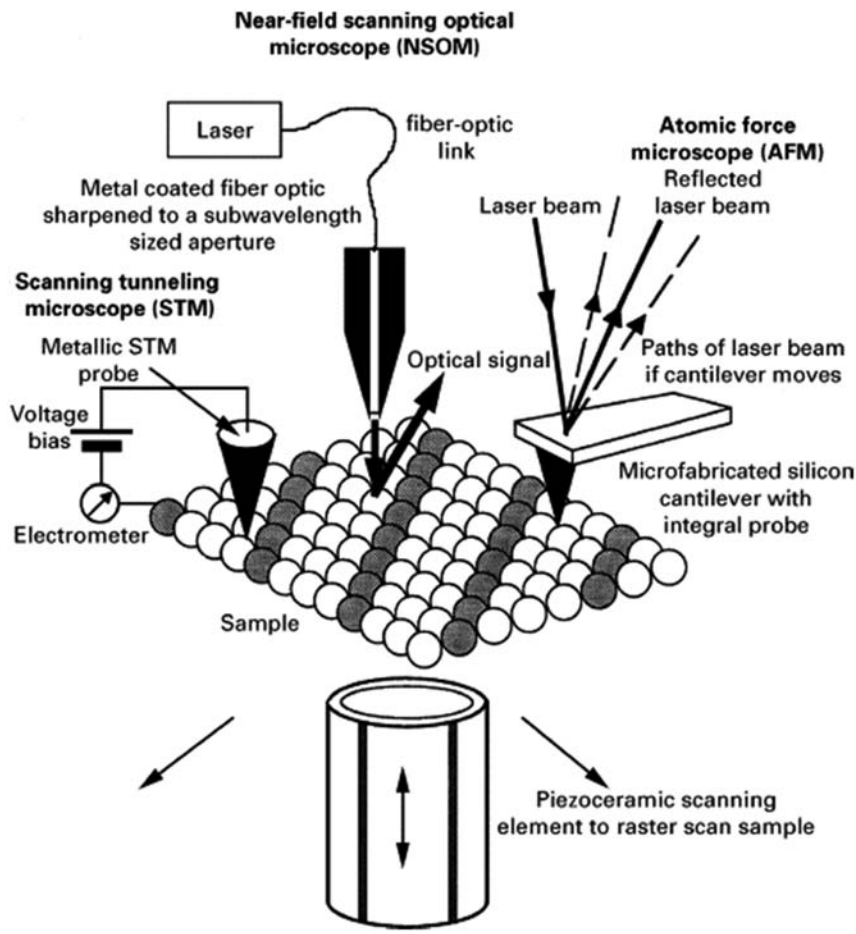


Figure 6.4 Schematic diagram of scanning probe microscope [43].

cantilever to move in response to an electric current, which scans the image across a screen. The scanner is mounted on a gantry that moves back and forth over the sample. As it does so, the piezoelectric crystal inside the tip expands and contracts, creating an electronic signal that represents the surface topography of whatever material is being scanned [44–46].

6.2.3 Data deposit technique

STM is a modern and recently developed SPM technology. One of the main features of STM is its ability to image the surface of a material at the atomic scale. In contrast to conventional microscopes which transmit light

and scan across the sample to build an image, in STM, the sample surface is scanned between the tip and conductive metal pin so that atoms are probed sequentially by alternating current (AC) fields. When the AC voltage is increased, one or more electrons flow between the metal tip and the surface. This can be converted into an electrical charge difference which may be proportional to either mass change or local chemical potential caused by the adsorption of electrons onto atoms at the surface. The STM tip is made of a highly conductive material such as tungsten, which is atomically sharp. When the tip is brought close to a surface and held at a constant distance above it, an electrical current flow between them. This current causes an electrostatic force that pulls the tip onto the surface if there are no other forces present. This can be recorded as a topographic image at the atomic scale of the material. The STM instrument uses a superconducting magnet to produce a very strong magnetic field, which prevents any other kind of electrical current from flowing inside the instrument. This allows electrons to be moved around by applying an electric current through them. An image is built up by scanning the tip over the surface while recording the signals produced by each point in the scan or by tunneling electrons through barriers [47,48].

6.3 Scanning probe microscope methods

6.3.1 Chemical force microscopy

The technology of chemical force microscopy (CFM) is a technique, which consists of modifying probes with covalently bonded molecules that terminate in a well-defined functional group or biological molecule. By using a suitable tip modification, chemically specific probing of the surface can be achieved when using 2D materials to detect AFM tips. A CFM experiment has been used to probe fundamental adhesion and friction forces at the solid-liquid interface. The tip of the probe is usually made out of silicon nitride or silicon carbide. The tip can be modified with a variety of chemical groups including biotin and streptavidin, which are used to bind with biological molecules or proteins on surfaces. CFM experiments are also used to probe the physical properties of 2D materials. In addition, CFM can be used to probe the surface chemistry of solid surfaces such as photonic crystals and graphene. The most common way to perform CFM is by using the Wilhelmy method, which was first developed in 1869. This method involves placing a liquid drop on top of a solid surface and then measuring the contact angle with respect to the

horizontal plane. CFM can be used to study biological molecules, proteins, and cells at the nanoscale. The CFM experiment is an extension of the AFM technique. The measurement is the mapping of surfaces with chemical contrast. Specific imaging of biological surfaces, imaging of hydrophilic/hydrophobic contrasts, direct determination of intermolecular forces, determination of adhesion forces on induction of chemical reactions on local scale pKa-value determination [49–52].

6.3.2 Magnetic force microscope

The magnetic force microscope (MFM) is a technique used to determine the number and type of magnetic domains on a sample in order to study the magnetic properties of materials. MFM is a conducting cantilever that has a coating such as (Co-Cr). The interactions between the probe and the surface can be detected via the deflection of the cantilever (contact mode). The changes in the magnetic field shift the resonant frequency of the cantilever—this shift can be monitored. A key aspect of this measurement is that “background is taken” prior to the MFM measurement to ensure that it is due to magnetic domains and not topography. First, the topography of the sample is measured, then the measurement of magnetic domains on a surface can be done using MFM. The main advantage of MFM is that it is low-cost and easy-to-use method. The main disadvantage of MFM is that there are no macroscopic quantities derived from this technique, as only the spatial distribution of magnetic domains can be determined. Due to these limitations, MFM has been used mainly as an imaging alternative to other techniques such as AFM and SEM. In order to measure the magnetization, a sample may be placed on an MFM tip that is made out of permalloy (NiFeCo), which has a very large magnetic moment. Another disadvantage is that it is not possible to determine the direction of magnetization from MFM images [49–52].

6.3.3 Lateral force microscopy

Lateral Force Microscopy (LFM) is a sensitive method used to detect molecular interactions in the contact mode. During scanning, the cantilever bends not only in the vertical direction, but also undergoes torsional deformation as a result of physical impediments. This imaging mode offers nanometer-scale resolution with sensitivity to variations in surface composition, molecular organization, mechanical properties, and acid-base characteristics. The cantilever extends from a thin metal tip that is attached to

a flexible substrate. LFM can be used to image both static and dynamic interactions of molecules at the solid-liquid interface. It is a powerful tool for investigating how molecules interact with each other, or how changes in the surface affect their behavior. The method is based on the principle of surface force microscopy, which utilizes cantilever geometry and tip-sample interactions to measure nanometer-scale forces. In LFM, the cantilever is mounted into a holder that allows torsional deformation without affecting vertical bending. This enables analysis of lateral forces, which provide information on the local mechanical properties of materials in contact. This imaging mode provides nanometer-scale resolution with sensitivity to variations in surface composition, molecular arrangement, mechanical properties, and acid-base characteristics. The cantilever is a thin silicon probe that moves laterally across the surface of interest at a constant speed while being scanned by a laser beam. The cantilever bends not only vertically but also undergoes torsional deformation as a result of physical impediments it encounters during scanning [49–52].

6.3.4 Phase imaging

Phase Scanning is a powerful, new extension of tapping mode AFM. It detects variations in composition, adhesion, and friction by mapping the phase of the cantilever oscillation during tapping mode. Some applications include the identification of contaminants and mapping of different components in composite materials differentiating regions of high and low surface adhesion or hardness. In addition to the mapping of phase, the cantilever oscillation can be used to measure force and torque. This feature allows for high-resolution detection of contamination or different components in composite materials. The technique is non-destructive and has a resolution down to 1 nm. Phase scanning can be used as a powerful tool in materials science and engineering. It is often used to identify contaminants or impurities, map out different regions of material with different phase properties and even differentiate between materials with high and low surface adhesion. The phase scan is carried out by exciting the cantilever at its resonance frequency, which causes it to oscillate in both amplitude and phase. The cantilever motion is converted into a voltage signal that can be measured at any time during the tapping cycle. The cantilever is loaded with a sample that has been deposited on the surface. The cantilever motion is then scanned through various tapping cycles, which are typically defined by the ratio of amplitude to phase shift and the number of cycles required for the cantilever to return to

equilibrium. The phase scan is typically carried out by exciting the cantilever at its resonance frequency, which causes it to oscillate in both amplitude and phase. The cantilever motion is converted into a voltage signal that can be measured at any time during the tapping cycle. The amplitude and phase of the cantilever motion are then used to calculate Young's modulus (stiffness), Poisson's ratio (elasticity), and other material properties. The phase scan is an important and powerful tool in materials science and engineering. It is often used to identify contaminants or impurities, map out different regions of material with different phase properties and even differentiate between materials with high and low surface adhesion. The phase scan can be used to determine the frequency shift of the cantilever motion, which is proportional to the depth of penetration of the sample surface. By measuring this shift at different positions on the material surface, it is possible to build up a picture of its structure and composition. The phase scan is also particularly useful for inspecting materials with high surface adhesion. When the cantilever is moved across a material surface with low adhesion, it can easily be detached from the surface as it moves, causing a large frequency shift. The phase scan is an important and powerful tool in materials science and engineering. It is often used to identify contaminants or impurities, map out different regions of material with different phase properties and even differentiate between materials with high and low surface adhesion. The phase scan is also used to measure the surface roughness of a material and can be used as a tool for quality control in the production line. This technique is particularly useful when measuring materials with very small features, such as nanomaterials or microelectronic devices. The phase scan is mainly used to characterize the surface topography of a material. The technique can be used to identify contaminants or impurities, map out regions of material with different phase properties and even differentiate between materials with high and low surface adhesion [49–52].

6.4 Scanning probe microscope applications

SPM-based techniques, in comparison to most microscopes, can scan living biological systems with an unprecedentedly low signal-to-noise ratio. Due to the increasing complexity of such living systems, users are frequently challenged to identify specific cellular features and must either compare the sample topography to known morphologies (for example, structural references) or combine SPM with fluorescence microscopy, where a subset of structural details has been fluorescently labeled. The approach might be

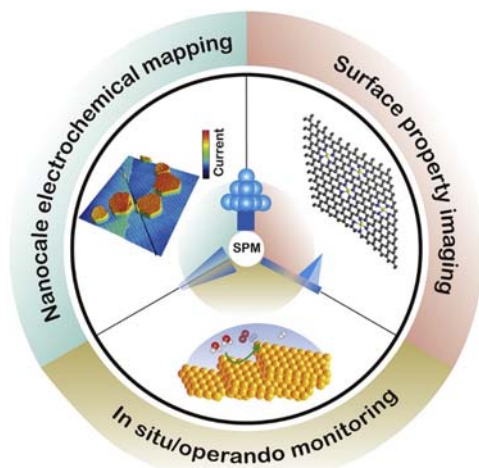


Figure 6.5 Wide application of scanning probe microscope [1].

AFM-based functional imaging, which employs the AFM tip as a nanoscopic instrument to concurrently scan, measure, morphologically map, and control particular interactions of biological components. Biological systems are highly dynamic, changing state either actively or passively in milliseconds to minutes. So the status of complex biosystems recorded by SPM must be constantly monitored and should not be influenced by factors such as evaporation, adsorption of a 3D item onto a substrate, non-physiological temperature, or a buffer solution.

As shown in Fig. 6.5, the wide range of application are noted. Even biological systems can be monitored at work using time-lapse or elevated footage SPM if all of the SPM variables are appropriately tuned. Other microscopic techniques, such as cryogenic electron microscopy, can offer atomistic images of biological systems in action in 3D. As a result, SPM might be used as a superficial approach that can be recycled to investigate niches that no other technology can, such as concurrently photographing biological systems which in action can be viewed at the best quality at nanometer level and characterizing their mechanical, chemical, and biological features [53–56].

6.5 Conclusion

Surface and interface research has numerous key methodological techniques. Among the backbone analytical experiments of the atomic and molecular structure of compounds, SPM is currently regarded as one of

the best. Spectrometry is generally used to analyze macromolecules, however for nano and below-sized materials (atomic scale) SPM has proven to be an efficient tool for analysis. The fact that biomolecules are mobile and have dynamic structures that vary over time, is a basic hurdle to analyze biological systems using SPM. To rectify this advantage some methods are used such as shortening data acquisition times and, in some cases, boosting SPM's Scanning speed might be beneficial. This chapter solely focused on (1) various techniques used for imaging acquisition through SPM, (2) merits and demerits in the techniques used, (3) hazards faced during acquisition, and the solution used to rectify that.

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CHAPTER 7

Transmission electron microscope

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7.1 Introduction

Microscopes were the savior because whenever we struggled to observe something through the naked eye. Microscopes can be found in an irreplaceable spot in all science labs. Due to this enormous types of microscopes had been invented over the century. These types mostly differ by the usage of the light source. The most advanced innovation in the microscope field is Transmission Electron Microscope (TEM). The specimen is viewed by passing a beam of electrons through a thin spectrum. This is the same as a light microscope, but the difference is the Light microscope uses natural light whereas TEM uses electrons to view the specimen. In this chapter, the principle, featuring applications, instrumentation, and applications of the TEM were discussed [1–3].

7.2 Principle

The usage of electron beams was implemented due to the Abbe theory. This theory reported an equation [Eq. (7.1)] of the resolution limit for the optical microscope.

$$d = \frac{0.61\lambda}{N} \quad (7.1)$$

where λ is the wavelength and N is the numerical aperture, the Numerical aperture is usually 1 excluding some special cases. Thus the resolution is based on the wavelength of the light. This clearly indicated that to produce a higher-resolution image, the wavelength of the light source should be shortened. Based on Einstein's theory light consists of energy which can have wave-like properties and de Broglie's matter-wave concept,

Ruska in 1931 developed the first TEM with an electron beam having wave properties and higher resolution. The light source of this instrument is a very fine accelerated electron beam which is allowed to pass through a thin layer of the specimen. The transmitted beam was then allowed to land on a fluorescent screen and magnified. The shorter wavelength of the electrons results in a higher resolution of the sample. By using scattered electrons, the resolution of the image will be much higher when compared to the light microscope in which the resolution is comparatively less. This helps the TEM expose the finest details of the specimen.

7.3 Instrumentation

The TEM mainly consists of three essential parts or systems (Fig. 7.1A). They are:

7.3.1 The electron gun

Electron gun generates the electron beam through which the specimen is viewed. The element in it is usually a sharp-edged material that acts as a cathode surrounded by a control grid. The cathode and control grid is at a negative potential. The final electrode of an electron gun is the anode. The intensity of the beam is controlled by a condenser lens. Table 7.1 shows the advantages and disadvantages of types of electron gun.

Tungsten and Lanthanum hexaboride uses high temperature to produce electron beam. Electron guns using temperature are typically known as thermionic emission. In contrast, electron gun that uses an electric field to release electron beam is known as a field emission gun (EFG). EFG is categorized into two namely (1) cold and (2) Schottky. Cold FEG does not need any temperature criteria to produce a beam since its name. It contains a single crystal of tungsten and needs a very high vacuum to maintain its contaminant free. Schottky FEG is made up of a single crystal of tungsten coated with zirconium oxide (ZrO). Unlike Cold FEG, this required high temperature (1800K). The coating of ZrO lowers the work function. This helps in high current density and low energy spread which enables high brightness of imaging.

Hairpin look-alike filament made up of W wire of 100 μm is typically used for electron generation. In a thermionic emitter, using resistive heating the filament at the cathode is heated up to 2000K–2700K. The beam is accelerated through a small hole at the anode where it was measured for current. This is used to adjust the power supply for the electron gun [4].

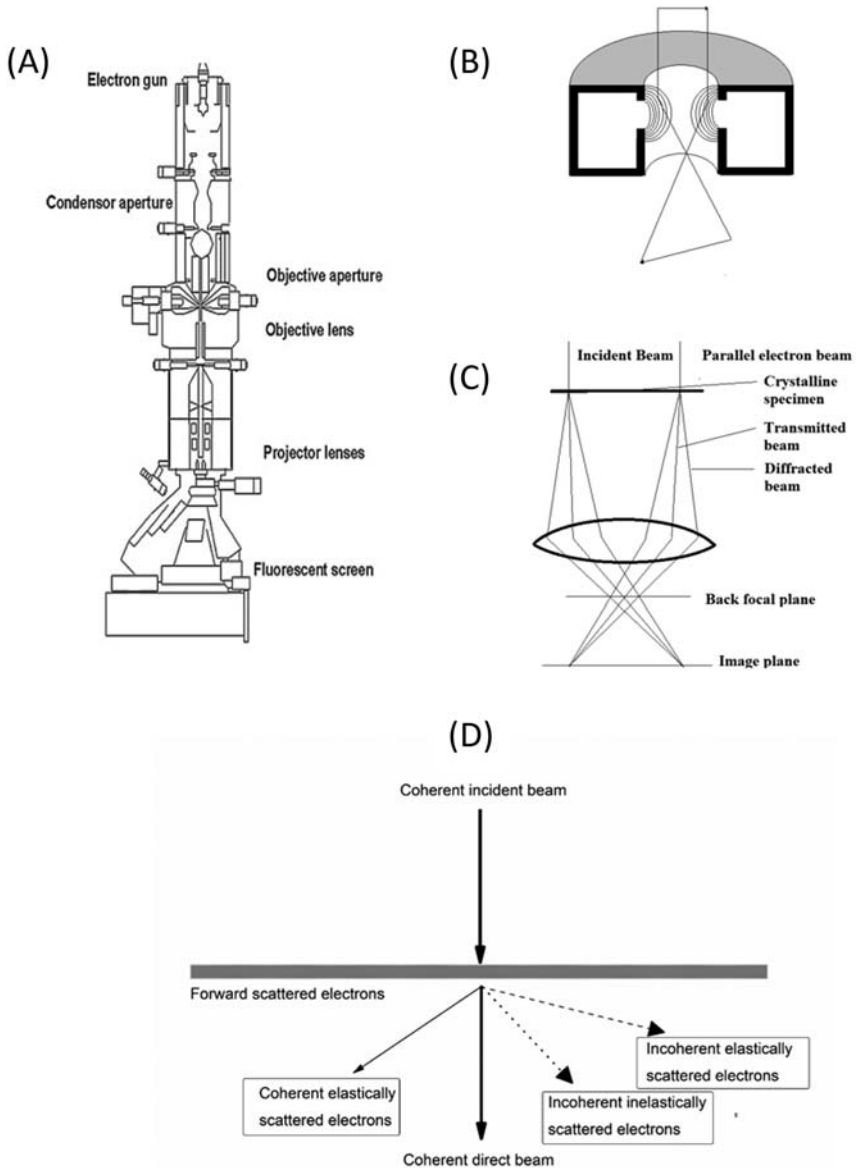


Figure 7.1 (A) Illustration of TEM, (B) Magnetic lens, (C) Beam path around sample, (D) Beam paths after incident on the sample.

Due to high temperatures, the wire of tungsten evaporates and easily breaks. The brightness is also low on tungsten filament. The brightness can be increased by replacing the tungsten filament with lanthanum

Table 7.1 Types of electron gun with advantages and disadvantages.

Types	Advantages	Disadvantages
Tungsten (W)	Handling: easy vacuum: Moderate stability: long time total beam current: high	Brightness: lowlife time: low (≈ 100 h)
Lanthanum hexaboride (LaB ₆)	Brightness: high total beam current: highlife time: long (500–1000 h)	Handling: fragile vacuum: high stability: long time instabilities
Field emission gun (FEG)	Brightness: extremely highlife time: very long (2000h)	Handling: very fragile stability: current instabilities vacuum: ultra high vacuum

hexaboride (LaB₆). The single crystal of LaB₆ is mounted on a graphitic carbon or rhenium base. The LaB₆ could be contaminated easily thus requiring a better vacuum. This also increases the lifetime of the gun to 1000 h. More brightness and lifetime could be obtained by using EFGs. These are electrically charged at the magnitude of 10 V/nm, by doing so the electron escapes the cathode by reducing the potential barrier. The cold field emitter produces a huge amount of mechanical stress, metal such as tungsten which has the strength to withstand the stress was soft-welded on a wire of tungsten. The potential difference between the first electrode and the tip is maintained in the order of 3–5 kV to produce 10 μ A electron emission. The beam energy was regulated by the potential difference between the tip and the second electrode. Despite of high vacuum, the CFE tip needs to be cleaned daily by flashing to a temperature of 2500K. The emission would be high after flashing however it reduces soon and stabilizes once the surface is covered. After continuous flashing (several years), the tip becomes more blunt rendered unfit, and has to be changed. To overcome this flashing process, SFE was introduced. SFE is operated at high temperatures. Thus it self-cleans itself through high temperature. Table 7.2 shows the characteristics of the types of electron guns. The work function reduction is improved by coating the tip surface using ZrO₂ which has a finite lifetime and needs to be replaced every year [5].

7.3.2 Lens

The TEM has different types of lenses in it. One is the Condensor lens and the other is the Objective lens. This lens magnifies the specimen and

Table 7.2 Types of electron gun with their characteristics.

Material used in gun	Source size (nm)	Energy speed (eV)	Brightness (A/cm ² SR)	Short-term beam current stability (%RMS)	Operating vacuum (Torr)	Approximate service life (hours)
Schottky	15	0.3–1.0	5×10^8	<1	10^{-9}	6000
Cold field	3	0.2–0.3	10^9	4–6	10^{-10}	2000
LaB ₆	104	1.0	10^7	<1	10^{-7}	1000
W	>104	1.0	10^6	<1	10^{-5}	100

also increases the resolution of the image. A single projector lens may provide a range of magnifications of 5:1. If the final image should be obtained in higher magnification, photographic or digital enlargement methods are used. The quality of the image depends upon the accuracy of the mechanical and electrical adjustments by which the various lenses are aligned to the illuminating system [6].

When an electron passes through an electromagnetic field it undergoes rotation (Fig. 7.1B). After crossing the center of the lens, the rotation is reversed as the radial component of the magnetic field reverses. An electron wandering away from the axis of the path will spiral toward the optic axis. The point beam begins bending to the point where it crosses the axis of the lens is called the focal length. The focal length of the optical lenses is fixed though the focal length of the electron lens can be varied by changing the current in the coils. The magnetic field at the center would be contributed by each turn of the solenoid. The center flux density is calculated by

$$B = \mu \left(\frac{NI}{l} \right) \quad (7.1)$$

Where μ = permeability of surrounding material,

N = number of turns

I = current flowing in the coil

L = length of the solenoid

$\left(\frac{NI}{l} \right)$ could be substituted as H . Since at high magnetic fields, iron reaches magnetic saturation therefore $\mu = 1$. Thus the strength of the magnetic field defines flux density at the center ($B = H$).

7.3.2.1 Condensor lens

Condensor illuminates a specific part of the specimen. Dissimilar to the glass lens used in the optical microscope, TEM has an electromagnetic lens since electrons cannot pass through glass. These electromagnetic waves are produced by copper wires coiled on iron pole pieces placed on both sides of the beam path. This makes the beam deflect by converging before hitting the specimen. Condensor has a large focal length due to the large bore.

These lenses play a crucial role in adjusting the intensity, illumination angle, and area autonomously. This allows fixing the resolution. The solenoid is covered around soft iron, and the magnetic field along the axis is increased. If the entire coil except at a narrow annular gap is made of soft iron, a greater concentration of the magnetic field along a short axial distance occurs. The annular rings (pole pieces) focus the magnetic field at a given location.

7.3.2.2 Objective lens

The aperture mainly consists of lenses that are electromagnetic, it has conical pole pieces as an extension. The conical pole forms a small gap in which the specimen holder is placed. The objective lens will produce a diffraction pattern/image in the focal plane on the back side. The image or pattern obtained by the diffraction is taken for further magnification process. Some apertures which have a size of a few micrometers (approximately 10–15 μm) will produce diffraction. Aperture will screen the stray electrons while allowing a narrow beam to fall on one plane resulting in high-resolution images [7].

7.3.3 Detector

The main purpose of using a detector is to record the images. It also plays a crucial role in the conversion of fast-moving electrons into light with the help of a screen layered with phosphorescent. The obtained light is shifted to Charge Coupled Device converting light to electrical charge (Fig. 7.1C). Nowadays, two methods were developed, (1) direct electron detectors have been developed which convert directly fast-moving electrons into slow-moving electrons. (2) The detectors are digitalized, which converts light to images. These digital detectors converts images based on the value of optical density and also with the help of scanners.

There are two types of beams transmitted after passing through the sample, (1) transmitted beam, (2) diffracted beam. By capturing any one we can get either bright field or dark field images. A suitable aperture is

used to exclude the unwanted transmitted beam. This aperture is placed before the focal plane of the objective lens. Particular diffracted beams and transmitted beam can be captured to obtain dark and bright field images respectively. Either moving the aperture or tilting the magnetic field are the techniques applied to capture dark field images [8].

7.3.4 Image recorder

This system helps in converting the electron image to some optical image that our human eye can view. Fundamentally electron image produced is monochromatic which will then be converted to be visible to the human eye. This is done by allowing the electrons to fall on a fluorescent screen at the base of the microscope. This can be an aid to the visual interpretation and to create a visually attractive picture from the raw image. Although elastically and inelastically scattered electrons were obtained from the electron sample interactions, elastically scattered electrons are mostly used to form bright field images (Fig. 7.1D).

7.4 Features

Over the years many innovative modifications were coupled with the TEM to get varying results. These modifications could be majorly categorized into three; (1) spectroscopy, (2) imaging, and (3) diffraction (Fig. 7.2).

These different combinations could be used for identifying

1. nature of crystal (single, poly, or amorphous), orientation
2. orientation
3. crystal structure

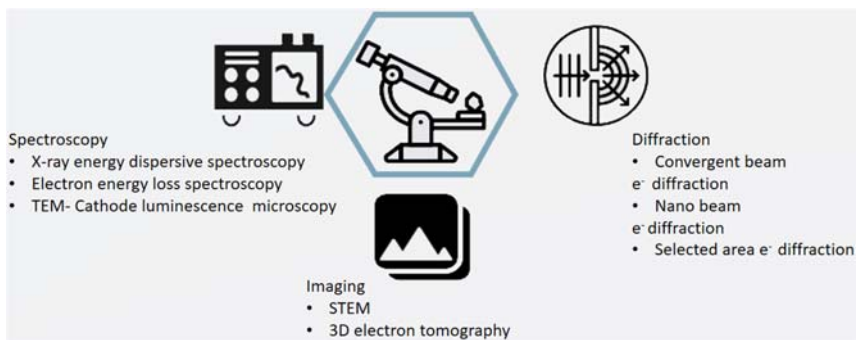


Figure 7.2 Features of transmission electron microscopy with modification and varying approach.

4. quality
5. dislocations in lattice
6. grain boundaries
7. distribution
8. analytical attachments [X-ray energy dispersive spectroscopy (EDX), Electron energy loss spectroscopy (EELS)]

7.4.1 Spectroscopy

Three types of measurements were possible in instrumentally modified TEM (Fig. 7.3).

7.4.1.1 X-ray energy dispersive spectroscopy

When the beam of high energy ejects the electrons in the inner shell of atoms in the sample, the excited ionized atoms replace the missing electrons with electrons from outer shells. This jump produces either auger electrons or X-rays. The difference in the energy of electron shells involved can be used to identify the atom. In EDX, this unique signature is characterized by the atoms of different elements in the sample.

The most used spectroscopy among them is EDX, which basically reveals the percentage of elements present in a specific area. This is possible by including an X-ray detector. EDX-TEM has a wide range of applications from environmental monitoring to improving catalysts. Fig. 7.3A shows the spread of cobalt, aluminum, and molybdenum elements over the specific area of the specimen. Further MoS₂ stacks positioned in voids among alumina and S-deficient cobalt-molybdenum phase were identified using EDX [9].

7.4.1.2 Electron energy loss spectroscopy

Electron energy loss spectroscopy (EELS) is mostly used for atom identification and chemical bonding. Basically, two types of electron energy loss take place when electrons interact with the sample. (1) Low loss of energy (<50 eV) corresponding to the interaction between weak outer-shell electron and beam. (2) High energy loss (> 50 eV) of the electron that has been scattered inelastically by inner electron shells. The high and low contains information regarding the characteristics of the atom and electronic information of the sample, respectively.

An EELS consists series of peaks at low energies loss and peaks at high energy loss. The former is created by plasmon oscillations while the latter is evaluated by the unique onset potential of the atoms. In Bloch waves

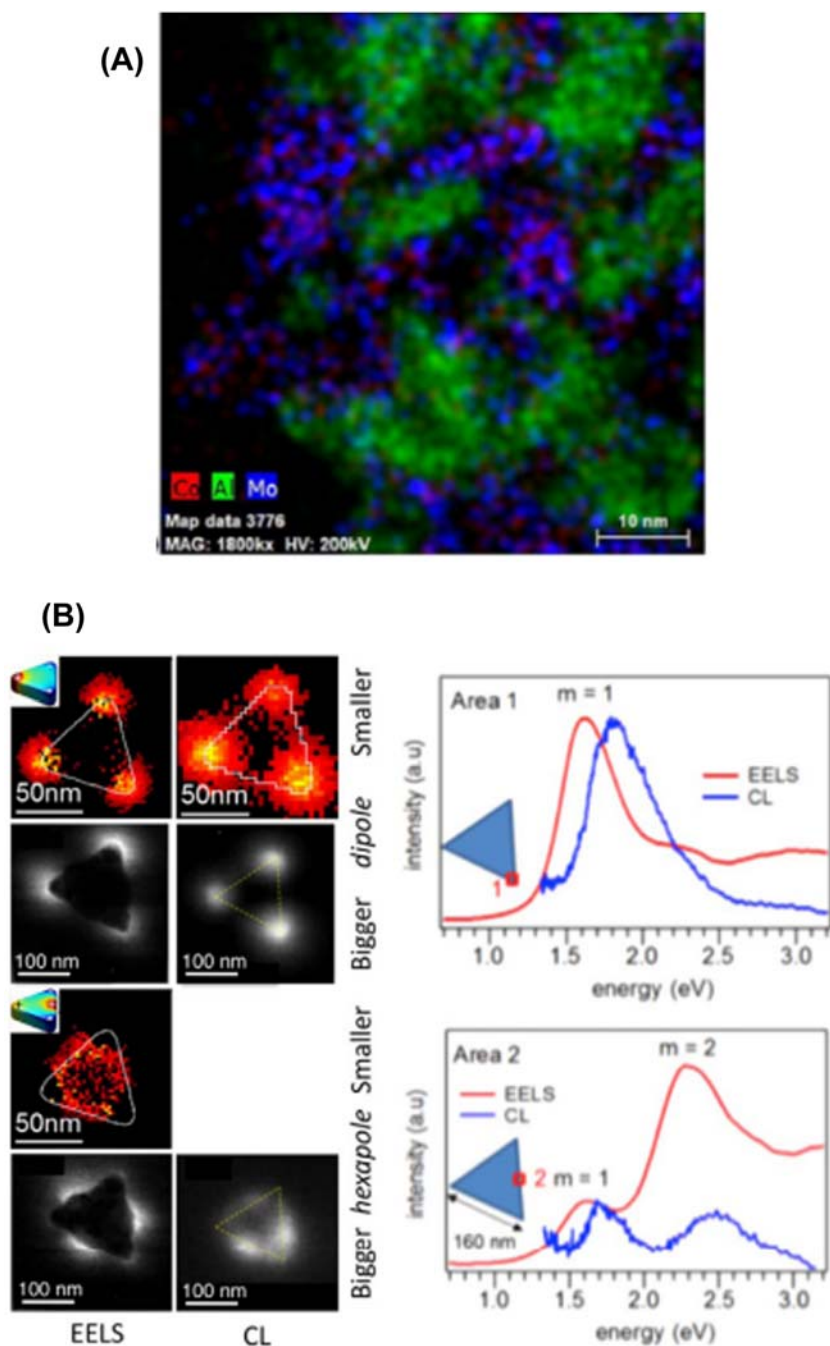


Figure 7.3 (A) EDX TEM [9] (B) CL and EELS of TEM [10]. Reproduced with permission (A) S. Eijbouts, L.C.A. van den Oetelaar, M. Rayner, H. Govaers, T. Boonen, Combined HR TEM and STEM-EDX evaluation—the key to better understanding of the Co-Mo sulfide active phase in real-life Co-Mo-P/Al₂O₃ catalysts, *J. Catal.* 403 (2021) 56–73. <https://doi.org/10.1016/j.jcat.2021.01.024>. (B) M. Kociak, L.F. Zagonel, Cathodoluminescence in the scanning transmission electron microscope, *Ultramicroscopy* 176 (2017) 112–131. <https://doi.org/10.1016/j.ultramic.2017.03.014>.

(nondissipative modes) in a photonic band gap, all the energy lost by an electron is transformed into radiation. This can be seen in Fig. 7.3B where the difference between EELS and CL was shown. In CL, the tip of the triangle (dipolar) was radiative and thus visible, however in EELS all modes are visible in EELS.

7.4.1.3 Cathodoluminescence

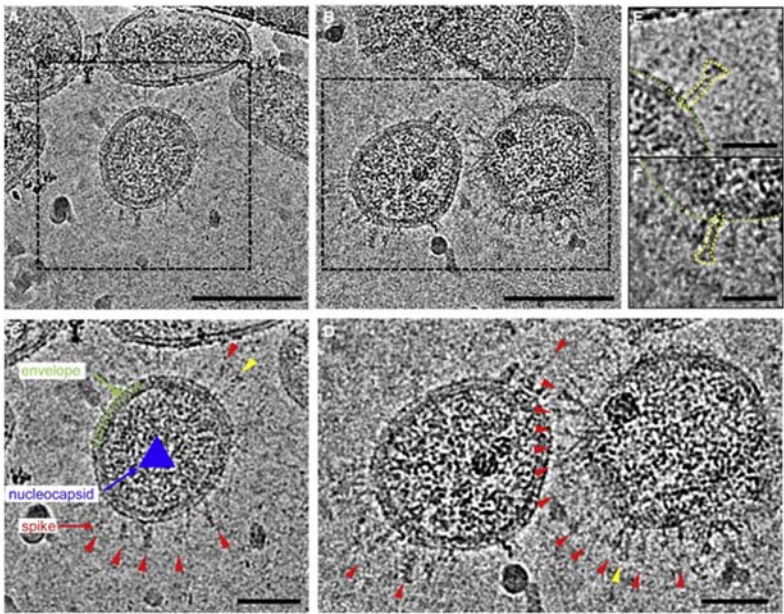
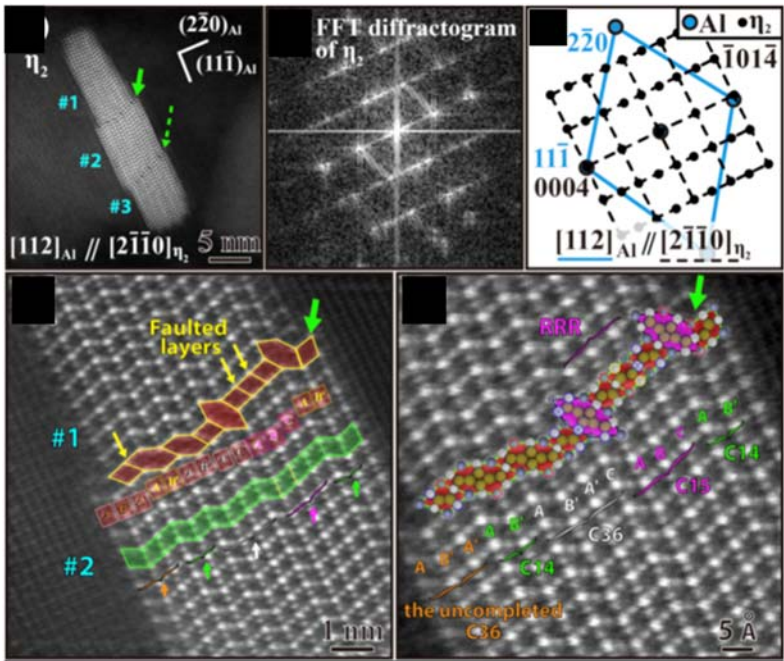
Emitting of a photon when exposed to high-velocity electrons is known as cathodoluminescence (CL). These phenomena can be widely observed in inorganic materials. Fluorophores are used to get high-resolution images. CLM can be highly informative for Rare Earth elements due to their characteristics such as narrow spectral lines, high photostability, and sharp fluorescence emission. CL can be used for high-resolution investigations of plasmonics and quantum-confined materials. New applications, such as time-resolved STEMCL or bio-imaging are most likely promised a great future [10]. Due to differing techniques, damped excitation shifts the CL and EELS which can be seen in Fig. 7.3B. This is because of the ability to map plasmon by CL.

7.4.2 Imaging

Fig. 7.4 describes STEM showing defect chains.

7.4.2.1 Scanning transmission electron microscope

A scanning transmission electron microscope (STEM) is a type of TEM. Conventional TEM passes the electron beam through a thin specimen, however in STEM electron beam is focused on only a tiny fine spot (0.05–0.2 nm). The beam parallel to the optical axis is illuminated on the entire specimen through a raster illumination system. This is suitable for analytical methods like dark field imaging, EDX, and EELS. STEM can run both spectroscopic data and imaging simultaneously [13,14]. STEM is highly useful in detecting diffraction patterns, atom arrangement, and crystal defects. The best example is the investigation of crystal defects in Al alloy. Fig. 7.4A shows the atomic projection showing the zig-zag rhombic stackings with the irregular subunit defect chains (as indicated by solid and dotted arrows in green). Fig. 7.4B and C show the corresponding FFT diffractograms and simulated diffraction patterns of Fig. 7.4A, showing the orientation relationship of the plane with respect to the aluminum matrix. Fig. 7.4D and 7.4E shows the enlarged images of 7.4A. Fig. 7.4D shows the detailed atomic columns of the rhombic stackings



nearby the irregular subunit defect chain with the accompanying faulted layers (indicated by yellow arrows). Fig. 7.4E shows the atom arrangements of the adjacent area being constructed by the model of Komura array model and the possible unit stacking being displayed: the uncompleted C36 [11].

7.4.2.2 ET

Since a typical TEM produces only 2D images, Cryoelectron tomography is the exception in producing 3D images of the specimen. Tomogram is constructing a 3D image by compiling the 2D images taken from different angles of the same object. Generally, the sample is tilted from + 60 to −60 degrees by taking a 2D TEM image at every 1 or 2 degree intervals (Fig. 7.5). Shows the simple instrumentation of ET. The images taken at each angle are used to construct a 3D image computationally. Through this method high resolution (1–4 nm) 3D samples can be inspected. Thus the method is highly useful for biological samples, especially macromolecules, and cells.

Since biological samples contain water that can alter the vacuum or other substances that can easily react with the surroundings, the samples are prepared in two ways. (1) The samples are prepared by dehydration and fixation. (2) The sample was mixed with a standard aqueous media and placed on the grid. The grid is then immersed in cryogens that are highly effective and can form vitreous ice. The vitreous ice is formed by water without any crystalline lattice. This preserves the native cellular structures. The cryogen-treated samples were imaged at liquid nitrogen temperatures to prevent water crystalline formation. Usually, viruses,

Figure 7.4 STEM showing defect chains (top left), FFT diffractogram (top middle), simulated diffraction patterns (top right), showing the atomic columns of the rhombic stackings nearby the irregular subunit defect chain with the accompanying faulted layers (indicated by yellow arrows) (middle left), the atom arrangements of the adjacent area being constructed by the model of Komura array model and the possible unit stacking being displayed: the uncompleted C36 (middle right) [11], and electron tomogram (bottom four images) [12]. *Reproduced with permission T.F. Chung, Y.L. Yang, C.L. Tai, M. Shiojiri, C.N. Hsiao, C.S. Tsao, et al., HR-STEM investigation of atomic lattice defects in different types of η precipitates in creep-age forming Al–Zn–Mg–Cu aluminum alloy, Mater. Sci. Eng. A. 815 (2021) 141213. <https://doi.org/10.1016/j.msea.2021.141213> C. Liu, L. Mendonça, Y. Yang, Y. Gao, C. Shen, J. Liu, et al., The architecture of inactivated SARS-CoV-2 with postfusion spikes revealed by cryo-EM and cryo-ET, Structure 28 (2020) 1218–1224.e4. <https://doi.org/10.1016/j.str.2020.10.001>.*

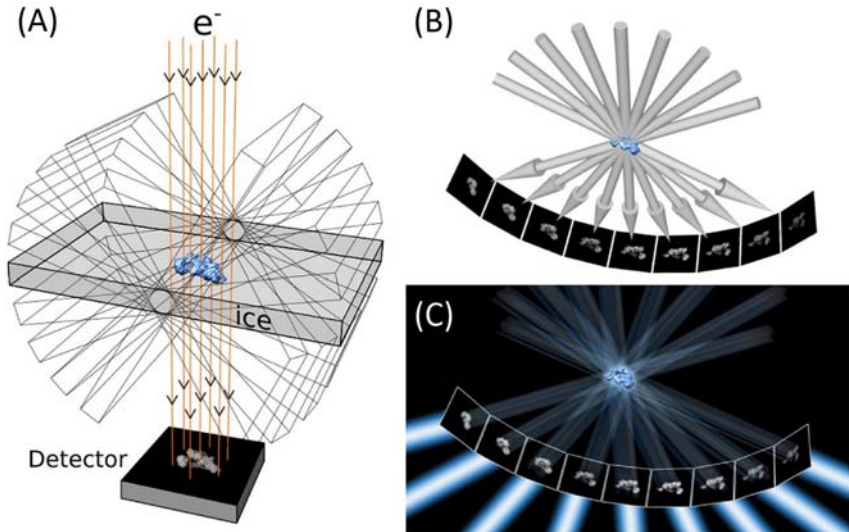


Figure 7.5 (A) Instrumentation of electron tomography, (B) The resulting projection images of the specimen from different angular views yields a so-called tilt-series. (C) This tilt-series is computationally back-projected to form a 3D volume, the tomogram. Reproduced with permission R.I. Koning, A.J. Koster, T.H. Sharp, *Advances in cryo-electron tomography for biology and medicine*, *Ann. Ana. - Anatomischer Anzeiger*, 217 (2018) 82–96, <https://doi.org/10.1016/j.aanat.2018.02.004>.

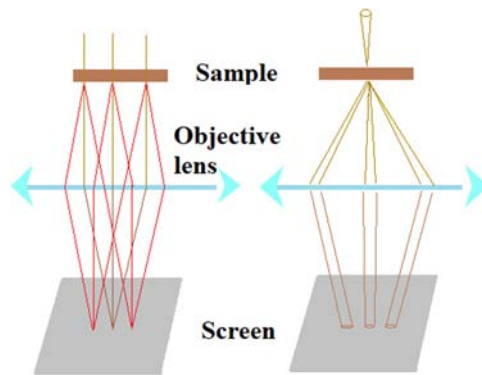


Figure 7.6 SAED versus CBED instrumentation.

archaea, and bacteria were imaged using ET. Fig. 7.4F shows the 3-D images of Inactivated SARS-CoV-2 [12].

7.4.3 Diffraction

A pictorial representation of SAED versus CBED instrumentation has been provided in Fig. 7.6.

7.4.3.1 SAED

When a thin sample was passed through by electrons, the interaction with the sample atoms causes a phase shift in the wave of electrons as shown in Fig. 7.8. The interference of the electron wave at lattice planes of materials results in electron diffraction. Diffraction patterns thus reflect the atomic arrangement in the sample. For SAED, the paralleled electron beams illuminate the sample with the diffraction spots formed in the back focal plane of the objective lens.

Selected area electron diffraction is obtained by an aperture placed in the objective lens. The diffraction pattern at the far field is imaged by the rays that are passing through this aperture. The apertures are placed in a specific place under the thin sample. The evaluated area would be a few hundred nanometers. The result would be either spot patterns corresponding single crystal diffraction or ring patterns resulting from powder diffraction from multiple crystals. Using the formula $R = \frac{\lambda L}{d}$, (where d is d -spacing of crystal, λ is wavelength of the electron, L -constant of TEM, R = radius) the d -spacing and hkl values can be calculated. This technique is used generally for phase identification, determination of growth, and direction. Additional to this, crystalline or amorphous, if crystalline, phase and lattice constant can be calculated (Fig. 7.7). A. reveals the sole crystal-line phase of a cubic diamond with a lattice constant of 0.357 nm [15].

7.4.3.2 NBED

Nano beam electron diffraction is mainly used to determination of strain with high spatial resolution in materials. This will image a nanometer sized area in TEM. The electron beam is focused on the focal plane pre field of the objective lens which forms a parallel beam that is illuminated on the sample. The beam size is much smaller than SAED but the patterns would be similar to SAED.

There are ever going innovations being included in TEM. The perfect example is shown in Fig. 7.7B. Recently this work tried a rocking beam approach to get less strained artifacts and revealed their inference [16]. The black profiles in Fig. 7.7B show the strain for single disk evaluation. The red profile shows the opposite-disks evaluation, for the precession-like summation and the rocking beam case. The green curves show the evaluation of the standard NBED series without tilt from opposite-disks evaluation. There might be deviations between lines scans carried out at slightly different specimen positions. The fact that the profiles in Fig. 7.7B do not perfectly show the expected symmetries that can be attributed to

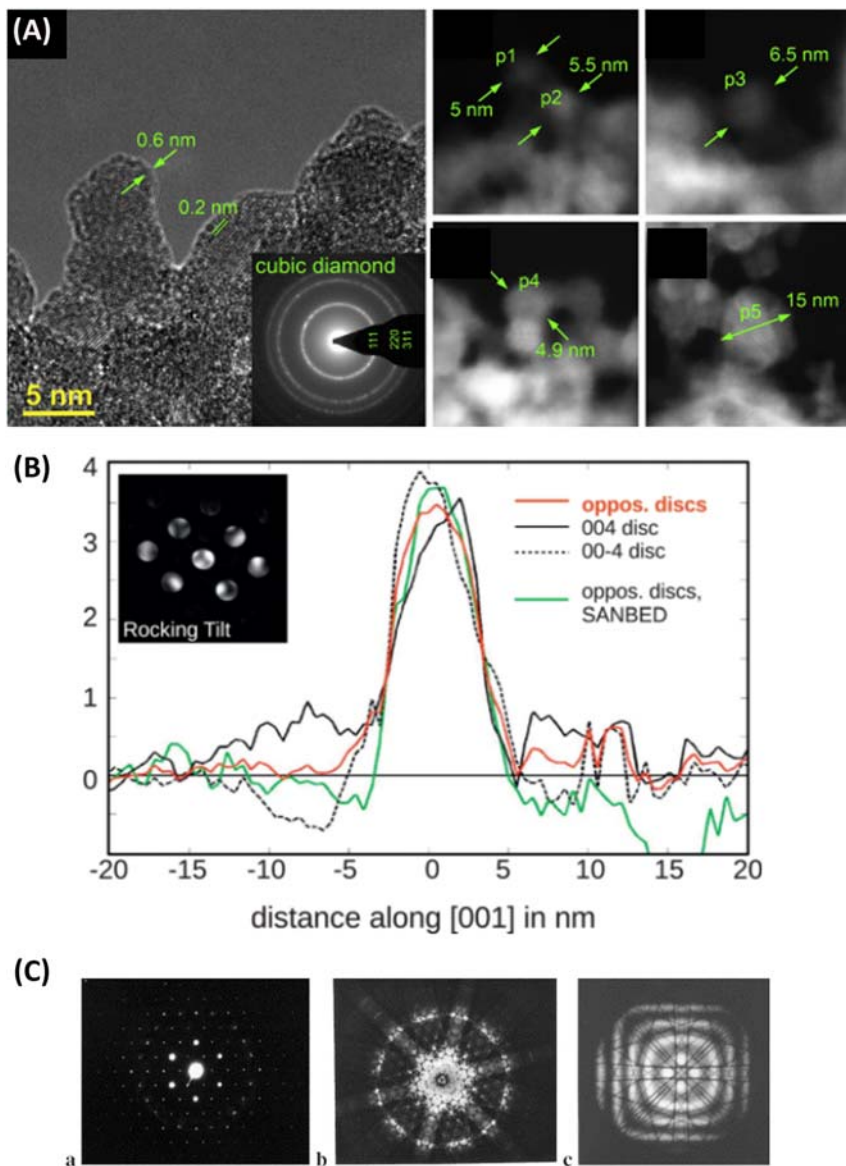


Figure 7.7 SAED pattern [15], (B) NAED pattern [16], (C) CBED pattern [17]. Reproduced with permission (A) S. Bogatyrenko, A. Kryshchal, Thermal expansion coefficients of Ag, Cu and diamond nanoparticles: in situ TEM diffraction and EELS measurements, *Mater. Charact.* 178 (2021) 111296. <https://doi.org/10.1016/j.matchar.2021.111296>. (B) T. Grieb, F.F. Krause, M. Schowalter, D. Zillmann, R. Sellin, K. Müller-Caspary, et al., Strain analysis from nano-beam electron diffraction: Influence of specimen tilt and beam convergence, *Ultramicroscopy* 190 (2018) 45–57. <https://doi.org/10.1016/j.ultramicro.2018.03.013> (C) I. De Wolf, V. Senez, R. Balboni, A. Armigliato, S. Frabboni, A. Cedola, et al., Techniques for mechanical strain analysis in sub-micrometer structures: TEM/CBED, micro-Raman spectroscopy, x-ray micro-diffraction and modeling, *Microelectron. Eng.* 70 (2003) 425–435. [https://doi.org/10.1016/S0167-9317\(03\)00372-1](https://doi.org/10.1016/S0167-9317(03)00372-1).

this. Concluding, the suggested rocking-beam approach has the potential to significantly optimize strain measurements from NBED disk-detection. The presented experimental implementation via scripting is mainly limited by the restricted access to the microscope's alignment procedures over external software. However, the positive results suggest further development in this field [16].

7.4.3.3 CBED

CBED is performed with a convergent incident beam (with a beam convergence in the range 0.1 to 1 degree) focused on a specimen (Fig. 7.6). The patterns are observed in the back focal plane of the objective lens and are made of disks containing excess and deficiency lines

Convergent beam electron diffraction is created by focusing the electron probe on the sample. This is mainly used for recording individual atomic columns. For crystallographic applications, CBED patterns are typically recorded with a probe of a few to tens of nanometers (Fig. 7.7C). Fig. 7.7A and B show the comparison of SAED and CBED, respectively. CBED is very useful for symmetry determination and quantitative analysis of electron diffraction patterns. The comparison of the three diffraction techniques is reported in Table. 7.3.

7.5 Application

Application of TEM in different platforms have been shown in Fig. 7.8.

Providing high magnification images of the internal structure of a non-destructive sample is the main application of a TEM. There are different ideal numbers of fields in TEM. Life science, nanotechnology, medical, biological, and material research, forensic analysis, gemology, metallurgy, industry, and education. TEM provides information on compositional, crystalline, topographical, and morphological.

TEM images allow us to view samples on a molecular level and allow researchers to analyze structure and texture. This information is useful to study crystals and metals. Colleges and universities can utilize TEM for research and studies. It is used in semiconductor analysis and production and the manufacturing of computer and silicon chips. In technology companies, they used TEM's to identify flaws, fractures, and damages to objects in micro-sized. This information or data can help to fix the

Table 7.3 Comparison of diffraction types.

Diffraction type	Modification	Advantages	Disadvantages
SAED	Placing an aperture in the imaging plane of the objective lens	(1) Can observe large area of specimen with a bright beam. (2) Image plane can be magnified (50 μm aperture can magnify a 2 μm area). (3) Thick films can be even studied	(1) Due to spherical aberrations area less than 1 μm cannot be selected. (2) Individual nanoparticles or thin films are difficult to evaluate.
NBED	Focus the beam on the front focal plane of the objective lens and use a small condenser aperture to limit beam size	(1). A parallel beam without selection errors. (2) A 10 mm aperture can form a ~ 50 nm probe size. (3) Useful to investigate individual nanocrystals and superlattices	(1) Very weak beam—difficult to see and tilt the sample. (2) More complex alignment than conventional TEM. (3) High resolution images are difficult to obtain.
CBED	Focusing the electron probe on the specimen	(1) Much smaller area can be viewed with a focused probe (2) CBED can be recorded from individual atomic column (3) Smallest electron probe currently available in a high-resolution FEG-STEM is close to 1 $\text{\AA}$.	(1) High current density produced by focused beams can strip the atom from the surface of the sample.

problems or help to make more durable efficient products. The wide areas TEM is being used are shown in Fig. 7.7. A few other techniques are being developed now [18,19]. The scientific challenges and suggested improvements of the TEM are tabulated in Table 7.4 which might be focused on the development of TEM [20].

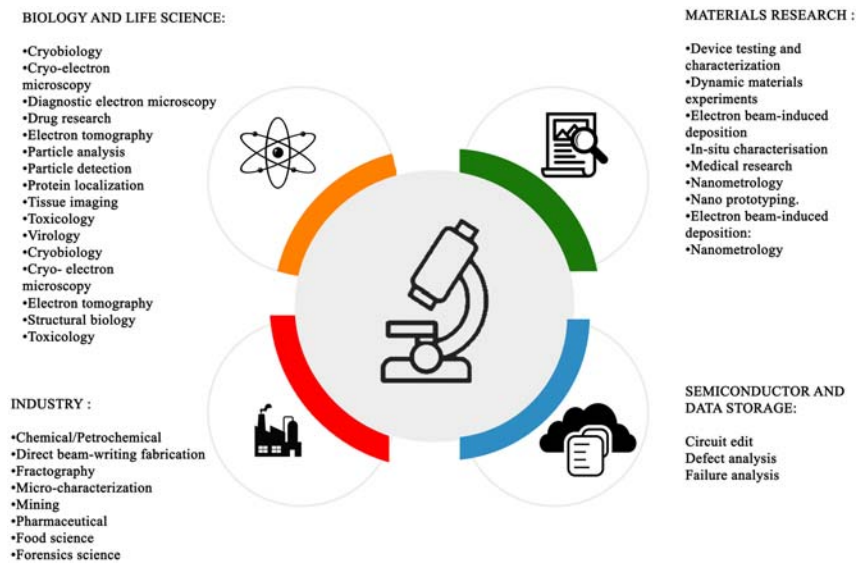


Figure 7.8 Application of transmission electron microscopy in different platforms.

Table 7.4 Categories and their challenges and suggested improvements.

Category	Current applications	Suggested improvements	Scientific challenges
Heating holders	(1) Phase transformation (2) Gas-solid reactions (3) High temperature electrochemistry (4) Nucleation and growth of Precipitates	(1) Higher temperature limit (2) Local, precise temperature measurement (3) Uniform temperature across the sample grid/ chip	(1) Phase transformations in ceramic materials. (2) Nano scale kinetic and thermodynamic measurements

(Continued)

Table 7.4 (Continued)

Category	Current applications	Suggested improvements	Scientific challenges
Indentation holders	(1) Mechanical property measurement. (2) Structure-property relationship. (3) Stress induced phase transformation	(1) Higher mechanical stability for high magnification tests (2) Versatile testing modes, such as compression, tensile, bending etc. (3) Coupling with thermal/electrical/gas fields. (4) Different tip geometries and grip styles, for example, for doing tensile experiments different sample geometries	(1) Noises resulted from both the instruments and the environment (2) Thermal drift upon heating. (3) Decouple the effects from different sources, like e-beam, thermal etc. 3-D stress state analysis as a function of crystal orientation
Liquid cell holders for electrochemistry	(1) In-situ synthesis. (2) Liquid-solid interactions Liquid electrochemistry	(1) Robust windows. (2) Uniform thickness for entire viewing region Heating in liquid	(1) Nucleation and growth mechanisms. (2) Phase transformations of solid materials in liquids. (3) Improve life time of batteries by understanding electrode poisoning.

(Continued)

Table 7.4 (Continued)

Category	Current applications	Suggested improvements	Scientific challenges
High pressure gas cells with heating device	(1) Gas solid reactions. (2) Catalytic reactions atmospheric chemistry climate research.	(1) Robust windows. (2) Temperature measurement. (3) Gas Composition measurement.	(1) Nanoscale kinetic and thermodynamic measurements. (2) Heterogeneous catalysis. (3) Gas-solid reactions involving corrosive and/or contaminating gases. (4) Understand the sites for catalytic reactions, Improve efficiency.
High gas pressure ETEM emission source/electron gun	(1) Catalytic reactions. (2) Gas effect on mechanical properties. (3) Gas-effect on electrical resistance.	(1) High pressure and high resolution. (2) Integration with spectroscopic techniques High energy resolution High intensity	(1) Controlled nanostructure growth (2) Beam-induced contamination in TEM parts (3) Interaction of e-beam, materials and gases (4) Understand ice nucleation in aerosols
Ultrafast TEM	Phase transformation in a few systems.	Better time resolution in movie mode, more images in a movie, higher spatial resolution, more in situ capabilities	(1) Understand the nucleation of phase transformation on an atomistic level. (2) Application to radiation sensitive systems in soft matter research.

(Continued)

Table 7.4 (Continued)

Category	Current applications	Suggested improvements	Scientific challenges
Concurrent Microscopy and spectroscopy: Large polepiece gap	Not available.	(1) Multi-probes. (2) High tilt tomography	Perform complex chemical experiments completely inside a TEM -> better understanding of chemical and electrochemical reactions
High speed data acquisition	In situ nucleation and growth of nanostructures.	(1) High spatial and high Temporal resolution. (2) Embedment of metadata of in situ parameters.	Understanding of defect dynamics in 2D materials Controlled nanostructure growth

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CHAPTER 8

Neutrons—characteristics and sources

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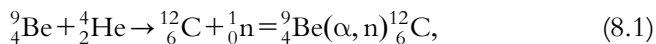
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8.1 Introduction

8.1.1 History

One of the great breakthroughs in the early days of nuclear physics was undoubtedly the discovery of the neutron by James Chadwick in 1932, for which he was awarded the Nobel Prize in Physics in 1935. As early as 1920, in one of his lectures, Ernest Rutherford already postulated a so-called “neutral doublet”—a closely combined state of an electron and a proton that “should be able to move freely through matter” [1]. American nuclear chemist William Draper Harkins finally introduced the term “neutron” for this hypothetic combination [2]. In their experiment in 1930, Herbert Becker and Walther Bothe bombarded beryllium with alpha particles from a polonium source and found a highly penetrating type of radiation, which they misinterpreted as gamma radiation [3]. One year later, Irene and Frederic Joliot—Curie observed no effect in the ionization chamber if directly exposed to this remarkable “beryllium radiation.” However, when hydrogen-containing paraffin wax was placed in between, the electric current increased. They explained these findings with the recoil of protons after the interaction with extremely hard gamma radiation (~ 50 MeV). At the same time, this interpretation contradicted the law of conservation of energy, and such nuclear reactions are usually lower in energy. James Chadwick improved this experiment and finally postulated a new electrically neutral particle with proton-like mass—the neutron. Its kinetic energy was found an order of magnitude smaller, which solved the problems with

energy conservation. The original publication of his results appeared in February 1932 [4]. Nowadays, this reaction used is written as:



where the target nucleus of beryllium ${}^9\text{Be}$ reacts with an α particle (helium nucleus, ${}^4\text{He}$) resulting in a carbon nucleus and one free neutron. Residual energy can be released by the emission of gamma photons.

Chadwick's research paved the way for the discovery of neutron-induced artificial radioactivity by Enrico Fermi in 1934 [5,6] as well as the man-made nuclear fission, whose experimental evidence was given by Otto Hahn (Nobel Prize in 1944) and Fritz Strassmann [7], and its first theoretical description by Lise Meitner and Otto Frisch [8]. Their works eventually led to the development of the first nuclear reactors, which also provided unprecedented neutron fluxes for scientific research and technical development. The study of the neutron itself [9], the application of neutrons as “probes of choice” for materials analysis, as well as the development of new sources and instrumentation, have always been working hand in hand. In the following, a brief introduction to neutron methods is provided, including the basics of neutron properties, differences in comparison with X-rays, the production of neutrons, and the available neutron sources. Neutron applications in imaging and chemical analysis are described in Chapters 9 and 21.

8.1.2 The neutron

To understand why neutrons can be used efficiently as “probes” for materials analysis in a wide range of applications, one has to look at the properties of the particle and its possible interactions. We will focus on the aspects that are relevant to practical neutron-based techniques in the field of materials science. Table 8.1 lists some neutron properties and their relevance for neutron imaging and chemical analysis with neutrons.

Together with the protons, the neutrons form the atomic nuclei. While the proton number, also called atomic number or nuclear charge number, is fixed for each chemical element, the varying number of neutrons defines the different isotopes of an element. The sum of the number of neutrons (N) and protons (Z) results in the atomic mass number ($A = N + Z$). If neutrons are bound in the nucleus, they are stable, but free neutrons decay.

Table 8.1 Fundamental parameters of the free neutron.

Parameter	Unit	Value	Relevance for neutron imaging/element analysis
rest mass	kg	$1.67 \text{ E} - 27$	subject to gravity (neutron beams)
diameter	m	$1.60 \text{ E} - 15$	not really
electric charge	C	0^*	deep penetration into materials, capture without Coulomb barrier
electric dipole moment	$\text{C} \cdot \text{m}$	0^*	not really
spin ^{parity}		$1/2^+$	polarized neutron imaging
magnetic moment	μ_n	-1.913	interaction with magnetic fields
life time	s	881.5	not really
particle composition		3 quarks, u-d-d	not really
classification		baryon, fermion	not really
interaction with matter		scattering, absorption	high importance

For (*), it is unclear if exactly zero, but can be considered as zero from a practical point of view.

Neutrons underlie all four *fundamental forces of physics*. The *strong nuclear force*, which holds together the positively charged nuclei and defines the binding energy, interacts with neutrons and protons in the same way. For instance, the strong force responsible for the neutron capture by nuclei. Neutrons and protons are collectively called “nucleons,” which are distinguished by the quantum number “isospin” with the representation $I_Z = -1/2$ for neutrons and $I_Z = +1/2$ for protons. Of more practical importance for the methods described in this book, is the fact that, unlike the proton with positive elementary charge $+1e$, the neutron is electrically neutral.¹ This enables a deeper penetration through matter compared to charged particles like electrons, protons, or ions. However, the neutron

¹ It should be noted that it is not yet theoretically understood if the electric charge is strictly quantized or not. The search for a deviation from zero—although it would be negligibly small from a practical point of view—is the subject of fundamental research. According to Baumann et al., the upper limit for the electric charge is $(-0.4 \pm 1.1) \times 10^{-21}e$ [10,11]

interacts with the *electromagnetic force* because of its magnetic moment of -9.66×10^{-27} J/T. This is for instance important for imaging with polarized neutrons. However, in many cases, magnetic fields are insufficient for the effective guidance of neutrons due to low deflection. This can be practically realized with low-energy neutrons, that is, very cold and ultracold neutrons, but the applications mentioned in this book work with higher neutron energies. Still, the neutrons can be delivered to a large distance using neutron guides, but that makes use of the wave nature of neutrons and the total reflection principle rather than a field. Enrico Fermi and Walter Henry Zinn were the first to describe the reflection of neutrons on mirrors [12]. Although the mass of a neutron is small, the *gravity force* of the earth can influence its flight path if the velocity is low. Slow neutrons fly along a parabolic trajectory and may displace from the straight line by millimeters over flight distances of tens of meters. For higher energies, these effects are negligible, while for lower energies the deviation is more pronounced and ultracold neutrons can be even trapped by gravity. The *weak interaction* is responsible for the decay of the free neutron: The lifetime of the free neutron is large compared to the time to pass the distance from the source to the experiment and thus not of practical relevance for imaging, element analysis, or scattering methods. Neutrons decay with a half-life of approximately 10 minutes² into a proton p^+ , an electron e^- , and an electron antineutrino $\bar{\nu}_e$:



In matter, neutrons interact typically only with the atomic nuclei in form of elastic (the kinetic energy of a particle is conserved in the center-of-mass framework, but its direction of propagation is modified) or inelastic (the energy of the incident particle is changed) scattering, capture (absorption), and transfer reactions, such as (n, p) or (n, α), while a fraction of neutrons might pass through without any interaction (transmission). Neutron capture and transfer result in a transmutation of the target nucleus and the emission of different reaction products, for example, gamma photons, protons, and alpha particles. In certain heavy nuclei, neutrons can induce fission reactions. Probabilities for reactions, such as scattering and capture, are nuclide-specific and can be quantified by the *microscopic cross sections* (unit barn = 10^{-24} cm²), σ_i relating to a single

² Because the exact lifetime contributes essentially to the understanding of the weak interaction and primordial nucleosynthesis, intensive basic research is still ongoing.

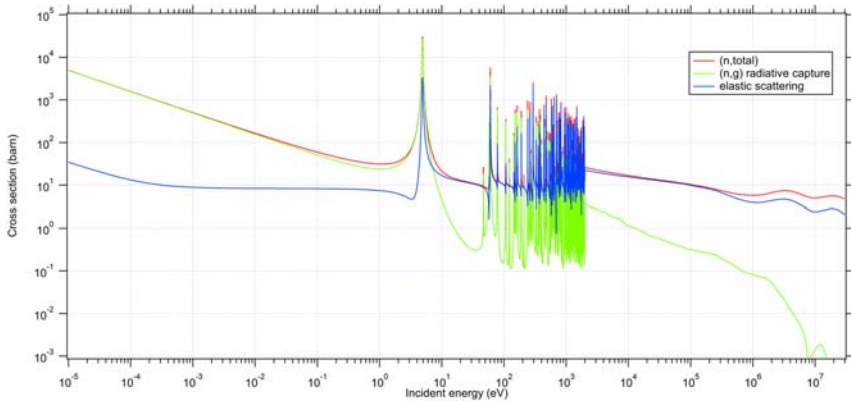


Figure 8.1 The cross section as a function of neutron energy, for Au-197. The capture (green), the elastic scattering (blue), and the total cross sections (red) are plotted. The nuclear data were taken from the ENDF/B-VIII.0 database. Drawing by L. Szentmiklósi.

target nucleus, and a certain reaction i . An illustrative example presents the capture—(green), the elastic scattering—(blue), and the total (red) cross sections of Au-197 nuclide as functions of the neutron energy (Fig. 8.1). The noticeable characteristic in the middle of the curves is caused by resonances. The graph is monotonous for lower energies—the cross section increases with less velocity ($1/v$ law). It is important for imaging and chemical analysis because it is directly linked to the energy-dependent quantities such as absorption coefficients and partial gamma-ray production cross sections.

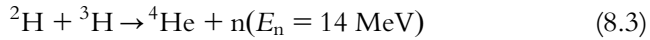
From this, the macroscopic cross section, Σ_i , can be calculated by multiplication with the atomic density. The *total cross section* is the sum of the contributions from all i reactions. For the sake of completeness, it should be mentioned that interactions of neutrons with nuclei can be angle-dependent, and one can therefore further distinguish between the *differential cross section* in an infinitesimal angular range and the *integral cross section* over the entire solid angle. Cross sections directly influence attenuation coefficients in imaging, k_0 values in neutron activation analysis, and scattering lengths in neutron scattering techniques.

8.1.3 Production of free neutrons

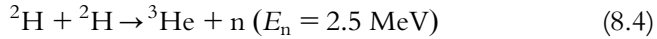
There are several ways of producing free neutrons. First, the general nuclear processes are described, followed by an overview of modern neutron facilities. In the introduction, we have already seen that neutrons can

be released from the atomic nucleus by alpha-particle bombardment. With the high-energy gamma radiation from a ^{124}Sb source, the ^9Be nucleus splits into two ^4He particles and one neutron. Similar reactions on nuclei with relatively weakly bound neutrons are possible using the irradiation with protons (p) or deuterium nuclei (d), for example, $^2\text{H}(\gamma, n)^1\text{H}$, $^7\text{Li}(p, n)^7\text{Be}$, $^7\text{Li}(d, n)^8\text{Be}$, $^9\text{Be}(d, n)^{10}\text{B}$, and $^{51}\text{V}(p, n)^{51}\text{Cr}$. The special case of photon-induced reactions by high-energy gamma radiation is called photonuclear. Also, accelerated electrons with energies of at least 10 MeV are suitable to release neutrons from the nuclear bond in (e, n) reactions.

Another way to generate neutrons is the fusion reactions of light elements. The most important one related to neutron production is the D-T reaction with tritium (T, or ^3H) and deuterium (D, or ^2H) as educts and helium ^4He and neutron as products:



The kinetic energy of the neutron, E_n , is given in parentheses. The D-D reaction produces neutrons with a lower E_n :



In the typical energy ranges of accelerators, the cross section of the D-T reaction is up to two orders of magnitude higher than that of the D-D reaction. This has a branching ratio of 1:1 in terms of the alternative production of a proton.

Nuclear fission is a highly efficient process to produce neutrons, during which a heavy nucleus splits into two medium-heavy ones. A distinction is made between *spontaneous* and *induced fission*. Some heavy, neutron-rich nuclei fission spontaneously without external influence and with a certain probability per unit of time. A famous example is ^{252}Cf with a half-life of 2.6 years.

Much higher neutron fluxes can be obtained by using induced fission in a nuclear reactor reaching a neutron source flux level of about $10^{15} \text{ cm}^{-2}\text{s}^{-1}$ as described in the following sections. The induced nuclear fission is schematically shown in Fig. 8.2. The capture of the neutron by a heavy nucleus, especially the one with an odd neutron number, results in the formation of a shape-unstable compound nucleus. With a high probability, a double “drop-let” is formed, which is finally only connected at a narrow waist. Then the repulsion of the positively charged parts gains the upper hand over the short-range strong interaction holding the nucleus together. In the end, the nucleus

almost two thousand times larger. For the same kinetic energy, their wavelength is therefore of a different order of magnitude. The energy E , momentum p , velocity v , wavelength λ , and frequency f are all dependent quantities. Their relation for particles with mass m was described by Louis–Victor de Broglie as follows:

$$\lambda_{\text{dB}} = \frac{h}{p}, \text{ with } p = \frac{mv}{\sqrt{1 - \beta^2}} \quad (8.5)$$

Here, h is the Planck constant and β is a term for the relativistic correction. The wavelength λ_{dB} is called the de-Broglie wavelength. Moreover, according to Ludwig Boltzmann, the equation $E = 3/2 k_{\text{B}}T$ is valid for the mean energy, with the Boltzmann constant k_{B} and the temperature T , so that the above quantities are also directly linked to the temperature:

$$\lambda_{\text{dB}} = \frac{h}{\sqrt{3mk_{\text{B}}T}} \quad (8.6)$$

The wave nature of the neutron is particularly important for neutron guiding, neutron scattering methods, and special wavelength-resolved neutron imaging. In conventional imaging and chemical analysis, however, not monoenergetic neutrons are used, but neutrons with polychromatic energy distributions. Especially the Maxwell–Boltzmann distribution is important because it is valid for the case of thermal equilibrium with the surrounding moderator. Quickly, after a few collisions with light atomic nuclei like hydrogen, deuterium, or carbon, the neutrons take the temperature of a moderator material reaching the equilibrium. The most famous example is the thermal neutron distribution in the moderator tank of a nuclear reactor. In the literature, mostly the average neutron energy or the most probable value is usually given. For thermal neutrons, the most probable value is 25 meV. Cold neutron moderation can be realized by using liquid hydrogen or deuterium. This shifts the most probable neutron energies to the 1–5 meV range. The Maxwell–Boltzmann distribution with the neutron density can be expressed as a function of the velocity $n(v)$ or as a function of the energy $n(E)$:

$$n(v) = 4\pi \left(\frac{m}{2\pi k_{\text{B}}T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_{\text{B}}T}} \quad (8.7)$$

or

$$n(E) = 2\pi \left(\frac{1}{\pi k_{\text{B}}T} \right)^{\frac{3}{2}} \sqrt{E} e^{-\frac{E}{k_{\text{B}}T}} \quad (8.8)$$

In Table 8.2, a rough classification of neutrons is given based on their kinetic energies, temperatures, and velocities, while Fig. 8.3 shows some natural and artificial sources and uses of selected neutron energies. Note that for fast neutrons the distribution mentioned above is no longer applicable. For instance, fission neutrons are distributed according to the so-called Watt distribution. Values for energy intervals vary slightly in the literature, except for thermal energy. For very high neutron energies, the specification for the temperature makes little sense, and relativistic corrections for the calculation of the velocity must also be taken into account. For 10 MeV, the velocity is already about 15% of the speed of light c .

Table 8.2 Neutron energy ranges.

Designation		Energy range	Temperature	Velocity
slow neutrons	ultracold	$\sim 10^{-7}$ eV	<0.01 K	<10 m/s
	cold	<0.025 eV	<290 K	<2200 m/s
	thermal	~ 0.025 eV	290 K	2200 m/s
	epithermal	$0.025\text{--}1$ eV	290 K–1200 K	2200–14 000 m/s
	resonance	$1\text{--}1000$ eV	1200 K– 12,000 K	14–440 km/s
intermediate neutrons		$1\text{--}1000$ keV	10^4 K– 10^{10} K	440–14 000 km/s
fast neutrons		$1\text{--}10$ MeV	$>10^{10}$ K	$>14\,000$ km/s – relativistic
ultrafast neutrons		>10 MeV		relativistic

Note that the classification varies slightly in the literature. Very cold neutrons with velocities from 10 to 200 m/s are also occasionally defined.

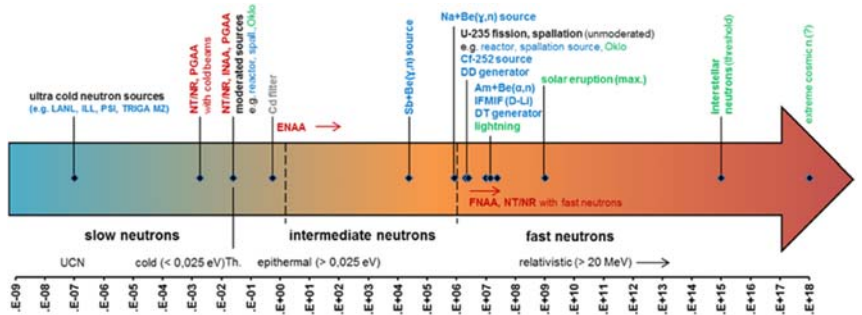


Figure 8.3 Some natural (green) and artificial sources (blue) and applications (red) for selected neutron energies. Drawing by C. Stieghorst.

In a nuclear reactor, the energy distribution of the neutrons is—depending on the grade of thermalization—a combination of a Maxwell–Boltzmann distribution at the lower energy region, a fission Watt distribution at high energies around 2 MeV, and an epithermal slope in between (see detailed description in Chapter 21, Chemical analysis with neutrons).

Finally, the intensity of a neutron beam or in an irradiation position in the reactor is described by the scalar quantity of the neutron flux $\varphi(v)$. The (nonnormalized) flux can simply be calculated from the product of the velocity and the neutron density $v n(v)$. Therefore, the unit $\text{cm}^{-2}\text{s}^{-1}$ for the flux results from the distance traveled per second (here in cm/s) multiplied by the number of neutrons per cubic centimeter (1 cm^{-3}). The neutron flux integrated over a certain time is called neutron fluence.

8.1.5 Differences in comparison with X-rays

The major practical difference between neutrons and X-rays is their penetration depth, these are either used for chemical analysis or imaging. Neutrons and gamma rays are capable of penetrating samples up to a few cm in thickness, while X-rays are limited to a few mm, depending on the composition of the material. Their microscopic cross sections (i.e. probability of interaction with the material) also differ greatly. This is due to their different reaction mechanisms. Neutrons interact with the nuclei of the target atom, while X-rays with the electrons of the atomic shell. For this reason, the neutron cross section is nuclide-specific and large differences can be observed even between different isotopes of an element. X-rays react with the shell electrons mainly via the photoelectric effect, therefore the cross section highly increases with the atomic number (=number of electrons in the atom). X-ray absorption cross sections are generally higher than neutron absorption cross sections, especially in the case of metals, and elements with higher Z . In the case of neutrons, scattering is a coequal interaction with the atomic nuclei besides absorption. The scattering cross section might affect the penetration of the neutrons into the sample if its value is dominant over the absorption cross section, by modifying the propagation direction and the energy distribution of the neutrons. There are various online databases available containing X-ray [15] and neutron cross sections [16]. Fig. 8.4 shows the mass attenuation coefficients (derived from the linear attenuation coefficient based on the $\mu_m = \frac{\mu}{\rho}$ formula, where μ_m is the mass

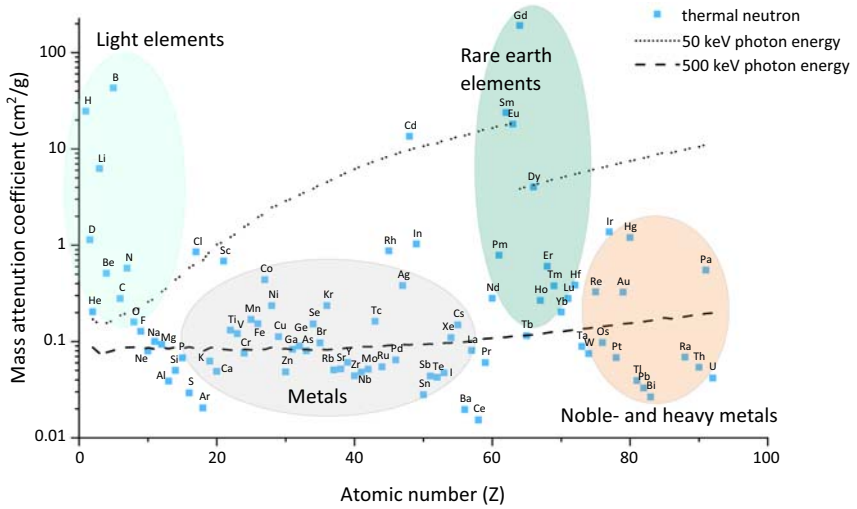


Figure 8.4 Mass attenuation coefficients valid for thermal neutrons (blue symbols) and photons (50 and 500 keV). Graph by L. Szentmiklósi & B. Maróti.

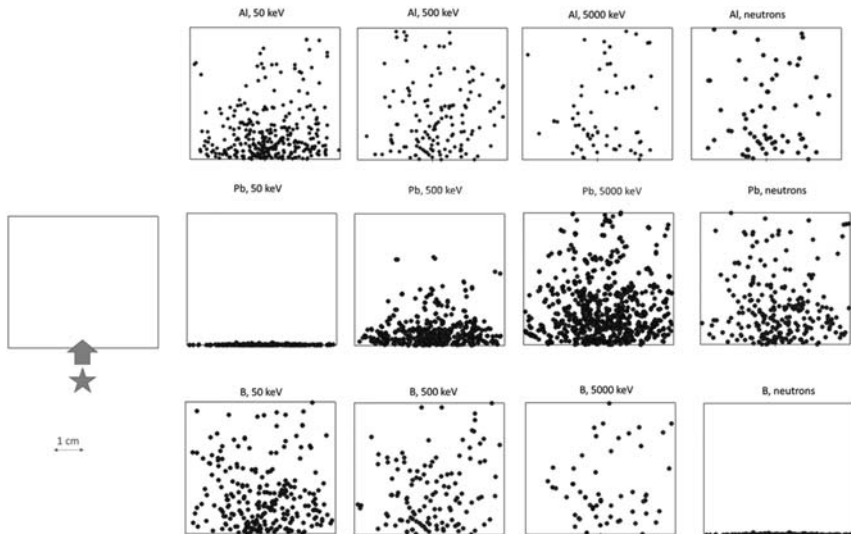


Figure 8.5 The penetration of incident X-rays, gamma photons, and thermal neutrons into cylinders made of aluminum (weak interaction with both photons and neutrons), lead (weak neutron absorber, strong gamma absorber), and boron (strong neutron absorber, weak gamma absorber). The dots represent the positions of the interactions whose spatial distributions are remarkably different for the three selected materials. Higher attenuation means that there are more interaction spots and they are concentrated near the entry plane of the radiation. The star symbol indicates the position of the radiation source that emits particles in 4π (Monte Carlo simulation, MCNP code) Drawing by L. Szentmiklósi.

attenuation coefficient, μ is the linear attenuation coefficient, and ρ is the density of the material) of various elements in the case of thermal neutrons, X-rays, and gamma photons. The higher the mass attenuation coefficient, the larger the cross section. X-rays are insensitive to lighter elements, while neutrons have a high cross section for hydrogen and boron. Fig. 8.5 depicts the computer-simulated penetration of various radiations into copper, aluminum, lead and boron.

The main interactions of neutrons and X-rays with matter are discussed in more detail in Chapters 9 and 21.

8.2 Neutron sources

8.2.1 Radioisotope sources

The so-called radioisotopic neutron sources contain either a spontaneously-fissile nuclide (^{252}Cf) or a mixture of an alpha-emitting radionuclide and Be ($^{238}\text{Pu-Be}$, $^{241}\text{Am-Be}$). The relatively low neutron yield, the related administrative burden, and the fact that they cannot be switched on and off make them obsolete in research applications.

8.2.2 Neutron generators

Neutron generators based on D-D or D-T reactions are widespread in industrial applications. They can produce 10^8 – 10^{10} fast neutrons in a second in 4π and can be switched off when not used. Some of them are installed in a lab environment [17], while others are field-portable for applications in landmine detection, cargo screening, borehole logging, or material feed analysis.

8.2.3 Research reactors

The research reactors produce the most intense stationary neutron field and therefore they are indispensable in neutron-based element analysis, imaging, and radioisotope production. There are several decades of operational experience and this technology became mature. However, the neutron density cannot be further increased due to the cooling limits. Few new research reactors with innovative concepts are deployed, while many existing ones, after 50–60 years of service, reach the end of their lifetimes and are being decommissioned. A comprehensive registry of research reactors is maintained by the International Atomic Energy Agency (IAEA) [18].

The research reactors can be subdivided according to the design: pool type (MTR, TRIGA, SLOWPOKE), tank-type (VVR), or tank-in-pool type (MNSR, FRM II, OPAL), according to the enrichment of the uranium fuel (low- and highly enriched), or based on the moderation (heavy- or light-water), pulsed by rotating reflectors (IBR-2). Based on reactor power, one can distinguish between small-scale (<1 MW), medium-sized (1–10 MW), and high-power reactors (10–100 MW). The reactor, its instrument suite, and the competence of the staff form a neutron research center.

8.2.4 Spallation sources

A spallation neutron source requires advanced accelerator technology, but it is not a nuclear facility, because there is no chain reaction and excursion of power possible. Since the spallation process requires irradiation of a heavy target with protons of energy well above 200 MeV, the costs of establishing spallation sources are high. The spallation process produces about an order of magnitude less heat than fission in nuclear reactors to produce the same number of free neutrons, and thus spallation is the more efficient nuclear reaction for producing the highest neutron intensities. A typical number is about 15–20 neutrons per incident proton. However, this number grows proportionally with increasing proton energy and mass number of the target. In terms of waste management, they are also more favorable than reactors. It can provide stationary or pulsed neutron beams. Prominent examples of this class of neutron sources are ISIS in the United Kingdom, SINQ in Switzerland, SNS in the United States, and the European Spallation Source (ESS) to be built in Lund, Sweden.

8.2.5 Compact and high-current accelerator-driven sources

${}^7\text{Li}(p, n){}^7\text{Be}$ or ${}^7\text{Be}(p, n){}^7\text{B}$ nuclear reactions can be initiated with a low-energy (5–10 MeV) proton accelerator. Such a compact accelerator-driven facility (CANS) is again nonnuclear, its operation is cheap, and it offers easier access to the premises. Although the overall number of neutrons produced is much smaller, the flux at the measuring equipment can be as high as it is now in medium-power research reactors, especially for scattering instruments. The affordable price could make it accessible to the industry or for medical applications, such as boron neutron capture therapy. There is a Low Energy Neutron Source already operational at Indiana University, United States and the LvB source at Martonvásár,

Hungary is under commissioning. Many others, even with higher brilliance (HiCANS), are in the design phase (Jülich High Brilliance Neutron Source, Germany, CEA SONATE, France).

8.3 Outlook and further perspectives

The evolution of the neutron sources over the last 80 years is summarized in the Brugger–Price–Carpenter–Lander diagram (Fig. 8.6). It displays clearly that the peak thermal neutron flux of research reactors has been saturated since the 1960s, while an increasing sophistication in safety and control systems and the instrument suite is experienced. The performance limit can be superseded for instance by switching technology and transitioning from steady sources to pulsed ones. This will be demonstrated by the upcoming state-of-the-art spallation source ESS with instrumentation for diffraction, reflectometry, small angle scattering, spectroscopy, and imaging. For activation analysis, material aging studies, and radioisotope production, however, the steady-state research reactors are still the more favorable sources.

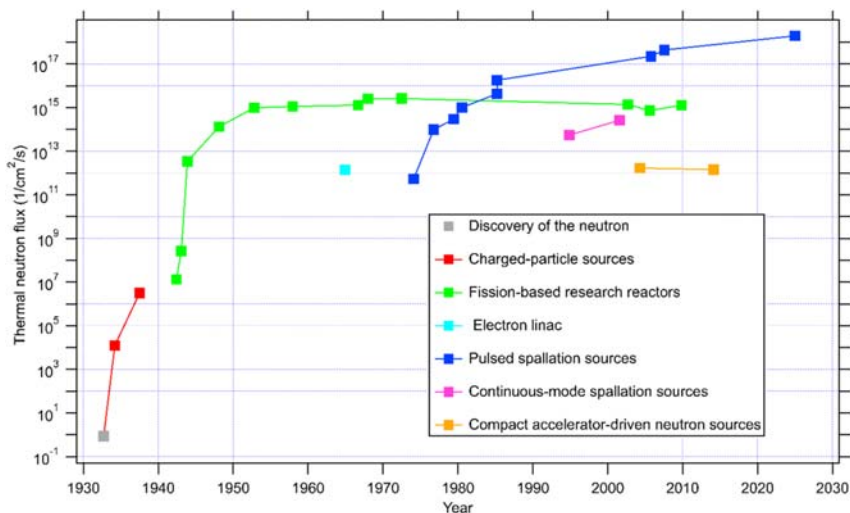


Figure 8.6 Brugger–Price–Carpenter–Lander diagram: the evolution of the neutron sources over the past 80 years. The first gray point represents the discovery of the neutron in 1932 [19]. Graph by L. Szentmiklósi. Data are taken from figure 3 of ESFRI Physical Sciences and Engineering Strategy Working Group - Neutron Landscape Group, *Neutron scattering facilities in Europe – Present status and future perspectives*, ESFRI Scripta Volume I, Università degli Studi di Milano, 2016, pp. 1–74.

Due to the high investment and operation costs, the concentration of the large-scale neutron infrastructure is foreseen, that is, to have fewer, but more equipped neutron centers in the future neutron research landscape. In parallel, to replace the fleet of small-scale university and training reactors, one can envisage the spread of CANS installations, which are easy to operate and are affordable solutions for specific non-destructive material-testing functions, as well as for education and training purposes.

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CHAPTER 9

Neutron imaging

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9.1 Introduction

Neutrons have the ability to penetrate cm-sized objects, with the penetration depth depending on the composition and thickness of the material and the energy of the used neutrons. For typical imaging measurements, the transmission of neutrons carries information about the interaction of the neutron beam with the material, which can be used to characterize the material properties.

Neutron imaging is a well-established method today, where the two-dimensional distribution, or transmission, of the neutrons across an object is measured. This behavior is essential for non-destructive testing of technical samples regarding defects and manufacturing failures, and also to understand unknown material distributions, for example, in old archeological artifacts. If many images are taken in a time sequence, the change of material distributions can be observed dynamically, that is time-dependently.

To compensate for beam inhomogeneity and detector response, an image with (raw data) and without the object (open beam) in the beam is acquired in practice as shown in a very simplified sketch in Fig. 9.1. This approach was adopted from X-ray imaging, in place just after the observations by C. Röntgen at the end of the 19th century, which nowadays is a sophisticated and indispensable technology in medicine, as well as in non-destructive testing for industry and research.

The complementarity between neutron and X-ray imaging is provided by the very different interaction principles of these two kinds of radiation with matter. Although providing images with similar quality, the contrast is vastly different. This is demonstrated by the example in Fig. 9.2, a historical sword from the 15th century.

Neutrons, as the name suggests, are neutral or uncharged particles and have a deep penetration ability. They only interact with nuclei, very specifically from one nuclide to the next, even differently for isotopes of the

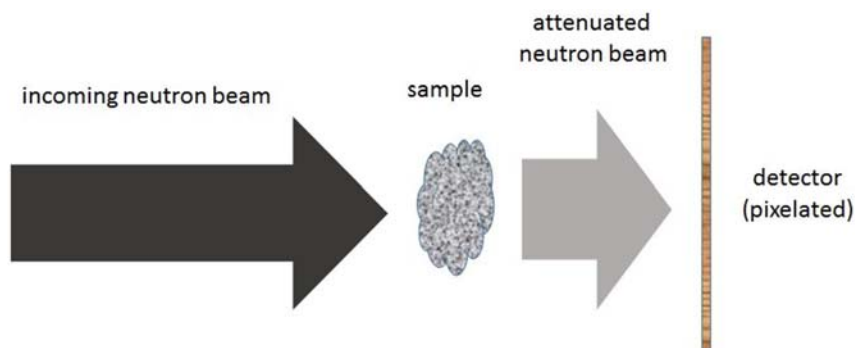


Figure 9.1 Basic principle in neutron imaging: the incident beam from a source is attenuated by the sample and measured with a (pixelated, two-dimensional) neutron detector positioned behind the sample. This signal can be used to characterize and quantify the sample dimensions and properties.

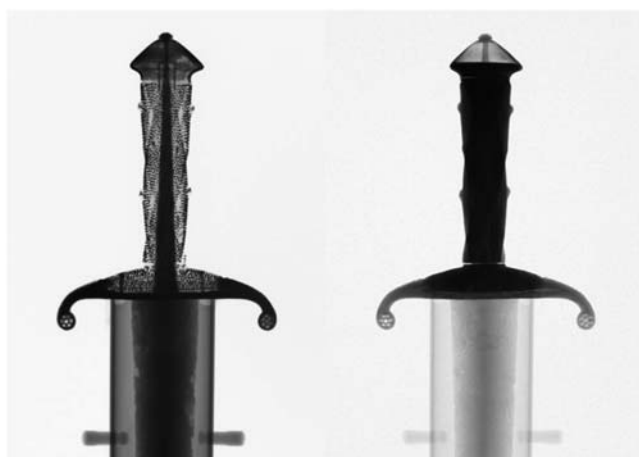


Figure 9.2 Handle of a sword of the 15th century, found in a Swiss lake [1]. Comparison of an X-ray (left) and neutron (right) transmission image. The x-ray image delivers a strong contrast for all metallic parts (including the decoration in the wooden handle). In comparison, the neutron image delivers a strong contrast for the wooden parts, containing hydrogen [2]. Adapted from D. Mannes, F. Schmid, J. Frey, K. Schmidt-Ott, E. Lehmann, *Combined neutron and x-ray imaging for non-invasive investigations of cultural heritage objects*, *Phys. Procedia* 69 (2015).

same element. Most of the nuclides interact by neutron scattering, where the arriving neutrons from the beam are deflected and thus removed from the beam behind the object. The second interaction process is the absorption of neutrons, where the arriving neutron is absorbed via a nuclear reaction in the sample.

X-rays, on the other hand, mainly interact with electrons in the shell via absorption (photoelectric effect) or via Compton scattering. It is obvious, that the number of electrons in the shell is important for the interaction probability with the matter. Therefore, light elements (like hydrogen, lithium, and boron) are mostly “transparent” while heavy elements (like iron, lead, and uranium) are “opaque” already at millimeter thicknesses.

Nowadays, X-ray imaging is common in each hospital and also in many dedicated inspection facilities (even at airports). In contrast, neutron imaging requires high flux neutron sources, often based on nuclear fission, spallation, or other interaction of high-energy particles. As a result, only a few imaging facilities that provide high-performance neutron imaging capabilities are available worldwide. An overview of the worldwide status is given on the ISNR homepage [3]. To access also the third spatial dimension of objects, neutron tomography has been established on a routine basis [4].

Therefore, neutron imaging is often applied for cases where X-ray methods failed and neutron imaging can advantageously be used. This article is prepared to show such examples and to explain how the investigations were performed in detail.

Nowadays, not only the simple transmission image with neutrons can be used. There are also more advanced methods available using for example, the neutron spin or its wave properties for image formation, which are still under further development. Moreover, neutrons with different energies can be used for either higher penetration or higher contrasts. Because most of the crystalline solid state material provides a characteristic scattering behavior, energy-selective imaging enables the noninvasive determination of the lattice properties—and their changes under load.

Additionally, also neutrons with higher than the common “thermal” energies can be used for material characterization. Fast neutrons with about 1 MeV can penetrate samples with 10 cm thickness—and even more, depending on the material composition.

Neutrons have no charge, but spin- $1/2$ particles carry a magnetic moment in two polarization states (spin up and down). Their interaction with magnetic materials or magnetic fields becomes measurable, in particular, if only one spin state is selected from the incoming beam and the investigations are performed with polarized neutrons. Combining polarized beams with neutron imaging can provide valuable, spatially resolved

information on magnetic field distributions or magnetic properties of samples [5–8].

But even the scattered neutrons can be studied more by using methods for their investigations. On the one hand, “diffractive imaging” is enabled with a second imaging detector, sitting aside from the beam direction and observing the scattered neutrons, for example, from a single-crystalline sample. A more sophisticated method was developed for small-angle type scattering effects in the direct beam, using the neutron grating interferometry (nGI) technique [9].

Such methods will be explained in detail with the aim to give potential users an idea, if and which neutron imaging method can be applied to their specific problem in material characterization and defect analysis.

9.2 Principles of neutron imaging

To perform imaging studies with thermal or cold neutrons it is necessary to extract a beam of such neutrons from the primary source. This can only be done through channels between the source region and the end of the beam line with the help of a collimator device. This collimator defines two parameters: the neutron beam intensity and the possible spatial resolution. The larger the initial pinhole (aperture) the higher will be the resulting beam intensity, but the higher is also the inherent blurring by the less collimated neutrons.

To establish a neutron imaging facility according to the principle shown in Fig. 9.1, several other components are needed, as indicated in Fig. 9.3 for a generic layout.

As mentioned in the introduction and shown in Fig. 9.2, slow neutrons can be used to investigate samples and objects and to show inner, hidden features and structures. Because different materials interact in different manners and different amounts, clear contrast deviations become visible. As already shown in Fig. 9.1, the two-dimensional imaging detector registers the resulting attenuated beam after passing through the object. Modern imaging detectors provide a pixel-wise digital image.

The interaction of slow neutrons with the sample material can be attributed to two mechanisms: absorption and scattering by the nuclei. Both reactions withdraw the neutrons from the initial beam (see Fig. 9.1) thereby reducing the intensity in the resulting image. While the absorbed neutrons are really permanently removed from the beam, some scattered neutrons can return back into the image region and disturb the

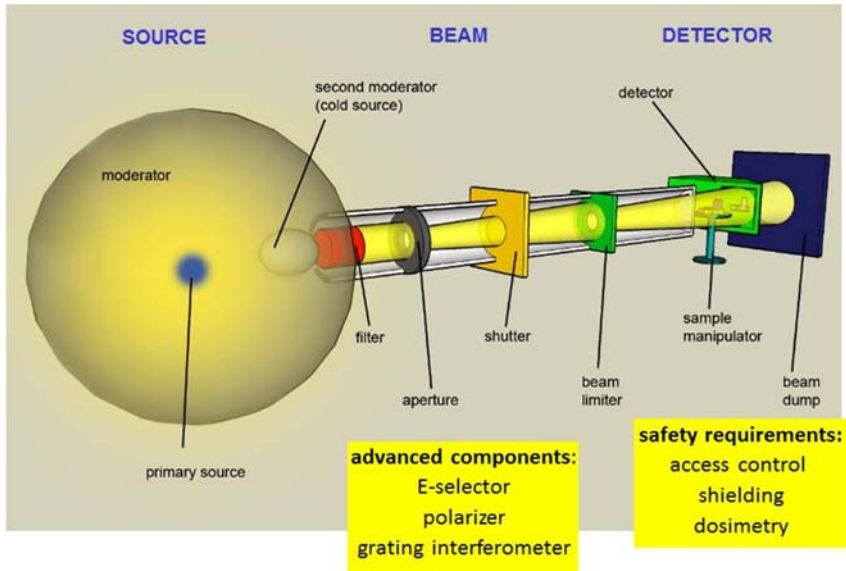


Figure 9.3 Generic layout of a neutron imaging facility.

interpretation of the image data. This is mainly valid for more bulky samples. Sophisticated techniques have been developed to account for the artifacts arising from such scattering contributions to image formation both during data acquisition and evaluation.

9.2.1 Fundamental differences in x-ray interactions

Because neutrons only interact with the nuclei of the studied materials, the electrons in the shell are irrelevant for the absorption process highlighting the difference to interactions with X-rays, whose energy is not high enough to tackle the nucleus, but makes interactions with the electrons around. As visible in the example displayed in Fig. 9.2, images with both X- and neutron radiation provide similar quality, but the mechanism behind each differs in principle. Because the number of electrons is increasing with the charge Z of the material, the interaction probability is also increasing according to about Z^n ($n \sim 3$). This situation becomes visible in the data shown in Table 9.1, where the attenuation coefficients μ [cm^{-1}] are given for all elements of the periodic table. They are similar to $\sum$ (common to describe neutron attenuation), introduced below, because X-rays also follow an exponential law of attenuation.

Table 9.1 Attenuation coefficients μ [cm^{-1}] for all elements (natural abundance) of the periodic table when exposed with x-rays of 100 keV.

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	H 0.02																	He 0.02
2	Li 0.06	Be 0.22											B 0.28	C 0.27	N 0.11	O 0.16	F 0.14	Ne 0.17
3	Na 0.13	Mg 0.24											Al 0.38	Si 0.33	P 0.25	S 0.30	Cl 0.23	Ar 0.20
4	K 0.47	Ca 0.26	Sc 0.46	Ti 0.73	V 1.04	Cr 1.29	Mn 1.32	Fe 1.57	Co 1.78	Ni 1.96	Cu 1.97	Zn 1.94	Ga 1.42	Ge 1.33	As 1.50	Se 1.23	Br 0.90	Kr 0.73
5	Rb 0.47	Sr 0.89	Y 1.61	Zr 2.47	Nb 3.43	Mo 4.29	Tc 5.06	Ru 5.71	Rh 6.08	Pd 6.13	Ag 5.67	Cd 4.84	In 4.31	Sn 3.98	Sb 4.28	Te 4.05	I 3.45	Xe 2.53
6	Cs 1.47	Ba 2.73		Hf 19.70	Ta 25.47	W 30.46	Re 34.47	Os 37.92	Ir 39.01	Pt 38.61	Au 36.94	Hg 25.88	Tl 23.23	Pb 22.81	Bi 20.28	Po 20.22	At -	Rn 9.77
7	Fr -	Ra 11.80		Rf -	Db -	Sg -	Bh -	Hs -	Mt -	Ds -	Rg -	Uub -	Uut -	Uuq -	Uup -	Uuh -	Uus -	Uuo -
Lanthanides				La 5.04	Ce 5.79	Pr 5.23	Nd 5.45	Pm 7.33	Sm 7.68	Eu 5.06	Gd 8.69	Tb 9.46	Dy 10.17	Ho 10.17	Er 11.70	Tm 12.49	Yb 9.32	Lu 14.07
Actinides				Ac 24.47	Th 28.95	Pa 39.65	U 49.08	Np -	Pu -	Am -	Cm -	Bk -	Cf -	Es -	Fm -	Md -	No -	Lr -

The attenuation of the neutron beam follows (to first order) Beer–Lambert’s law of exponential decay:

$$I(x, y) = I_0(x, y) \cdot e^{-\int_0^d \Sigma(x, y) \cdot dz} \quad (9.1)$$

Here, the intensities before the sample I_0 and behind it I along the beam (in direction z) are related to the attenuation coefficient Σ (total macroscopic cross-section), integrated over the thickness of sample d .

The attenuation coefficient is a property in the interaction with a specific material, which is related to the “microscopic cross-section” σ as:

$$\Sigma = \sum_i N_i \cdot \sigma_i \quad (9.2)$$

The nuclear density N is obtained from the density ρ of the material i , its molecular weight M and Avogadro’s constant L :

$$N = \frac{\rho \cdot L}{M} \quad (9.3)$$

The microscopic cross-sections are well-known parameters that are tabulated in extensive libraries [10,11] for all energies from slow neutrons up to many MeV. This database has played an important role in the design of nuclear reactors, which are based on the interaction of neutrons with all materials in the reactor core. Fig. 9.4 shows the cross-section of Al for the

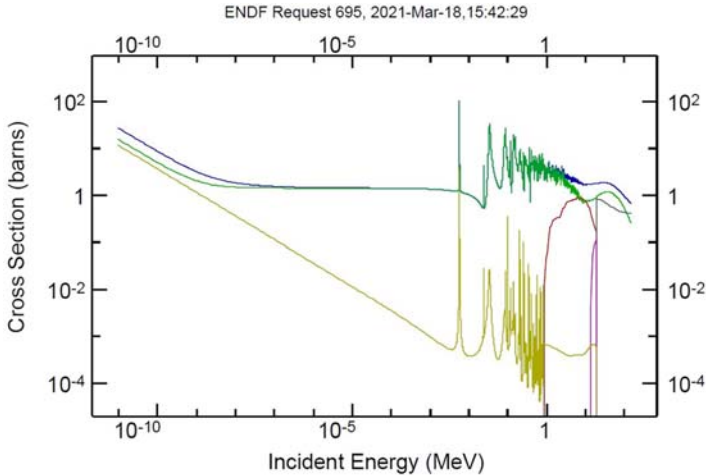


Figure 9.4 Microscopic cross-sections for Al, taken from the ENDF/B-VIII library [11]: yellow—absorption; green—scattering; blue—total; red—inelastic.

different possible nuclear reactions and for the whole energy range (in log scale).

For the interpretation of the experimental data from neutron imaging measurements, it is common to use the total cross-sections (as a sum over all induced nuclear reactions: absorption, scattering) because any neutron lost in the interaction with the sample is not registered in the transmitted beam. When scattered neutrons will return to the detector behind the sample, their contributions have to be taken into account by experimental means or with scattering correction algorithms [12].

It is important to mention that the interaction with neutrons is strongly dependent on the particular individual isotope. Because the number of nucleons in the nuclei differs for the isotopes, the reaction during neutron exposure can result in very different features. Looking, for example, at boron with its two stable isotopes, B-10 and B-11 with 19.9% and 80.1% fractions in the natural abundance, the capture cross-sections are 3840 barn and 0.005 barn, respectively. Such a significant difference between isotopes holds for other elements and their isotopes in a similar manner. Table 9.2 represents the macroscopic attenuation coefficients Σ [cm^{-1}] only for the natural compositions according to relation (9.2).

In contrast to Table 9.1, there is no systematic rule visible for the interaction of thermal neutrons with the different elements and their isotopes. It is obvious that some light elements (H, Li, B, ...) have

Table 9.2 Macroscopic attenuation coefficients Σ [cm^{-1}] for all elements (natural abundance) of the periodic table when exposed to thermal neutrons (25 meV).

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	H 3.44																	He 0.02
2	Li 3.30	Be 0.79											B 101.6	C 0.56	N 0.43	O 0.17	F 0.20	Ne 0.10
3	Na 0.09	Mg 0.15											Al 0.1	Si 0.11	P 0.12	S 0.06	Cl 1.33	Ar 0.03
4	K 0.06	Ca 0.08	Sc 2.00	Ti 0.60	V 0.72	Cr 0.54	Mn 1.21	Fe 1.19	Co 3.92	Ni 2.05	Cu 1.07	Zn 0.35	Ga 0.49	Ge 0.47	As 0.67	Se 0.73	Br 0.24	Kr 0.61
5	Rb 0.08	Sr 0.14	Y 0.27	Zr 0.29	Nb 0.40	Mo 0.52	Tc 1.76	Ru 0.58	Rh 10.68	Pd 0.78	Ag 4.04	Cd 115.1	In 7.58	Sn 0.21	Sb 0.30	Te 0.25	I 0.23	Xe 0.43
6	Cs 0.29	Ba 0.07		Hf 4.99	Ta 1.49	W 1.47	Re 6.86	Os 2.24	Ir 30.46	Pt 1.46	Au 6.23	Hg 16.21	Tl 0.47	Pb 0.38	Bi 0.27	Po -	At -	Rn -
7	Fr -	Ra 0.34		Rf -	Db -	Sg -	Bh -	Hs -	Mt -	Ds -	Rg -	Uub -	Uut -	Uuq -	Uup -	Uuh -	Uus -	Uuo -
Lanthanides																		
	La 0.52	Ce 0.14	Pr 0.41	Nd 1.87	Pm 5.72	Sm 171.47	Eu 94.58	Gd 1479.0	Tb 0.93	Dy 32.42	Ho 2.25	Er 5.48	Tm 3.53	Yb 1.40	Lu 2.75			
Actinides																		
	Ac -	Th 0.59	Pa 8.46	U 0.82	Np 9.80	Pu 50.20	Am 2.88	Cm -	Bk -	Cf -	Es -	Fm -	Md -	No -	Lr -			

macroscopic attenuation coefficients higher than for X-rays, while some heavy elements (Pb, Bi, U, Pt, ...) enable a much higher penetration for neutrons. These properties can favorably be used in practical neutron imaging applications (see below).

9.2.2 Neutron spectra

As shown in the example of Al, the cross-sections of the interaction with neutrons have a high energy dependence and are different for specific nuclear reactions. For neutron imaging and the interpretation and quantification of the transmission data we use first order the “total cross-section,” which just adds all reactions j and isotopes i together:

$$\Sigma_{tot} = \sum_{i,j} N_i \cdot \sigma_{ij} \quad (9.4)$$

This corresponds to the data in Table 9.2, there specifically for thermal neutrons. Here the cross-section values are high and free of resonances, which only occur for higher neutron energies. These resonances are specific properties of nuclides, which can only be accessed when neutrons are available with these particular higher energies. An example is given below.

For neutron energies above 100 keV and higher, more complex nuclear reactions than only capture and scattering can be induced.

However, the cross-sections are generally lower than for thermal neutrons, which makes imaging with such “fast neutrons” attractive for the study of very thick objects. For this purpose, either the initial, unmoderated source is used directly—or thermalized neutrons are re-converted by means of a U-235 target, as in the NECTAR facility at FRM-II [13]—see Chapter 3.5.

The slope of the cross-section in the energy range of a few meV is high and follows for most materials a “ $1/v$ ” law with v being the neutron velocity. Therefore, even a relative shift of the neutron spectrum, for example, from 25 meV (thermal neutrons) down to 3 meV (cold neutrons) becomes important when contrast and penetrability of different materials are considered. This is presented in Fig. 9.5 for the three beam lines at PSI, which are used for neutron imaging purposes (BOA, ICON, and NEUTRA) in relation to prominent materials and their cross-sections.

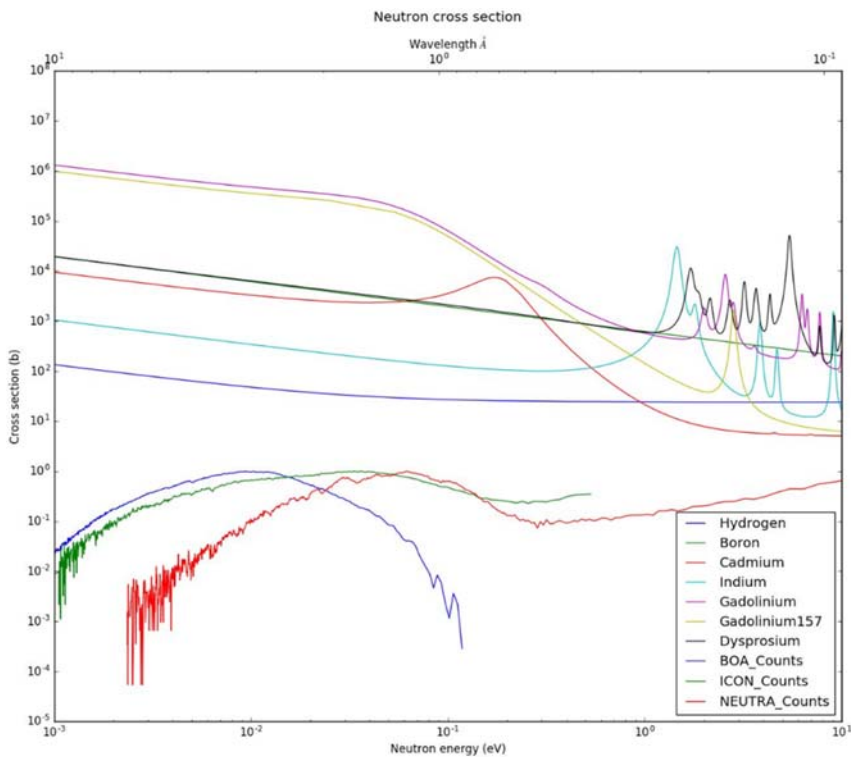


Figure 9.5 Neutron spectra at facilities in use for neutron imaging at PSI (BOA, ICON, NEUTRA) in comparison of the total cross-sections of different relevant materials; please, consider the double logarithmic scale.

9.2.3 Beer—Lambert's law and quantification

Based on the relation (9.1), the well-known exponential attenuation law, it becomes possible to derive material properties within the neutron imaging process. Comparing the neutron beam intensity distribution without a sample in front of the two-dimensional detector $I_0(x, y)$ with the same when the sample is placed in front of the detector $I(x, y)$, the transmission $T(x, y)$ can be derived:

$$T(x, y) = \frac{I(x, y)}{I_0(x, y)} \quad (9.5)$$

Inverting the relation (9.1), and assuming a homogenous material with the thickness d along the integration direction z , the following relation occurs:

$$\sum (x, y) \times d = -\ln(T(x, y)) \quad (9.6)$$

In this manner, the attenuation coefficient $\sum(x, y)$ of planar material distribution, integrated into beam direction z , is the value suited for quantification, because it is directly linked to the material density, according to (9.2). Here, we underline the perfect knowledge of the data of the microscopic cross-sections $\sigma(E)$, for comparison and interpretation of the data.

However, this approach has some limitations, which have to be considered in a precise quantification process:

1. If the sample contains more than only one material, the integration in beam direction is a mix of all components involved, often difficult to distinguish. This problem can be overcome in neutron tomography, where the sample is observed from different angular positions (projections), and the material distribution in the third direction is derived by mathematical procedures (reconstruction algorithms)—see below.
2. The neutron interaction process with the matter, expressed by the microscopic cross-sections (see Figs. 9.4 and 9.5), is strongly energy dependent. Because the neutron spectrum in the imaging process is spread over a relatively broad energy range (Maxwellian distribution in the case of thermal neutrons, see Fig. 9.5), the resulting imaging data represent therefore an average over the whole involved energy range.
3. Furthermore, the used neutron imaging detectors, based on the neutron absorption by Li-6, B-10, or Gd, also have an energy-depending response, which has to be considered as a weighting function. This is less important for Gd, which absorbs nearly all neutrons equally due to the very high capture probability than for the other two detector materials.

4. Most of the sample materials under investigation interact with the neutrons in the beam more by neutron scattering than by neutron absorption. There are two consequences: neutrons might return into the image area at different positions in the beam compared to their initial one, contributing to the signal as a perturbation; neutrons can additionally be slowed down or even pushed up in energy (as for cold neutrons) in the scattering process, and are registered with a different probability (see point 3).

The mentioned problems can be overcome in different ways, experimentally by using specific setups and analytically by means of accompanying simulations, using Monte-Carlo methods [14,15].

If the neutron beam is well-collimated, the sample can be placed at a certain distance from the detector, sacrificing only some spatial resolution. In this way, the contribution of the scattered neutrons is reduced and can be ignored more and more. It depends on the particular material and its amount, from which distance on the “scattering free” measurements are possible.

As hydrogen is a strongly scattering material, all investigations with hydrogenous materials need more attention if higher amounts are involved in the imaging and quantification process. Examples are all moisture distribution measurements, the process of hydrogen storage, or studies for corrosion. Here, we need calibration or correction methods for the consideration of the scattered neutrons [12].

9.2.4 Pinhole-based neutron imaging

It is the goal in a neutron imaging setup to provide a beam of well-defined neutrons (spectral distribution), as parallel as possible (collimation), ideally larger than any object to be investigated (FOV), without disturbing, accompanying gamma-background and of the highest intensity (short acquisition time).

Because neutrons cannot be guided by magnetic fields and focusing neutron optics are still rather limited for neutron imaging applications, the common way to form such a beam is to place a suitable aperture with a diameter D (e.g., with 2 cm diameter) near the source/moderator and to provide a long flight path L for the selected neutrons (over about 10 m). This defines the collimation ratio L/D , which would be $L/D = 500$ for this case, which is a typical value in many state-of-the-art instruments. In this way, the image blurring by the limited beam collimation can be reduced towards the inherent resolution of the (digital) detector.

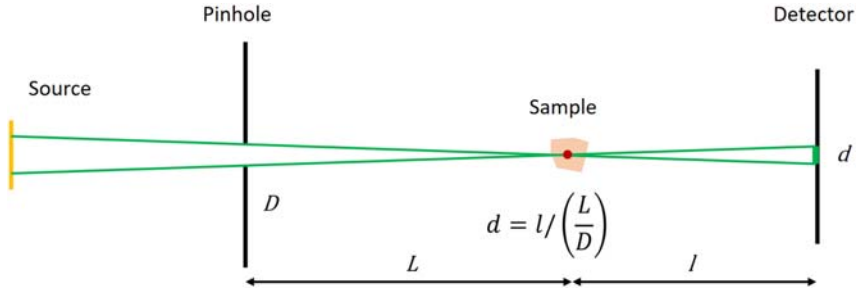


Figure 9.6 Sketch of the geometric blurring d arising from the finite pinhole size D , the neutron flight path to the sample L and the distance between sample and detector l . A point within the sample (indicated by a red dot) is blurred to a disk of diameter d on the detector.

The geometric blurring d due to the limited beam collimation of a sample placed at a distance l away from the detector can be estimated as (see Fig. 9.6)

$$d = \frac{l}{L/D} \quad (9.7)$$

In contrast to X-ray imaging, neutron imaging employs quasi-parallel beams with essentially no magnification. In order to minimize the geometric blurring, the sample is typically placed as close as possible to the detector, that is, the value of l is reduced to the minimum.

Modern neutron imaging facilities are able to change the aperture for either smaller diameters or larger ones. By opening the aperture more, the beam intensity can be increased while the spatial resolution is getting worse. It is worth noting that the intensity increases quadratically with the aperture diameter D , while the resolution only decreases linearly.

Fig. 9.3 demonstrates such a setup, which is realized in many cases at the relevant neutron sources. The particular performances differ, however, from facility to facility strongly.

9.2.5 Neutron tomography

At the end of the last century, tomography using x-rays was already on the way to becoming a routine method in hospitals. It enables “slice” the human body at arbitrary levels and delivers insight into deeper structures of the patient.

The method is based on a mathematical formalism, where information is obtained for the third dimension when two-dimensional data (projections)

for angular positions over at least 180 degrees are used. Due to the limited computing power at that time (calculation speed, data storage volumes), the demand was quite high and the investigation very time-consuming.

The approach to use also neutrons than X-rays enabled a further step into material research, which started around 1995 in Munich and other places [16]. Compared to medical imaging applications, where neutrons fail due to the high hydrogen content of human bodies, the strength of neutron imaging is the application for heavier elements, including many metals. Here, the X-ray methods come to their end due to the limited penetration power.

The methods, how reconstructing the data volume, based on a voxel matrix of attenuation coefficients $\sum_{i,j,k}$, are well described in the relevant literature, for example, [17], and will not be explained here again. There are programs available on a commercial basis to perform the reconstruction process very quickly today, for example, [18]. The final step to analyze the voxel data, derive slices in all directions, segment inner structures, and enhance volume features, is today also possible with suitable programs.

In Fig. 9.7, the process in tomography studies is shown symbolically.

The following examples shown in this chapter contain also neutron tomography data, performed either on the macro level (up to 40 cm sample size) or on the micro level (down to a few micrometer resolutions). However, the analytical process for all sample sizes is the same.

9.2.6 Neutron imaging facilities and instrumentation

Modern neutron imaging takes place at dedicated facilities at beam ports of large-scale facilities (strong research reactors, spallation neutron sources).

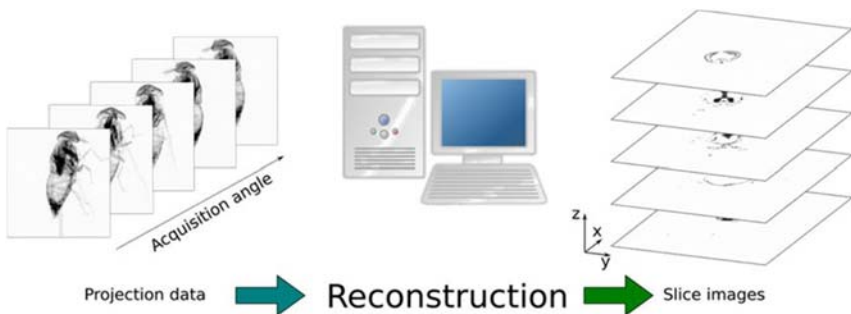


Figure 9.7 Workflow during neutron tomography experiments: based on the projections over the angular range of at least 180 degrees, the slices in the third direction are reconstructed according to the beam properties (parallel, conical, or fan geometry).

Because the various techniques of neutron imaging are today well-accepted tools for material research with high relevance to industrial applications, they are operated similarly to neutron scattering investigations within well-organized access programs for external users.

Due to the complexity of modern neutron imaging instrumentation and the need for relatively high beam intensities, there are only about 15 such facilities in operation worldwide [3]. However, even weaker neutron sources, for example, research reactors with power less than 250 kW, are able to perform neutron imaging on a reasonable level for several interesting applications [19].

As already shown in Fig. 9.3 symbolically, a setup for neutron imaging consists mainly of the three components: neutron source, beam forming collimator, and a neutron imaging detector. There are many additional supporting devices necessary to enable the best performance of the facility in order to provide the best data for further analysis (sample manipulator, monochromator, polarizer, sample environment, cooling/heating devices, beam dump, and complex shielding).

One key element of such installations is the neutron imaging detector, which records the two-dimensional distribution of the neutron beam after the interaction with the sample. Today, nearly all detection systems are based on digital sensors (cameras, semiconductor panels) which observe the light from a neutron-to-photon conversion in scintillation screens. The state of the art is presented in [20]. In order to improve the performance of these devices, some development is still on the way [21,22].

It has to be mentioned that all new projects for advanced neutron sources and all leading facilities have taken neutron imaging into the suite of instruments [13,23–30]. Most recently, ILL Grenoble joined the field by installing the NeXT facility [31].

9.3 Examples from neutron imaging studies

9.3.1 Neutron imaging for battery research

Modern high-performance batteries are typically based on lithium in combination with a liquid electrolyte. While the electrolyte and lithium electrodes are typically not visible with x-rays, the high contrast of neutrons for both hydrogen (contained in the electrolyte) and lithium predestines neutron imaging as an ideal tool for the investigation of such batteries (see e.g., [32,33]).

It is possible to study dynamic processes and material transport phenomena in-situ during discharging and/or charging of the batteries on instruments providing sufficiently high neutron flux. Here, we want to highlight two recent applications in battery research where neutron imaging was performed.

Lithium-ion pouch batteries have a wide range of applications for mobile devices or electro-mobility due to their compact shape that allows for a high packaging density of multiple cells [34]. One major cost driver during the production of these cells is the process of electrolyte filling [35]. Here, a stack of electrodes and separators is inserted into a metalized plastic pouch into which the electrolyte is then injected. In order to facilitate the wetting of the electrodes with the electrolyte, this is typically done inside a vacuum chamber at low pressure [36] and requires a significant amount of technical effort and time to reach a homogeneous distribution of the electrolyte in the cell. Optimization of the wetting process, therefore, has a significant potential to reduce the manufacturing costs of such cells. The excellent contrast of the electrolyte provided by neutron imaging was used to visualize the electrolyte movement during the wetting process non-destructively under vacuum conditions and to study the effect of the application of different pressure cycles on the time required to reach a homogeneous wetting of the cells in a series of studies [34,37–39]. For this purpose, a vacuum chamber made from aluminum including a dosing and a sealing mechanism for the cells was installed on the beam line ANTARES at FRM II [25]. An open pouch cell with a stack of electrodes was inserted in the vacuum chamber and the pressure was reduced to 50 mbar before dosing the electrolyte into the cell and sealing the pouch. The pressure inside the chamber could be controlled remotely during the experiment and pressure cycles were applied to enforce a stronger movement of the electrolyte inside the cell. During the experiment, images were taken every 15 seconds. By normalizing the images to the first image in the dry condition, the movement of the electrolyte was separated from the static material of the cell. The influence of different pressure profiles during the wetting period was studied in order to minimize the time required to achieve a homogeneous wetting. Examples of wetting states after different times are shown in Fig. 9.8. The electrolyte is very nonhomogeneously distributed at $t = 0$ seconds directly after the injection and mainly located at the bottom and the sides of the cell and in several folds of the pouch. After sealing the pouch and application of higher pressure in the vacuum chamber the liquid gradually moves

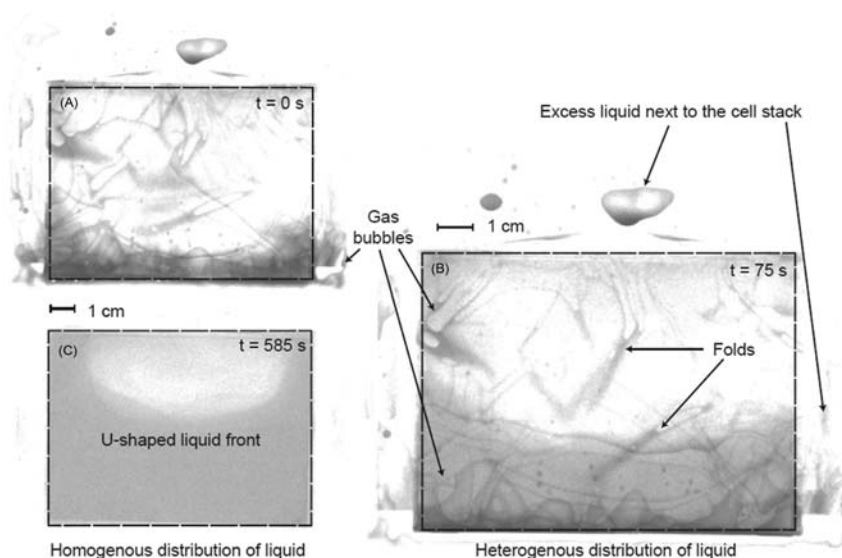


Figure 9.8 Radiographs showing the electrolyte distribution at different times after dosing. Before increasing the pressure in the vacuum chamber, a large part of the liquid electrolyte is located at the bottom and the sides of the cell as well as in server folds of the pouch. After pressurizing the vacuum chamber, the electrolyte distribution becomes more homogeneous. A full wetting was not achieved within the experiment time of 600 s. From T. Knoche, V. Zinth, M. Schulz, J. Schnell, R. Gilles, G. Reinhart, *In situ visualization of the electrolyte solvent filling process by neutron radiography*, *J. Power Sources* 331 (2016) 267.

from the folds into the cell's stack and slowly wets the cell. A full wetting was not achieved within the experimental time of 600 seconds. Using this data, it was possible to identify the flow paths of the liquid in the cells and to study the influence of the process parameters on the wetting time providing pathways to optimize the wetting process at a lower cost and more consistent cell performance.

In the second study which we want to highlight, neutron imaging was used to investigate the degradation of metallic Li electrodes during the discharge of LiSOCl_2 primary batteries [40]. In this type of battery, the metallic Li-anode serves as a current collector while at the same time being consumed in the chemical reaction producing the electrical energy of the battery. The partial consumption of the electrode may lead to loss of electric conductivity in some regions of the battery, therefore reducing the realistic capacity of the battery compared to the theoretical value given by the total amount of metallic lithium. Here, x-ray

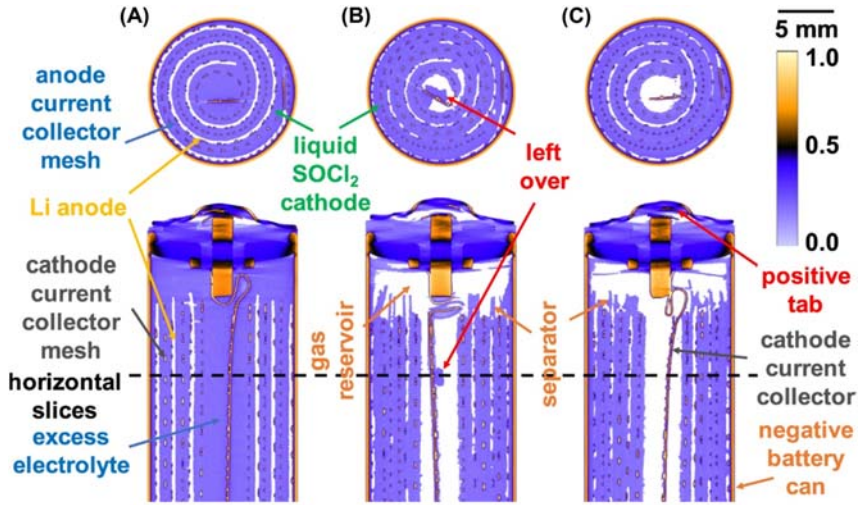


Figure 9.9 Orthogonal slices of X-ray CT data of a battery cell in (A) pristine condition and discharged at rates of (B) 300 mA and (C) 100 mA. The Li anode shows very low attenuation and is only indirectly visible as a white spiral in the images. From R. F. Ziesche et al., Editors' Choice—4D neutron and x-ray tomography studies of high energy density primary batteries: part II. Multi-modal microscopy of LiSOCl₂ cells, *J. Electrochem. Soc.* 167 (2020).

CT fails to visualize the Li-anode due to the low attenuation arising from the low atomic number of Li, while at the same time, the metal parts of the case produce significant artifacts in the CT reconstruction (see Fig. 9.9).

In contrast, time-resolved *operando* neutron CT provides good contrast for the lithium and the electrolyte and allows for the time resolved determination of the shape and volume of the Li-anode during discharge. The experiments were performed at the NEXT beam line at ILL, which currently offers the highest neutron flux for neutron imaging. Applying a reduced pixel resolution and a continuous sample rotation allowed to record of a full CT scan over 180 degrees in 15 minutes, therefore enabling a real time resolution to follow the degradation of the electrode during the discharge process, which lasted between 4.4 and 14.6 hours depending on the discharge current. Fig. 9.10 shows the 3D visualization of the rolled Li-anode of the batteries at different times during the discharge process. At the end of the discharge process, insulated lithium regions are observed which are not electrically connected to the

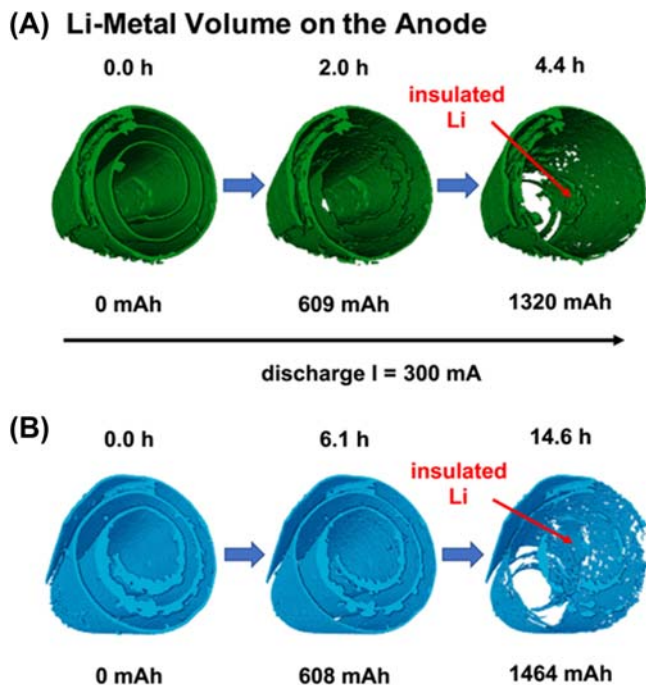


Figure 9.10 3D visualization of the metallic Li-anode at different states of charge for two different discharge rates of 300 mA (A) and 100 mA (B). In both cases, insulated Li areas are visible in the fully discharged battery. From R. F. Ziesche et al., *Editors' Choice—4D neutron and x-ray tomography studies of high energy density primary batteries: part II. Multi-modal microscopy of LiSOCl₂ cells*, *J. Electrochem. Soc.* 167 (2020).

remaining electrode and therefore can no longer contribute to the power generation. These studies show the great potential of neutron imaging for in-situ and in-operando studies of Li-based batteries.

9.3.2 Intermetallic connections—gluing, brazing and welding

Many metallic components of industrial products are joined together by means of permanent connections. On the one hand, adhesives and brazing agents are added between the joining pieces as a third component. On the other hand, the same, but molten material is taken as filler in the case of welding joints.

The value of neutron imaging in these cases is the high penetration through metals in general, but also the often higher contrast for the connection material itself. Therefore, there is a completely non-destructive method available to check and evaluate the quality of the metallic interface.

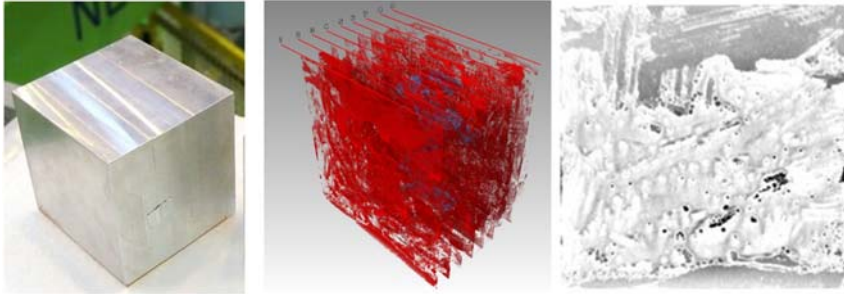


Figure 9.11 Adhesive connections between 10 Al plates of 10 mm each to form a cube of 10 cm $\times$ 10 cm; photo—left; tomography view of the adhesive material distribution—middle (the metal is rendered transparent); view onto one single adhesive layer—right, also derived from the tomography data [41]. Adapted from C. Grünzweig, D. Mannes, A. Kaestner, F. Schmid, P. Vontobel, J. Hovind, et al., *Progress in industrial applications using modern neutron imaging techniques*, *Phys. Procedia* 43 (2013).

Adhesives often contain a high amount of hydrogen, which delivers a high neutron imaging contrast even in thin layers between the metallic structures. This was demonstrated by means of a test sample of 10 Al plates with 10 mm thickness, connected in layers to form a cube of 10 cm by 10 cm (Fig. 9.11). By means of a neutron CT it became possible to look precisely onto each of the nine adhesive layers after its completion (hardening) in the structure. Although the adhesive material was distributed homogeneously on the surfaces before the connection was built, quite unequal glue distribution is created in the process of combining. This behavior may not be dangerous for the strength of the connection, but is a surprising result, which could only be obtained in a destructive manner (disassembly)—if neutron imaging would not be available. In the common industrial praxis, such glue distribution patterns are only visible after dismantling.

This knowledge has practical applications, as shown in Fig. 9.12, where the gluing connection between two components of a car door is inspected by means of neutron radiography. Because the door is much larger than the neutron beam and the detector area, the final image is composed of many single images—without showing gaps between them. However, the spatial resolution of the data and the high image contrast by the adhesive layer enable a very careful inspection which would be done otherwise in a destructive manner. If the glue connection is imperfect, the door undergoes a corrosion process during its lifetime.

Brazing or soldering connections are performed with liquid metals. We investigated the connections between stainless steel components

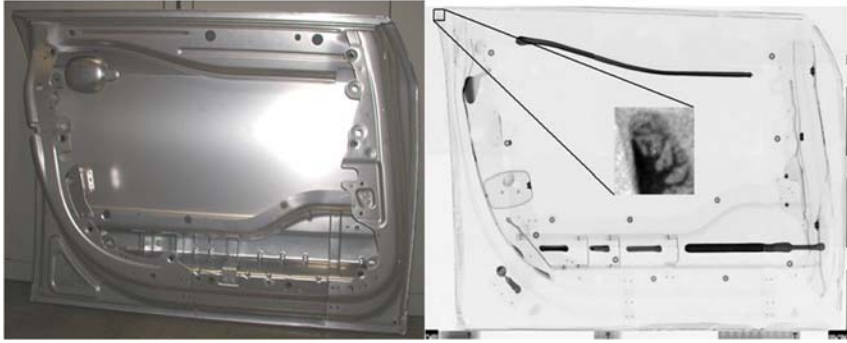


Figure 9.12 The inner and outer parts of the car door are connected with glue, which can be inspected with neutron imaging means, as shown on the right side image and the cut-out.

carefully by using neutron radiography and tomography. In this particular case, the brazing agent contains a relatively high amount of boron, which is a strong neutron-absorbing material. Therefore, it is obvious find a high contrast in the brazing connections and very sensitive control of the agent is enabled after the treatment. In particular, the brazing process is performed by heating the sample in an oven after putting the still-solid agents between the two components in a suitable manner. The melting and solidifying take place without any interference from outside. Therefore, some “random” agent distributions might happen—which can be determined with neutron imaging methods in the best way. An example of the inspection of the brazing connection is shown in Fig. 9.13.

Welding connections are very common within steel or aluminum structures, where the weld is built with approximately the same material as the components to be joined. The best welding connection should have about the same composition and crystalline structure as the basic material.

Here, a more sophisticated method: energy selective neutron image needs to be used. The common approach in neutron imaging with either thermal or cold neutrons is to use the full spectrum delivered from the neutron source and integrate/average of all energies in one image. The pixel-wise data correspond to the attenuation coefficient $\Sigma(x, y)$ with the beam in the z -direction, ϕ is the neutron flux spectrum, and ε the detector efficiency, both in the dependency on the neutron energy E :

$$\Sigma(x, y) = \frac{\int \Sigma(x, y, E) \cdot \phi(x, y, E) \cdot \varepsilon(E) dE}{\int \phi(x, y, E) \cdot \varepsilon(E) dE} \quad (9.8)$$



Figure 9.13 Brazing connections inside a stainless steel dummy sample (diameter about 50 mm) demonstrate the high contrast of the boron containing the brazing agent and its distribution after the treatment in the heat [42].

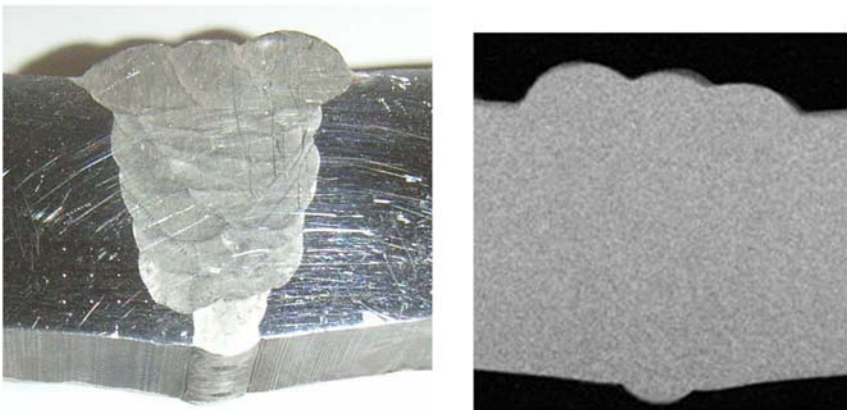


Figure 9.14 A steel weld (photo left, [43]) and the transmission neutron image with the full thermal beam for the sample with a thickness of 12 mm; because all neutron energies contribute to the averaged image, no structural details can be observed—in contrary to the behavior at selected neutron energies—see Fig. 9.16. (left) From E. H. Lehmann, S. Peetermans, L. Josic, H. Leber, H. van Swygenhoven, *Energy-selective neutron imaging with high spatial resolution and its impact on the study of crystalline-structured materials*, *Nucl. Instrum. Methods Phys. Res. A* 735 (2014).

Therefore, a steel weld as shown in Fig. 9.14 shows no internal structure or material distribution deviations for the case of equal thickness in beam direction z .

It is however well known, that in particular Fe, Al, or Ni have a specific behavior in the neutron scattering process. Given the crystalline

lattice structure, elastic scattering of equally oriented grains in the metal happens according to the Bragg diffraction law:

$$2d \cdot \sin\theta = n \cdot \lambda \quad (9.9)$$

In this equation, the neutron wavelength λ corresponding to the energy E in Eq. (9.1) fulfills this condition if the scattering angle θ and the lattice distance d are just fitting. Therefore, it becomes possible to determine sample properties like grain size and grain orientations if an energy-dependent investigation in the imaging mode is performed.

There are several methods available to select narrow energy/wavelength bands from the broad Maxwellian spectrum at the imaging beam line. Neutron velocity selectors, which are turbines with twisted, absorbing blades are available, which allow the transmission only for small energy bands according to the rotation frequency. By changing that speed, variable energies can be chosen. The finer energy resolution is possible with “double crystal monochromators (DCM)” where two single crystals of pyrolytic graphite are used to select the suitable energy band by a zig-zag reflection [44]. With the technique of “time-of-flight,” (TOF) best implemented at a pulsed neutron source the energies are selected according to their arrival at the detector.

Because the real cross-section data of for example, Fe (Fig. 9.15) have the characteristic “saw tooth” structure, particularly at a wavelength above 0.3 nm (cold spectrum), the selection of cold neutrons out of the spectrum is most important. From the selection methods, DCM has been found to present the best image quality in the particular case of the steel weld, as shown in Fig. 9.16. We can clearly see the different crystals and their size. The contrast by the different grain orientations and their sizes were verified by Electron Backscattering Diffraction measurements, as shown in Fig. 9.17.

9.3.3 Soot particulate filters

The majority of cars on our streets are still driven by combustion engines, using gasoline or Diesel oil as fuel. Besides the conversion of carbon into carbon dioxide during the combustion process, there are other by-products, which have a high environmental impact. Next to nitrogen oxides, which are handled and reduced by means of catalytic chemical processes, there are emissions of soot and ash particles into the air. This kind of pollution is a problem, in particular in big cities and agglomerations.

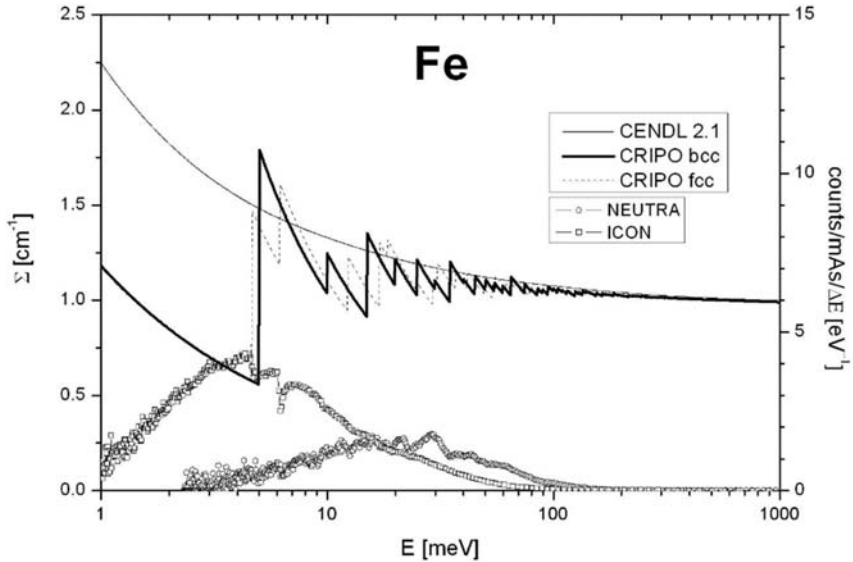


Figure 9.15 Cross-section data for iron in the cold and thermal energy range with the characteristic Bragg edges corresponding to the scattering effects at different lattice planes of the crystalline material.

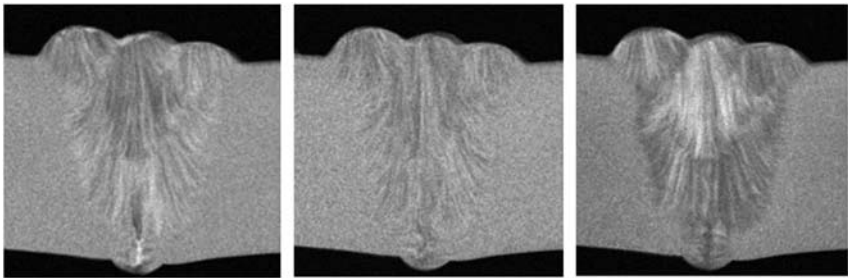


Figure 9.16 The same steel weld as shown in Fig. 9.14, now measured at selected neutron wavelength: from left to right—0.35, 0.37, 0.40 nm.

The car manufacturers found a solution to this problem through the installation of soot particulate filters, especially for Diesel engines. Although there are different types of filters on the market, the basic concept is about the same: a ceramic matrix with internal channels is flooded with exhaust gases and the semipermeable walls remove soot, ash, and other solid particles from the gas flow.

The application of neutron imaging methods for inspections was found very useful for the following reasons: the structural materials (steel cover,

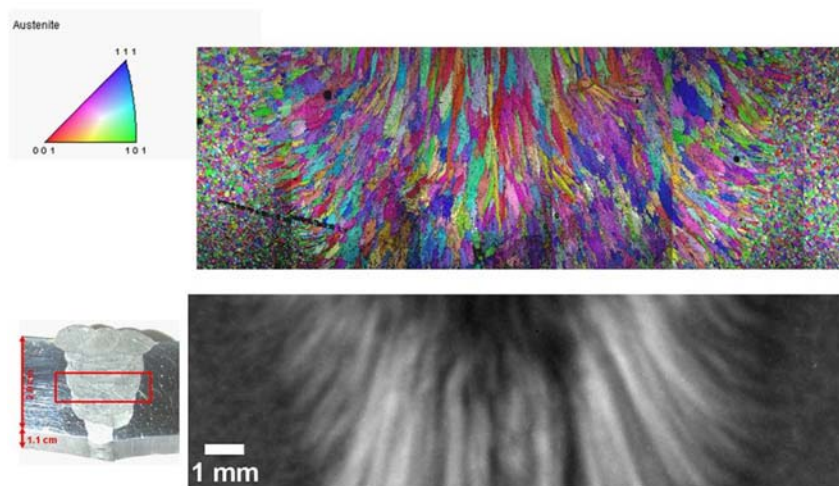


Figure 9.17 Comparison of the EBSD measurement (*above*) with the energy selective transmission image (*below*) for the part of the steel sample as shown on the left. The grain sizes in the weld and in the base material and their orientation (described by the colors) fit well together. From E. H. Lehmann, S. Peetermans, L. Josic, H. Leber, H. van Swygenhoven, *Energy-selective neutron imaging with high spatial resolution and its impact on the study of crystalline-structured materials*, *Nucl. Instrum. Methods Phys. Res. A* 735 (2014).

ceramic structure of the filter) are quite transparent for neutrons; the hydrogenous soot particles can be detected and observed with high sensitivity. This is caused by the specific attenuation behavior of neutrons, as already described above.

There are two inspection strategies for neutrons, mainly neutron tomography: (1) to investigate the whole sample with a coarse resolution but the corresponding large field-of-view OR (2) to cut out relevant pieces of the ceramics and to study in a high-resolution mode all sedimentations in more detail.

Results of such kinds of studies are shown in Fig. 9.18 for case (1) and in Fig. 9.19 for cases (2).

The strength of the neutron imaging methods is the ability to distinguish the different substances and to determine the content quantitatively. In this manner, the soot accumulation can be followed during all stages of the combustion process, completely noninvasively [45].

Because the intention of purification of the environment is not only related to Diesel engines alone but will also be introduced to gasoline-driven ones, the application of the neutron methods for even smaller amounts of soot is essential in the near future.



Figure 9.18 Photo (*left*) and neutron tomography results (*right*) of a Diesel particulate filter, where the structure, but also the amount of soot and ash can be determined quantitatively.

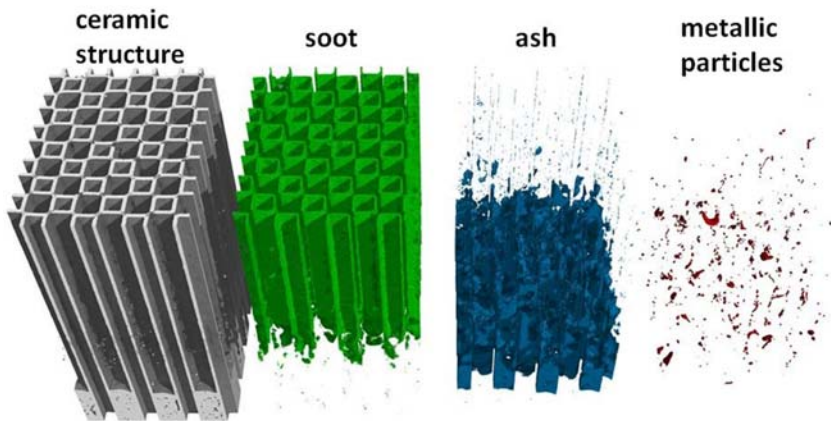


Figure 9.19 Tomography data of a smaller cut-out of the filter ceramics, where different contents are separated by image processing tools.

9.3.4 Absorption resonance imaging of nuclear fuels

Neutron cross sections at energies >0.4 eV can exhibit strong variations that can vary drastically between isotopes of the same element. The underlying

reason for these variations in neutron cross sections throughout the periodic table is the nuclear shell structure that confines protons and neutrons to subshells that are preferentially filled. Light elements have fewer neutrons and protons and therefore fewer possible ways to arrange them, which results in few energy levels at energies often ranging from keV to MeV. Heavy nuclei, on the contrary, have more neutrons and protons, therefore, providing more possible ways to fill the subshells, resulting in more energy levels, often reaching energies as low as in the eV range. This nuclear structure is generally too complicated to directly calculate the energy configurations. As a consequence, nuclear cross-sections are typically extracted from experimental databases.

As an example, the measured cross sections of the two isotopes ^{238}U and ^{186}W are shown in Fig. 9.20. It is noticeable that the spectrum can be roughly divided into two different regions. The first region is one of thermal neutrons with energies $<0.4\text{ eV}$, where the cross sections are inversely proportional to the neutron velocity. The second region is one of epithermal neutrons with energies $>0.4\text{ eV}$, where a discrete structure in the cross sections appears. These strong and sudden increases in the cross sections for epithermal neutrons can be attributed to so-called resonances. Resonances occur when the energy of an incoming neutron

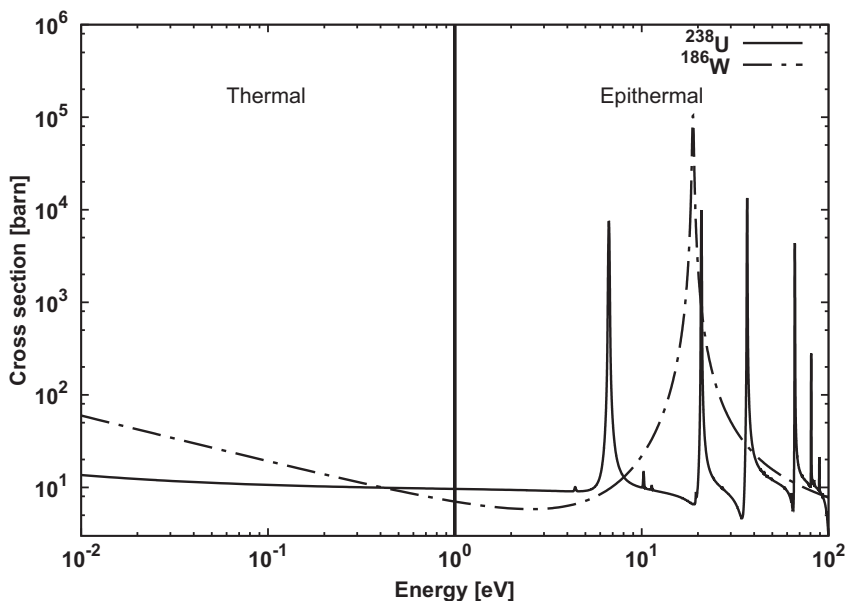


Figure 9.20 Cross sections for ^{186}W and ^{238}U extracted from the ENDF data-base.

matches the energy difference ΔE of two discrete energy states of the nucleus, the neutron is absorbed and the nucleus adopts an excited state. The shape of such nuclear resonances can be described with the Breit–Wigner formula [46]. It should be noted that each element or isotope exhibits its own resonance spectrum, thus measuring the resonances can be used to fingerprint what element or isotope is present in the material. After absorption, the compound nucleus then typically decays into a lower-energy state through radioactive decay by emission of α , β , or γ rays; this can lead to additional contributions in the background radiation. In principle, there is a third region in the fast neutron-energy range with energies $> 10^5$ eV (not shown in Fig. 9.1). This region is also called “unresolved” since the density of energy states has increased to a point that individual resonances often cannot be experimentally resolved anymore.

Access to these resonances for imaging can be obtained via energy-resolved neutron imaging at a spallation source using TOF neutrons. As an example, energy-resolved neutron imaging of a dUO₂ fuel rod assembly (dUO₂ pellets contained in a stainless-steel rod) is shown in Fig. 9.21 was performed at the Los Alamos Neutron Science Center—Lujan Center. Fig. 9.21A shows a CT reconstruction of the assembly using cold neutrons based on an integrated data set using the cold spectrum only, similar to that of a data-set one would acquire at a cold neutron source. Mapping of the ^{186}W distribution was accomplished by using the energies

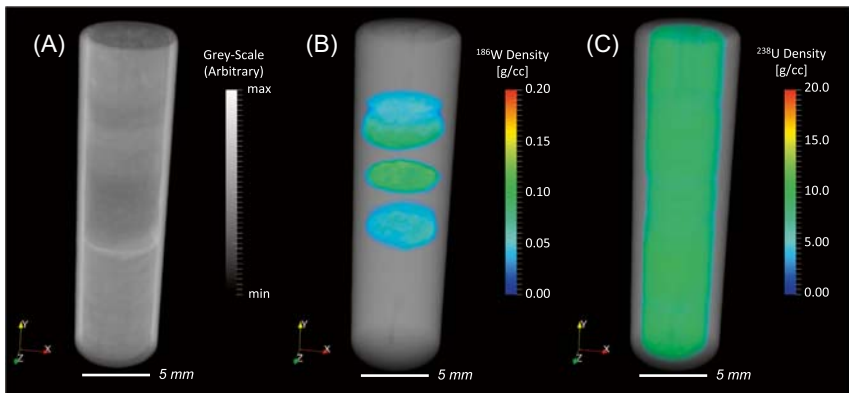


Figure 9.21 Attenuation based cold neutron CT-reconstruction of a fuel pellet assembly containing dUO₂ pellets in (A). Absolute CT-reconstruction of the assembly via use of absorption resonance of ^{186}W and ^{238}U in g/cc shown in (B) and (C), respectively. The measurements were performed at the Los Alamos spallation neutron source.

of tungsten resonances and is shown in Fig. 9.21B. The distribution of ^{238}U was mapped similarly to that of ^{186}W by using the non-saturated energies of the uranium resonances and is shown in Fig. 9.21C.

While this technique offers unique characterization capabilities for nuclear materials [47–50] other applications of this technique to date include in-situ measurements of dopant transport in crystal growth [50–52], mapping of ions in porous materials during water uptake [53] and imaging of elemental composition of a natural gold single crystals [54].

9.3.5 Imaging of hydrogen storage using fast neutrons

In general, increasing the energy of a particle increases its mean-free path in the medium through which it is traveling. Thus, higher-energy particles will exhibit higher penetration. This principle is deployed at fast neutron imaging beam lines to probe large and dense objects (generally objects larger than a cubic centimeter) by use of neutron energies in the MeV range.

Due to the comparatively low attenuation of fast neutrons, they are inherently difficult to detect. The main detection mechanism for MeV neutrons in imaging is via proton recoil, that is scattering of the neutron off a proton, whereby visible light is emitted by slowing down or stopping the recoil proton in the scintillator material. This makes hydrogen rich materials, such as plastic, in combination with a scintillating material, for example, zinc sulfide, the material of choice for fast neutron imaging detectors. However, to even reach the percent range in detection efficiency, mm-thick scintillators are required, consequently providing relatively low spatial resolution in the sub mm-range.

Nonetheless, fast neutrons are often deployed when X-rays or thermal neutrons do not provide sufficient penetration for imaging studies, such as shown in [55] for in-situ fission neutron radiography of metal hydride based hydrogen storage systems, whereby steel walls of 24 mm in total thickness were required to penetrate before being able to receive a signal from the metal hydride samples exposed to hydrogen. It was shown that the use of fission neutrons can provide unique insights into the spatial distribution of hydrogen for that matter, even for scaled-up components, and therefore enabled a direct study of hydrogen storage tanks. Moreover, the quantification of time-resolved data and a priori material distribution allowed for an optimization of the manufacturing process of the hydrogen storage systems. The samples measured within the steel tank for that study

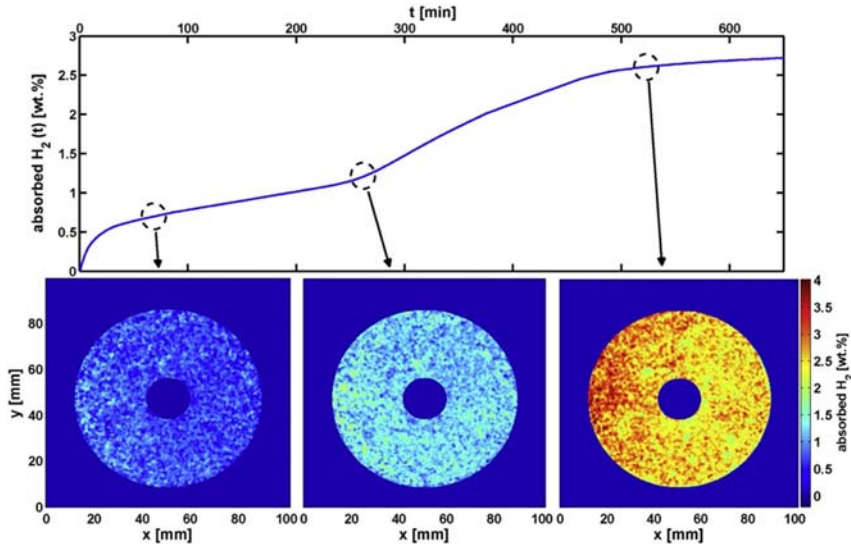


Figure 9.22 Time evolution of absorbed hydrogen (*top*) with quantitative, spatially resolved hydrogen distribution in the material (*bottom*) for selected time steps, indicated by dashed circles in the overall time evolution image [55].

were compacted pellets of a metal hydride, doped with NaHe-Al, with dimensions of 77 mm (outer diameter) and 12 mm (inner diameter) and a thickness of 10.5 mm, that were then exposed to hydrogen gas. Fig. 9.22 shows the time evolution of the charging of the samples with hydrogen.

An important aspect when working with fast neutrons is to account for the scattering when performing quantitative analysis. While thermal neutrons generally scatter isotropically for powder samples, fast neutrons scatter predominantly in the forward direction, making it more so important to place samples at a distance from the detector to reduce the solid angle for the disturbing scattered neutrons in the transmission radiographs. For the study on hydrogen storage, this was accounted for by placing the samples at a 15 cm distance from the detector.

In conclusion, fast neutrons become invaluable when material distributions of scaled-up experimental setups are measured, providing quantitative insight even for dynamic processes. Moreover, scientific experiments using X-rays or thermal neutrons are often carried out with simplified sample containers due to the limitations in penetrating dense and bulky objects. Additionally, the attenuation of fast neutrons for different elements is similar throughout the entire periodic table. Thermal neutrons for example are heavily limited in their penetration capability for samples

that contain large amounts of hydrogen, while aluminum in comparison is fairly transparent. For fast neutrons, with a mean energy of 1.8 MeV, as is the case for the imaging beam-line NECTAR [13,26] utilized in the study above, both elements provide similar contrast. Therefore, this can provide an advantage when imaging very light materials in the presence of heavy materials.

9.3.6 Mapping of crystallographic phases using energy selective neutron imaging

As discussed before, the neutron absorption cross section depends on the wavelength λ and increases linearly in the thermal neutron range. In contrast, the coherent scattering cross section of neutrons on the lattice structure of polycrystalline materials shows characteristic edges related to the crystal lattice spacing d by $\lambda = 2d$. These edges arise because Bragg's law cannot be fulfilled for wavelengths $\lambda > 2d$ for a particular lattice spacing d , leading to a sudden drop of the scattering cross section—also denotes as “Bragg edge.” The theoretical attenuation coefficients for α and γ iron are shown in Fig. 9.23 as a function of λ where several Bragg edges are clearly visible [56].

Manifold information can be extracted from the position, shape, and height of the Bragg edges. The relation between the position of the Bragg edge and the lattice spacing d can be used to determine stress in a material

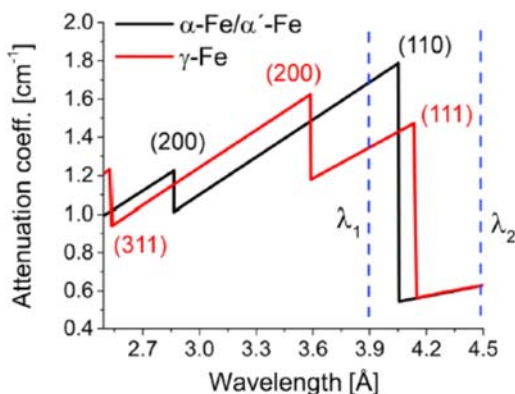


Figure 9.23 Theoretical calculation of the Bragg edges of α and γ iron. The Bragg edges arise from the different crystal structure of the two phases (hcp and bcc). From S. R. Soria, X. H. Li, M. Schulz, M. Boin, M. Hofmann, Determination of martensite content and mapping phase distribution on austempered ductile iron using energy-selective neutron imaging, *Mater. Charact.* 166 (2020).

based on a shift of the Bragg edge position [57–59]. In a multi-phase material, the relative heights of the characteristic Bragg edges for each phase are related to the fractions of crystallographic phases present in the composite [60,61]. Lastly, the shape of the edges can reveal information on the presence of texture (preferred orientation) in the material [62,63]. From a technical point of view, the determination of the position and shape of the Bragg edges requires the transmission of the sample to be measured as a function of wavelength. This is only possible on instruments that provide devices for monochromatization on continuous sources or by using TOF techniques on pulsed neutron sources (see Chapter 27). In particular, the measurement of stress requires very fine wavelength resolution, which can typically only be achieved with TOF.

Here we selected two examples of applications of this technique for the quantitative determination of phase fractions in materials undergoing a phase transition under mechanical deformation, also known as transformation-induced plasticity effect [64], typically found in stainless steels. Here, austenite showing an fcc structure transforms to martensite (hcp and bcc structure) under deformation, which is accompanied by a change of the mechanical (in particular low-cycle fatigue) as well as the magnetic properties of the material [65]. Consequently, an investigation of the phase transformation is of great importance for industrial applications and with other non-destructive techniques is generally limited to the surface of the material. Here, based on their high penetration, neutrons provide an ideal tool for the spatially resolved investigation of phase distribution inside the bulk material.

In the first study [60], a radiographic approach was used to determine the 2D spatial phase distribution in cylindrical samples of cast ductile iron with a diameter of 6 mm and an original thickness of 7 mm after compression along the cylinder axis between 0% and 45%.

As indicated in Fig. 9.24 (*left*) the samples were aligned with the cylinder axis parallel to the neutron beam direction and the neutron transmission was measured in a wavelength range from 1.6 to 6.0 Å. An example of the transmission measurements at $\lambda = 3.9$ Å is shown. After correction of the transmission for the different sample thicknesses, the attenuation coefficient was plotted as a function of wavelength in the middle panel. While the individual Bragg edges of alpha and gamma-iron are not discernible due to the limited wavelength resolution of the monochromator [44] used for these measurements, a clear change in the height of the Bragg edge with deformation is found, which can be correlated with the change of the phase fraction of alpha-iron as indicated in the right panel.

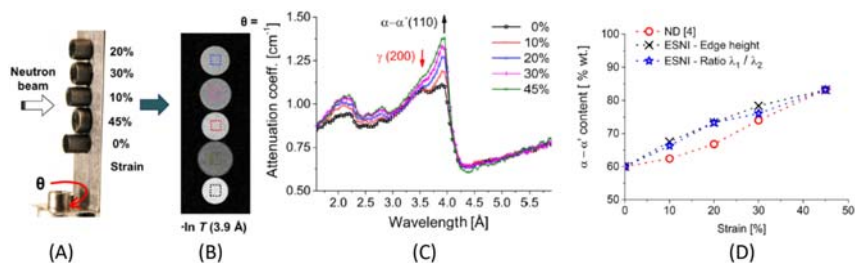


Figure 9.24 Bragg edge imaging results of ADI samples with different deformation from 0% to 45% (A). Transmission image at 3.9 Å (B). Measured wavelength dependence of the attenuation coefficient for the samples with different deformation (C). The phase content can be determined from the height of the Bragg edge and shows good agreement with neutron diffraction results (D). From S. R. Soria, X. H. Li, M. Schulz, M. Boin, M. Hofmann, *Determination of martensite content and mapping phase distribution on austempered ductile iron using energy-selective neutron imaging*, *Mater. Charact.* 166 (2020).

For this technique, a calibration of the relation between edge height and alpha-iron phase fraction was performed for two points based on the phase fractions determined in neutron diffraction measurements [61].

Another approach to determine the phase fraction is to perform transmission measurements at two selected wavelengths shortly before and shortly after the Bragg edges of alpha- and gamma-iron. Thereby, the required measurement time compared to a full wavelength scan can be greatly reduced. This was used by Woracek et al. [66] to map the 3D phase distribution of various samples after deformation by performing two monochromatic neutrons CTs at 4.3 Å (after the Bragg edges of both alpha- and gamma iron) and 4.1 Å (at the maximum height of the alpha-iron Bragg edge) and dividing the reconstructed 3D volumes. The resulting value of each voxel can then be correlated with the alpha-iron phase fraction after calibration with two known phase fractions. In this case, a 3D distribution of the phase fractions can be visualized as seen in Fig. 9.25 for samples that have undergone different deformations such as pure torsion, where the martensite content is strongly increased towards the edge of the sample where the largest deformation is expected, while the center of the sample remains in the austenitic phase. Similarly, for a sample after tensile deformation, the martensite concentration is again largest in the areas with the highest deformation.

These examples clearly demonstrate the potential of energy resolved neutron imaging for the determination of phase fractions in engineering

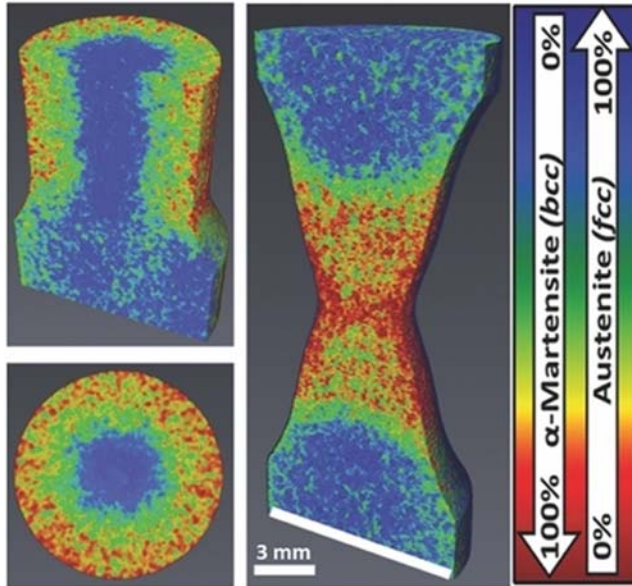


Figure 9.25 Ferritic and martensitic structure can be distinguished by means of energy—selective neutron imaging. From R. Woracek, D. Penumadu, N. Kardjilov, A. Hilger, M. Boin, J. Banhart, et al., 3D mapping of crystallographic phase distribution using energy-selective neutron tomography, *Adv. Mater.* 26 (2014).

applications. The 3D approach is not limited to a particular sample shape and can be extended to arbitrarily shaped samples taken from production processes.

9.3.7 Magnetic flux guidance in electrical steel employing stress induced by embossing

Another advanced neutron imaging technique is nGI [67–69], which offers additional and complementary contrast modalities to regular attenuation-based neutron imaging by installing a spatially resolved interferometer setup into a regular neutron imaging beam line. There are different approaches to the implementation of this technique with the most prominent one being a Talbot-Lau interferometer. By implementing a linear phase grating into the beam line, an interference pattern with a periodicity of a few μm will be generated on the detector. In addition, typically two absorption gratings are required to create a spatially coherent neutron beam and to analyze the resulting interference pattern. When a sample is placed into the beam—in addition to classical absorption—it will alter the neutron wave front by refraction or

ultra small angle neutron scattering (USANS). By analyzing the influence of the sample on the position and amplitude of the interference pattern at the detector, two additional images can be obtained. The information about the phase shift of the neutron wave introduced by the sample is contained in the differential phase contrast image, while from the amplitude of the interference pattern information about USANS scattering of the sample can be extracted via the dark field image (DFI). In particular, the DFI has recently seen tremendous interest as a spatially resolved USANS technique containing information shown in scattering of neutrons on structures of length scales in the range from 100 nm to 10 μ m. Such information cannot be extracted by regular neutron imaging due to the current limitations of the spatial resolution of imaging detectors. Due to the sensitivity of the neutron scattering length density to magnetic fields, the USANS scattering can not only arise from structural inhomogeneities but also from ferromagnetic domains [6,9,70]. This has extensively been used to investigate the magnetic domain distribution in the bulk of electric steels as typically employed in electric drives or transformers. An example of such an application [71] will be reviewed in the following (Fig. 9.26).

High energy efficiency is a key component to combat global warming. In electric drives, especially in reluctance and permanent magnet synchronous machines, this can be achieved by optimizing the magnetic flux guidance in their magnetic core [72]. Conventionally, cutouts in the electrical steel sheets comprising the magnetic core are used for magnetic flux guidance [73]. However, this compromises the mechanical strength of the rotating magnetic core and, as a result, reduces the maximum angular velocity. In a series of works, the use of embossing the electrical steel to guide the magnetic flux is investigated [74–77]. The stress induced by embossing changes the local magnetic properties and decreases the local magnetic permeability. Guiding the magnetic flux by means of embossing allows to an increase in the mechanical stability of the electric steel and consequently leads to higher possible angular velocity as well as the power density of electric drives.

The nGI setup installed at the ANTARES beamline at FRM II allows probing the local magnetic properties of the embossed electrical steel. In particular, nGI maps the ultra-small-angle scattering of neutrons off magnetic domain walls.

In the first step, electrical steel sheets with a single, large embossing acting as a magnetic flux barrier were investigated. Fig. 9.26 shows the variation in the signal arising from different punch geometries. Here, a

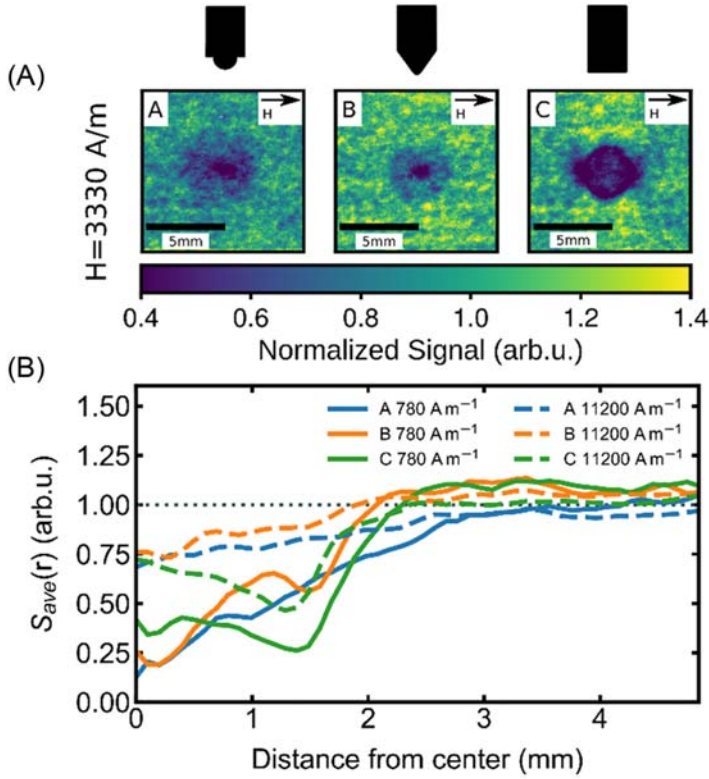


Figure 9.26 Analysis of the influence of embossing on the scattering contrast. A DFI-signal of samples A, B, and C in an applied magnetic field $H = 3330 \text{ A/m}$. The data is normalized using a virgin reference sample also exposed to H . A signal smaller than $S = 1$ indicates more scattering in the embossed sample than in the non-embossed reference. B Normalized signal $S_{ave}(r)$ as obtained by radially averaging the images of samples A (blue), B (orange), and C (green) exposed to two different magnetic fields. From T. Neuwirth, A. Backs, A. Gustschin, S. Vogt, F. Pfeiffer, P. Böni, et al., A high visibility talbot-lau neutron grating interferometer to investigate stress-induced magnetic degradation in electrical steel, *Sci. Rep.* 10, (2020).

signal $S_{ave} < 1$ corresponds to a reduced local magnetic flux in the material compared to the virgin material. The results indicate that ideally the deformation of the electrical steel sheet is kept localized, as achieved with a flat punch used in sample C. This also provides the highest stability of the flux barrier with respect to the applied magnetic field.

Building on these results, flux barriers comprised of finely distributed small embossing points have subsequently been studied as an alternative

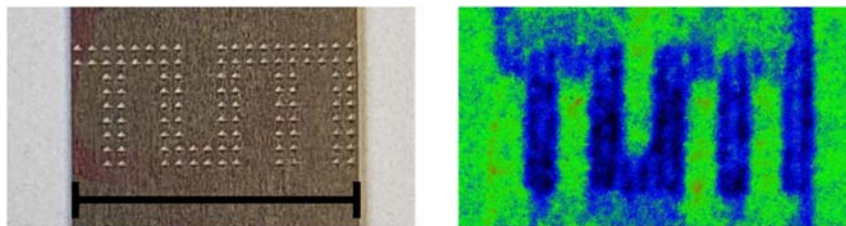


Figure 9.27 Examples of finely distributed embossing points acting as magnetic flux barriers. The logo of TUM was embossed into electric steel sheets using a large number of fine embossing points as shown in the photo on the left. The black scale bar indicates a length of 10 mm. A magnetic field is applied in the vertical direction. Lower DFI values (*blue*) show decreased magnetic flux within the embossed patterns, while the flux is increased (*green*) at the sides as seen in the DFI image on the right side.

for flux guidance. This change allows reduction of the deformation of the electrical steel necessary to form a flux barrier. Examples of such embossing patterns are shown in [Fig. 9.27](#).

These results will help towards the development of electric drives using embossing to guide the magnetic flux, resulting in increased angular velocity. The combination of measuring local and global magnetic properties supported by mechanical simulations enables a deeper understanding of the influence of embossing induced stress on the local magnetic properties of electrical steel sheets.

9.4 Outlook

This article has focused on the application of neutron imaging as a tool for industrial applications, in particular the noninvasive study of relevant materials and processes. The given examples of previous studies demonstrate the different options and methods available today.

The direct link to industrial partners has two important aspects: assistance of companies in the development and improvement of their products—and the motivation for the operators of NI facilities to develop their methods even further.

Unfortunately, the number of neutron sources is limited and will even be reduced more since the research reactors are aging and shut down consequently. A summary of currently available “user facilities” is given in [Table 9.3](#) together with information about the access procedures via the facilities' home pages.

Table 9.3 Overview about user facilities for neutron imaging, status May 2022.

Institution	Country	Neutron source	Source type	Operation mode	Name of the facility	Neutron spectrum	Imaging system	Status	User lab link
TUM	D	FRM II	Reactor	Stationary	ANTARES	Cold/ thermal	Digital		https://mlz-garching.de/user-office
TUM	D	FRM II	Reactor	Stationary	NECTAR	Fast/ gamma	Digital		https://mlz-garching.de/user-office
PSI	CH	SINQ	Spallation source	Stationary	NEUTRA	Thermal	digital		https://www.psi.ch/en/useroffice
PSI	CH	SINQ	Spallation source	Stationary	ICON	Cold/ thermal	digital, film		https://www.psi.ch/en/useroffice
PSI	CH	SINQ	Spallation source	Stationary	BOA	Cold	digital		https://www.psi.ch/en/useroffice
JPARC	JP	MLF	Spallation source	Pulsed 25Hz	RADEN	Cold	Digital, TOF		http://is.j-parc.jp/uo/en/index.html
NIST	USA	NCNR	Reactor	Stationary	BT-2	Thermal	digital		https://www.nist.gov/ncnr/obtaining-beam-time
NiST	USA	NCNR	Reactor	Stationary	NG-6	Cold	Digital		https://www.nist.gov/ncnr/obtaining-beam-time
ILL	EU, F	ILL reactor	Reactor	Stationary	NEXT	Cold	Digital		https://www.ill.eu/users/contacts
ANSTO	AUS	OPAL	Reactor	Stationary	DINGO	Thermal	digital	Construction	https://www.ansto.gov.au/user-access
ESS	SWE, EU	ESS	Spallation source	Pulsed 14 Hz	ODIN	Cold	Digital, TOF		https://europeanspallationsource.se/science-support-systems/scuo
ORNL	USA	HF1R	Reactor	Stationary	CG-9	Cold	Digital	Construction	https://neutrons.ornl.gov/users/become
ORNL	USA	SNS	Spallation source	Pulsed 60 Hz	VENUS	Cold	Digital		https://neutrons.ornl.gov/users/become
Rutherford Lab	UK	ISIS	Spallation source	Pulsed 10 Hz	IMAT	Cold	Digital, TOF		https://www.isis.stfc.ac.uk/Pages/User-Office.aspx

(Continued)

Table 9.3 (Continued)

Institution	Country	Neutron source	Source type	Operation mode	Name of the facility	Neutron spectrum	Imaging system	Status	User lab link
KFK1	H	WWS-M	Reactor	Stationary	NORMA	Cold	Digital	Upgrade	https://www.bnc.hu/?q=beam_time_app
KFKI JINR	H RUS	WWS-M IBR-2	Reactor Pulsed reactor Reactor	Stationary Pulsed 5 Hz Stationary	NRAD NR	Thermal Thermal	Digital Digital		https://www.bnc.hu/7qsbeam_time_app http://flnph.ji-nr.ru/en/facilities/ibr-2
NECSA	ZA	SAFARI-1			SANRAD	Thermal	Digital		not available

New sources should be based more on accelerator-driven reactions proposed in the concept of the Compact Neutron Source by FZ Jülich, Germany [78]. Also there, state-of-the-art neutron imaging facilities are foreseen which will use the TOF options for energy resolution.

Acknowledgements

The authors want to thank all persons, involved in the particular investigations at the imaging facilities at FRM-II (TUM, Germany) and SINQ (PSI, Switzerland), which are mentioned in the different shown examples. Here, the beamline scientists and their users played an important role, in particular in the further development of neutron imaging methods and their best possible application.

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CHAPTER 10

Infrared thermography: philosophy, approaches, analysis—processing, and guidelines

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10.1 Introduction

10.1.1 Infrared thermography

The first “Image of Heat” was produced in 1840 by Sir John Herschel [1]. Sir John was also able to show a primitive heat image in his study, which he called thermography.

Infrared was discovered between 1900 and 1920. Numerous patents were granted for devices that can detect people, artillery, airplanes, ships, and even icebergs. In particular, the earliest operating system was developed during World War I, whereas, in the interwar period, two revolutionary new infrared detectors were built, namely, the image converter and the photon detector [2].

The tactical military disadvantages of the so-called “active” thermal imaging systems provided the opportunity, after World War II, for further military-secret infrared research aimed at developing “passive” systems. It was only in the mid-1950s that thermal imaging devices began to be available to science and industry.

Recently, governments and airport security used infrared thermography (IRT) to detect suspected swine flu and other viral diseases during

both the 2009 and 2020 pandemic emergencies [3]. The use of IRT has increased dramatically in recent years in several sectors.

In modern thermographic cameras, the live thermogram reveals temperature variations very clearly, thanks to the use of innovative algorithms [4]. A demonstration is provided in this chapter.

10.1.2 Basic principle

IRT utilizes an infrared (thermal) camera to extract and analyze a thermal pattern based on the principle that each body at a temperature above absolute zero (-273.15°C) emits electromagnetic (EM) radiation. The EM radiation emitted by an object is sensed by the infrared camera and transformed into an electronic signal, which is then processed to produce a thermal image.

10.1.2.1 Basic infrared radiation

Fig. 10.1 shows an overview of the EM spectrum. Within the EM, infrared radiation occurs at frequencies above those of microwaves and just below those of red visible light (VL). The infrared band lies between 0.74 and $1000\text{ }\mu\text{m}$ of the EM spectrum and is divided into five parts: near-infrared (NIR) lying between 0.74 and $1\text{ }\mu\text{m}$, short wavelength infrared (SWIR) lying between 1 and $3\text{ }\mu\text{m}$, medium wavelength infrared (MWIR) lying between 3 and $5\text{ }\mu\text{m}$, long wavelength infrared (LWIR) lying between 8 and $14\text{ }\mu\text{m}$, and very long wavelength infrared which lies between 14 and $1000\text{ }\mu\text{m}$. SWIR, MWIR, and LWIR are the regions where infrared imaging devices exist [5].

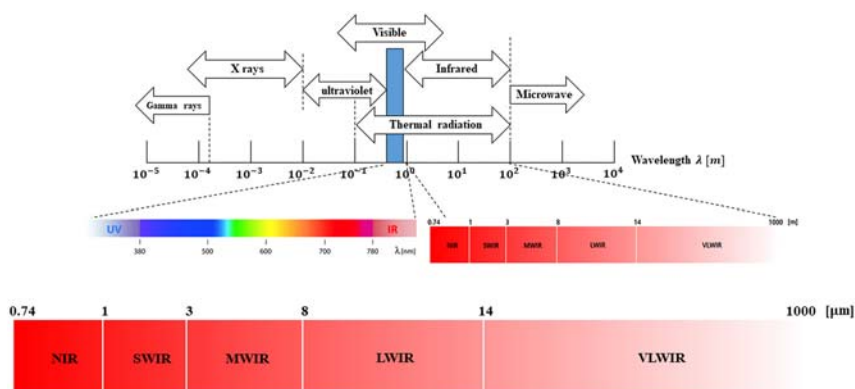


Figure 10.1 Electromagnetic spectrum with different infrared bands.

10.1.2.2 Radiation laws of the black body

A blackbody is a theoretical or model body that absorbs all radiation falling on it, reflecting or transmitting none. It is a hypothetical object that is a “perfect” absorber and “perfect” emitter of radiation at all wavelengths. The characteristics of blackbody radiation are explained with the help of Planck’s law, Wien’s displacement law, and Stefan–Boltzmann law.

Planck’s law describes the spectral distribution of radiation emitted by a black body and can be expressed by Eq. (10.1) [6]. Fig. 10.2 depicts the graphic representation of a series of blackbody spectra for various temperatures following Eq. (10.1):

$$E_{\lambda,b}(\lambda, T) = \frac{C_1}{\lambda^5 \left(e^{\frac{C_2}{\lambda T}} - 1 \right)} \quad (10.1)$$

where $E_{\lambda,b}[\text{W}/\text{m}^2 \mu\text{m}]$ is the blackbody spectral radiant emittance at wavelength $\lambda [\mu\text{m}]$ and temperature $T [\text{K}]$, $C_1 = 2\pi hc = 3.742 \times 10^8$

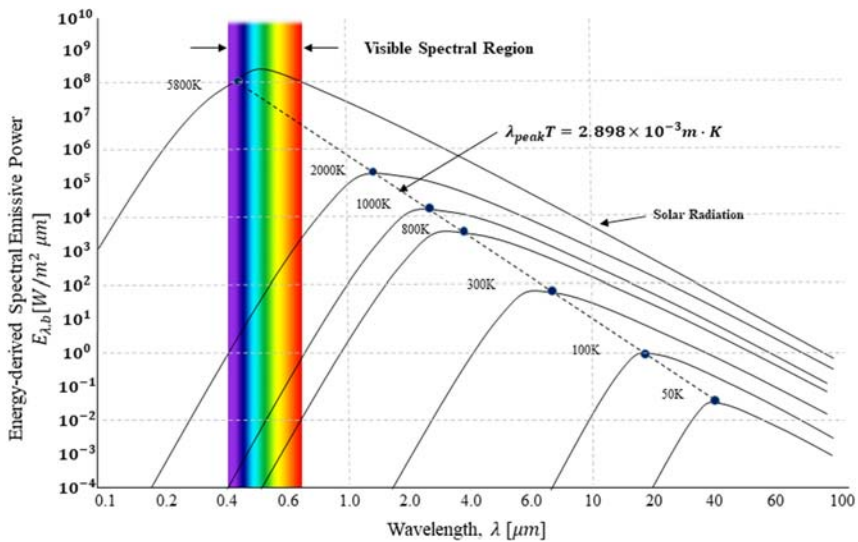


Figure 10.2 Spectral distribution of the radiation intensity from a blackbody according to Planck’s law, plotted for various absolute temperatures. The dotted line represents the maximum radiant emittance points at each temperature according to Wien’s Displacement Law. The maximum intensity of radiation emitted is within the infrared spectral band with the material under study at the temperatures it is usually found. Hence the cameras are sensitive to the infrared spectrum to measure the temperature, in addition to the atmospheric absorption is minimal between the body emitting radiation and the camera reading the emitted radiation.

$[W \mu m^4/m^2]$ is the first radiation constant, and $C_2 = \frac{hc}{k} = 1.439 \times 10^4 [\mu m K]$ is the second radiation constant, with $c = 2.998 \times 10^8 [m/s]$ being the velocity of light in vacuum, $h = 6.626 \times 10^{-34} [J s]$ and $k = 1.381 \times 10^{-23} [J/K]$ the universal Planck and Boltzmann constants, respectively.

Wien's Displacement Law states that "The wavelength of the maximum intensity of blackbody radiation is inversely proportional to the temperature [7]." Graphically, this is represented in Fig. 10.2 and marked as a straight dotted line. It is found that the peak energy is proportional to their corresponding λ for varying temperatures and can be expressed by Eq. (10.2):

$$\lambda_{\max} = \frac{C_3}{T} \quad (10.2)$$

where $C_3 = 2897.8 [\mu m K]$ is the third radiation constant.

The Stefan–Boltzmann law can be obtained by integrating Planck's law over the entire spectrum ($0 < \lambda < \infty$) which states that "The total flux density $E_b [W/m^2]$ emitted by a black body is proportional to the fourth power of its absolute temperature T " [7]. It can be expressed by Eq. (10.3):

$$E_b = \sigma T^4 \quad (10.3)$$

where $\sigma = 5.6697 \times 10^{-8} [W/m^2 K^4]$ denotes the Stefan–Boltzmann constant, which depends on C_1 and C_2 values.

10.1.2.3 Radiation laws of the real body

Objects in the real world are not perfect black bodies. Not all the incident energy upon them is absorbed; therefore, they are not perfect emitters of radiation. A real generic object may have a different ability to absorb (emit), reflect, and transmit energy concerning the black body owing to its bulk material nature and surface finishing, which can be expressed by Eq. (10.4) [7]:

$$\alpha + \rho + \tau = 1 \quad (10.4)$$

which links the total absorptance (α) to the total reflectance (ρ) and the total transmittance (τ).

10.1.2.4 Heat transfer mechanism

Heat transfer is the process of transferring heat from a high-temperature medium to a low-temperature medium. It is an essential tool that explains abnormal surface temperature patterns. The three heat transfer mechanisms are conduction, convection, and radiation. When dealing with transient thermal problems and inspection using IRT, conduction is the most important heat transfer mode, as this mechanism defines the amount of heat reached and finally emitted by the surface of the solid. Different materials conduct heat at different rates, and these rates are related to their thermal properties. The main thermophysical properties related to IRT are thermal conductivity, density, specific heat, diffusivity, and effusivity.

10.1.3 Thermography approaches

There are two approaches in thermography, that is passive and active thermography, which will be discussed in detail later. Moreover, defects can be active or passive. Passive defects are at the same temperature as the surrounding environment and hence need to be heated or cooled to produce defect indications. Whereas active defects emit or absorb thermal energy and can be detected in a passive mode [8].

10.1.3.1 Passive thermography

There is no extraneous energy required in passive thermography to stimulate a gradient of temperature at the structure or material being investigated. The aspects of importance are inherently below or above ambient temperature due to the object's self-heating or friction. This approach works well in two spectral regions, 3–5 μm (MWIR) and 8–12 μm (LWIR), in which the amount of IR radiation energy relies on the desired range of wavelength. The passive thermography consists of an IR camera, a control device, and a computer (processing unit) as shown in Fig. 10.3A.

It is generally a qualitative method with the primary aim of identifying discontinuities. This approach is widely applied as a standard quality control technique and has numerous applications, including condition monitoring, predictive maintenance, structural health monitoring, medical imaging, power station monitoring, building thermal efficiency, process monitoring, fire forest detection, road traffic monitoring, agriculture, and biological sciences [9]. Nevertheless, such an approach is sometimes restricted to NDT applications because there should be sufficient natural thermal contrast.

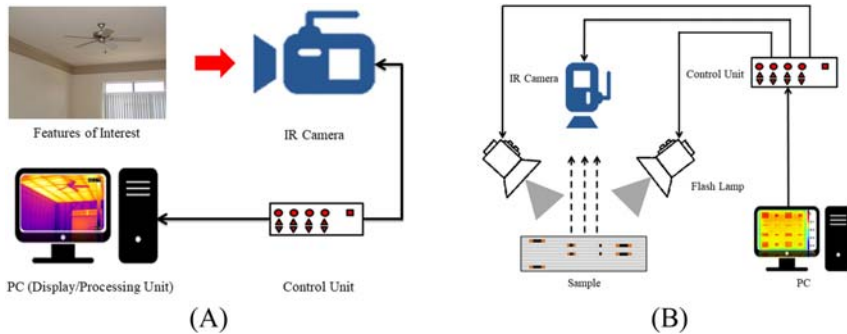


Figure 10.3 Experimental setup (A) passive, and (B) active thermography.

10.1.3.2 Active thermography

Active thermography integrates infrared imaging with an external energy source; that is, an external energy source is supplied to the subject being inspected, which was previously thermally balanced, and a temperature difference is generated to expose the details of interest. Active thermography, therefore, comprises an external energy source, a supply source, an IR camera, a control device, and a computer (processing unit), as shown in Fig. 10.3B. The experimental setup of active thermography is similar to passive thermography except that an external energy source is needed to produce a thermic inconsistency in the object or system. The heating or cooling energy can be generally supplied in pulsed or harmonically modulated form [10]. A wide range of energy origins can be employed for active thermography. Laser heating, optical flash lamps, halogen lamps, hot or cold air guns, electrical heating, ultrasonic excitation, eddy currents, microwaves, and other techniques are instances [11].

When a sample is heated or cooled, heat propagates by diffusion through the material, which has a direct impact on the surface temperature's temporal changes. Then, the thermal response of the investigated object, recorded by an IR camera, is evaluated to disclose the existence of imperfections. The assessment can take place in either transmission or reflection mode. In the transmission mode, the heating unit and the IR camera are on opposite sides of the object under examination, while in the reflection mode, the heating source and the IR camera are on the same side of the sample. Controlled testing conditions, including the quantity and type of stimulation, enable not only the detection of abnormalities but also the quantification of defects [12,13].

Active thermography provides different inspection methods as well as a variety of measuring techniques. Thus, the measurement procedure can be optimally adapted to different materials and parts with different structural properties. The inspection methods mainly differ in the type of excitation source used, the way thermal energy is applied, and the data/signal processing methods [14].

The primary classical practices are pulsed thermography (PT), step heating thermography (SHT), and lock-in thermography (LIT). In PT, short and high-power thermal energy is applied to the object's surface being inspected, and the thermal response of the stimulated surface is observed in a transient mode. PT is a fast and popular thermal imaging technique in non-destructive testing and evaluation (NDT&E). SHT is similar to PT, but in contrast, a longer pulse, from a few seconds to several minutes, is used for thermal stimulation, and the surface temperature of the stimulated object is monitored during both the heating and cooling phases. Whereas in LIT, the surface of the object being inspected is energized by a periodically modulated thermal wave, and the thermal response of the surface is observed in a steady-state condition [12,15].

Concerning the defect information, both filtering and efficient signal processing are of primary importance. By using the adapted image and signal processing strategies, it is possible to visualize discontinuities of different sizes inside structures or to inversely retrieve material thermal properties. Working with a reduced amount of thermal images speeds up the process, but inaccuracy increases, and these cons must be kept in mind. [16].

In NDT&E applications, active thermography can be used for the inspection of components/processes in various industries. Examples include investigation of interior structures such as lightweight honeycomb structures and recognition of deeper material deficiencies; detecting and characterizing defects such as metal corrosion, cracks, subsurface defects, coating wear, debonding, and impact damage; determining material properties such as thermophysical properties like diffusivity and thermal conductivity, adhesion strength, anisotropic material characterization, etc. [17].

10.1.4 Recent trends and developments

Since each NDT&E technique has its inherent limitations, integrating different methods is suggested for better inspection. In this regard, the fusion of IRT with other existing NDT&E techniques is rising. It will result in

better inspection capability, and more information can be acquired in a single test compared to the results of an individual technique.

The potential of combining thermography with shearography, an optical approach for identifying and characterizing subsurface defects in structures, has been investigated. Investigations have shown that by integrating two image-based NDT approaches, the suggested approach is suitable for defect detection [18].

Ultrasonics is the most mature and widely used method for NDT&E. The main advantage of ultrasound sensing is its outstanding capability to probe inside the object, with the disadvantage of being contacted and a low-productive technique. Hence, the integrated use of IRT with ultrasonic sensing may be advantageous to detect both shallow and deep defects, saving time during the inspection of large surfaces [19]. In this integrated approach, heating of the material under inspection can be accomplished via the application of sonic or ultrasonic energy using a device such as an ultrasonic welding horn known as vibrothermography, thermosonics, or sonic infrared.

Eddy current can be combined with IRT, in which the object under inspection is heated by an inductively generated current flow, which is known as induction thermography. This integrated technique uses induced eddy currents to heat the material being tested, and defect detection is based on the changes in the induced eddy current flow revealed by the thermal distribution captured by the infrared camera.

In some cases, even more than two NDT methods can be fused. For example, eddy current, IRT, and laser scanning were used in combination to inspect aeronautical structures such as honeycomb sandwich panels that have been damaged by low-velocity impacts [20].

10.2 Data analysis

Raw thermal data are generally not suitable for the quantitative evaluation of defects. Several preprocessing and processing techniques to enhance the detection capability and evaluation metrics to characterize the performance of the processing techniques have been developed.

10.2.1 Conventional techniques

Some preprocessing techniques such as pseudo-colorization, histogram equalization, image filters—a median filter and a gaussian low filter—segmentation, image fusion, image building, image subtraction, etc. are integrated features

in the typical R&D software in infrared cameras. These preprocessing techniques mainly help to reduce the effects of nonuniform surface emissivity, temporal noise, spatial image noise, and outliers caused by dead pixels. Besides these, several studies demonstrate the development of processing techniques and their effectiveness in detecting and assessing defects. Table 10.1 depicts a simple classification of thermal data processing techniques based on image

Table 10.1 Classification of thermal data processing based on image processing groups [21,22].

Groups	Techniques	Remarks
Thermal contrast	Absolute contrast running contrast normalized contrast standard contrast differential absolute contrast	1-D solution of Fourier’s diffusion equation for pulsed thermography and enables to model the time evolution profiles of the sample surface temperature. Enhanced the defect contrast for pulsed thermography data.
Transforms	Harmonic approximation (four point method)	Fast method and only valid for sinusoidal stimulation. Enhanced the defect detectability for modulated thermography.
	Fast Fourier transform Wavelet transform	Enhanced the defect detectability for both pulsed and modulated thermography. Also used in the passive thermography approach.
	Pulsed phase thermography	Enhanced the defect detectability for pulsed thermography data.
	Principle component analysis	Usually used to enhance the defect detectability for pulsed thermography data. But can also be used for modulated thermography, though efficiency needs to be evaluated. Also used in the passive thermography approach.
Statistical	Signal reconstruction, derivatives, skewness, kurtosis	Enhanced the defect detectability for Dirac and square pulsed thermography.

processing groups, that is, techniques based on thermal contrast, techniques based on transforms, and techniques using statistical methods.

Although there are several data processing techniques, computation of the amplitude image and phase image using the Fourier transform is the most popular technique in active thermography, specifically for both pulsed and modulated thermography. The Fourier transform is used to pass from time to the frequency domain in thermal images. The Discrete Fourier Transform (DFT) is implemented for each pixel of the thermographic data set and can be expressed by Eq. (10.5) [17]:

$$F_n = \Delta t \sum_{k=0}^{N-1} T(k\Delta t) \exp \frac{j2\pi nk}{N} = Re_n + Im_n \quad (10.5)$$

where Δt is the sampling interval, j is the imaginary number, n is the frequency increment ($n = 0, 1, \dots, N$), and Re and Im are real and imaginary parts of the transform, respectively. To simplify, the Fast Fourier Transform is used instead of the DFT and is available in the standard software package. With the transformation of data to the frequency domain, the amplitude (A_n) and phase angle (φ_n) in different frequencies are computed using Eqs. (10.6) and (10.7), respectively [17]:

$$A_n = \sqrt{R_e^2 + I_m^2} \quad (10.6)$$

$$\varphi_n = \tan^{-1} \left(\frac{Im_n}{Re_n} \right) \quad (10.7)$$

The phase image is not directly linked to local disturbances, for example, nonuniform heating and emissivity; in fact, it is related to the depth attained by the thermal wave. Hence, phase images are used in the identification of defects.

Literature shows different types of evaluation criteria to characterize the performance of the processing techniques. The signal-to-noise ratio, also known as the contrast to noise ratio (CNR), is an evaluation metric to determine and qualify the advantages and limitations of each processing technique. Also, the CNR metric is used to differentiate the two regions of interest (ROI). The quantification of a defect is based on the information of two areas: the defective area and the reference or sound area. Contrast is the absolute difference between the defective area information and the sound area information. Noise is the standard deviation of the

noise area information. Information may be in temperature, amplitude, or phase angle, depending on the type of image. For this purpose, two ROIs, one for each defective area and one adjacent to the defective area (i.e., sound area), are selected. ROI in the defective area will be considered as “signal” (DROI), and ROI in the sound area will be considered as “noise” (SROI). The CNR metric for a defect can be calculated by using Eq. (10.8) [22]:

$$\text{CNR} = 20\log_{10}\left(\frac{|\text{DROI}_{\text{mean}} - \text{SROI}_{\text{mean}}|}{\sigma}\right) \quad (10.8)$$

where $\text{DROI}_{\text{mean}}$ is the arithmetic mean of the defective area; $\text{SROI}_{\text{mean}}$ is the arithmetic mean of the sound area; and σ is the standard deviation of the defective area.

10.2.2 Advanced techniques

The analysis of temperature evolutions in both defective and sound regions is central to IRT data processing. In both passive and active thermography, the data recorded with infrared cameras can be considered in three different forms in order to be processed: a 1-D model which is independent of spatial information and where input is a vector of temperature history in terms of time for a pixel; a 2-D model which is independent of temporal information and where input is thermal images; and a 3-D model with the input of thermal images (video) series combining the 1-D and 2-D models.

Artificial intelligence’s rapid advancement, particularly Machine Learning (ML) and Deep Learning (DL), makes IRT increasingly automated and intelligent, broadening its scope of applications significantly [23]. For instance, Recurrent Neural Networks (RNN) and 1D Convolutional Neural Networks (CNN), 2D CNN, and 3D CNN are the popular DL methods based on the format of the input corresponding to 1D, 2D, and 3D models, respectively. On the other hand, compared to visible images, the quantity of labeled thermal images is significantly lower; thus, various challenges arise. Utilizing labeled VL data to minimize the quantity of data necessary for IRT algorithms in DL is a fascinating topic. Transfer learning [24] is an ML method that focuses on storing and transferring information obtained while addressing one problem to a different but related task. Domain adaptation [25] is a particularly effective approach to transfer learning when the data is diverse but the tasks are the

same. Common VL tasks, like object detection, offer passive IRT with a wide range of expertise and data [23]. The DL algorithms that have recently been used to analyze IRT data are explained in the following within the two categories of passive and active IRT.

10.2.2.1 Deep learning in passive infrared thermography

In passive IRT, the use of DL models such as RNN, CNN, Generative Adversarial Network (GAN), Auto-encoder (AE), and Restricted Boltzmann Machine is often more prevalent than in active IRT. Since IR cameras have an inferior resolution to visual cameras, resulting in a poor-quality image and restricted use of passive IRT, several researchers have evaluated CNN [26] and GAN [27] to boost the resolution of IR projections. To increase the resolution of thermal images, single-frame super-resolution technology might be used. For instance, the enhancement of the quality of infrared images for object detection was studied in [28]. To enhance target signature quality and maximize the baseline resolution of inputs, a method according to Super-Resolution CNN (SRCNN) and image bias correction has been suggested. The key goal is to improve the amount of usable information on the item to be identified, even if the quantity of target pixels is insufficient. The method improved target resolution substantially in experiments, allowing automated detection systems to recognize objects more efficiently. Instead of just merely improving the resolution of thermal data, some researchers are attempting to exploit the synergy of visual and thermal images to combine their information for super-resolution. For example, a DL method according to GAN was established, improving the resolution of thermal images by integrating VL and IRT data [29]. An approach combining a GAN with a residual network has been suggested to enhance the visualization of the fusion of thermal and visible images [27]. Experiments show that the suggested technique finally produces suitable results, outperforming nine representative thermal and visible image fusion methods in terms of visual resolution and objective assessment.

10.2.2.2 Deep learning in active infrared thermography

Although the use of DL in active IRT is currently lower than in passive IRT, its advancement and growing use are expected in this regard. DL in active thermography NDT&E can be categorized into three subdivisions depending on the format of the input data, as earlier mentioned above since active IRT generally creates thermal video.

10.2.2.2.1 1-D model

A Long Short-Term Memory Recurrent Neural Network (LSTM-RNN) model based on an array of temperature series [30] has been used to automatically classify prevalent defects in honeycomb materials, such as adhesive pooling, debonding, and liquid ingress. The proposed LSTM-based algorithm has a sensitivity of more than 90% in identifying water and hydraulic oil ingress and more than 70% in classifying adhesive pooling and debonding.

In LIT, a 1D CNN model is used to evaluate the thermal sequence of Carbon Fiber Reinforced Polymer (CFRP) specimens [31]. A new two-stream CNN structure is utilized to draw features from a pair of 1D thermal signal series to accurately classify faulty and healthy areas. In comparison to PCA and the Fourier transform, the results show that the 1D CNN improves resolution.

10.2.2.2.2 2-D model

For surface crack detection, 2D CNN has been employed [32]. A DL-based autonomous concrete fracture detection approach integrating vision and IRT data has been provided. By spatially inspecting via unmanned vehicles equipped with a hybrid imaging technology that includes IR and vision cameras as well as a continuous-wave line laser, concrete-made infrastructure on a large scale (like bridges and dams) can be efficiently assessed. To accomplish automatic crack detection and visualization, the reconstructed images have been categorized into multiple patches, and each patch has been categorized using a pretrained GoogLeNet using a transfer learning approach.

10.2.2.2.3 3-D model

Active thermography's growing development is the 3D model, which integrates temporal and spatial data. Nonetheless, since 3D input has the complexity to tackle, several approaches have been developed that can help, such as:

- **Reducing temporal data:** Since it is troublous to utilize DL to analyze temporal and spatial data at the same time, some researchers suggest compressing temporal data with a non-DL approach first, then processing spatial data with a DL one [23]. For instance, to provide accurate crack identification and localization, an end-to-end pattern deep region learning architecture has been suggested [33]. The temporal information was extracted from the thermal video using PCA and

compressed into a single frame (matrix) with a more substantial defect feature, while Faster-RCNN was used to detect faults from the matrix.

- **Dealing with temporal and spatial data independently:** This category, for instance, can be found in Ref. [34]. A technique integrating YOLO (Yolonet—you only look once) and a fully connected network (FCN) has been presented, according to the hypothesis that the spatial and temporal data in thermal sequences are unrelated. FCN forecasts the depth of defects, whereas YOLO evaluates if there are any. The approach may be considered as a fusion of a 1D feed-forward network and a 2D YOLO model.
- **Designing a fused temporal-spatial network:** To analyze merged temporal and spatial inputs, a hybrid spatial-temporal DL framework for automated thermography has been developed [35], notwithstanding the difficulty. An LSTM (with 3 layers) loop has been used to collect the material characteristics that reflect the character of thermal differences between the defective and the healthy point, and Visual Geometry Group-Unet (VGG-Unet) has been employed for identifying the faulty area out of the standard.

10.3 Modeling and simulation

Modeling is the process of representing an actual system in a mathematical form with its properties, while simulation is an experiment based on a developed model implemented into a computer program to study the performance of a system. Modeling and simulation provide insight into how systems can behave early in their lifecycle without the risk and expense of building the system and transporting it to the environment concerned. Thus, modeling and simulation enable rapid and cost-effective analysis of complex systems, thereby reducing development time and costs. Over the past few decades, modeling and simulation have been booming with their applications in engineering and computer sciences, military and defense, aerospace and transportation, education, health care and drugs, recreation and entertainment, architecture and construction, climate and environment, finance and economics, etc. [36].

Modeling and simulation consist of four main steps: conceptual modeling, mathematical modeling, numerical modeling, and computational modeling. Conceptual modeling puts the problem in the context of its physical phenomenology and allows the information needed for a

good system design to be structured and ordered. Mathematical modeling systematically analyzes phases and components together with the constitutive laws to derive the balance equations and the initial and boundary conditions. Numerical modeling choose a convenient way of discretizing equations based on the shape of the balance equations and the mathematical restrictions of the problem. Computational modeling chose a suitable computational platform with a computational language and software for writing the numerical model once the numerical model has been finalized [37].

Modeling and simulation studies typically fall into four types of applications: proof-of-concept, modification, comparison, and optimization. Proof-of-concept studies are executed in the predesign phase of a future system, support the determination of the viability of concepts, and provide information concerning the expected system performance. Modification studies are conducted on existing systems to allow inferences regarding system performance under proposed operating conditions and to allow parameter settings to be tuned for desired system prediction accuracy. Comparison studies involve competing systems. Finally, the determination of the best system operating conditions is based on optimization studies [38].

Modeling and simulation are used in many steps of the NDT&E process, specifically for the development and verification of new inspection methods. Many researchers from around the globe have used modeling and simulation to stimulate the propagation of the thermal wave in materials for IRT inspection. Shrestha et al. [13] developed a transient finite element model using commercial software, “ANSYS 15,” and simulated PT and LIT to evaluate the coating thickness, stimulated by a flow of heat, allowing experimental parameters to be tailored without the need for extensive, time-consuming, and potentially expensive preliminary experiments. The same authors [39] used modeling and simulation to develop a PT inspection process to detect artificial flat-bottomed hole defects in aluminum structures using “ANSYS 15.” Shrestha et al. [40] also developed a transient finite difference model and simulated the LIT inspection process to detect inclusions in glass fiber-reinforced plastic composite structures using the software “ThermoCalc-3D.” Shrestha et al. [41] used a transient finite element model and stimulated a flow of heat to simulate PT for the evaluation of ancient marquetry samples using “ANSYS 19.” Tighe et al. [42] created the finite element model of PT and PPT to detect the kissing defects in adhesive bonds.

To obtain the results shown in Fig. 10.4, the authors used commercial software “ANSYS 15” and modeled a square-shaped coating sample of size 180×180 mm with a nickel-based superalloy substrate of 4 mm, a bond coat of MCrAlY of 0.1 mm, and a top coat of zirconia varying from 0.1 to 0.6 mm. In this work, the authors used a tetrahedral fine mesh. Also, physical preference was taken into account as mechanical with a relevance equal to 100. Finally, the relative center worked in fine mode, while both proximity and curvature were used in the advanced size function. The final mesh had 162,000 elements, while the nodes were 854,685 in total. In PT configuration, an energy of 9 kJ was delivered via a single square pulse of heating lasting 10 ms. The frame rate was set at 0.01 seconds and the analysis lasted 5 seconds. In the LIT configuration, a 2 kW power was applied as a heat stimulus. The time step was retrieved by the modulation frequency, and the period of analysis was defined as $\frac{2}{100f}$. Here, f is the modulation frequency. Several modulation frequencies ranging from 1 Hz down to 0.01 Hz were used in the simulation. On this basis, the authors concluded that the simulation model helps a better understanding of PT and LIT modalities by both optimizing the experimental configuration and limiting the number of physical tests. It is possible to underline the fact that both thermographic techniques are useful for an accurate and fast determination of coating thickness.

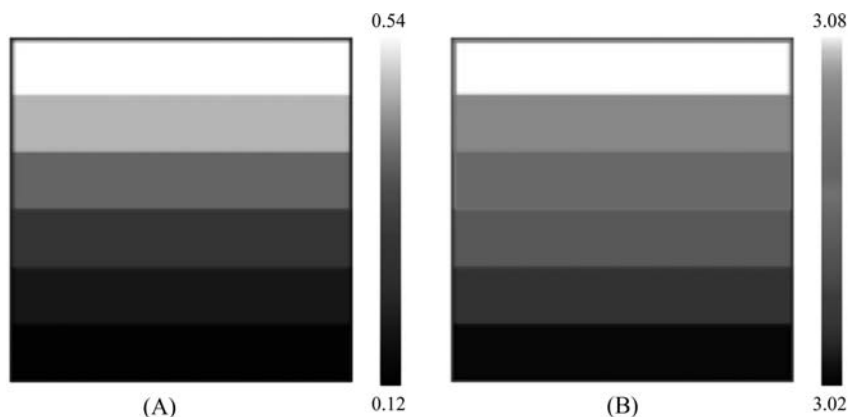


Figure 10.4 Phase angle data with respect to variation in coating thickness, (A) Phase image obtained after the processing of PT data using Fourier transform and (B) Phase image obtained after the processing of LIT data at the modulation frequency of 0.2 Hz [13].

10.4 Relevant standard

Recently, structural health monitoring of the components, specifically using IRT, has expanded rapidly in various areas. The effectiveness of IRT inspection depends on the proper use of the systems and equipment. The International Organization for Standardization (ISO) provides terms, basic principles, equipment, and test procedures, as well as matters related to international certification of thermal imaging. Currently, the ISO technical committee, ISO / TC 135/SC 8—Thermographic testing in NDT, is in the process of standardizing “Electrical Equipment Testing” as ISO 5750 in WG 4 and “Testing Method for Integrated Performance” as ISO 18251-2 in WG 3 [43]. Table 10.2 presents some of the ISO standards developed regarding IRT testing.

In addition, the American Society for Non-destructive Testing and American Society for Testing and Materials in the United States, the Deutsches Institut für Normung in Germany, the British Standards Institution in the United Kingdom, and the Japanese Society for Non-Destructive Inspection (JSNDI) in Japan standardize IRT tests, use standards for every measuring and diagnostic case, and also issue certificates.

10.5 Case study

The high quality of materials and structures is of paramount importance in different areas of human activity. Steel is used around the world because of its good chemical-physical and mechanical qualities.

It should be highlighted that multiple preparations and cautions should be taken into consideration in order to effectively perform IRT inspection and avoid further errors throughout the assessment of metallic samples. Since the reflectivity of the object’s surface, particularly for metal objects, is one of the key obstacles in IRT, an opaque (color) cover can be sprayed on the surface. This solution, however, cannot be used on any item, such as a painting or artwork [52]. Another situation is when IRT performance is being evaluated. Several mechanical and thermal characteristics should be considered and appropriately modeled in order to simulate a true representation of a realistic defect in the lab and research. The most important characteristic is the relative thermal conductivity of the primary material to the imperfection. For example, Teflon, which is commonly used to simulate defects such as delamination and detachments in composite structures including CFRP and GFRP, should not be used because of

Table 10.2 ISO standards related to thermographic testing.

Group	Standard identification	Remarks
ISO	ISO 10878: 2013— Non-destructive testing— Infrared thermography— Vocabulary [44]	Defines terms used in IRT for NDT and forms a common basis for standard general use.
	ISO 10880: 2017— Non-destructive testing— Infrared thermographic testing— General principles [45]	Provides general principles for IRT testing in the field of industrial NDT.
	ISO 18251–1: 2017— Non-destructive testing— Infrared thermography— Part 1: Characteristics of system and equipment [46]	Describes the main components and their characteristics, constituting an infrared imaging system and related equipment used in NDT. It also aims to assist the user in the selection of an appropriate system for a particular measurement task.
	ISO 22290: 2020— Non-destructive testing— Infrared thermographic testing—General principles for thermoelastic stress measuring method [47]	Provides general principles for thermoelastic stress measuring method of IRT testing in the field of industrial NDT.
	ISO 18434–1: 2008—Condition monitoring and diagnostics of machines—Thermography— Part 1: General procedures [48]	Introduces the application of IRT to machinery condition monitoring and diagnostics, where “machinery” includes machine auxiliaries such as valves, fluid and electrically powered machines, and machinery related heat exchanger equipment.
	ISO 18434–2: 2019—Condition monitoring and diagnostics of machine systems— Thermography—Part 2: Image Interpretation and diagnostics [49]	Provides specific guidance on the interpretation of infrared thermograms as part of a program for condition monitoring and diagnostics of machine systems.
	ISO 18436–7: 2014—Condition monitoring and diagnostics of machines—Requirements for qualification and assessment of personnel—Part 7: Thermography [50]	Specifies requirements for qualification and assessment of personnel who perform machinery condition monitoring and diagnostics using IRT.
	ISO 9712:2012— Non-destructive testing— Qualification and certification of NDT personnel [51]	Specifies requirements for principles for the qualification and certification of personnel who perform industrial NDT including IRT.

10.5.1 Lock-in thermography

The experiment was conducted with a lock-in system in reflection mode. The lock-in system consisted of an IR camera (SC 645, FLIR Systems, Danderyd, Sweden) with a 640×480 pixel resolution, a spectral range of $7.5\text{--}13\text{ }\mu\text{m}$, thermal sensitivity (NETD) $<50\text{ mk}$, accuracy $\pm 2^\circ\text{C}$, and a frame rate of 50 Hz; a heat source (two halogen lamps (OSRAM, Medium Flood, China) of 1 kW each); a programmable function generator (Agilent 33210A, Malaysia); a lock-in module (Answer Tech, Republic of Korea); and a personal computer (MSI GE620DX).

Fig. 10.6 shows the phase images acquired at modulation frequencies of 0.1, 0.05, 0.02, and 0.01 Hz. The phase image is considered superior to the amplitude image because it is independent of local disturbances such as nonuniform heating and emissivity and is primarily influenced by the

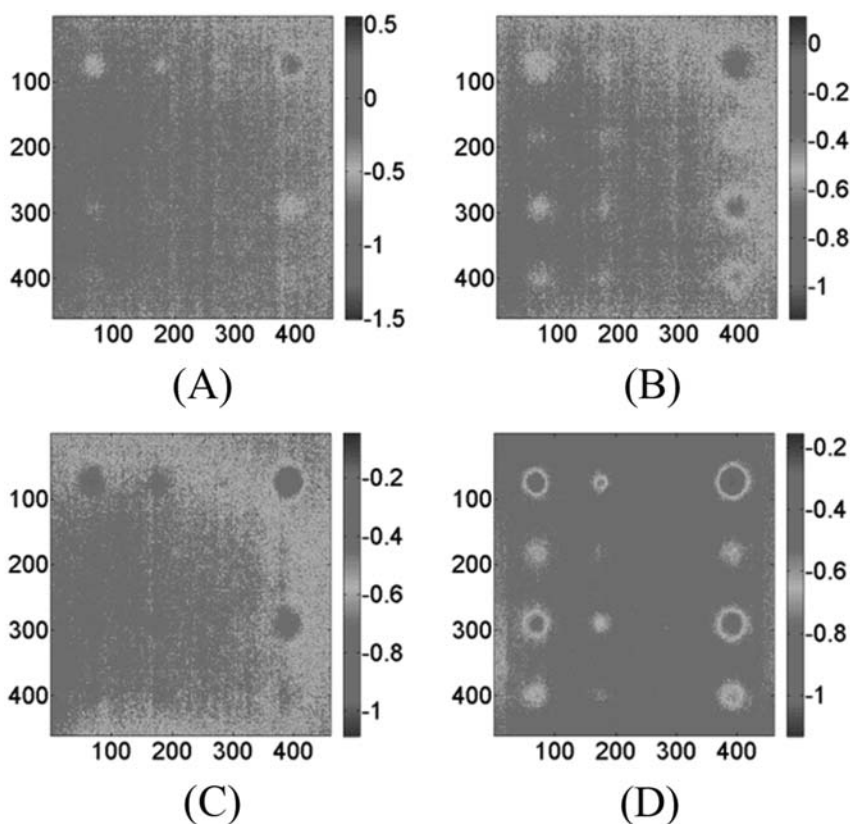


Figure 10.6 Phase images using LIT at modulation frequencies, (A) 0.1 Hz, (B) 0.05 Hz, (C) 0.02 Hz, and (D) 0.01 Hz.

depth attained by the thermal wave. It is possible to see that no defects were detected at the highest frequencies of 0.1 Hz. While the frequency is lowered to 0.05 Hz, the contrast begins to improve, and when it decreases to 0.01 Hz, the subsurface defects in phase images become clearly visible. It can also be seen that there is a phase contrast between the defective areas and the sound areas. Hence, the correct modulation frequency range has to be selected for the material to detect defects.

10.5.2 Pulsed thermography

The experimental setup is based on a short and high-power heating source lamp (Universal BALCAR, Rungis, Paris, France) of power 6400 W-s with the system controller (BALCAR Light System, Nexus A 6400, France), an infrared camera (FLIR Systems, Danderyd, Sweden) with a spectral range of 7.5–13 μm , thermal sensitivity (NETD) <50 mk, accuracy $\pm 2^\circ\text{C}$, a 640×480 focal plane array detector with a frame rate of 50 Hz, and a personal computer (MSI GE620DX). The front side of the sample surface was subjected to a heat pulse with a duration of ~ 10 ms. In addition, 5 seconds was the duration of the registration of the thermal response. The results obtained through some of the conventional and advanced techniques are discussed here.

10.5.2.1 Thermal signal reconstruction

The result of Thermal Signal Reconstruction (TSR) is illustrated in Fig. 10.7A. Also, in order to convert the obtained image to the binary one aimed at a better comparison, a thresholding method based on local intensity is utilized,

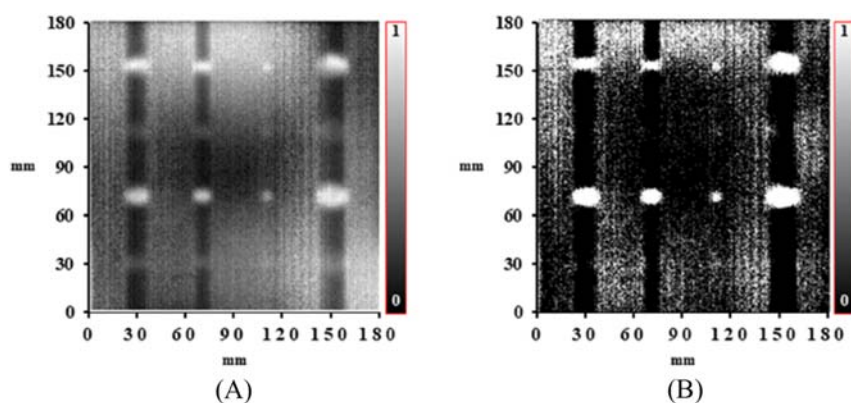


Figure 10.7 Results of TSR algorithm with the maximum kurtosis value among frames: (A) Gray image and (B) Binary image. Axes units are mm.

which determines a different threshold at each pixel by the Gaussian weighted mean in the neighborhood. Hereinafter, the results are converted to binary images using this local thresholding. The binary result of TSR is illustrated in Fig. 10.7B. The frame has been selected at the moment with the maximum kurtosis value for that frame having an acceptable contrast. The TSR method was able to detect shallower defects with a depth of 2 and 3 mm but not deeper defects with a depth of 5 and 4 mm.

10.5.2.2 Pulse phase thermography

The amplitude and phase of PPT, as well as their binary results, are shown in Fig. 10.8. The images have been selected with the maximum kurtosis value for that frame. Nevertheless, since the result of the amplitude of PPT at the maximum kurtosis moment is not proper, another (last) frame is also displayed in Fig. 10.8, in which all defects can be somehow traced. Nevertheless, the fault size cannot be precisely and simply approximated.

10.5.2.3 Principle component thermography

The first five principle components (PCs) obtained by PCT and their binary images can be seen in Fig. 10.9. The influence of nonuniform

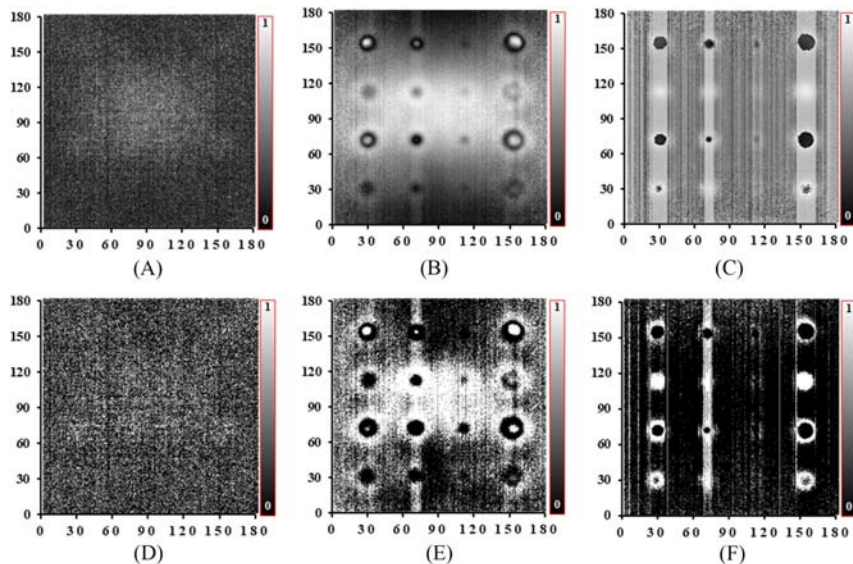


Figure 10.8 Results of PPT algorithm, (A) Gray PPT amp (Max Kurtosis) image, (B) Gray PPT amp (last frame) image, (C) Gray PPT Phase (Max Kurtosis) image, (D) Binary Gray PPT amp (Max Kurtosis) image, (E) Binary PPT amp (last frame) image, and (F) Binary Gray PPT Phase (Max Kurtosis) image. Axes units are mm.

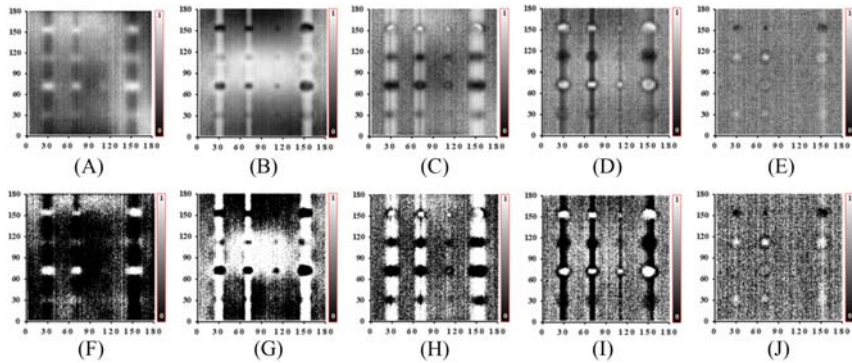


Figure 10.9 Results of PCT algorithm, (A) Gray image 1st PC, (B) Gray image 2nd PC, (C) Gray image 3rd PC, (D) Gray image 4th PC, (E) Gray image 5th PC, (F) Binary image 1st PC (G) Binary image 2nd PC, (H) Binary image 3rd PC, (I) Binary image 4th PC, and (J) Binary image 5th PC. Axes units are mm.

heating distribution may be noticed in the first and second PCs, and as a result, the third and fourth PCs can better confirm the existence of all defects. In addition, as shown in Fig. 10.10, some of the PCs can be combined in order to synergy of the performance because the resolutions of different defects in different PCs are varied, and it cannot be confirmed that one PC exists that has the highest resolution for all defects with different depths compared to other PCs.

10.5.2.4 Thermal signal area

Thermal Signal Area (TSA) combines each pixel's thermal response across a user-defined timespan [54,55]. The results of TSA for a time range from the 10th frame to the 100th frame are shown in Fig. 10.11. Although not all defects can be detected, particularly the deeper and smaller ones, this method is fast and simple to use. It should be noted that the TSA is more suitable for step and long pulse heating thermography methods. In addition, the TSA-inspired Adaptive Spectral Band Integration (ASBI) approach [56], considering the frequency domain instead of time domain, can be utilized to better analyze the thermograms.

10.5.2.5 Artificial neural network

In this section, a Pattern Recognition Neural Network (PRNN) in three simple architectures is used to classify the pixels. In fact, the thermal variation of each pixel over time is considered a timeseries signal, and as a result, a thermal video can be considered a multitimeseries. Then, a

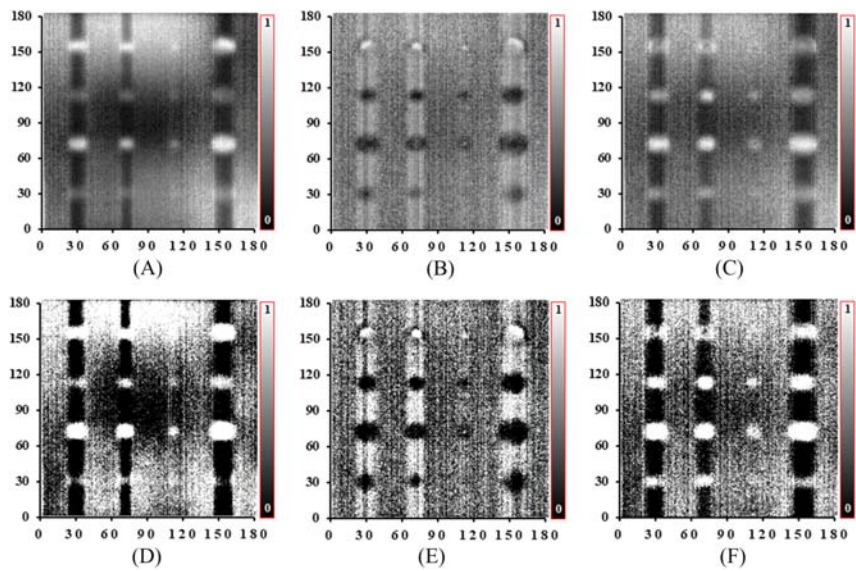


Figure 10.10 Results of PCT algorithm, (A) Gray image superposition of PC1 and PC2, (B) superposition of PC3 and PC5, (C) Gray image superposition of PC1, PC2, PC3, and PC5, (D) Binary image superposition of PC1 and PC2, (E) Binary image superposition of PC3 and PC5, and (F) Binary images superposition of PC1, PC2, PC3, and PC5. Axes units are mm.

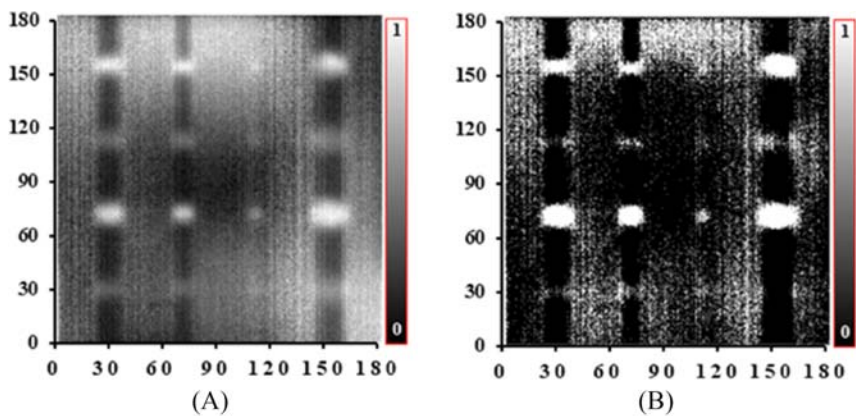


Figure 10.11 Results of TSA algorithm, (A) Gray image, and (B) Binary image. Axes units are mm.

PRNN can be used to classify these timeseries related to different pixels to determine which pixels are sound (intact area of the inspected sample) and which ones are defective (defective area of the inspected sample). Here, the problem is considered as a supervised NN for classification with

two classes: sound (0) and defective (1). Three architectures for PRNN are:

- 1st architecture: one hidden layer with 10 neurons.
- 2nd architecture: one hidden layer with 20 neurons.
- 3rd architecture: two hidden layers with 10 and 5 neurons, respectively.

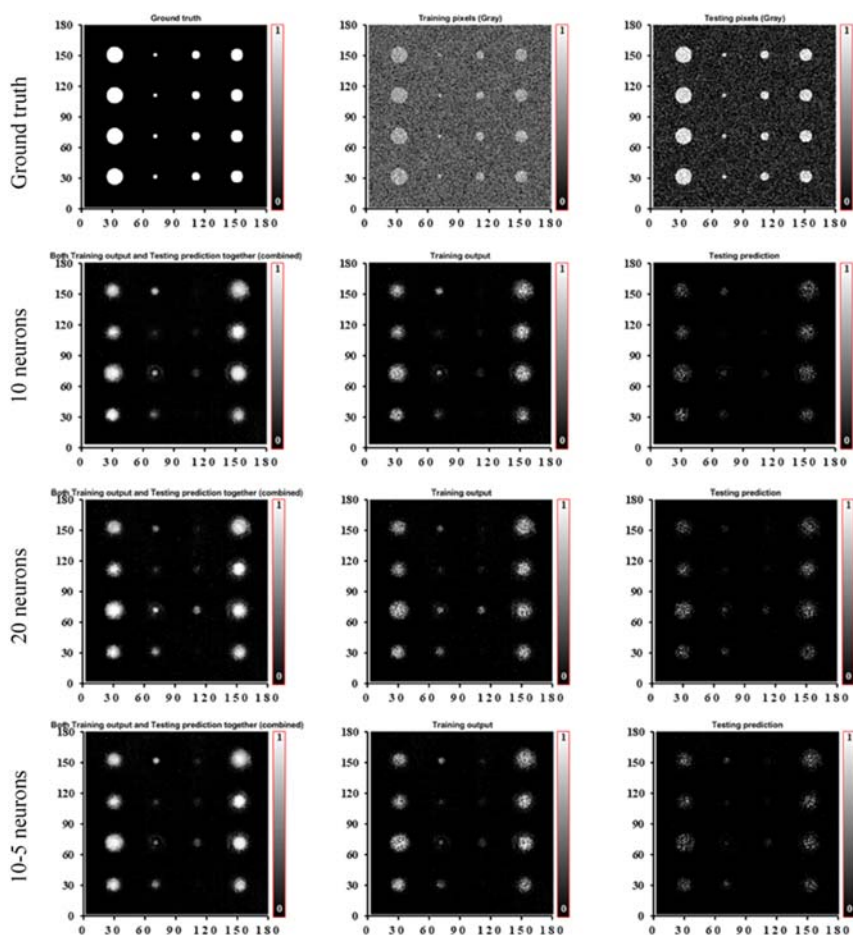


Figure 10.12 Results of PRNN on thermograms (raw data). First row: Ground truth image (*left side*), ground truth image including training (*gray*) pixels (*middle*), and ground truth image including testing (*gray*) pixels (*right side*); second row: the results of architecture 1; third row: the results of architecture 3; fourth row: the results of architecture 3. Axes units are mm.

Scaled conjugate gradient backpropagation is used to train the networks. First, a ground truth image is made in which 1 (white color) is a defective pixel and 0 (black color) is a sound pixel. Next, the dataset containing multitime-series signals is randomly divided into training and testing datasets by a ratio of 7:3. It should be noted that the training dataset itself is also divided into (pure) training and validation datasets by a ratio of 4:1 in order to perform validation checks during training. Thus, the ratio of the training to the total dataset is 56%. Since only one specimen is evaluated in the present work, this type of division for the training and testing



Figure 10.13 Confusion matrix of PRNN for the first architecture with 10 neurons on thermograms.

dataset is applied. Otherwise, if more specimens were available, the results would be improved. The ground truth image as well as the training and testing pixels highlighted in gray on the ground truth image can be seen in Fig. 10.12 (first row). Despite the lack of a sufficient training dataset for utilizing a supervised NN and the model's simplicity, the majority of the faults may be spotted.

The neural networks' performances are calculated based on cross-entropy. The performances (MAE) for architectures 1, 2, and 3 on the raw thermal data are 0.0884, 0.0832, and 0.085, respectively. Also, the

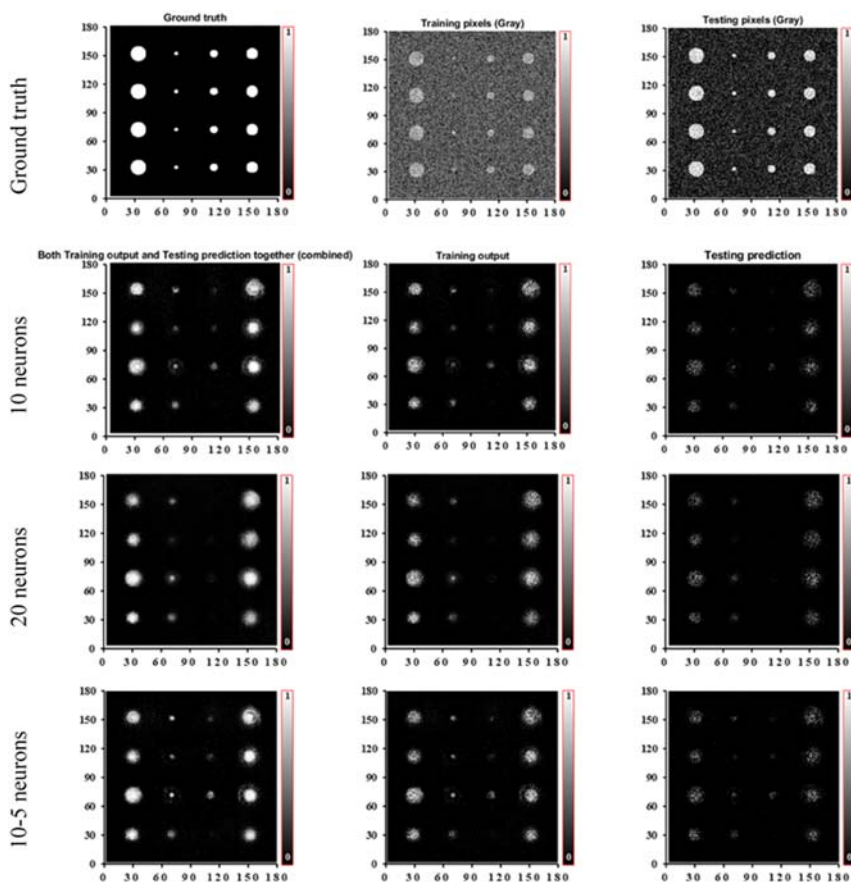


Figure 10.14 Results of PRNN on processed data (TSR). First row: Ground truth image (left side), ground truth image including training (*gray*) pixels (*middle*), and ground truth image including testing (*gray*) pixels (*right side*); second row: the results of architecture 1; third row: the results of architecture 3; forth row: the results of architecture 3. Axes units are mm.

confusion matrices for the first architecture are shown in Fig. 10.13. The results confirm that artificial neural networks (ANN) have strong efficiency in detecting defects in thermal videos.

In another scenario, the NN models can also be applied to the processed data by using some common algorithm. For example, the results of the three aforementioned PRNN architectures applied to the de-noised data by the TSR method can be seen in Fig. 10.14. The performance (MAE) for architectures 1, 2, and 3 on the TSR video are 0.0891, 0.0945, and 0.0793, respectively. The results are superior with the deeper NN, which has 10 and 5 neurons in the first and second layers, respectively.

The results are acceptable, and the defects can be detected, even though the PRNN architecture was not optimized and is simplistic. With a deeper neural network, the outcomes could be much improved. The application of the DNN in IRT has dramatically increased recently [57], and advanced, mature DNN frameworks and architectures were introduced for thermography [35,58].

10.6 Conclusions

The chapter has been organized into six sections, comprising this one. The logic follows a pyramid scheme, that is, the so-called top-down approach. Initially, an overall view of the IRT technique has been given; therefore, the authors have deepened the main concepts of data analysis; subsequently, experience in thermal modeling and simulation has been provided to the readers, who anticipated the state-of-the-art in relevant standards; and finally, a series of case studies has taken stock of the technique itself.

The chapter is actualized to 2022 since it provides the recent advances of numerical modeling as a facilitator to understanding experimental analyses. The latter rests on a case study dissected through the implementation of well-known and advanced algorithms for image processing, up to the core, that is, an ANN example applied to a stainless-steel sample having flat-bottomed holes representing subsurface defects of different sizes at varying depth levels. The results obtained can be considered of great interest and leave the doors open for future perspectives, such as the fusion of images with other NDT techniques.

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CHAPTER 11

Non-destructive material testing in welding: ultrasonic scanning

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11.1 Introduction

Inspection and testing of welded constructions must be carried out before, during, and after the execution of the welds. Before welding, it is necessary to verify the materials (base and filler), including joint preparation; machinery and accessories (e.g., jigs); working conditions (inside/outside the factory); personnel (from the welder to the welding coordinator); and the orders and manufacturing methods (drawings, specifications, welding procedures, etc.) [1]. During welding, compliance with welding specifications (and process parameters) should be ensured, as well as checking for preheat and interpass temperatures (if any), the sequence of passes and cleaning between passes, the correct use and handling of consumables (e.g., the use of a portable storage oven for coated electrodes). Sometimes, it is also important to take intermediate examinations to check the dimensions of both beads and inevitable distortions.

After welding a structure, depending on the level of safety or requirements, it is imperative to inspect the quality of the beads and the construction itself, for example, verify the presence of significant deformations. Thus, before selecting the inspection method, one should be considered the following points:

- Welding process used;
- Base metal, filler metal, and treatment (thermal or other);
- Dimensions, shape, and tolerances;
- Type of joint and geometry;
- Configuration of the component (accessibility, surface type, etc.);
- Required quality level (e.g., according to the ISO 5817 standards);
- Predicted type of imperfection (and its orientation);
- Results and records of postwelding work (e.g., heat treatments or straightening operation).

After welding, two types of inspecting methods can be considered: destructive and non-destructive. Destructive is naturally expensive because it involves destroying the structure (or part of it). Thus it makes sense to perform destructive testing in critical cases or the case of large series. Typically, these are compression, tensile, bending, fatigue, etc. tests, carried out until reaching failure. This test is intended to determine, for example, whether the failure is achieved in the welding bead (including the heat-affected zone [HAZ]) or the base material.

On the other hand, non-destructive inspection methods can be performed in several ways, typically known as non-destructive testing (NDT). Examples include visual and dimensional inspection, leak testing, penetrant testing, magnetic particle, eddy current, ultrasound, and radiography [2].

Ultrasonic testing comprises a vast list of advantages, including the following in a not limited manner: (1) high penetration, allowing deep flaw detection; (2) high sensitivity, making it possible to detect tiny flaws; (3) a part can be tested even if only one side is accessible; (4) greater accuracy than other NDT methods; (5) capacity for size, shape, orientation and nature of defects estimation; (6) testing of dissimilar structures composed of different alloy with differing acoustic properties; (7) low safety requirements and nonhazardous method unlike some other NDT methods; (8) Potential of automation and portability; (9) quick acquisition and data retrieval, making it possible to obtain results immediately.

NDT, such as ultrasonic examination, has been widely used to detect welding defects. This type of testing is particularly interesting for identifying internal flaws, otherwise not detected during visual inspection. The application of ultrasonic testing goes beyond fusion welding, for instance, to detect specific flaws such as root flaws and wormholes typically associated with Friction Stir Welding. In one example, Tabatabaeipour et al. [3] proposed an approach for the detection of root flaws using an immersion ultrasonic testing method in oblique incidence and backscatter mode, demonstrating the potential of backscattering mode (C-scan) for flaw detection of aluminum butt welded samples (7xxx series).

Another example of the application of ultrasonic testing in welding is the comparison between welding processes for one specific application. In one recent example, da Cruz Payão Filho et al. [4] used ultrasonic testing to compare the welds performed with the Gas Metal Arc Welding and Shielded Metal Arc Welding (SMAW) processes. These are two typically used welding processes to weld pipes for oil and gas industries. Ultrasonic testing made it possible to inspect and verify the better results produced with the SMAW process.

Additionally, simulation tools have also been used for welding flaws verification through ultrasonic testing. One example is the CIVA software, which is reported to provide reliable predictions for welding inspection [5] and to be an efficient tool in comparison to finite element solvers [6,7].

The following sections present the main characteristics of the ultrasonic scanning method to inspect the quality after welding.

11.2 Non-destructive characterization of welded parts—ultrasonic testing

This method is based on the emission of an ultrasonic beam, which will pass through the metal and be reflected when it finds some discontinuity or its limit (at the end of the thickness of the part). This reflection is then received (by the same probe, or not), and the closer the defect is, the stronger the signal (or, the shorter the time until the reflection reached the probe—time of flight diffraction). It is thus possible to find a defect and assess its size and even the thickness of the welded plates. The flaw detector, depending on the type of transducer/configuration used, makes it possible to implement the following techniques:

- Pulse-echo
- Through-transmission pitch-catch
- Direct pitch-catch
- Time of flight to diffraction

11.2.1 Pulse-echo

This method is known as the A-scan method. The transducer sends a signal to a test object and receives reflected echo signals from defects and the thickness or outer shape of the product. Based on the signal's arrival time, it is possible to identify the location of the defects and, based on the amplitude of the signal, the size of the defects. The disadvantage of this technique is the need for the defect to have a reflective surface perpendicular to the ultrasonic beam or be located near the part's surface. For example, this technique does not allow the detection of planar defects (cracks or defects due to the lack of fusion) that are not located near the product's surface under test.

11.2.2 Through-transmission pitch-catch

The pulse-echo technique does not allow the detection of planar defects (cracks and defects caused by lack of fusion) that are not located near the

structure's surface under test. Pitch-catch techniques—duet and tandem are used to recognize these defects. In the case of the through-transmission pitch-catch, this is achieved with a pair of transducers installed. The signal emitted by the first transducer is returned to the second transducer after reflection of the planar defect.

11.2.3 Tandem pitch-catch

The through-transmission pitch-catch technique does not guarantee the location of all defects that have different orientations. For this purpose, the tandem technique is used with the transducers placed on both sides of the bead so that the signal reflected on the back surface of the workpiece reaches the receiver. If there are sufficiently large defects (and of practically any orientation) by the wave path, the signal is shaded, evidencing its existence. However, this technique does not immediately provide accurate information about the location (coordinates) of the defects found. For accurate and localized readings, preliminary adjustments are necessary and possible with the help of reference blocks.

11.2.4 Time of flight diffraction

The time of flight diffraction (TOFD) technique is based on the interaction of ultrasonic waves with the limits of discontinuities (Fig. 11.1). This collision generates other diffraction waves with a wide range of angles. The diffraction wave test allows for establishing the presence of a discontinuity. The transmission time of the received diffraction signals allows us to measure the height of the discontinuity and, therefore, the movement of the probe will also give the size of discontinuity. In this method, the

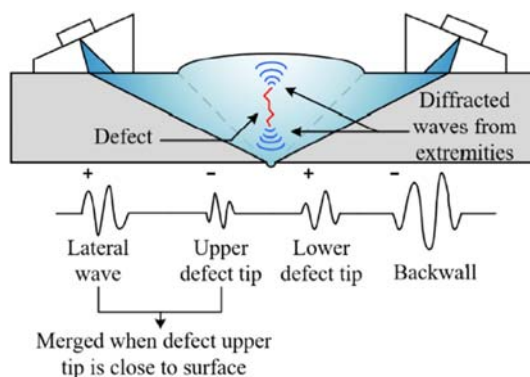


Figure 11.1 The time of flight diffraction technique (TOFD) [5].

signal amplitude is not used for size measurement. In this case, both longitudinal and cutting waves are generated and applied. The main feature of the information is the arrival time of the signal.

The TOFD technique has numerous advantages over conventional manual ultrasonic testing. For instance, much higher productivity, low sensitivity to the orientation of defects (i.e., the test is made regardless of the orientation of the defect), the possibility of measuring the actual sizes of planar defects, and a considerable level of visualization and perception of test results. To implement the TOFD technique, a piece of special equipment (a cart) with one or several pairs of transducers is placed on both sides of the bead and moved along the same during the inspection. To see the position, the user can use an encoder.

11.2.5 Ultrasonic testing and inspection of welded components

Welding inspection by current ultrasonic methods (manual contact test) is generally restricted to joints with thicknesses greater than 10 mm. In fact, for low thicknesses, the angle of the probe would have to be larger, which leads to a greater dispersion of sound and, therefore, loss of quality and the emergence of spurious phenomena. For example, in the area near the probe, does not measure appropriately due to the transition of the medium (from the probe to the contact liquid and the metal). In the inspection of welds, the ultrasonic technique forces the passage of the probe to sweep the entire bead and HAZ. When possible, due to geometrical constraints, welds must be inspected from at least two sides.

Generally, a zigzag path is usually made with some overlap to ensure 100% coverage. Sometimes, a slight rotational motion is added to the zigzag pattern back and forth to improve the detection of tilted defects. Also, scanning is usually possible in three directions:

1. 90 degrees to the centerline of the welding;
2. ± 45 degrees to the bead line.

The scanning speed should be slow enough to maintain coupling between the probe and the part and ensure that the operator can accurately visualize all events on the monitor. Fig. 11.2 depicts the coverage of the volumetric zone and the scanning patterns. Usually, to make a proper inspection, two probe angles are used. For thicknesses lower than 20 mm, a probe of 60–70 degrees is used and for thicknesses above 20 mm, it is recommended probe angles within 45 and 60 degrees.

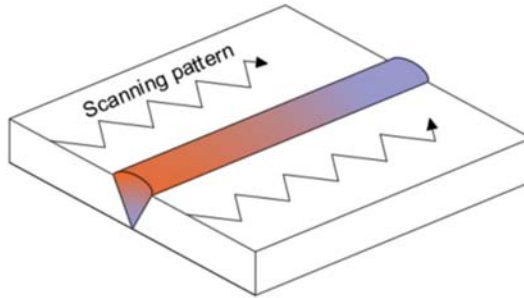


Figure 11.2 Zigzag probe path.

In order to eliminate or mitigate undesirable effects in the measurements, special care should be taken during sample and test setup preparation. For instance, it is necessary to guarantee that area around the weld is free from projections or other protruding defects that may damage the probe. This area must be large enough to ensure a distance between the probe and the cord to carry out the analysis. Also, it is appropriate that the surface between the probe and the tip contains a liquid for the scan to produce the best results. Oil or other viscous fluids are recommended.

Additionally, special care is necessary during the test and data analysis. Again, a fluid should always be used between the probe and test piece (e.g., water). It is recommended to draw a parallel line to the bead with a specified distance between the probe and the bead in order to eliminate measurement errors. The gain value is a variable that needs to be carefully monitored since it increases the sensibility, which may result in small errors being profoundly displayed. On the other hand, a low gain may hinder the detection of defects.

The remarkable evolution of electronics and computer science has made it relatively easy to perform complete weld scanning with just a few sweeps of the probe. Current scanners use phased array ultrasonic testing (PAUT) systems that generate and receive ultrasonic beams, allowing them an excellent coverage of the bead with the same probe position (Fig. 11.3). Thus ultrasonic scanners have some advantages over x-ray:

- There is no radiation;
- Faster inspection;
- Indication of the defect's height (in depth)—naturally impossible to obtain on the x-ray.

Traditional ultrasonic testing techniques are inadequate for detecting defects with directionality since inspection results are calculated with one

angle from a single element [9]. The PAUT technology has several advantages over general ultrasonic testing, where a single element or coupled element for applying various angles through time delay, beam property adjustment, and electronic scanning is applied [10,11]. This is particularly interesting for the scanning of pipelines and welded pipes. In a recent study, Lim et al. [9] developed a flexible PAUT array probe for welded pipes inspection and verified its high efficiency for flaw detection in complex curved-shaped welded structures.

11.2.5.1 Ultrasonic testing standards

The ultrasonic scanning of welds must comply with standards, for example, EN ISO 17640:2018. This European standard describes general ultrasonic testing techniques for the most typical welded joints for components within 0°C–60°C. This includes the specific requirements of the equipment, preparation, performance of the testing, and reporting [12]. Overall manual ultrasonic testing techniques are specified for fusion-welded joints of parts with a minimum thickness of 8 mm, exhibiting low ultrasonic

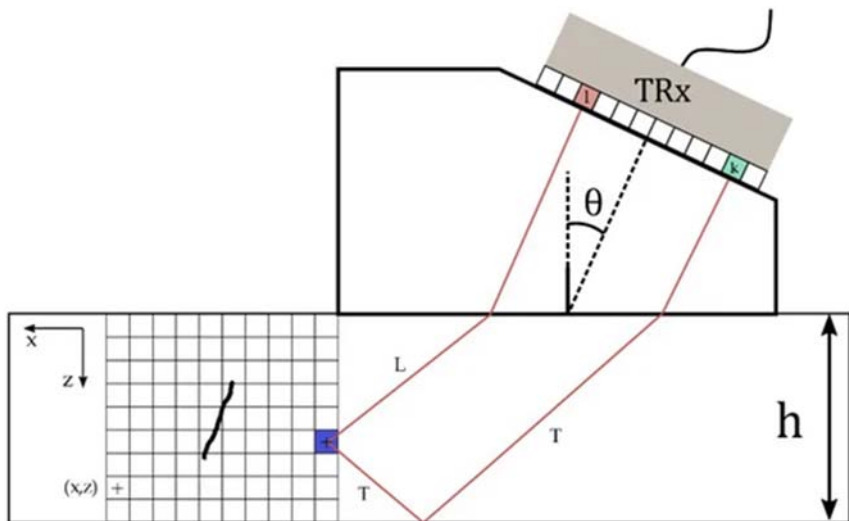


Figure 11.3 Illustration of phased array ultrasonic testing (PAUT) technology, which allows simultaneous inspection of all welding zones in the same position. Data acquisition principle through full matrix capture, where a signal is emitted by element i and received by element k . The image reconstruction area is divided into pixels, each one denoted by its position (x, z) . Placing a probe on each side of the weld enables easy, reliable, and complete bead coverage [8].

attenuation (especially due to scattering) within 0°C–60°C. It is primarily used on ferritic welded joints where full penetration is achieved.

The quality requirements are mainly associated with the material, welding process, and service conditions. ISO 17640 specifies four testing levels, from A to D, depending on the probability to detect a flaw. The chance of detection increases from level A to level C, which can be achieved by increasing the testing coverage, for example, number of scans. Finally, level D is intended for special applications. For instance, testing alloys other than nonferritic steel, welds with partial penetration, automated testing, or even testing outside the 0°C–60°C range. The testing level depends on the joint type, the thickness of the parent material, and the type of discontinuity (longitudinal or transverse) and how it defines the beam angles, probe position, scanning zone, and the total number of scans is defined in detail in ISO 17640 [12].

The ISO 17640 evaluation can be based on two techniques [12]:

1. On the length and echo amplitude of the discontinuity;
2. On characterization and sizing of the indication by probe movement techniques.

Other necessary standards considered indispensable when addressing ultrasonic testing are the following:

- ISO 5577 [13];
- ISO 9712 [14];
- ISO 11666 [15];
- ISO 16810 [16];
- ISO 16811 [17];
- ISO 16826 [18];
- ISO 17635 [19];
- ISO 23279 [20];
- EN 12668 (all parts) [21];

In this subsection, the main goal is to indicate and highlight the main aspects of ISO 17640 (NDT of welds—Ultrasonic testing—Techniques, testing levels, and assessment) [12] and other related standards [13–21]. For more specific details, the authors recommend that the reader consult the documents above, particularly their up-to-date versions.

In the case of welding components with different thicknesses, the thickness of the thinnest part to be joined should be considered. Also, requirements for additional tandem testing need to be following ISO 16826 [18]. There are also indications regarding the personnel, which

needs to be qualified to perform ultrasonic testing according to ISO 9712 [14] and have in testing welded joints.

The equipment needs to be following EN 12668 [21] requirements. The test frequency is also specified and within the range of 2–5 MHz. The selected value should consider the part properties in order to comply with ISO 11666 [15] acceptance levels. Nevertheless, testing at higher frequencies is possible when using ISO 23279 [20] standard for acceptable levels based on the characterization of discontinuities in order to improve the range resolution. Additionally, testing at lower frequencies can be carried out for long sound paths or when the material shows high attenuation.

In the case of transverse waves and techniques that require the ultrasonic beam to be reflected from an opposite surface, care shall be taken to ensure that the angle between the beam and the normal to the opposite reflecting surface is within 35–70 degrees. In the case of multiple beams, at least one needs to meet this requirement to ensure that the weld fusion faces are tested at normal incidence. In the case of multiple beam angles, there should be a minimum 10 degrees difference between the nominal beam angles. Angles of incidence at the probe and opposite reflecting surface, when curved, may be determined by drawing a sectional view of the weld or following the techniques given in ISO 16811 [17]. The setting of range and sensitivity need to be performed before each testing under ISO 17640 and ISO 16811 [12,17] and considering temperature effects. Temperature gradient during range, sensitivity setting, and testing must be within $\pm 15^\circ\text{C}$ [12]. Fig. 11.4 illustrates the significant effect of temperature gradients on the defect prediction of welded components.

When selecting the transducer size, the ultrasonic path and testing frequency need to be considered. The transducer's size is proportional to the length and width of the near field and contrary to the beam spread in the far-field. Therefore, probes with 6–12 mm diameter transducers (or rectangular ones with the equivalent cross-sectional area) are most valuable for short paths. For longer ones (greater than 100 mm for single-transducer or 200 mm for angle-beam probes), transducers with a diameter within 12–24 mm are recommended. Additionally, the distance between the sample's surface and the probe bottom should not exceed 0.5 mm, and the coupling media shall be following ISO 16810 [16]. The test surfaces need to be even and clean in order to eliminate or at least reduce interferences with the probe (e.g., rust and weld spatter).

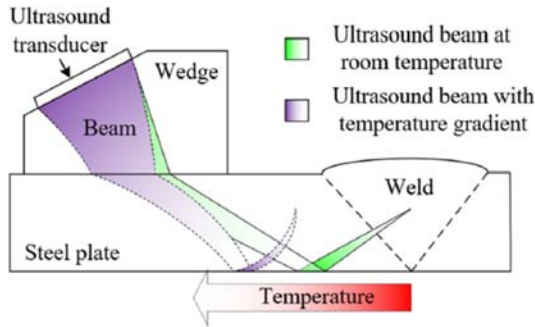


Figure 11.4 Effect of temperature gradient in the ultrasound beam—path deviation [5].

The testing technique should follow ISO 16810 [16]. Regarding the manual scan path, during angle-beam scanning (Fig. 11.2), swivel motions of 10 degrees should be performed [12]. Imperfections perpendicular to the testing surface is difficult to detect with single-transducer angle-beam techniques [12]. Therefore, specific testing techniques need to be employed, especially for thick components. The specification shall define the use of these testing techniques.

Independently of the direction, the discontinuity length should be determined using the technique specified in the acceptance levels standard, unless otherwise agreed. If defined, discontinuities shall be characterized by ISO 23279 [20].

11.3 Conclusions

Ultrasonic testing for weld inspection is a non-destructive test method that consists of detecting discontinuities in welds. The procedure is of fundamental importance for the identification of defects in order to provide the safety and excellence of the activity in an industry. Typically performed with modern, high-tech equipment, ultrasonic weld inspection strictly follows the standards and procedures, and products that pass through its application, ASME, AWS, DIN, and ASTM, among others. This chapter focuses on EN ISO 17640:2018 (NDT of welds—Ultrasonic testing—Techniques, testing levels, and assessment) and its related standards. Overall, this inspection technique is relevant for several industrial sectors such as petrol, automotive, aerospace, railway, etc. The interest in employing such a technique is mainly justified by its advantages:

- Non-destructive testing;
- Performed without prejudicial chemicals;
- Access to only one side of the sample;
- The results are highly repeatable and reliable (if the test was correctly configured);
- Without potential health risks, unlike radiography;
- It does not require strict safety measures.

Nevertheless, there are also limitations linked to ultrasonic testing, which represent the current challenges and will guide future developments of related technologies:

- Requires qualified and experienced personnel for inspection and data interpretation;
- False positives related to spurious signals that may result from tolerable anomalies or even from the component geometry;
- Lower sensitivity for volumetric flaws than radiographic testing, particularly in the case of metal inclusions,
- Complex geometries, rough objects, irregular shapes, and very small/thin, or inhomogeneous components are challenging to inspect

In this chapter, some advancements were previously highlighted, such as the flexible PAUT probe developed by Lim et al. [9] to inspect welded pipes in complex configurations. Another example is empirical wavelet transform and deep convolution neural networks for PAUT signal enhancement and classification, which proved to be a more efficient and accurate methodology for welding defect classification [22].

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Further reading

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CHAPTER 12

Diffraction with X-rays and neutrons

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12.1 Introduction

Diffraction/scattering is one of the most established methods for non-destructive materials characterization. The use of X-rays and neutrons as a probe for the investigation of the structure of matter by diffraction/scattering methods has a long and profound history. Since X-rays and neutrons are endowed with strong penetrating power to materials in comparison with electrons, these probes are more usable than electrons to non-destructively study the material structures by diffraction technique under in situ and/or operando conditions. Also, since both X-rays and neutrons weakly interact with materials, multiple scattering effects can be neglected so that the first Born approximation (kinematical approximation) can safely be used. Moreover, the advent of synchrotron radiation (SR) X-ray sources has accelerated such situations [1], and made possible the development of high-resolution studies of surface and interface even under the conditions of film deposition and layer-by-layer crystal growth.

We will present, in the first part of this chapter, concepts of X-ray diffraction in qualitative terms, restricting the use of mathematical descriptions to a minimum, including the review of the method for surface and interface structural investigation using SR X-rays. Since the energy tunability of incident X-rays is one of the fascinating properties of SR sources, we will introduce an anomalous diffraction technique that carries out the diffraction experiment by changing the incident X-ray energy around the atomic absorption edge energies.

Since Neutron diffraction, which is complementary to X-ray diffraction, is well known as a non-destructive materials characterization method, its method with a spallation neutron source will be explained in the last part of this chapter, and show some of the results applied to battery electrodes.

12.2 Interaction of X-rays with electrons (materials)

12.2.1 Scattering from an electron

X-rays are transverse electromagnetic waves with wavelengths (λ) in the region of atomic distance in materials. For simplicity, considering a plane wave of X-rays, its electric field can be written as $\vec{E}(\vec{r}, t) = \vec{\epsilon} E_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$, where E_0 is a maximum electric field amplitude, $\vec{\epsilon}$ is the polarization of the electric field, $\vec{k}$ is a wavevector along the direction of the propagation ($|\vec{k}| = 2\pi/\lambda$), $\hbar\vec{k}$ is a momentum of the incident X-ray photon and $\hbar\omega$ is a quantized photon energy of X-rays. When we consider the scattering event, the differential scattering cross section is generally defined. Fig. 12.1 shows a schematic diagram of the differential scattering cross section by a free single electron, where I_0 is the number of photons passing through a unit area per second, I_S is the intensity of the scattered X-rays in unit area per second detected at r from the electron as a scatterer, and $d\Omega$ is a unit of solid angle.

Then the differential scattering cross section is defined by $\frac{d\sigma}{d\Omega} = \frac{I_S \cdot r^2}{I_0}$. Since I_0 and I_S are proportional to $|\vec{E}_{in}|^2$ and $|\vec{E}_{rad}|^2$, where $\vec{E}_{in}$ and $\vec{E}_{rad}$ are incident and radiated electric fields, respectively, $\frac{d\sigma}{d\Omega}$ can be written as $\frac{|\vec{E}_{rad}|^2 \cdot r^2}{|\vec{E}_{in}|^2}$. Also, the ratio of radiated to incident electric fields is expressed as $\frac{E_{rad}(r, t)}{E_{in}} = -r_0 \cdot \frac{e^{ikr}}{r} \cdot |\vec{\epsilon} \cdot \vec{\epsilon}'|^{(1)}$. r_0 is the classical radius of the electron (or Thompson scattering length), which is equal to $\left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right) = 2.82 \cdot 10^{-5} \text{ \AA}$, and $\vec{\epsilon}'$ is the polarization of the scattered X-ray. Therefore the differential scattering cross section by a free electron becomes $\frac{d\sigma}{d\Omega} = (r_0)^2 |\vec{\epsilon} \cdot \vec{\epsilon}'|^2$. In the case of the experiment using X-rays produced at synchrotron sources,

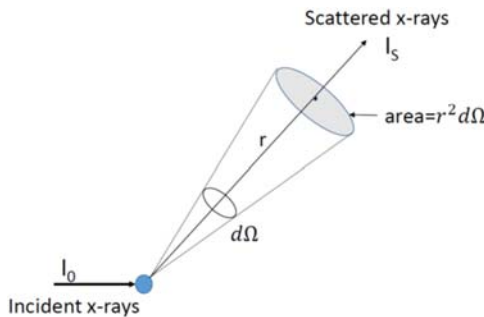


Figure 12.1 Schematic diagram defining the differential scattering cross section.

which are 100% linearly polarized in the horizontal plane of the synchrotron, a vertical scattering plane should be accepted for the best performance in terms of intensity because of the factor of $|\vec{\epsilon} \cdot \vec{\epsilon}'|^2$.

12.2.2 Scattering from an atom

12.2.2.1 General

Let us consider the scattering from a single atom with z electrons. Fig. 12.2 shows the case that a plane wave X-ray with a wave vector $\vec{k}_0$ impinges on an atom and is scattered to the direction specified by $\vec{k}$. The electron distribution in the atom is specified by a number density $\rho(\vec{r})$. A minute volume $d\vec{r}$ around point A has $\rho(\vec{r}) \cdot d\vec{r}$ electrons. Therefore $\int \rho(\vec{r}) \cdot d\vec{r}$ should be z for the atom with z electrons. When the scattering is elastic, the relation of $|\vec{k}_0| = |\vec{k}|$ is kept in all the scattering events by electrons in the atom. The scattered radiation field is a superposition of contributions from different volume elements of the charge distribution in the atom. The phase difference between the origin (point O) and the one at position $\vec{r}$ of point A is given by $(\vec{k}_0 - \vec{k}) \cdot \vec{r} = \vec{q} \cdot \vec{r}$, where $\vec{q} = \vec{k}_0 - \vec{k}$ is known as the scattering vector, and its magnitude $|\vec{q}|$ is equal to $(4\pi/\lambda)\sin\theta$ for the scattering angle of 2θ . Then, finally, the total scattering length of a single atom is expressed as

$$-r_0 f^0(\vec{q}) = -r_0 \int \rho(\vec{r}) e^{i(\vec{q} \cdot \vec{r})} d\vec{r} \quad (12.1)$$

where $f^0(\vec{q})$ is known as the atomic form factor (, or atomic scattering factor). As you can see the right-hand side of the equation of the atomic form factor, this is recognized as a Fourier transform of the distribution of electrons in the atom.

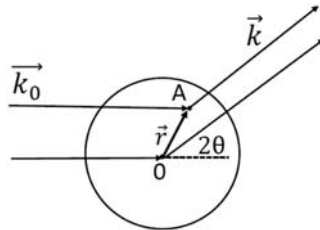


Figure 12.2 Diagram of the scattering from an atom.

As an example, let us consider that the electron distribution in the atom is spherically symmetric. In such a case, the $\rho(\vec{r})$ depends only on the length of the vector $\vec{r}$. Therefore the atomic form factor becomes

$$f^0(\vec{q}) = \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin qr}{qr} dr \quad (12.2)$$

In general, as seen in Eq. (12.1), the atomic form factor can be numerically calculated if the electronic wave functions are known, and those of an isolated atom and ion are given in the International Table of Crystallography [2].

12.2.2.2 Anomalous dispersion correction

The calculation of the atomic scattering factor in the previous section is valid in the case that the incident X-ray energy is large compared to the absorption edges of the scattering atom. When the incident X-ray energy approaches a critical value that can excite the strongly bound electrons, for example, K-shell electrons, to the unoccupied electronic states, an anomalous dispersion correction on the atomic form factor should be taken into account. A quantum mechanical theory can be applied to this phenomenon to calculate the anomalous dispersion correction quantitatively, and as a result, the atomic form factor can be written in the form

$$f(\vec{q}, \omega) = f^0(\vec{q}) + f'(\omega) + if''(\omega) \quad (12.3)$$

where f' and f'' are the real and imaginary parts of the dispersion corrections which are X-ray energy dependent, and related to Kramers–Kronig relation to each other. This $f(\vec{q}, \omega)$ of Eq. (12.3) is called the anomalous atomic scattering factor. When this dispersion correction are dominated by electrons in the K shell (energy = ω_0), the electrons in these shells are so confined in the real space that their $\vec{q}$ dependence can be neglected. And the electrons in the L and M shells in the heavier elements, like rare earth and actinide elements, are also true. Fig. 12.3 shows the X-ray energy dependence of the dispersion corrections around the K edge in a schematic way. One interesting application of the anomalous atomic scattering factor is to the structural analysis of a crystal composed of two elements of neighboring atomic numbers, whose atomic form factors are numerically close. One example will be shown in the chapter of surface/interface diffraction.

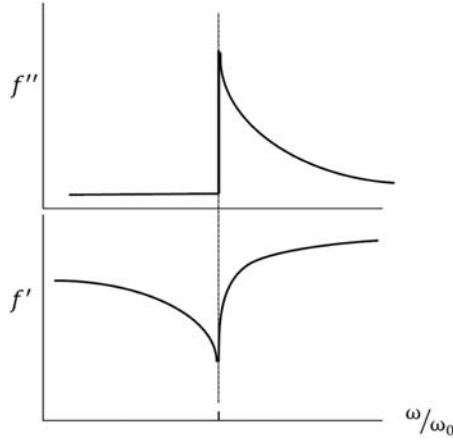


Figure 12.3 Energy dependence of the dispersion correction around K shell for an isolated atom. *Top panel:* the imaginary part $f''(\omega)$. *Bottom panel:* the real part $f'(\omega)$.

12.2.3 Scattering from a crystal

The crystal is composed of a group of a unit cell, which has a single or a group of atoms. Labeling the different atoms in the unit cell by index j , the scattering length of the unit cell can be written as

$$F_{unit}(\vec{q}) = \sum_j f_j(\vec{q}) e^{i\vec{q} \cdot \vec{r}_j} \quad (12.4)$$

where $f_j(\vec{q})$ is the atomic form factor of the j th atom in the unit cell, and the sum is over all the atoms in the unit cell. This is called the crystal structure factor. If $\vec{R}_n$ the lattice vectors that define the position of the unit cells in the crystal shown in Fig. 12.3, and $\vec{r}_j$ is the position of the atoms with respect to any one particular unit cell, the position of any atom in the crystal is given by $(\vec{R}_n + \vec{r}_j)$. Then, $\vec{r}_j$ Eq. (12.4) should be replaced by $(\vec{R}_n + \vec{r}_j)$ considering the crystal. Therefore the scattering amplitude for the crystal becomes

$$F_{crystal}(\vec{q}) = \sum_j f_j(\vec{q}) e^{i\vec{q} \cdot \vec{r}_j} \cdot \sum_n e^{i\vec{q} \cdot \vec{R}_n} \quad (12.5)$$

where the first term is the crystal structure factor, and the second term is a sum of the unit cell sites in the crystal. In the case that the basis vectors of the unit cell are $\vec{a}, \vec{b}, \vec{c}$, and (n_1, n_2, n_3) are integer, the lattice vector $\vec{R}_n$ are of the form:

$$\vec{R}_n = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c} \quad (12.6)$$

Then the second term can be expressed as:

$$G(\vec{q}) \equiv \sum_n e^{i\vec{q} \cdot \vec{R}_n} = \sum_0^{N_a-1} e^{in_1 \vec{q} \cdot \vec{a}} \cdot \sum_0^{N_b-1} e^{in_2 \vec{q} \cdot \vec{b}} \cdot \sum_0^{N_c-1} e^{in_3 \vec{q} \cdot \vec{c}} \quad (12.7)$$

where (N_a, N_b, N_c) are the number of the unit cell for $(\vec{a}, \vec{b}, \vec{c})$ directions, respectively, (Fig. 12.4).

When the scattering intensity is considered, $|G(\vec{q})|^2$ should be calculated:

$$|G(\vec{q})|^2 = \frac{\sin^2\left(N\vec{q} \cdot \frac{\vec{a}}{2}\right)}{\sin^2\left(\vec{q} \cdot \frac{\vec{a}}{2}\right)} \cdot \frac{\sin^2\left(N\vec{q} \cdot \frac{\vec{b}}{2}\right)}{\sin^2\left(\vec{q} \cdot \frac{\vec{b}}{2}\right)} \cdot \frac{\sin^2\left(N\vec{q} \cdot \frac{\vec{c}}{2}\right)}{\sin^2\left(\vec{q} \cdot \frac{\vec{c}}{2}\right)} \quad (12.8)$$

This equation is named as Laue Function. Finally, the scattering intensity $I(\vec{q})$ from the crystal becomes

$$I(\vec{q}) = (r_0)^2 |F_{\text{crystal}}(\vec{q})|^2 = (r_0)^2 |F_{\text{unit}}(\vec{q})|^2 |G(\vec{q})|^2 \quad (12.9)$$

Let's look up the character of the Laue Function. The sum of Eq. (12.7) is of order unity unless the scattering vector happens to fulfill the following condition:

$$\vec{q} \cdot \vec{R}_n = 2\pi \cdot (\text{integer}) \quad (12.10)$$

Usually, the crystal is much larger than the unit cell, that is, N_a, N_b, N_c are all big numbers.

Therefore $|G(\vec{q})|^2$ show a sharp local maximum value only when Eq. (12.10) is satisfied, and the maximum value is $(N_a N_b N_c)^2 = N^2$ (N is

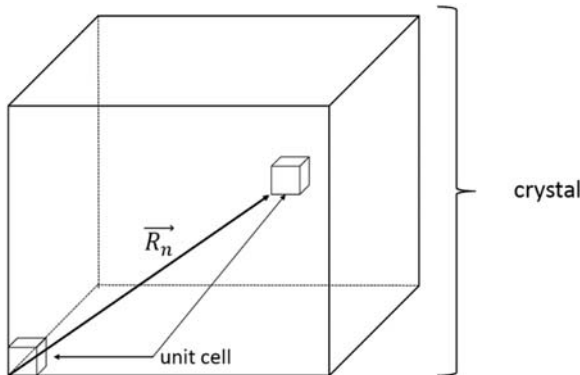


Figure 12.4 Schematic drawing of the relation between a unit cell and crystal.

the total number of the unit cell in the crystal). A unique solution to Eq. (12.10) can be found by introducing the concept of the reciprocal lattice, which is defined by

$$\vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}, \vec{b}^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})}, \vec{c}^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \quad (12.11)$$

Any lattice site in this reciprocal lattice is given by

$$\vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

where (h, k, l) are integers. When $\vec{q} = \vec{G}$ required, Eq. (12.10) is satisfied. This means that the crystal structure factor $F(\vec{q})$ is non-zero only if the scattering vector $\vec{q}$ coincides with a reciprocal lattice vector. This is a well-known Laue condition for the observation of diffraction from a crystal, which is equivalent to Bragg's law, $2d\sin\theta = n\lambda$ (d is a spacing of real space atomic plane involved in diffraction).

12.3 Data analysis: Patterson function

There are many excellent textbooks on the subject of structural analysis using X-ray diffraction data [3], and we do not have the space and knowledge to explain all the available methods here. As already seen in Eq. (12.4), all the information about the atomic geometry inside the unit cell is contained in the structure factors. Although the number of analysis methods is large, it is easily imagined that they are all based on Fourier analysis by considering Eqs. (12.1) and (12.4). As mentioned in the previous section the diffracted intensities are proportional to the square of the magnitude of the structure factor F [see Eq. (12.9)]. Then the electron distribution ρ cannot be calculated by the inverse transformation of F because the phase factor exists as an unknown factor. Patterson, however, showed that the structure factor could be used to obtain a pair-correlation function (autocorrelation function) of the electron density [4]. The Patterson function is defined by

$$P(\vec{R}) = \int F(\vec{q}) \cdot F^*(\vec{q}) e^{-i\vec{q} \cdot \vec{R}} d\vec{q} \propto \int \rho(\vec{r}) \cdot \rho(\vec{r} + \vec{R}) d\vec{r} \quad (12.12)$$

where $\vec{R}$ is a vector which has fractional coordinates along $\vec{a}$, $\vec{b}$, and $\vec{c}$ in the unit cell. The Patterson function has peaks at positions relative to the origin that correspond to interatomic distances in the F unit cell. In

particular, it is maximum for $\vec{R} = 0$. From Eqs. (12.1) and (12.4), the Patterson function can be written as follows:

$$P(\vec{R}) = \frac{1}{V_c} \sum_{h,k,l} \sum_{h',k',l'} \int_0^1 F(\vec{q}) \cdot F(\vec{q}') e^{i(\vec{q} \cdot \vec{r})} \cdot e^{i(\vec{q}' \cdot (\vec{R} + \vec{r})} d\vec{r} \quad (12.13)$$

where V_c is a unit cell volume, $\vec{q}$ and $\vec{q}'$ are the vectors which have integer coordinates (h, k, l) and (h', k', l') in the reciprocal space, respectively. All the terms of the sum in Eq. (12.13) are zero, except those where $h' = -h$, $k' = -k$, $l' = -l$. Thus, in the remaining terms,

$$F_{h',k',l'} = F_{-h,-k,-l} = F_{h,k,l}^*$$

Finally, Eq. (12.13) becomes

$$P(\vec{R}) = \frac{1}{V_c} \sum_{h,k,l} |F_{hkl}|^2 \cdot e^{i(\vec{q} \cdot \vec{R})} \quad (12.14)$$

Since $|F_{hkl}|^2$ is obtained experimentally, the Patterson function can be calculated directly from the experimental results. The Patterson function shows the interatomic distances in the unit cell, but we should be careful that it does not give an explicit picture of the real structure when the unit cell contains more than three atoms. In general, n atoms in the unit cell have $\frac{1}{2}n(n-1)$ independent vectors in the Patterson function. Then, in order to derive a correct atomic arrangement in the unit cell, iterative procedures are used to find atoms, and/or to search for known components of a structure systematically. The detailed technique of how to use the Patterson function for determining atomic arrangement can be given in reference [4].

12.4 Surface/interface diffraction

The physics of surfaces and interfaces is fascinating both from a fundamental and technological point of view. Structural studies of these systems are of considerable importance for the elucidation of surface and interface phenomena. Surface studies, for instance, have been made on some metals and semiconductors by using low energy electron diffraction, reflected high-energy electron diffraction (RHEED), transmission electron microscope, and scanning tunneling microscopy to investigate reconstructions appeared on surfaces. Paying attention interface structural studies, however, there were not many before the advent of SR X-rays because most of the probes used for the structural studies mentioned above cannot

penetrate deeply enough to investigate the interface structure. X-rays, on the other hand, penetrate matter easily, although the scattering from one or a few monolayers of interface with roughly about 10^{15} atoms/cm² is small by 10^4 , compared to the scattering from the bulk. This is a reason why the advent of intense SR X-rays has opened up the field of structural studies of the interfaces. Even though SR X-rays are intense, greater intensities are required to successfully analyze the interface structures in detail. Therefore the challenge is to employ the geometry of grazing incidence diffraction (GID) for the surface/interface studies. The pioneering work on a clean surface using the GID technique was done by P. Eisenberger and W. C. Marra [5] with the use of a rotating anode X-ray source, not SR X-rays. Their work has brought birth to the field of surface X-ray crystallography.

12.4.1 Grazing incidence diffraction method

Since the refractive index of all materials at X-ray wavelength is slightly less than unity, X-ray beams are totally reflected for a small glancing angle measured from a sample surface. The refractive index, n , can be given with neglecting absorption by the following equation,

$$n = 1 - \delta = 1 - 2.70 \times 10^{-6} \left(\sum_j Z_j / \sum_j A_j \right) \cdot \rho \lambda^2$$

where $\sum_j Z_j$ and $\sum_j A_j$ are the sum of atomic charges and the atomic masses in the unit cell, respectively, ρ is the mass density in g/cm³ and λ is the wavelength of the X-ray in angstrom. Under the condition of the incidence angle equal to the critical one, the electric field amplitude at the surface is doubled by the constructive interference between the incident and reflected waves, which results in a four times increase in scattered X-ray intensity compared with incoming waves. The situation holds true for the refraction of outgoing waves as predicted by the reciprocity theorem. This means that the diffracted intensity from the atoms in the surface layer is enhanced by a factor of 16 when the incident and exit X-rays approach exactly the critical angle. The scattering angle 2θ in such a configuration is mainly in the surface plane. The GID configuration brings the benefits of not only the intensity but also the reduction of the background. The main contribution of the background comes from the bulk. Then, by employing the GID configuration, an evanescent wave traveling parallel to the surface is created as described by the Fresnel equations of optics [6] and is strongly damped into the bulk crystal. As a consequence,

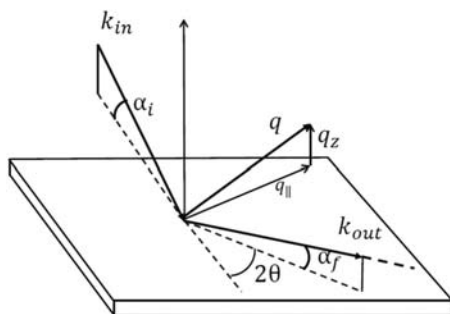


Figure 12.5 Principle of GID. See text in the detail explanation (this figure is taken from reference [7]).

the background is reduced significantly. Therefore a surface or a buried interface structure that is located between a material with refractive index n_1 in a few nm thickness and the bulk material with index n_2 ($n_2 < n_1$) can be studied by the GID method. The detailed description about the theory of diffraction under total external reflection conditions, the GID method, and the surface crystallography are given by G. Vineyard [6], R. Feidenhans'l [7] and I. K. Robinson [8], respectively.

A cartoon of the GID experimental geometry is shown in Fig. 12.5. The monochromatic X-ray beam of wave vector k_{in} is incident at an α_i to the surface. After diffraction through an angle 2θ , the X-rays are detected at an exit angle α_f to the surface. The momentum transfer $\vec{q}$ is composed of an in-plane component $\vec{q}_{\parallel}$, which is a reciprocal lattice vector of the surface lattice and $\vec{q}_z$ normal to the surface. In the GID configuration, $\vec{q}_z$ is usually small. A schematic drawing of the experimental configuration for GID is shown in Fig. 12.6. In order to probe along a rod in reciprocal space to investigate the structure perpendicular to the surface, $\vec{q}_z$ can be varied. I. K. Robinson defined “Crystal Truncation Rods (CTR)”, which are the diffuse rods of scattering in the direction normal to the surface for integer-order reflections. CTR originates from the truncations or termination of the surface [9]. The CTR has become an important tool for studying surface-related characteristics, such as the roughness of surfaces, the interfacial relationship between two materials, and the determination of adsorption sites.

12.4.2 Principle of data analysis

As it is seen in Chapter 2.3 that the diffraction from bulk crystals occurs only if the momentum transfer of the X-ray beam satisfies the three Laue

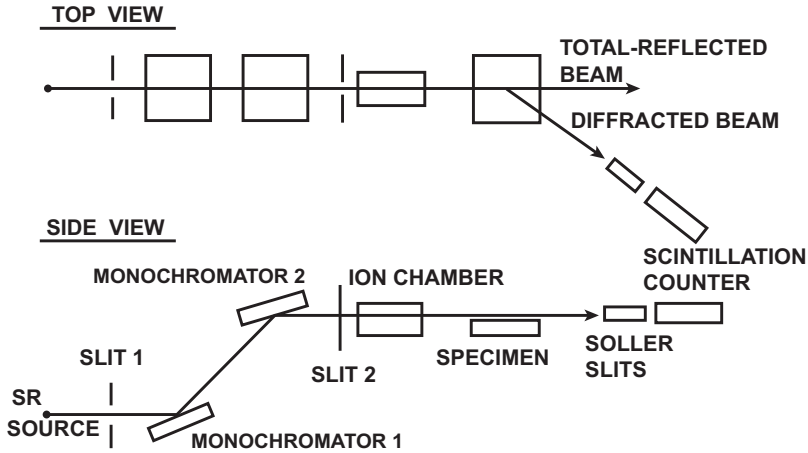


Figure 12.6 Schematic drawing of the experimental configuration for GID [10].

conditions given by a point (hkl) in reciprocal space (h, k, l are integers). In the case of the surface and interface, however, the third Laue condition, l , is relaxed, that is, the diffraction occurs if the two Laue conditions given by the in-plane indices (h, k) are satisfied. X-rays only interact weakly with matter and a single scattering (kinematical) approach is sufficient to analyze the experimental data. Especially, since the diffracted X-ray intensity for GID is very low, an analysis based on the Born approximation is applicable. This makes the structure analysis straightforward. In the two-dimensional case, $\vec{q}$ has a two-dimensional component, $q_x = h, q_y = k$. The structure factor, $F(\vec{q})$, is given by the following equation:

$$F_{unit}(\vec{q}) = \sum_j f_j(\vec{q}) e^{i\vec{q} \cdot \vec{r}_j} = \sum_j f_j(h, k) e^{i(h \cdot x_j + k \cdot y_j)} \quad (12.15)$$

The sum is over all the atoms in the surface unit cell. As for the data analysis, we already know that the Patterson function calculation is useful for analyzing the structure of bulk crystals. It easily imagines that we can apply this method to the surface/interface structure analysis. But there was no attempt to use the Patterson function in surface structure determination until 1983 by I. K. Robinson [11]. The important point for surface and/or interface structure determination, such as reconstructed structure, is that the reflections from the planes of integer Miller indices, which are related to the Laue condition, are not used in the data analysis because these reflections include the structural information of the substrate. This

absence of structure factors may distort the Patterson function slightly. The detail of structure determination for the two-dimensional system using the Patterson function is described in the literature by Robinson [8].

12.4.3 Application to metal/semiconductor interface systems

We would like to show here an application of GID to the interface structure analysis as an example [10]. The microscopic understanding of metal-semiconductor contacts has been important not only from a scientific but also from a technological point of view. The Al/GaAs(001) contact system has been especially interesting since it can be used as one of the Schottky barrier systems [12]. Although Wang reported that the Schottky barrier height (SBH) was dependent on the surface stoichiometry of GaAs, or the reconstructed structure on the GaAs surface [13], the relationship between the structure at the interface and the SBH was not fully understood. It is not obvious that the surface reconstructed structure is preserved at the interface, or rather it is natural to believe that its structure disappeared by the reaction with the metal over-layers.

Fig. 12.7 shows a cross-sectional view of the Al/GaAs(001) system we prepared, and we carried out the GID experiment with this sample [14]. The experiment was performed at the synchrotron facility, Photon Factory.

The observed diffraction peaks at the fractional reciprocal lattice point are shown in Figs. 12.8 and 12.9 shows the observed structure factor with some corrections. The radius of the circles is proportional to the observed structure factor. These results indicate that the reconstructed structure observed may be an overlap of the (4 × 1) and (1 × 6) domains. In the case of the surface structure, the overlap was suggested by our RHEED patterns from the clean (001) GaAs surface before the Al depositions. We

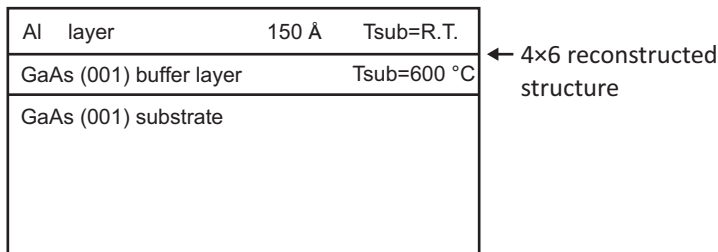


Figure 12.7 Cross-sectional view of the Al/GaAs(001) interface system having 4 × 6 reconstruction [14].

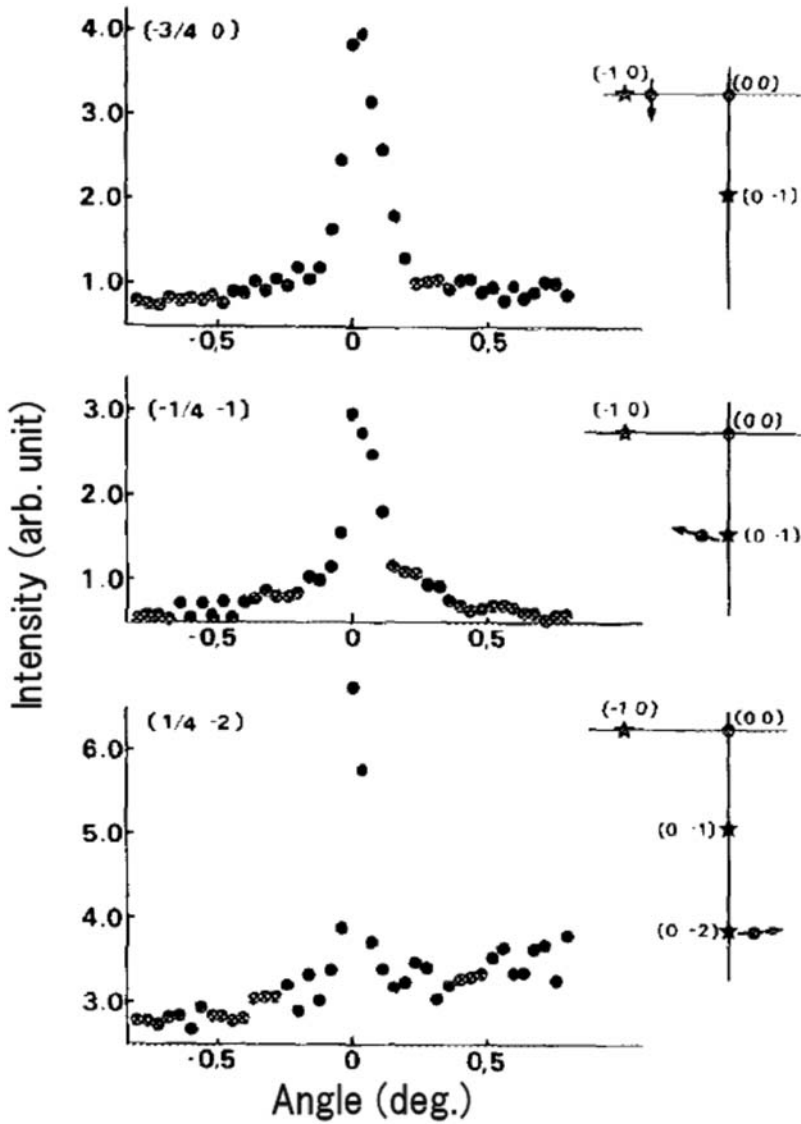


Figure 12.8 Experimental diffraction profiles from the reconstructed structure at the interface between Al and GaAs(001). The center (corresponding to the zero of the horizontal axis) and the direction of the scan in the reciprocal lattice space are indicated on the right-hand side of each figure. $(-1\ 0)$, $(0\ -1)$, and $(0\ -2)$ are the reciprocal lattice point of the bulk structure [14].

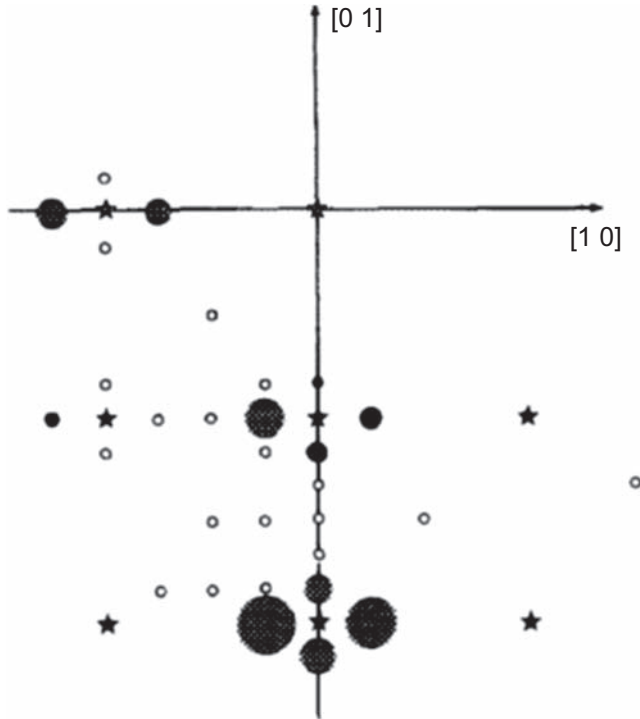


Figure 12.9 Observed structure factors. The area of each solid circle is proportional to the intensity. Open circles are reflections measured to be zero. Star marks are the fundamental reciprocal lattice points of the bulk structure.

would like to emphasize from these experiments that surprisingly a buried reconstructed structure at the interface between Al layers and GaAs(001) substrate was preserved. Regarding the relation between the interface structure and SBH, however, what we found in Al/GaAs(001) systems through these experiments was that the SBHs did not vary even when the interfacial structures were different from each other. SBH may be controlled by more local structures than long range ordered structures.

12.4.4 Application of anomalous dispersion correction to surface structure analysis

In the previous section, we showed that the 4×6 -reconstructed structure was preserved at the metal/GaAs(001) interface, but no detail of the 4×6 -reconstructed structure was discussed. Here, we will show the detailed surface structural analysis of GaAs(001)- $c(4 \times 4)$ [15], which is

used for technological applications such as InGaAs quantum devices and dilute magnetic semiconductors. For decades, this surface structure was discussed with some controversial models. The main problem on the c (4×4)-reconstructed structure was whether As-As homodimers or Ga-As heterodimers exist in the unit cell of this structure. Although we know that GID is a powerful technique to elucidate surface structures, the atomic numbers of Ga and As are so close that the contrast due to the difference in the number of electrons is too faint to differentiate Ga and As. So, the anomalous X-ray diffraction method with the anomalous dispersion correction comes over to solve this question. Molecular Beam Epitaxy (MBE) chamber of III-V compound semiconductors crystal growth is designed for an in situ X-ray diffraction experiment. The experiments were performed with a six-circle diffractometer [16] directly coupled to the MBE chamber at the experimental station BL11XU at the synchrotron facility, SPring-8. The measurements were performed in the symmetric z -axis mode where the surface normal of the substrate lies in the horizontal plane and where the incoming and outgoing beams make the same angle with respect to the sample surface. In this measurement, reciprocal lattice point L, which is perpendicular to the sample surface, is 0.03 in the reciprocal lattice unit. The observed structure factors are shown in Fig. 12.10, compared with the calculated structure factors based

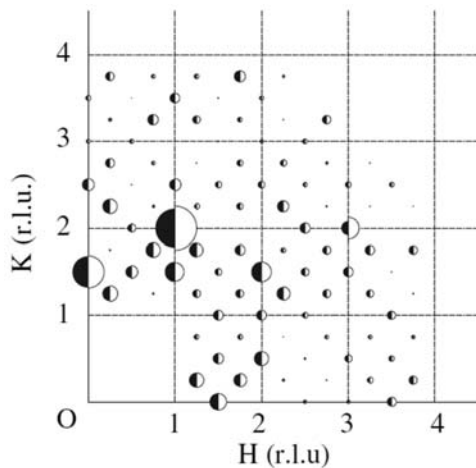


Figure 12.10 Structure factors measured by the X-ray diffraction technique at $L = 0.03$. The indices H and K are along $[\bar{1}10]$ and $[110]$ directions, respectively. The abbreviation r.l.u. denotes reciprocal lattice units [14].

on a buckled dimer model [16]. The radius of the open and solid half circles is proportional to the observed and calculated structure factors, respectively. The abbreviation r.l.u. denotes reciprocal lattice units.

Although the buckled dimer model shows the best fit result, it is hard to distinguish between As-As dimer (homodimer) and Ga-As dimer (heterodimer) by X-ray diffraction. Anomalous X-ray diffraction with the use of anomalous dispersion correction can resolve this uncertainty because this diffraction method has an element selectivity by tuning the incident X-ray energy. By changing the X-ray energy in the vicinity of the Ga K absorption edge, we measured six fractional-order reflections where only the reconstructed surface layers contribute. In this energy range, the scattering form factor from Ga atoms is strongly modulated, while that from As stays constant. Since we have already known the atomic coordinates of the $c(4 \times 4)$ structure, we can calculate the change in diffracted intensity in the two cases where the surface dimers are heterodimers or homodimers. Depending on the reflection indices, the phase of the diffracted wave can be different and thus the diffraction intensity makes either a peak or a dip at the Ga K absorption edge. By comparing the energy dependence of the diffracted intensity between the observation and calculation, the elements that contribute to the surface dimers can be distinguished. The energy dependence of the refractive index was calculated using anomalous scattering factors calculated by the Cromer-Lieberman method [17]. The observed results are presented in Fig. 12.11 which shows the structure factors of six surface peaks as a function of the X-ray energy. The solid and dashed lines indicate the results from calculations when the Ga-As and As-As dimers are assumed, respectively. Obviously, the Ga-As dimer model not only shows a better fit to the observed data but also reproduces the peak and dip at the Ga K -edge energy depending on the surface reflection points. This gives direct evidence for the formation of heterodimers on GaAs (001)- $c(4 \times 4)$. Although the qualitative agreement is good, the remaining quantitative disagreement between calculated curves and the observed data is due to the difficulty in the correct evaluation of X-ray anomalous scattering factors. For the surface atoms, the anomalous scattering factors can be different from the bulk values owing to the different chemical environments at the surface. In spite of this, however, the possibility of a buckled As-As dimer model can be excluded. Readers who are interested in the detail of this surface structure should visit the reference [15].

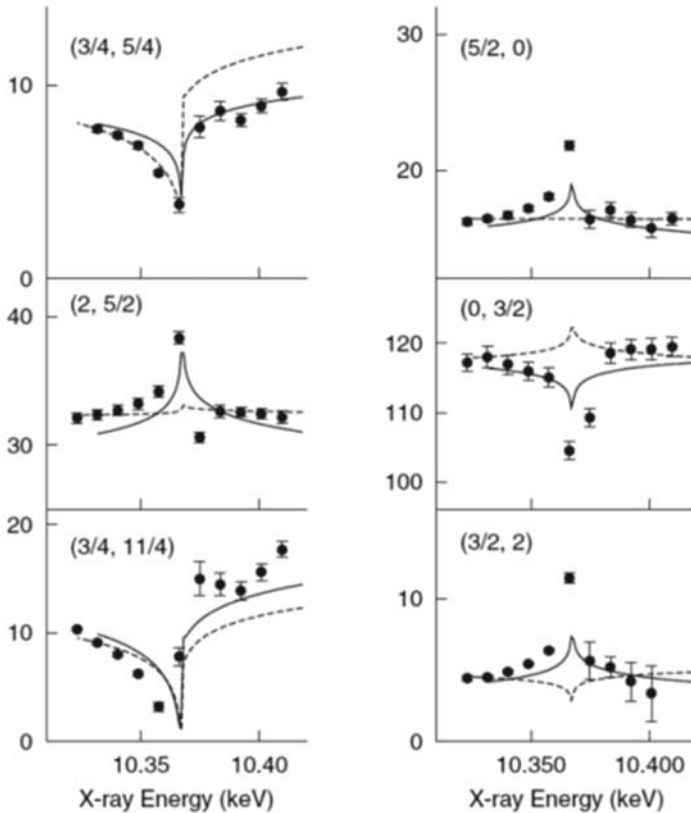


Figure 12.11 X-ray energy dispersion of the structure factors of (H, K) reflections. The solid circles are observed structure factors. The solid and dashed lines indicate the results from calculations when the GaAs and As-As dimers are assumed, respectively [15].

12.4.5 Coherent X-ray diffraction

The diffraction technique utilizing the improved coherence of the beam is explained briefly before closing this X-ray diffraction section. Coherent X-ray diffraction is rather a new technique developed by the advent of third-generation SR sources. Although most of the X-ray sources are only partially coherent, a microscopic beam from undulators at those sources is close to fully coherent, that is, the nearly coherent beam can be obtained by cutting down an incoherent beam to a size comparable with its transverse (or lateral) coherence length. The transverse coherent length, ξ , is determined by the source size, S , by $\xi = \lambda D/S$, where λ and D are the wavelength of X-rays and the distance from the source to the defining

aperture, respectively. ($\xi_{vert} = \lambda D / S_{vert}$, $\xi_{hor} = \lambda D / S_{hor}$) Another coherence needed to describe the beam is the longitudinal whose length, η , is determined by the monochromator resolution as $\lambda(\Delta\lambda/\lambda)^{-1}$. The resulting diffraction pattern is related to the Fourier transform of the entire object illuminated by the coherent beam. Therefore the diffraction pattern observed is sensitive to any fluctuations in space or in time. In other words, when a coherent X-ray is scattered from a disordered system, it gives rise to a speckle pattern, which is a result of interference between X-rays scattered from different places in the sample. When the disorder evolves in time, the speckle pattern changes in time. The expression of the coherent diffraction intensity is as follows. If the incident X-ray is fully coherent over all parts of the sample illuminated, the diffracted intensity is the square of their amplitude sum: $I(\vec{q}) = \left| \sum_j e^{i\vec{q} \cdot \vec{r}_j} \right|^2$

This intensity contains phase information about the relative positions of all the scattering grains (domains). This means that the intensity avoids the ensemble average normally associated with X-ray diffraction from disordered systems and we can see an interference pattern (speckle pattern) containing all the phase information of the sample illuminated by the coherent X-rays. The first observation of speckles using coherent X-rays was made on Cu_3Au , which has randomly arranged antiphase domains by Sutton, et al. in 1991 at National Synchrotron Light Source, Brookhaven National Lab [18]. Also, pioneering work for studying surface morphology was done by I. Robinson using the reflectivity of coherent X-rays [19].

12.5 Neutron diffraction

12.5.1 Scattering theory

Consider neutron with wavevector $\vec{k}_0$ is incident on two atoms whose position vectors are $\vec{r}_i$ with each other and scattered with wavevector $\vec{k}$; scattering vector is $\vec{q} = \vec{k}_0 - \vec{k}$. The scattered neutron waves from the two atoms are strengthened each other when the phases of the scattered waves are in phase. That is, strong interference occurs when the phase difference $\vec{q} \cdot \vec{r}_i$ is zero, where $\vec{r}_i$ is the relative position of two atoms. In a crystal, since atoms are regularly arranged and many atoms are at the same distance from each other, the scattered waves intensify and interfere with each other as a function of the scattering vector. This is the Bragg reflection. Even in non-crystallite materials, such as liquid or amorphous, there

are many atoms at approximately equal distances, so the scattered waves more or less interfere. By analyzing the interference pattern, that is, the Bragg-peak positions, their intensities, peak shape, or diffuse scattering, etc. we can learn information about how the atoms are arranged. Let us consider crystals in the following.

In crystalline solids, individual atoms are thermally vibrating around their average position. The atomic arrangements averaged in time and space is regular and has translational and rotational symmetry. The basic unit of symmetry is called the unit cell, and its repetition extends throughout the crystal.

To classify crystal structures by symmetry, we first consider that crystal structures are composed of a crystalline “lattice” and “basis”. The symmetries of the lattices can be classified into seven crystal systems (or six crystal families) and 14 Bravais lattices. Taking into account the symmetry of the basis, the crystal structures can be classified into 32-point groups. Furthermore, by introducing translational symmetry operations such as screw operations or glide operations, a total of 230 space groups are obtained. The basic unit of translational symmetry is the unit cell, but not all atoms in the unit cell are independent; many are linked by symmetry operations corresponding to each space group. So, there are many equivalent sites, called Wyckoff positions. Details of symmetry operations, Wyckoff positions, and other important information for each space group are compiled in the International Table for Crystallography A [20].

Scattering from the crystal produces strong interference peaks called the Bragg reflections, which can be analyzed (crystal structure analysis) to obtain an average picture of the crystal structure. If the deviation from the average structure is significant, diffuse scattering (weak broad scattering) is obtained. Analysis of Bragg scattering and diffuse scattering can reveal an overall picture of the crystal arrangement (both average structure and local structure), which has been also the crystal structure analysis in the broad sense.

On the other hand, since it has been revealed that both average structure and local structure are more or less involved in materials function, there is a growing interest to apply PDF (Pair Distribution Function) analysis, in which the Fourier transform is performed without separating Bragg scattering and diffuse scattering.

The neutron Bragg scattering intensity $I(\vec{q})$ can be expressed by the product of two functions, the unit-cell crystal structure factor $F(\vec{q})$ and

the interference function $G(\vec{q})$.

$$I(\vec{q}) = |F(\vec{q})G(\vec{q})|^2 \tag{12.16}$$

The unit-cell structure factor can be written as $F(\vec{q}) = \sum_j b_j e^{i\vec{q} \cdot \vec{r}_j}$, where b_j is the neutron scattering amplitude of the j th atom in the unit cell, and the sum is over all the atoms in the unit cell. $F(\vec{q})$ can be calculated from the atomic arrangement in the unit cell. Some selective b_j are shown in Table 12.1.

The interference function $G(\vec{q})$ corresponds to the position and shape (profile) of the Bragg reflection. From the positions of Bragg reflections, the *Bravais* lattice and unit-cell parameters can be specified, and from the profile of Bragg reflection, the crystal imperfection information such as effective strain and effective crystallite size, stacking fault density, dislocation density, etc. can be calculated.

Table 12.1 Examples of neutron scattering lengths in the unit of 10^{-13} cm.

Elements	b (10^{-13} cm)
^1H	−3.7423
^2D	6.674
Li	−1.9
^6Li	2
^7Li	−2.22
B	5.3
^{10}B	−0.1
^{11}B	6.65
C	6.6484
O	5.805
F	5.654
Na	3.63
Mg	5.375
Al	3.449
Si	4.149
P	5.13
S	2.847
Cl	9.5792
Mn	−3.73
Fe	9.54
Co	2.5
Ni	10.3

When single crystals cannot be obtained, crystal structure analysis must be performed using powder samples. Since powder diffraction data are one-dimensional, it is necessary to solve the three-dimensional crystal structure from the one-dimensional diffraction data. The first step is to determine the crystal system (and *Bravais* lattice) by searching for the three-dimensional lattice using the regularity and the extinction rule in the projected Bragg-peak positions in one dimension; this process is called 'indexing' since h , k , and l are assigned to each Bragg reflection. Various methods are proposed and a lot of software is available on the internet [21].

Once indexing is completed, the next step is to determine the atomic arrangement in the unit cell by analyzing the intensity of the Bragg reflections. This is called "unknown structure analysis". Since various methods have been proposed and a lot of software are available now, the unknown structure analysis is popular among researchers who synthesize new crystalline materials in powder forms [22]. The conventional methods for solving the unknown structure analysis are to determine the crystal structure using a list of Bragg reflections and their respective integrated intensities: the direct method and the Patterson method. The newly proposed methods are often called the real space methods, where diffraction patterns are fitted with the structural model which are modified using global optimization methods such as Monte Carlo and genetic algorithms.

If the crystal structure is completely unknown, do we have to carry out the unknown structure analysis? But wait for a while. The measured powder diffraction pattern may be similar to one of the diffraction patterns in a huge database. The *Hanawalt* method proposed in 1936 has been widely used to date, and the database has been succeeded by ICDD (International Centre for Diffraction Data) [23]. Currently, an electronic file PDF (Powder Diffraction File) with over 1,000,000 registered data and a search system are provided by ICDD.

If the structure is known, the next step is to refine the structural parameters using the least-squares method with the known structural parameters as initial values. This process is called structural refinement. The well-known structural refinement method exclusively used for powder diffraction data is the *Rietveld* method, which was proposed by H. M. Rietveld in 1966 for analyzing neutron powder diffraction data of the Petten nuclear reactor [24], and later extended for the use for X-ray powder diffraction data [25].

The Rietveld method is a method to optimize lattice constants, atomic coordinates, atomic displacement parameters, profile function parameters,

etc. so that the calculated pattern $h_i(x)$ based on a crystal structure model reproduces the measured pattern y_i as closely as possible. The nonlinear least-squares method is used to find the combination of parameters that minimizes $S(x)$.

$$S(x) = \sum_i w_i |y_i - h_i(x)|^2 \quad (12.17)$$

The *Rietveld* analysis enables the extraction of structural parameters from overlapping diffraction patterns of Bragg reflections. There are many software packages such as GSAS, FullProf, TOPAS, RIETAN, MAUD, and Z-Rietveld, each with its own advantages and disadvantages, but each has a large number of users. From the results of *Rietveld* analysis, crystallographic information such as lattice parameters, atomic coordinates, atomic displacement parameters, and other structural parameters and their standard deviations can be obtained, from which interatomic distances and angles and their standard deviations can be automatically calculated. Further analyses using the Maximum Entropy method to obtain electron density (X-ray) and scattering amplitude density (neutron), and/or various electronic structure calculations, etc. are routinely carried out.

It is also emphasized in situ measurements by changing the external environment (temperature, pressure, magnetic field, etc.) and operando measurements (charge-discharge process, chemical reaction, etc.) are more and more popular. The detailed crystal structural changes during these measurements can be studied using the Rietveld analysis.

In order to analyze an unknown structure, it has been claimed [26] that, more than 10 times separated reflections than the number of crystallographically independent atoms are required. In the Rietveld analysis, it is claimed at least five times more separated reflections are required. However, it depends on the number of structural parameters and the agreement of the fitting, which further affects the reliability of the obtained results.

The above is an overview of the flow of analysis of neutron diffraction data. The flow of analysis is not so different from that of the X-ray diffraction data analysis, and therefore, users should consider the difference between X-ray (looking at electrons) and neutron (looking at nuclei), and use the two methods in complementary ways. For example, by analyzing synchrotron diffraction and neutron diffraction data simultaneously, the number of light elements such as lithium and hydrogen (the quality of neutron data is generally higher), the presence of covalent bonds

(which can only be obtained with X-rays), the distribution of electrons and ions (new information can be obtained by combining both), the framework structure, its changes, mobile ions in the framework and so on.

12.5.2 Time-of-flight neutron diffraction

The time-of-flight neutron diffraction method (TOF method) is an energy dispersive diffraction method, where the time required for neutrons to propagate over a certain distance is measured, and from the time, neutron velocity hence energy, and wavelength is calculated. Since the neutron speed is slow enough and measurable, the TOF method has been used for a long time in the field of atomic physics.

Buras et al. were the first to use pulsed neutrons as a means of investigating materials structures. They showed TOF diffraction patterns from Al, Si, and Pb powders by using a Fermi-type chopper at research reactors [27]. Kimura et al. succeeded to utilize pulsed neutrons by (γ , n) reactions using electron linac in 1967 [28,29]. They developed the TOF Debye–Scherrer camera (it was later called Kimura Sputonick by Carpenter because of its shape) and solved crystal structures and magnetic structures of simple systems such as Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, MnP, etc. In the same year 1967, other electron linacs facilities at Harwell (UK) and Rensselaer (USA) also succeeded in TOF neutron scattering experiments [30]. Proton spallation has been started in 1972 in Argonne National Laboratory (USA) and later established itself as a promising source; the user programs started in KENS (1980–2006, High Energy Accelerator Research Organization, Japan), IPNS (1981–2008, Argonne National Laboratory, USA), LANSCE (1983–present, Los Alamos National Laboratory, USA), ISIS (1984–present, Rutherford Appleton Laboratory, UK), SNS (2007–present, Oak Ridge National Laboratory, USA), J-PARC MLF (2008–present, joint project between Japan Atomic Energy Agency and High Energy Accelerator Research Organization, Japan) and China Spallation Neutron Source (2018–present, Institute of High Energy Physics, China).

The pulsed neutrons are generated by colliding protons at a heavy-metal target in frequencies of 50 Hz (ISIS), 60 Hz (SNS), and 25 Hz (MLF and CSNS). The generated high-energy neutrons are reduced their energies by moderators to produce neutrons with energies of 0.1 meV–100 eV (0.03–100 Å). Each facility has developed several moderators depending on objectives: a high-intensity moderator, a high-resolution moderator, etc. Most of the TOF diffractometers utilize high-resolution

moderators where neutron pulses are sharp. Most of the small-angle scattering instruments utilize high-intensity moderators where neutron intensities are maximized.

In TOF diffractometry, the elapsed time is measured from the time when the neutrons are generated at the neutron source, till the neutron arrives at the detectors. Although neutrons with various energies (wavelengths) are generated at the same time, the time when the neutrons finally reach detectors through the sample is different, reflecting the difference in neutron velocity. If the neutron velocity is v and the distance from the moderator to the detector is L , the neutron velocity can be calculated by $v = \frac{L}{t}$. Combining this equation with the *de Broglie* relationship of $\lambda = \frac{h}{mv}$ (λ : neutron wavelength, h : Planck's constant, m : neutron mass), it becomes $\lambda = \frac{ht}{mL}$ and λ is obtained from time t . The d -spacing that Bragg scattering occurs can be calculated from Bragg's conditions $\lambda = 2d\sin\theta$ and $\lambda = \frac{ht}{mL}$

$$d[\text{\AA}] = \frac{t[\mu\text{sec}]}{505.555 \left[\frac{\mu\text{sec}}{\text{\AA m}} \right] L[\text{m}] \sin\theta} \quad (12.18)$$

In Fig. 12.12, neutrons are generated at time 0 and distance 0 (lower left of the graph), and travel at a constant speed (straight line with a

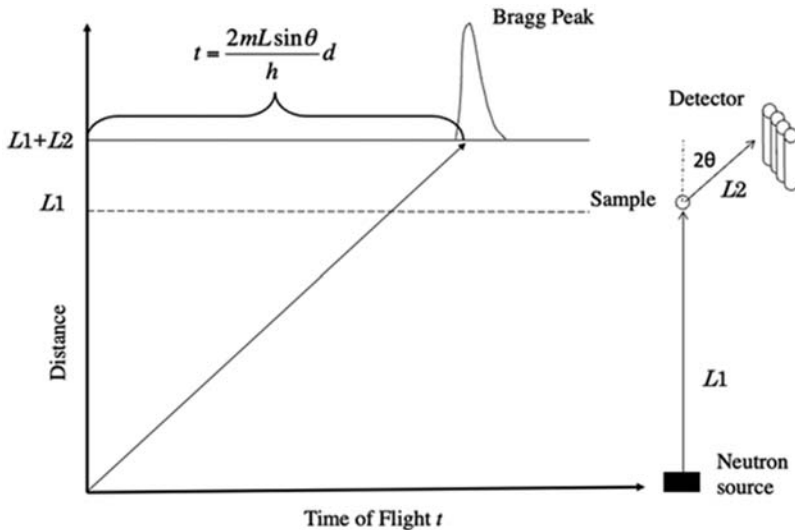


Figure 12.12 Conceptual diagram of diffraction experiments using the TOF method. The Bragg reflection position, t , is a function of the d -spacing, d , flight length, L , and scattering angle, 2θ .

constant inclination in the figure) depending on the wavelength and energy. In diffraction experiments, where the neutron is elastically scattered by the sample at the position L_1 , since the velocity is maintained before and after scattering, the slope is constant. The time t at which the Bragg reflection with the d -spacing is observed at the detector position $L_1 + L_2$ is calculated by Eq. (12.18).

When the proton accelerator is operated at 25 Hz, pulse neutrons are generated every 40 [msec]. TOF diffractometers usually use wavelengths of about 0.1 to 10 Å. Since the neutron velocity is as slow as several [km/sec], the wavelength can be obtained with high accuracy. The time of arrival of each neutron at the detector as well as the arrival position at the detector is recorded for every neutron; the time and the position are called neutron event data. So, each neutron event is recorded. The time information in neutron event data is measured by a time analyzer. The time analyzer is used to measure the elapsed time between the neutron-generated time indicated by a kicker pulse, and the time of arrival at the detector position. Typically, $10^6 - 10^8$ neutron events are accumulated for crystal structure analysis for the time channel of 10^4 . The neutron event data is usually converted to histogram data with time channels of few μsec intervals for further data analysis such as Rietveld analyses.

According to Eq. (12.18) and Fig. 12.12, in a TOF diffractometer with $L_1 = 30$ [m] and $L_2 = 2.0$ [m], the Bragg reflections with $d = 1, 2, 4$ [Å] measured at the backward detector ($\sin\theta = 1$, $L_1 + L_2 = 32.0$ [m]) are observed at $t = 16.178, 32.356, \text{ and } 64.711$ [msec], respectively. However, when pulsed neutrons are generated every 40 [msec] (25 Hz) and the speed of shorter wavelength neutrons are fast, the neutron of 64.711 [msec] is overtaken by the newly generated neutron. This phenomenon is called frame overlap. The measurable wavelength range is limited by the frame overlap. Then, how do we observe the Bragg reflection of $d > 2.776$ [Å] arriving at a time exceeding 40 [msec] at the backward detector ($\sin\theta = 1$)?

As can be seen from Eq. 12.18, a low-angle detector bank is often used to observe Bragg reflections with large d (reducing $\sin\theta$). For example, in a low-angle bank of the iMATERIA diffractometer in J-PARC, Bragg reflections exceeding $d = 20$ Å can be easily measured.

There are other methods to extend the limit of the wavelength range due to the frame overlap. Using multiple disk choppers which restrict transmitted neutrons and a T0 chopper that removes short-wavelength neutrons, reduced repetition such as the 12.5 Hz mode (1/2 of 25 Hz, 80 msecinterval)

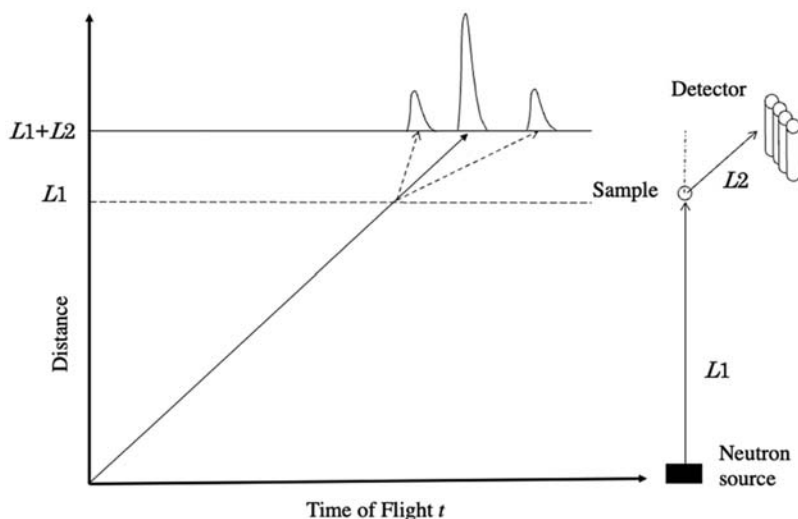


Figure 12.13 Conceptual diagram of inelastic neutron scattering. When neutrons receive energy from the sample material when scattered, the neutrons arrive earlier at the detector, and later when neutrons lose energy.

or 5 Hz mode ($1/5$ of 25 Hz, 200 ms interval) is available, which extends the limit of the measurement up to 80 or 200 ms, respectively. So, neutrons arriving at 64.711 [msec] can be detected. On the other hand, the phase can be shifted by using a disk chopper. Even within 25 Hz, the measurement range can be, for example, 30–70 [msec].

So far, we have discussed the case where Bragg's reflection occurs. In inelastic scattering, since there is an exchange of energy between neutrons and the matter of the scatterer, the energy and thus the velocity change after scattering. So, neutron reaches the detector earlier or later than elastic scattering. So, the slope of the line in the graph changes at the sample position. This makes it possible to calculate the energy transfer during inelastic scattering easily (Fig. 12.13).

12.5.3 Structural analysis of lithium-ion battery materials using neutron diffraction

Rechargeable batteries use redox reactions to convert electrical energy into chemical energy (charging), convert the stored chemical energy into electrical energy and extract it (discharging). In lithium-ion batteries, lithium moves between the cathode, electrolyte, and anode, and inserts into the cathode or anode, accordingly the structures of the cathode and the

anode change, and at the same time electrons also move in the circuit. They dominate battery properties.

The electrodes consist of active materials, binders, and conductive materials, in which lithium atoms are inserted and dis-inserted through conductive paths of lithium ions. Wide spatial scale of characterization is of interest where lithium-ion transfers at the interfaces between active materials and electrolytes in several nm, ion diffusion in the active material in tens of μm scale, and reaction distribution in electrodes in the mm to cm scale. The phenomena in these spatial scales dominate the performance of rechargeable batteries.

Neutrons are powerful probes for extracting static and dynamic information about rechargeable batteries on these spatial scales. In order to precisely determine the atomic arrangement, it is advantageous to use scattering: interference of waves of quantum beams such as X-rays, electron beams, and neutrons with wavelengths about atomic distances is most precise. Neutrons are advantageous to identify light elements among heavy elements because the intensity of scattering does not depend on atomic numbers such as X-rays and electron beams (Fig. 12.14). Neutron scattering is the only means by which atomic arrangement information of light elements such as lithium can be determined with 1% accuracy.

Table 12.1 shows the scattering lengths of the selective elements and their isotopes. If b is large, the scattering is strong, and if b is small, the scattering is weak. b has a dimension of the length of the scatterer. The

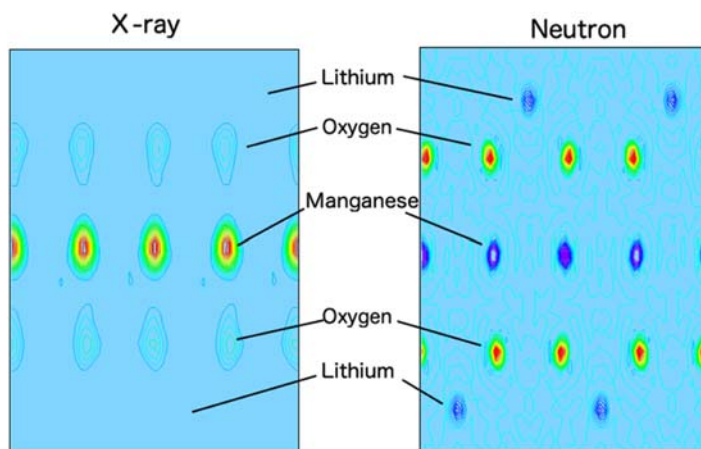


Figure 12.14 Fourier map of LiMn_2O_4 obtained from X-ray diffraction (*left*) and neutron diffraction (*right*).

table shows some b is negative, which indicates that the phase of the scattered neutron waves is inverted. Therefore, if two elements with the same absolute value of b with the opposite sign exist on the same Wyckoff site in the crystal, the coherent scattering is canceled.

Since the scattering amplitude depends on the isotope, the scattering contrast can be changed using isotopes. In particular, in the case of lithium, since the scattering amplitude can be widely changed from negative to positive by changing the isotope ratio, various studies using isotopes can be possible. For example, as shown in Table 12.1, the scattering amplitudes of natural lithium, lithium 6, and lithium 7 are $b(\text{Li}) = -1.90 \times 10^{-13}$ cm, $b(^6\text{Li}) = 2 \times 10^{-13}$ cm, $b(^7\text{Li}) = -2.22 \times 10^{-13}$ cm, respectively. By mixing isotopes with different ratios, the average scattering amplitude can be varied from -2.22×10^{-13} to 2×10^{-13} cm.

As outlined in Table 12.2, when lithium is replaced with lithium 6, the scattering amplitude of the lithium site varies greatly from negative to positive, and by adjusting the ratio of lithium 6 to lithium 7, the scattering from the site can be reduced or zero.

Table 12.2 Average scattering amplitude b^* at Wyckoff positions in LiMn_2O_4 and $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$.

(a) LiMn_2O_4					
site	x	y	z	Atom	b^*
8a	1/8	1/8	1/8	Li	-1.90
				^6Li	2
				$0.5\ ^7\text{Li} + 0.5\ ^6\text{Li}$	-0.11
16d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	Mn	-3.73
32e	0.2627	$= x$ (32e)	$= x$ (32e)	O	5.805
(b) $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$					
3a	0	0	0	$0.975\ \text{Li} + 0.025\ \text{Ni}$	-1.60
				$0.975\ ^6\text{Li} + 0.025\ \text{Ni}$	2.2
				$0.975\ (0.5\ ^7\text{Li} + 0.5\ ^6\text{Li}) +$ $0.025\ \text{Ni}$	0.15
				$1/3\text{Mn} + 1/3\text{Co} +$ $0.309\text{Ni} + 0.025\text{Li}$	2.73
3b	0	0	$\frac{1}{2}$	$1/3\text{Mn} + 1/3\text{Co} + 0.309\text{Ni} +$ $0.025\ ^6\text{Li}$	2.82
				$1/3\text{Mn} + 1/3\text{Co} + 0.309\text{Ni} +$ $0.025(0.5\ ^7\text{Li} + 0.5\ ^6\text{Li})$	2.77
6c	0	0	0.241	O	5.805

In the Rietveld analysis program Z-Rietveld, complex ion distributions can be determined by analyzing multiple data with different isotope ratios simultaneously with the same crystal structure model. For example, in the case of (Li, Ni) (Mn, Co, Ni, Li) O₂, occupancy information can be retrieved by performing measurements on multiple samples of $(1-x)$ ⁶Li + x ⁷Li with different x and analyzing the obtained multiple data with a same structural model.

Isotopes can also be used as labeling and tracer. For example, by using different isotopes for the positive electrode, the negative electrode, and the electrolyte, it is also possible to know how lithium moves before and after the charge/discharge reaction. Combining isotopes with various techniques in this way will be effective in future structural analysis of battery materials.

12.5.4 Operando neutron diffraction of batteries

The functional materials that make up a device exhibit their properties in response to changes in external conditions, resulting in the functioning of the device as a whole. Improving the properties of functional materials is directly linked to improving the performance of the device. However, it is not possible to maximize the performance of the device only by the optimum combination of constituent materials. Therefore it is necessary to detect how the constituent materials change during the operation of the device, that is, the operando study. Here, we think about a battery as a device.

Since neutrons have no charge, they can enter batteries deeply without being disturbed by the coulomb force. This means it is possible to observe changes in an atomic arrangement under operating conditions without dismantling the actual battery [31,32]. Fig. 12.15 is a result of an operando neutron diffraction measurement while actually discharging a commercially available battery. This operando neutron diffraction combined with the structure analysis makes it possible to precisely compare and verify the structure change in atomic level in relation to the discharging reaction.

Finally, it is worth comparing the advantages and disadvantages of a neutron with laboratory/SR X-ray in the operando diffraction measurements as well as the reliability of their data analysis [32–35]. Using a laboratory X-ray diffractometer with CuK α radiation (8 keV), the X-ray penetration is limited to several tens of micrometer. Since the real battery with steel casings cannot be used, specially designed batteries should be used. Then, the result can be compared with that of a real battery.

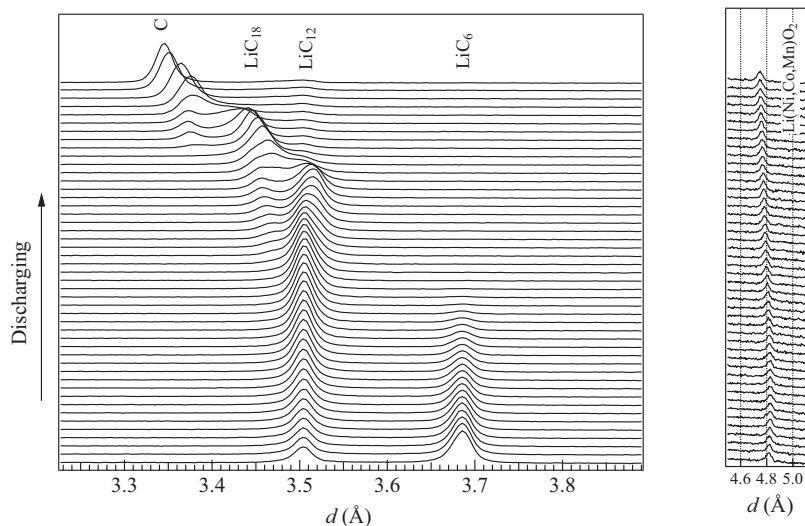


Figure 12.15 Neutron operando diffraction measurement during discharging. From the Rietveld analyses of the operando data, we can elucidate how Lithium atoms are extracted from the anode and enter the cathode, and how the anode and the cathode structures change during discharging with reasonable precision of Lithium occupancies.

Using synchrotron X-ray with $\lambda = 0.44 \text{ \AA}$ (28 keV), only 1% X-ray will be transmitted through the 0.26 mm thick steel casings of commercial 18,650 batteries, which makes it difficult to extract quantitative information [32]. The high-energy synchrotron X-ray with $\lambda = 0.108 \text{ \AA}$ (115 keV) is most probable, with higher spatial resolution and more rapid charging/discharging conditions than neutron [35]. But, Bragg intensities suffer from poor grain averaging, and information of Li atoms is relatively less than a neutron.

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CHAPTER 13

Raman spectroscopy—part one

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13.1 Introduction

13.1.1 Theory and basic principle of Raman spectroscopy

The Raman phenomenon was first reported by K. S. Krishna and C. V. Raman in 1928 [1]. C. V. Raman received the Nobel prize in physics in 1930 for the discovery. When monochromatic light with frequency ν_0 was illuminated to samples, most scattered light maintains its frequency (energy). However, a small portion of the light is scattered with shifted frequency. When scattered light is red-shifted (energy loses during the scattering), it is called Stokes Raman. When scattered is blue-shifted (energy gain during the scattering), it is called anti-Stokes Raman. Stokes Raman intensity is stronger than anti-Stokes Raman except low-wavenumber regions near zero Raman shift. Energy loss/gain correspond to vibrational transition. By analyzing the shift and intensity, the chemical composition of the sample can be performed. For the next 50 years after the discovery, Raman spectroscopy had been considered a laboratory technique with bulky and expensive instruments for limited applications. Raman research were focused on the investigation of physical phenomena while the most recent Raman research are focusing on chemical analysis. The limited application of Raman spectroscopy was due to fundamental issues such as intrinsically weak Raman signal from small Raman cross section (Raman conversion efficiency) and dominant fluorescence background signal (especially from nontransparent samples).

Inelastic Raman scattering has the same energy range as infrared (IR) absorption spectroscopy. The vibrational information from Raman and

IR absorption measurements are similar. However, the Raman signal is several orders of magnitude weaker than the strong absorption signal, which has been one of the fundamental issues for wide spread application of Raman spectroscopy. With advancing electronic detector technology, this intrinsically weak Raman signal became detectable. Charge-coupled devices (CCDs) with dispersive spectrographs significantly improved signal-to-noise ratio (SNR). Further, bright imaging spectrographs with low f-number enabled parallel measurements from multiple sample locations with high sensitivity. Another practical issue for Raman spectroscopy is the unwanted background signal. Strong fluorescence signal from sample or impurities and associated noise level frequently dominates weak Raman signal on top of the background. Raman spectroscopy experiments were mostly performed using a bulky light source in the visible range such as an Argon-ion laser. For example, the Raman spectrum from the skin includes small Raman peaks from collagen and fat on top of strong tissue autofluorescence signals mostly from melanin. Often, many small Raman peaks are not visible due to the shot noise from the background. Therefore, how to detect a weak Raman signal with an existing fluorescence signal has been a practical concern. The development of compact near infrared (NIR) diode lasers including Nd:YAG laser (1064 nm) and Al:GaAs (790–900 nm) solved much of the issue. Raman intensities decrease with longer wavelength (λ^{-4}) but fluorescence signal decreases faster for most samples as many fluorophores are not excited by low energy NIR photons. Availability of NIR diode lasers widely opened new applications including biomedical Raman spectroscopy. Technical advances in optical fibers and optical filters helped wide spread usage of Raman spectroscopy, too. Unlike Fourier Transform infra-red (FTIR) measurements, most Raman spectroscopy uses visible-to-NIR excitation/collection. This wavelength region can harness advanced optical fiber technology. Sensing through optical fiber enabled remote sensing from distant locations, in-situ monitoring during the biochemical process, and in-vivo sensing from inside the human body. Suppressing excitation light has been another technical challenge for Raman spectroscopy as Rayleigh light is several orders stronger than inelastically scattered Raman light. Bulky monochromators have been used to separate Rayleigh light from Raman measurement. Advanced filter technology including holographic notch filters and multilayer dielectric filters effectively rejected Rayleigh light and removed traditional monochromators from Raman instrument. This reduced the cost and size of the Raman system. Another key

component is the development of compact computer systems. Modern Raman instruments are controlled and analyzed by a computer. Fortunately, the advance of computer technology allowed easy access to computing power and storage without much cost. This also helped develop sophisticated chemometric analysis.

Combined advances in NIR laser, CCD detector, optical filters, optical fibers, and powerful low-cost computers helped to bring Raman spectroscopy to real world applications 50 years after its discovery. Integrated compact Raman system is becoming popular and attracts researchers without optics background. Improving individual components such as compact turn-key laser, miniature Raman optical fiber sensor, and more sensitive CCD are happening in parallel and will only help the more wide spread of the Raman technology in the future.

13.1.1.1 Comparison with other analytical techniques non-destructive characterization of materials

In the case of non-destructive testing, the measurement of a functionality, a property, a value of a component of the material, or a technique sensitive to the property or the value to be measured is then required. This technique has to be fast to be compatible either with specific medical constraints or simply with industrial times (a few seconds) of the monitoring of the considered process (specific characteristic of a material, pollutant concentration into the environment, or industrial process). It has to be sufficiently sensitive to the value to be measured or analyzed (desired or desired precision of the measurement) too.

Due to recent technological innovations, vibrational spectroscopies, and in particular Raman spectroscopy, are excellent candidates for non-destructive techniques applications. But this still sometimes requires learning and often correlations with other analytical techniques. In this context, chemometric (statistical) methods do have an important contribution, necessary, and significant innovation, allowing the development of these non-destructive techniques. A theoretical approach of non-destructive characterization of materials based on Raman spectroscopy cannot be built considering the wide panel of situations (analysis on the surface or into the bulk material, liquid or solid state, the maximum allowed or possible duration of the control, threshold detection, specific configuration of the Raman probe, heterogeneity in material composition). The Raman non-destructive characterization of material could be then considered through a progressive approach. The first step will consist of measurement to identify a peak characteristic of a chemical bond

or specie justifying a control. A second step will allow to establishment of a relationship between collected Raman spectra and a specific physical characteristic. A control could also be considered on an extended area, and Raman imaging is a solution to generate a hyper-spectral cube to identify to what extent a chemical specie or a physical characteristic has evolved over a given investigated zone. If the previous situations do involve bringing the sample to a Raman spectrometer, some situations do need to bring the spectrometer to the field to perform measurements, raising additional constraints (ambient light, compliance of the Raman probe with measurements conditions, information collected over a given distance in the case of mobile measurements).

The main technical and technological innovations that allow the use of Raman spectroscopy in this context are the following ones [2]:

1. Lasers and in particular the new powerful laser diodes (a few hundred mW), and very stable in the near-infrared wavelengths which often allows getting rid of the effects of fluorescence (or photoluminescence) of the materials.
2. Adapted rejection filters (Notch and Edge) to reduce the size of spectrometers and promote the detection of weak signals.
3. CCD and other detectors are more and more efficient, improving the signal to noise ratio, and affordable, allowing to obtain cost-effective spectrometers.
4. Chemometrics tools are sometimes freely available and are now present in many commercial spectrometers software.

In the following table, advantages, limits, and some recommendations are presented for the use of Raman spectroscopy in the non-destructive characterization of materials. (Table 13.1).

Many other details can be deduced from a Raman spectrum of a material. Indeed, the variations of positions or the presence of peaks can be used to identify a substance. Table 13.2, summarizes some information that can be deduced from Raman spectra.

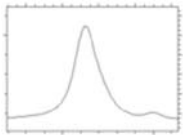
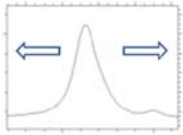
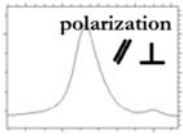
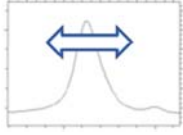
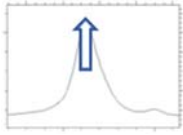
To illustrate the elements in Table 13.2, an example can be considered. It consists in monitoring two very important properties of polymer material in the framework of the followup of their mechanical behavior or molecular orientation for example, useful in the case of crash tests. Thus the two properties to be followed in an in-situ way are the rate of crystallinity and the rate of molecular orientation. The requests or requirements a sensor must then meet for a non-destructive followup are that it

Table 13.1 Advantages and limits of Raman spectroscopy as a non-destructive characterization of materials.

Advantages	Limits
Structural and chemical information • Configuration (amorphous or crystal, and the ones of some crystals) • Effect of stress • Composition • Crystallinity • Fast ($\approx 1-60$ s) • Transportable, possibility to perform on-line measurements Easy to use for monitoring industrial processes	Weakness of the Raman signal with only $1/10^7$ to $1/10^6$ of Rayleigh scattering
Non-destructive, noninvasive	Intense laser power can cause damage on studied material depending on its absorption of the laser wavelength • Fluorescence • Ability to change the wavelength of the laser to reduce or attenuate its effects • Difficult interpretation of the Raman spectra • Overlap of Raman peaks of different chemical bonds • Number of chemical bonds, increasing the risk of an overlap • Geometry, symmetry of some vibrational units, with necessity to implement polarizers
Possibility of measurements in hostile environments through windows or containers	Daylight or ambient can affect the measurement, although modeling of this light is still possible to remove it from the spectrum
No preparation of samples (no need to collect samples, no polishing, or drying)	
Possibility of remote measurement with optical fibers up to 200 m long with adequate quality Variety of probes configurations (immersion and noncontact several tens of cm)	

must obviously be non-destructive, fast, effective to monitor the chosen property, and cost-effective. A comparison with some usual analytical techniques to follow these two properties is detailed in [Table 13.3](#), with respect to several criteria. Considering X-ray diffraction as a reference,

Table 13.2 Information deduced from a Raman spectrum of a material.

Illustration of the spectrum, or of spectrum modification	Modification in the spectrum	Extracted information	Application to non-destructive characterization
	Raman shift position of the peak maximum intensity	Nature of the chemical bond, material chemical composition	Material composition, crystallinity [3]
	Change in the Raman shift position of the maximum peak intensity	Stresses, strains	Mechanical properties, doping structure [3–6]
	Polarization effects of Raman peaks	Symmetries, orientations	Orientations of molecular chains flow of a fluid [7]
	Broadening of Raman peak	Structural disorder	Presence of defects, identification of the nature of the defects [5,8]
	Raman peak intensity, ratio of Raman peaks intensities	Determination of the amount of a substance	Composition, determination of a mixture presence [7]

although it is not as cost-effective as some other techniques, is not miniaturized, and needs safety measures with respect to X-ray radiation, Raman spectroscopy meets all criteria. It has taken benefits of new technological innovations, especially in recent years. It is still recommended to obtain a correlation with one or more other conventional analytical techniques, in particular, to elaborate an important learning phase. It will then be possible to correctly monitor the property or phenomenon, through the development of statistical techniques to correlate with these conventional techniques and then generate a predictive model [9].

Table 13.3 Comparison between Raman spectroscopy with some other analytical techniques with respect to some selected criteria for materials characterization.

	Microstructural information	Selected criteria for materials characterization				
	Crystallinity rate	Molecular orientation	Non-destructivity	Measurement duration	Convenience compactness	Cost-effectiveness
Conventional analytical techniques						
Xray diffraction						
Calorimetry/dilatometry						
Thermogravimetric analysis						
Optical microscopy						
Scanning electron microscopy, transmission electron microscopy						
Near-field microscopy						
Birefringence measurements						
Infrared spectroscopy						
Raman microscopy						
	Good		Neutral		Poor	

13.1.1.2 *Chemometrics inputs and benefits in Raman spectra analysis*

As with many other analytical techniques, Raman spectroscopy is generating large amounts of data and has many variables, that is the wavenumbers or Raman shifts. Multivariate data analysis, also called chemometrics, is an appropriate method to identify signal differences and singularities in large data sets. Chemometrics is the science that applies and develops mathematical and statistical methods to design or select optimal measurement procedures and experiments but also to provide a better characterization, modeling, and understanding of reaction systems and/or complex samples [10,11]. It brings thus together the design of experiments and data analysis. Until recently, it was still difficult to exploit a very large amount of data from materials characterizations by different analytical techniques due to its heterogeneous and multiscale nature. This obstacle, which seemed insurmountable, is in fact a real asset.

It is in this context that the term chemometrics was first introduced in 1972 by the Swedish physical organic chemist, Svante Wold when submitting a grant application. Afterward, a few years later, he joined the American analytical chemist Bruce R. Kowalski to establish the International Chemometrics Society (ICS) [12,13]. The objective was to lay foundations of a new discipline in chemistry to acquire a more detailed knowledge of complex samples that may have proteiform data. Since then, this science continues to grow and is widely applied to different fields of chemistry, especially analytical chemistry. Of course, in the 1970s, some analytical groups were already working with mathematical tools on mainframe computers which are ascribed nowadays to chemometrics [14]. The development of this discipline is strongly related to the use of computers in chemistry. That is why, in the 1980s, the emergence of personal computers has allowed a new age for the acquisition, processing, and interpretation of chemical data. In the 1990s, advances in computing gave industries and research centers the opportunity to generate data at a relatively low economic cost, in particular with regard to the pharmaceutical industry (R. G. Brereton, n.d.). Modern instruments can now automatically generate large amounts of data, and in a very short period of time, in particular, to continuously monitor a chemical process on a material or simply after the spectral mapping of a given area. Data complexity is always higher and will be more so with the advent of big data. The interpretation of this dataset will then require the use of advanced mathematical approaches to extract the most relevant information from it in physicochemical.

To reach this goal, Chemometrics includes then several fundamental approaches from mathematics: reduction in dimension of data, classification methods [15,16], multivariate data analysis [17,18], modeling [19,20], prediction [21,22] and topology [23,24]. All of these methods cannot be used anytime, anyhow. Beyond the fact that the chemometricians aim to develop complex mathematical aspects in order to make their use more practicable, or even simple, it is important to focus on the scientific method. Indeed, data analysis is first and foremost dictated by experience (the way the data comes from). The Fig. 13.1 presents the chemometrics approach from data acquisition to interpretation. It is important to formalize the experiments needed to save time and to have the lowest possible economic costs. Thus, the amount of data as well as its nature may vary. In analytical chemistry, data obtained from multiple sources is frequently encountered to solve a scientific question [25,26]. The dataset is called a multiblock one due to the fact that it comes from a multiplatform analysis of the same sample. Unlike the single block (or single mode), the data is not simply multivariate but is also multimodal that is multivariate and multisource. An example of this would be data generated by two different spectroscopic techniques, like Raman spectroscopy and mid-infrared (MIR) spectroscopy from the same sample. However, multimodal data can also be obtained when working under different conditions, like for an industrial process with multiple batches, that is different processing conditions [26]. In the case of multiblock data, traditional chemometric

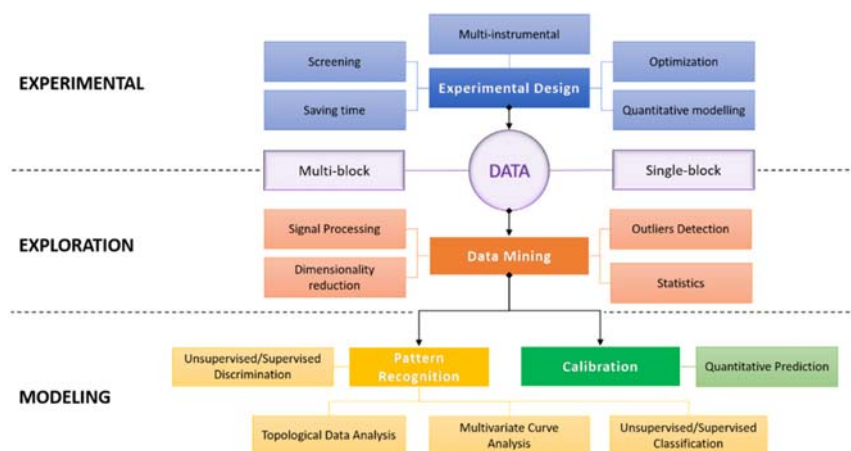


Figure 13.1 Chemometrics summary in three main sections for a given scientific question in analytical chemistry: experimental, exploration, and modeling.

approaches from single blocks, such as principal component analysis (PCA) [27], partial least squares (PLS) regression [28], etc., will extract only a limited part of the information present in the data [26]. Indeed, even if the mathematical methods differ between multi- or single-block, the objectives of the exploration and modeling sections remain the same.

In this book chapter, the data analyzed are single blocks in Raman spectroscopy for non-destructive material characterization. The first thing to do is therefore to explore the Raman data in order to identify and remove the effects of unwanted signals. A typical issue known in Raman spectroscopy is that spikes can appear in the Raman signal. Indeed, spikes are defined as high-energy cosmic rays that impact the CCD detector used to collect Raman photons. The signal of a spike is positive and very narrow bandwidth peaks at random positions on the spectrum. These spikes are problematic as they might hinder subsequent analysis, particularly if multivariate data analysis is required. Therefore one of the first steps in the preprocessing of Raman spectra is their removal. To do this, different strategies can be used. For example, different PCA can be applied to locate spikes contaminated spectra [29,30]. Once they are spotted, it is possible to replace the spectrum found with the median or the mean between the spectrum acquired on the time before and after. If it is Raman imaging, the median or the mean of the surrounding pixels can be also used. There are also preprocessing approaches to correct them directly on the Raman signals with the use of dedicated filters [31,32]. However, like any correction, it may not be perfect and induce weak false chemical contributions that may affect the chemical interpretation (especially in self-modeling curve resolution in pattern recognition).

The second preprocessing is to correct the baselines which can change from spectrum to spectrum with intense and irregularity shaped. In Raman spectroscopy, the intense background is commonly associated with fluorescence contributions. It is a real challenge in Raman spectroscopy because it is an inherent phenomenon (especially for biological samples). The fluorescence background is often many times more intense than the weak Raman signals. Also, ambient light and detector thermal noise may contribute to the background [33]. Therefore various approaches can be applied in order to remove or at least reduce the influence of this interference and then, extract the least biased information Raman signals from each raw spectrum.

1. Polynomial fitting based methods: This is by far the most commonly used approach for baseline removal on a signal. The objective of

Raman spectroscopy is to choose certain points in the spectrum identified as baseline points and a polynomial is fitted through these points. Then, this polynomial is subsequently subtracted from the raw Raman signal [34]. On a simple Raman signal, typically a spectrum without fluorescence, a straight line fit through a couple of points could be sufficient enough whereas a complex Raman signal could need many base point selections with a high order polynomial at the risk of being inconsistent [35].

2. Asymmetric least square based methods: The algorithm was originally proposed by Eilers et al. to subtract shifts in chromatography. It is based on a recursive local fitting of the entire spectrum with a baseline obtained by using Whittaker smoother [36,37]. In other words, a smoothed signal is estimated from a given raw Raman signal as a baseline. The corrected Raman signal is deduced iteratively by the residual signal between the raw Raman signal and the estimated baseline. The ordinary least square method is used for this with an objective function defined to have a bias toward positive residual errors. This preprocessing is fast even for complex signals, requires fewer parameters, and is really effective for Raman spectra [33].
3. Differentiation based methods: Generally, the vertical offsets and linearly sloping baselines are removed with the 1st or 2nd derivatives. However, it is important to do a smooth after-differentiation. Indeed, the baseline has broad bands and low-frequency components compared with genuine Raman bands. The differentiation of the raw signal Raman amplifies higher frequency components and suppresses lower frequency. As a consequence, the fluorescence background is suppressed whereas, the noise present in the raw Raman signal is also enhanced with the Raman bands. To do this, one of the most commonly used methods is called the Savitzky–Golay (SG) filter [38].
4. Frequency domain analysis: As discussed above, the baseline is the low frequency component of the raw Raman spectrum compared to Raman bands. As a consequence, the Raman spectrum is considered here as a time series of frequencies (Raman shifts) and the objective of these methods is to separate the relevant underlying Raman shifts from frequencies analysis. To do that, different methods exist like the Fourier Transform (FT) or the Wavelet transform (WT) based [12,39–41].

Once the interferences observed on the Raman spectra are corrected or even removed, it is important to proceed to a normalization step as a preprocessing. Indeed, different Raman spectra of the same sample may

have been recorded at different times and/or under different instrumental conditions such as laser alignment, power levels, or in imaging a slight defocus (in other words an overall scaling or gain effects). The objective of the normalization is thus to consider the disparity observed in intensity levels due to slightly different experimental conditions. In the literature, there are numerous normalization techniques available, and here presented some of them.

1. **Min-max normalization:** It is one of the simplest and most common normalizations. Indeed, the maximum and the minimum values of all intensities of a given spectrum noted here are calculated. Then, each Raman intensity is subtracted from the minimum and divided by the range between the minimum and maximum:

$$x_{\text{inew}} = \frac{(x_i - x_{\min})}{(x_{\max} - x_{\min})} \quad (13.1)$$

In this case, the relationship between the original and the normalized data is still linear. All the normalized data are between 0 and 1 [42].

2. **Z-score normalization:** The preprocessing data are conforming to the normal distribution that the average and standard deviation respectively are 0 and 1 [42]. This method is also called standardization and the mathematical expression is as follows:

$$x_{ij}^{\text{new}} = \frac{x_{ij} - \mu}{\sigma} \quad (13.2)$$

The average and the standard deviation are calculated with the values from the spectra.

3. **Metrics based normalization:** The normalized preprocessing method calculates one of several metrics using all the selected variables of each

sample, as the L1-Norm $w_i = \sum_{j=1}^n |x_{ij}|$ (it returns a vector with unit area) or the L2-Norm $w_i = \sqrt{\sum_{j=1}^n x_{ij}^2}$ (it returns a vector with unit

length).

4. **Standard Normal Variate (SNV) Normalization:** The SNV transformation was introduced by Barnes et al. [43] to reduce the multiplicative effects of scattering and particle size, and also to reduce differences in

the global intensities of the signals [44]. Each spectrum is centered and then scaled by dividing by its standard deviation.

$$x_{ij}^{\text{SNV}} = \frac{(x_{ij} - \bar{x}_i)}{\sqrt{\frac{\sum_{j=1}^n (x_{ij} - \bar{x}_i)^2}{p-1}}} \quad (13.3)$$

x_{ij}^{SNV} is the element of the transformed spectrum and x_{ij} is the corresponding original element of the spectrum i at j , $\bar{x}_i$ is the average of spectrum i , and p is the number of Raman shifts variables in the spectrum. SNV normalization is a weighted one (i.e., not all point contributes to the normalization equally). Furthermore, it is possible to correct an offset. Indeed, the user-defined offset can be used to avoid over-normalization samples with a standard deviation near zero. The mathematical expression is then [43]:

$$x_{ij}^{\text{SNV}} = \frac{(x_{ij} - \bar{x}_i)}{\sqrt{\frac{\sum_{j=1}^n (x_{ij} - \bar{x}_i)^2}{p-1} + \delta^{-1}}} \quad (13.4)$$

δ is a user-definable offset. SNV normalization should be carefully compared to other normalization methods for quantitative models.

1. **Multiplicative signal correction (MSC) normalization:** MSC is also a common technique for correcting additive and multiplicative scattering effects observed on the baseline [45,46]. The objective is to model each spectrum as a linear combination of a reference spectrum, having undergone an additive effect and a multiplicative effect. The reference spectrum is generally the average spectrum of the data set, but the median can also be used. The idea is that this reference spectrum best represents the optical path:

$$x_{\text{mc}} = x - \bar{x} \quad (13.5)$$

$$r_{\text{mc}} = r_{\text{median}} - \bar{r}_{\text{median}} \quad (13.6)$$

Then, the unknown multiplicative factor (i.e. slope) is determined using the following equations:

$$r_{\text{mc}} b = x_{\text{mc}} \quad (13.7)$$

$$b = (r_{\text{mc}}^T r_{\text{mc}})^{-1} r_{\text{mc}}^T x_{\text{mc}} \quad (13.8)$$

The corrected spectrum $\hat{x}$ is then calculated by this final equation:

$$\hat{x} = \frac{x_{mc}}{b} + \bar{r}_{median} \quad (13.9)$$

Note that there is also the extended MSC called EMSC [33]. But, in the EMSC model, a polynomial is also included along with the MSC and it is used for a baseline correction. Generally, it is a second order polynomial but one can choose to include a higher order polynomial if required.

Once the spectra are corrected, it is always interesting to explore the new preprocessed dataset in order to check if the various corrections have worked correctly or if there are still outliers. Indeed, it is extremely important to omit these spectra before applying a pattern recognition or a calibration approach to get desired results in the modeling step (Fig. 13.1). The elements described above will be used in the different situations described below, from Raman spectra collected during a chemical reaction process, or a Raman image up to field measurements.

13.2 Immersion in turbid media and reactive media

Many situations do involve reactive and turbid media where reaching information about the chemical reactions taking place is difficult to apprehend. The development of specific Raman probes eases access to these media when collecting the sample is either difficult if not dangerous, or simply when it will not allow us to reach the knowledge on the physicochemical processes at stake. Such a configuration for non-destructive characterization implies facing some specific challenges and coping with some difficulties among which respectively signal to noise ratio, fluorescence, the dimension of the Raman probe, and the preservation of its integrity, media heterogeneity, and threshold detection. Two situations will illustrate the way relevant and decisive pieces of information were obtained through a non-destructive characterization by Raman measurements, along with chemometrics tools. The first one is related to the pollutant biodegradation of fluorinated molecules in an environmental matrix, while the second deals with cementitious materials.

13.2.1 Pollutant biodegradation

Anthropogenic water and soil pollution is extensively discussed in the literature, along with the biodegradation of anthropogenic pollutants and their effects on the environment. Specific literature is dedicated to fluorinated aliphatic molecules used as surfactants in fire-fighting foams, as reported by

Marchetti et al. [47], considered toxic according to the literature with questions about their environmental impact. In airports, fire-fighting foams, contain fluorinated molecules in order to smother the fire and its extinguishment. But because of environmental concerns, it becomes mandatory to both characterize these molecules and their biodegradation in a non-destructive way, and Raman spectroscopy appeared as the appropriate method [48]. An OECD protocol [49] is usually implemented to characterize the environmental fate, considering the fluorinated molecule is the only source of dissolved organic carbon in the environmental matrix. Considering a fire-fighting foam is a mixture of at least two organic components (ethylene glycol 2-(2-butoxy ethoxy) ethanol and fluorinated ether molecules), this sole OECD protocol is unable to properly characterize the degradation of the fluorinated ether, and the kinetics of this biodegradation. The implementation of Raman spectroscopy into the OECD protocol will then enable the specific detection of fluorinated bonds (Table 13.4), a fire-fighting foam having a specific Raman signature (Fig. 13.2) due to strongly polarized C-F bond. If the OECD protocol needed sample collection at specific moments, a Raman continuous monitoring with an immersion probe avoided such constraints, and allowed almost continuous monitoring of the environmental fate of the fire-fighting fluid during 28 consecutive days, with a 30-s-integration time and a 15-min-interval between each

Table 13.4 Raman shift of chemical bonds of a fire-fighting fluid in the 400–1500/
cm spectral range.

Raman shift (cm)	Vibration type
530	C–F deformation
765	C–F deformation vibration in aliphatic monofluorinated compounds, C–F scissor
830	Symmetric stretch C–O–C C–F deformation
800–990	CH ₂ rocking
990–1110	C–F stretch in CH ₂ F aliphatic monofluorinated compound
1000–1110	Aliphatic monofluorinated compound CH ₂ F with C–F stretch and CH ₂ rocking
1040–1060	C–F stretch on aliphatic difluorinated compound
1050–1250	Aliphatic difluorinated compounds C–F stretch
1130	Asymmetric stretch C–O–C C–F stretch
1300	CF ₃ attached to an alkyl group CF ₃ attached to an aromatic group
1450	CH ₂ vibration of deformation

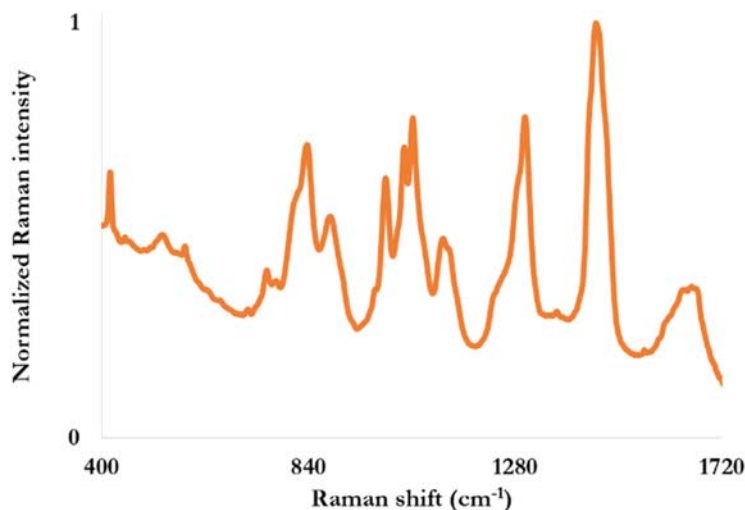


Figure 13.2 Normalized Raman spectrum of a pristine fire-fighting fluid constituted of a fluorinated ether (laser 785 nm, 30 s integration time) obtained with an immersion probe.

Raman spectrum. A large number of collected Raman spectra in a non-destructive way is significantly greater to properly and accurately describe this 28-day-long biodegradation process than the 15 measurements conventionally required by the current OECD protocol. The monitoring is performed on two reactors dedicated to the biodegradation, one containing the fire-fighting fluid, and a second without, the fluid both being turbid and almost black, and generating significant light diffusion and fluorescence. The probes were designed to cope with aggressive environments, with a stainless-steel body and a sapphire lens.

Furthermore, because of the involved volumes, the concentration of fire-fighting foam in the reactor is 1% v/v. Considering the number of Raman spectra, a principal components analysis was performed on this data set, revealing a structure illustrated in Fig. 13.3. In this scores' plot, data points from the biodegradation reactor without the fire-fighting still are grouped, while the ones from spectroscopic measurements in the biodegradation reactor with the fire-fighting fluid pure are dispersed and did converge towards the ones of the other reactor, without reaching them. Therefore this non-destructive characterization by Raman spectroscopy did indicate the biodegradation of the fluorinated molecules contained in the fire-fighting fluid is not complete.

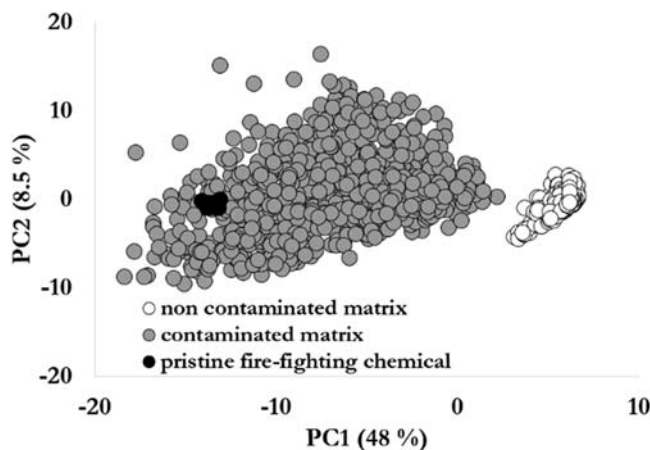


Figure 13.3 Scores plot for the first two principal components for a PCA conducted on Raman spectra (after baseline and Singular Normal Variate (SNV) corrections) from reactors without and with fire-fighting fluid during the 28-day biodegradation process, obtained with an immersion probe.

13.2.1.1 *Setting of cement paste and carbonation of cementitious materials*

If the previous situation involved a diffusive fluid, this one is occurring in a complex matrix evolving from a viscous reactive paste to a solid mixture of several materials and phases. Cementitious materials and other ones used in civil engineering represent a tremendous proportion of the ones encountered in the buildings and infrastructures construction. About 4.1 billion tons of cement were produced in 2019 [50], with cement only representing 12%–15% of the concrete mass. The water adjunction to cement powders constituted of tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$, dicalcium silicate $2\text{CaO} \cdot \text{SiO}_2$, tricalcium aluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and tetracalcium aluminoferrite $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ causes several chemical reactions [51–55]. Many analytical techniques allow the monitoring of this hydration process (TGA, SEM, TEM, NMR, DSC ...). Their destructive aspect with respect to samples is among their main criticisms. Haque et al. [56] quoted other analytical techniques, including non-destructive ones, among which Raman spectroscopy, though not presented from a favorable standpoint. The hydration process of cement was also specifically investigated by this technique, as summarized by Marchetti et al. The literature reported the use of green (514, 532 nm), red (633 nm), or near infrared (785, 1064 nm) lasers. Measurements were mostly conducted

at the sample surface, raising questions about the impact of carbonation. The setting stage is differently investigated according to the literature, from its earliest part to a few days and up to nearly a year. In the cases of studies related to early stage setting, only Zhang et al. [57] and Martinez-Ramirez et al. [58] investigated the process at a timestep in the 5–10-minute range. The results presented in these articles do rely on high-performance Raman spectrometers, while interesting results on civil engineering materials can be obtained with a portable instrument [59,60]. As a consequence, the hydration reaction of a cement paste is only described either by destructive and long analytical techniques or by surface spectroscopic measurements not providing in detail the evolution of the different present phases, which are presented through their detection, not through a qualitative evolution of their concentration. To do so, a Raman probe has to be inserted into a cement paste, and Raman spectra collected while the chemical process (hydration, carbonation, or external sulfatic attack as possible examples), as illustrated in Fig. 13.4. The probe aim is then to detect the chemical change in the material and therefore the occurrence of an interface between pristine and modified materials., this interface either being a conventional interface or a critical zone to be detected to trigger an alert.

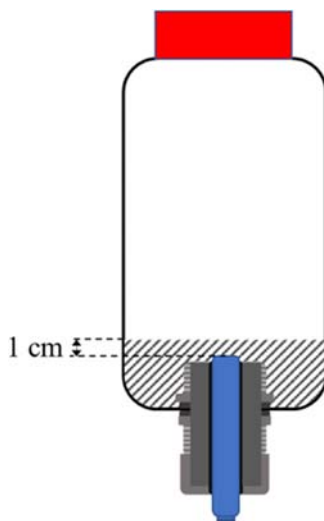


Figure 13.4 Experimental set-up to monitor its hydration reaction and to identify the chemical reactions at stake during 28 days with the insertion of a 785 nm non-contact Raman probe in a cement paste sample, 1 cm below its surface.

In this specific case, spectroscopic measurements are not affected by any ambient light, the Raman probe being immersed within studied materials. Raman spectra of the cement paste during the hydration phase do indicate the chemical evolution of the material along the process. Similar evolutions are easily observable in the case of carbonated Portlandite (Fig. 13.5). In both cases, the Raman probe was located below the surface, into the bulk materials, covered with a glass tube not presenting any absorption nor Raman fingerprint at the selected laser wavelength, only generating some signal attenuation. Baseline and spikes corrections were needed in this non-destructive evaluation of civil engineering materials to cope with their fluorescence. Raman spectroscopy was again perfectly adapted to characterize the materials without any alteration. It's coupling with chemometrics methods was also the opportunity to spectroscopically identify the different steps of both hydration and carbonation reactions of these cementitious materials. As illustrated in Fig. 13.6 with the carbonation process of a cementitious material, the scores plot of a PCA on obtained Raman spectra do show the chemical evolution this non-destructive spectroscopic approach provided.

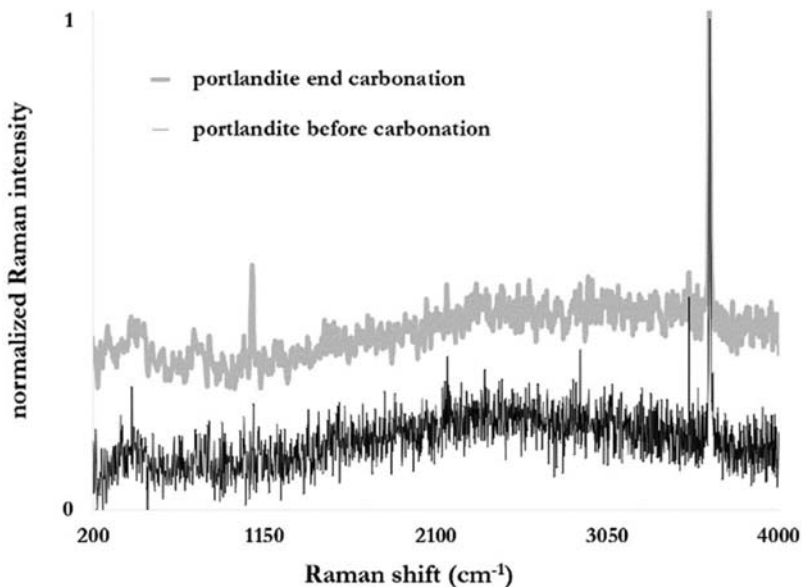


Figure 13.5 Raman spectra of compacted Portlandite powder before and after a carbonation process in a 4%-CO₂ enriched atmosphere, obtained with a 785 nm without contact Raman probe, located 4 mm below the surface into the bulk material.

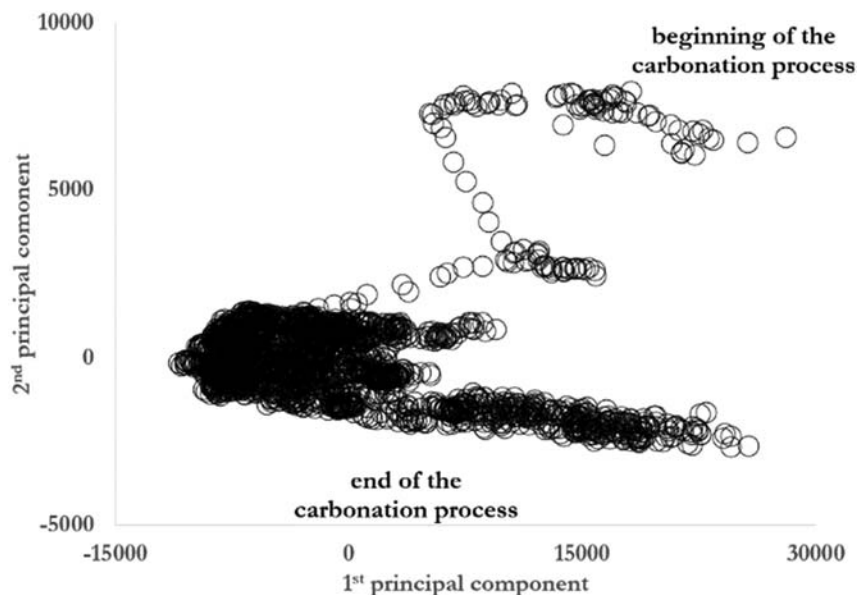


Figure 13.6 Scores plot after a PCA conducted on Raman spectra obtained during a carbonation process of a cementitious material (4% CO₂-enriched atmosphere, 532 nm laser, the integration time of 10 s, data acquisition every 30 s during nearly 14 days).

13.3 Conclusion

Raman spectroscopy is an evolving technique, in particular, due to technological innovations such as lasers, more and more efficient and sensitive detectors, and rejection filters. Thus this technique is increasingly appropriate for in situ monitoring of materials and in particular for non-destructive characterization of materials. In this chapter, a few scientific domains were presented where Raman spectroscopy was successfully implemented for non-destructive purposes. There were differences in environment, and civil engineering. The difference also concerned materials, mainly in their solid or liquid state, from turbid aqueous solutions to inorganic materials for different types of applications. Raman spectroscopy as a non-destructive technique was used here to monitor a specific chemical bond, characteristic of a material, so as to detect given chemical species in a turbid or a reactive media through continuous monitoring of some specific spectral band, or the growth a given spectral peak, synonymous of the occurrence of another compound not initially present in the studied matrix. This non-destructive spectroscopic approach was implemented to

avoid a tedious collection of samples when it is neither impossible nor cost-effective or simply poorly adapted to obtain a proper characterization of the studied system. Most common characteristics of Raman spectroscopy such as the absence of any material preparation, the need for a small amount of material, and fast measurements definitely appeared as the main advantages of such an approach with respect to some other analytical techniques (thermogravimetric analysis, SEM, LIBS ...). The kinetics of a chemical alteration, the identification of the interface before a critical zone could be directly identified, overtaking difficulties of ambient light, managing the fluorescence, or improving the signal to noise ratio. Immersion Raman probes have opened larger applications' contexts, avoiding a destructive step when again the necessity to collect samples from the bulk materials comes. In addition to these hardware evolutions, algorithmic developments allowed to removal of fluorescence artifacts, to improve signal to noise ratio. It's coupling with chemometrics methods provided tremendous benefits when numerous Raman spectra are collected. These methods eased the detection of unseen spectral variations when dealing with complex or heterogeneous media. In conclusion, Raman spectroscopy appeared as an efficient, accurate, able to discriminate materials, non-destructive method to characterize them, that can be considered as a reference method through standardized protocols.

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CHAPTER 14

Raman spectroscopy—part two

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14.1 Introduction

A previous chapter dedicated to Raman spectroscopy implemented for non-destructive purposes showed the benefits of the analysis of peaks at given Raman shifts. It presented the benefits of this spectroscopic approach with respect to other analytical techniques of investigation. Chemometrics was also introduced and helped the analysis of collected spectroscopic data. Such local measurements helped with materials characterizations, up to chemical reaction monitoring. This included the occurrence of new chemical species or the understanding of an alteration process. Collected Raman spectra without damaging the samples did contain the relevant information, either in some specific Raman peaks or in the spectra as a whole. This chapter will now focus on other aspects of non-destructive characterization of materials by Raman spectroscopy, from the monitoring of a specific physical characteristic, a mapping of a given area, and up to field measurements. Gathered spectral data, including at low wavenumbers, will be transformed and directly related to a property relevant for a non-destructive appreciation of a given situation, establishing a relationship between a microstructure (stretching of molecules, spectral anomaly...) of a material with a macroscopic situation (mechanical behavior, human health indicator...). This chapter will also describe some specific instruments settings to reach

14.2 Monitoring of a specific physical characteristic

If the immersion in a turbid media allowed the detection of a specific chemical bond and one of a material, in particular in the case of a

chemical reaction, non-destructive testing is also about the determination of a specific characteristic of a studied system. It can be a temperature of phase transition [1], a mechanical property, or a physiological element related to human health [2]. This paragraph will present some illustrations where Raman spectroscopy measurements were used to elaborate an index, a parameter that can be directly handled to contribute to a decision process.

14.2.1 In situ measurement of polymer mechanical properties by Raman spectroscopy

The study of polymers, in particular their composition or their mechanical behavior, is essential both for the fundamental understanding of materials and for several aspects of their industrial process monitoring. The protocol or the approach for in situ measurement of the properties or functionalities of a polymer will be highlighted here, through an example of the monitoring of the mechanical behavior of polymers [3]. The protocol or work approach consists of several steps if we want to follow physical properties or control an industrial process. It is first important to make a learning phase with a correlation with one or more conventional analytical techniques such as chromatography, X-ray diffraction, or differential scanning calorimetry (DSC). This learning phase is completed, and it will then allow us to make applications in particular for real-time measurements. This phase can be done thanks to a statistical approach using chemometrics methods such as Partial Least-Square regression

To understand and control the mechanical properties of solid polymers, it is then fundamental to perform tests as they usually are, but also to establish a relationship between the mechanism of deformation particularly at the microstructural scale. To do so, a tensile test, typically providing a curve of loading and unloading of considered material, is usually implemented. An applied strain causes the deformation of the sample, its unloading followed by an absence of strain for 3 hours allowed its recovery. Nevertheless, the microstructure is different when the strain is applied than the one once it is removed. Conventional analytical techniques are used on postmortem samples, once unavoidable relaxation processes have taken place. In situ and real-time measurements are then mandatory to get access to both a microstructure and a mechanical characteristic, especially in order to make a sensor that could be installed in an industrial context. Spectroscopic measurements, with a Raman probe near the

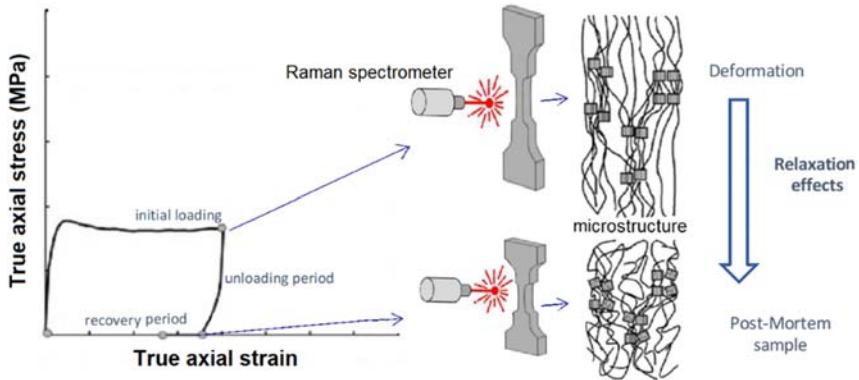


Figure 14.1 Illustration of the experimental approach to establish the relationship between the stress applied to a polymer specimen during a tensile test and the microstructure of polymer chains, with the appreciation of their microstructure by means of Raman spectroscopy.

polymer specimen, will provide elements to elaborate the relationship between microstructure and mechanical behavior (Fig. 14.1).

Connecting a mechanical characteristic of a material (a polymer in this illustration) does need a learning phase. This one consists in indexing the different Raman lines, in studying the material in temperature, by measuring the Raman spectrum of the polymer while its temperature changes, knowing the melting temperature of the crystals. In the specific case of isotactic polypropylene, the melting point is around 165°C, the material being semicrystalline below and amorphous above this temperature threshold (Fig. 14.2).

The nature of the sample (crystalline or amorphous) when the polymer is under strain can then be identified, assimilating the effect of strain on polymer chains to a temperature increase. The vibrational modes are different in each case, and this allows for identifying the attribution of modes to an amorphous or to a crystalline phase, and thus to establish a crystallinity index X_c , once a correlation has been established with a reference technique (either DSC or X-ray diffraction) (Fig. 14.3). This index translates the crystallinity rate determined by Raman spectroscopy, on the basis of peak intensities as detailed in the equation below [4,5]. Real-time monitoring of the crystallinity of the material can be obtained by Raman spectroscopy throughout tensile tests repeated 10 times until failure and particularly during the strain hardening regime, a regime difficult to observe by the conventional techniques. X_c curve, with error bars

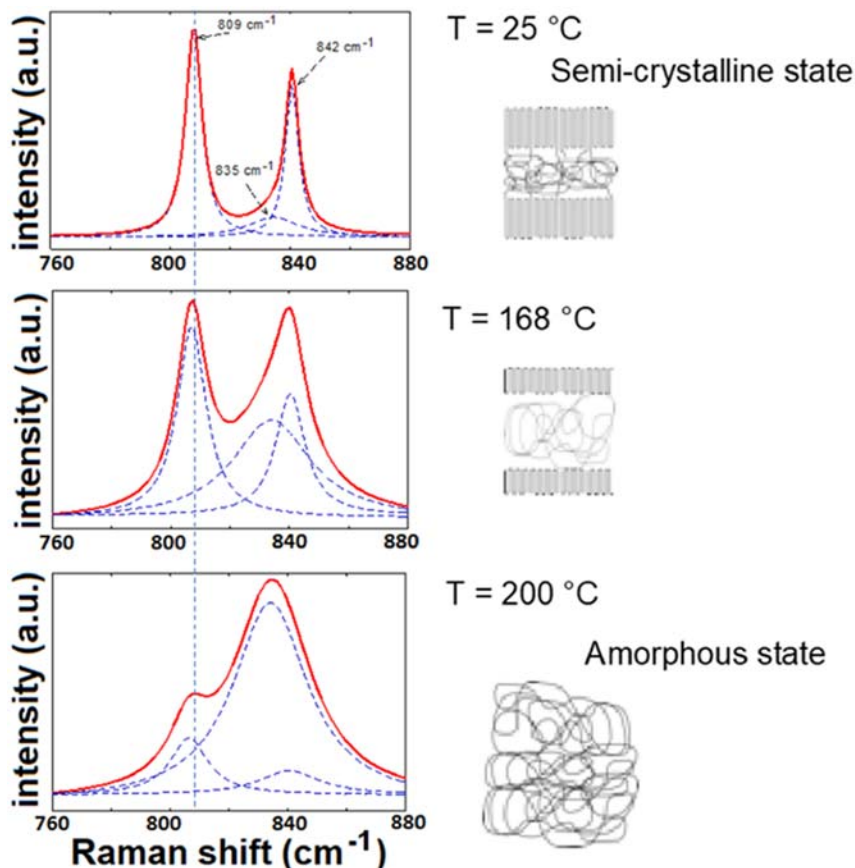


Figure 14.2 Raman spectra of isotactic polypropylene (iPP) as a function of temperature and illustration of corresponding microstructures of polymer chains ($\times 50$ objective, focal distance of 12 mm, 785 nm laser wavelength, 300 mW laser power).

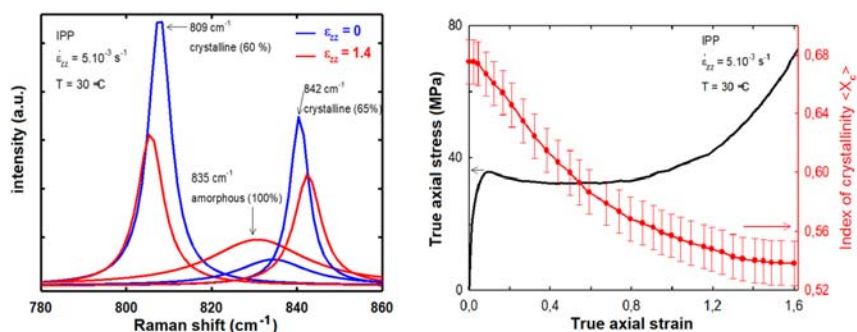


Figure 14.3 Part of the Raman spectrum of isotactic polypropylene (iPP) at two different drawing rates of the material, showing different responses depending on the amorphous or crystalline character of the polymer (left) and in situ Raman measurement of the crystalline index X_c of a polymer material during a tensile test to failure (right).

established on the basis of repeated tests, does reveal a three-stage decrease of the crystalline phase as axial stress increases.

$$X_c = 0.8 \left(\frac{I_{809} + I_{842}}{I_{809} + I_{835} + I_{842}} \right) + 0.2 \quad (14.1)$$

Within the context of real-time monitoring of the functional properties of a polymer, either as a function of temperature or of mechanical deformation, Raman spectroscopy appeared as a very effective technique. A learning phase is still necessary to elaborate a correlation between spectroscopic results and the ones from a conventional analytical technique, as already indicated above, contributing to promoting Raman spectroscopy as a non-destructive testing technique.

14.2.2 Glucose monitoring

Developing a less invasive, more accurate, and lower cost technology for continuous glucose monitoring (CGM) can significantly improve patient care and may reduce medical costs. This task has become only more urgent with the rapidly increasing population of diabetes worldwide [6–8]. While fingerstick blood glucose monitoring is the gold standard for patients to regulate their own glucose levels, the painful lancing process often deters many people from sampling with sufficient frequency [9]. Several studies report that more than half of people with type 1 diabetes (T1D) do not follow the daily self-monitoring recommendation [10,11], even though it is highly recommended for reducing the risk of various complications such as cardiovascular diseases, ketoacidosis, and renal failure. Improving glucose monitoring technologies that are noninvasive or minimally invasive, pain-free, and convenient may motivate patients to provide more frequent measurements. Recently, minimally invasive CGM sensors from Dexcom, Medtronic, and Abbott have become popular alone or in combination with an insulin pump or injections among those with T1D or type 2 diabetes. However, subcutaneous insertion, skin irritation caused by imbedded wire, and adhesive are barriers to uptake and can be reasons for device discontinuation. High operating costs (~\$2000–\$6000 annual) and short lifetimes (1–2 week per sensor) also limit the universal adoption of these devices.

Photonic solutions have long been sought as a viable path towards entirely noninvasive CGM with low-operating costs. Various optical techniques have tried to measure glucose levels directly and indirectly. Indirect

method estimated glucose concentrations in tissue by measuring refractive index changes or optical path length changes. Many interferometry-based methods, such as tissue reflectance [12] or optical coherence tomography [13] could measure glucose changes by quantifying induced refractive index variations. However, the indirect measurement could not overcome its fundamental limitation that glucose is not the only cause of tissue refractive index changes.

Among direct glucose monitoring methods, near-infrared (NIR) absorption [14–16] and Raman [2,17–21] spectroscopies have been the two leading technologies. Since NIR absorption provides a much stronger signal and is easier to be implemented as a miniature sensor, it was originally thought to be the superior approach. However, NIR absorption technology translations have all failed due to difficulty in extracting accurate glucose-specific features in the presence of confounding background noise and temperature variations in vivo. MIT Laser Biomedical Research Center has been working on a Raman solution for the past two decades. Quantitative analysis for diagnostic feasibility has been reported using various biological systems such as serum [22], blood [23] and in vivo skin [2,18,19]. Although these reports have shown promises, the inability to directly observe the characteristic Raman peaks and the inability to implement true prospective prediction have been major points of criticism. Using a novel offset detection geometry, has shown strong evidence in a swine model that these limitations have been overcome. The prospective prediction was achieved with an accuracy of 10% mean absolute relative difference (MARD) which is comparable to the accuracy of commercial CGM devices (9%–10% MARD). This next-generation Raman CGM sensor has the potential to dramatically improve current diabetes management.

Direct glucose signal was observed from in vivo skin [2]. This was mainly enabled by the illumination-collection geometry to regulate the sampling volume using a noncontact off-axis system. The noncontact off-axis system minimized the instability of the probe by illuminating a relatively large tissue under custom-designed large collection fiber bundles. The off-axis illumination and vertical collection geometry spatially filter out the specular Rayleigh reflection from the skin surface, and this can reduce the burden of the Rayleigh rejection filter at the probe tip. Finally, the noncontact measurement is less sensitive to the device-tissue interface, which is important for stable long-term measurement.

In order to demonstrate direct glucose Raman signal from transdermal measurements, glucose clamping measurement was performed in swine

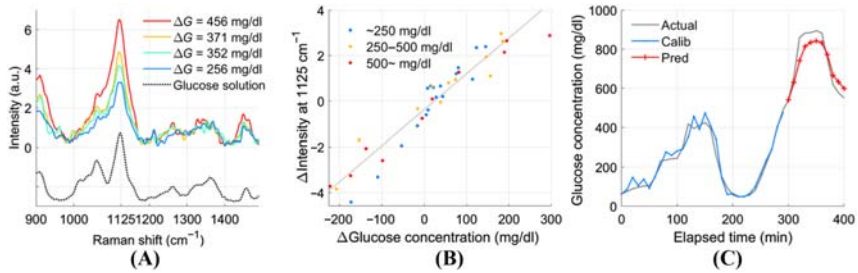


Figure 14.4 Glucose Raman spectra from in vivo experiments (A) and linearity between their spectral intensity and the corresponding blood glucose concentration (B), with prospect prediction, achieved based on the linearity (C).

models and calculated the subtraction spectrum between two tissue spectra with different glucose levels (G_1 and G_2), and further compared it with the Raman spectrum from pure glucose solution. In Fig. 14.4A, four subtraction spectra with four glucose level differences ($\Delta G = G_1 - G_2$) are plotted along with the reference Raman spectrum from the pure glucose solution. These in vivo subtraction spectra and the reference glucose solution spectrum exhibit a high degree of similarity as indicated by the Pearson correlation coefficient, $R = 0.90$ on average. One of the characteristic glucose Raman peaks appears at 1125 cm^{-1} and its intensity increases as the glucose difference (ΔG) increases. These observations confirm that the in vivo Raman peaks indeed originate from glucose molecules in the tissue. A linear relationship was observed between those glucose signal intensities and the corresponding glucose concentration differences during the entire measurement period. Fig. 14.4B demonstrates the high linearity of $R = 0.95$ between the change in spectral intensity and the glucose difference (ΔG) over the entire measurement time. Based on the linearity between the intensity of the glucose Raman peak and the glucose concentration difference ΔG , the prospective prediction was performed. Before this work, the direct glucose Raman signal was not visible from the raw spectrum. Therefore, the prediction was based on heavy computation and sensitive to environmental fluctuations such as changes in background signals due to the subject movement. As a result, frequent recalibration was required which hinders successful translation. In contrast, prospective prediction based on glucose peak intensity is very intuitive and robust. Prediction based on visible glucose peak intensity is a huge progress towards successful translation, with glucose concentration monitoring starting when it is delivered into the body (Fig. 14.4C).

14.2.3 Low-frequency Raman spectroscopy

The detection of Raman-scattered photons requires prior filtration of the (at least) 10^6 times more intense quasielastic Rayleigh scattering process. This filtration is critical not only when the vibrational modes peak close to the laser excitation but also over the first few hundreds of cm^{-1} , where the Rayleigh tail may otherwise appear as a sloped background. Until recently, the filters equipping commercially available Raman spectrometers had a cut-off around 100 cm^{-1} (3 THz), and going below that limit was possible only using triple monochromator stages (where the first two gratings scatter Rayleigh photons away from the entrance slit of the third one), at the cost of a dramatic intensity reduction (Table 14.1).

This was unfortunate since the low-wavenumber domain carries quite a lot of useful information, in particular intermolecular and lattice modes (Table 14.2). The breakthrough came with the introduction of Volume Bragg Gratings (VBGs) to suppress Rayleigh scattering, as first proposed in 1990 [24,25]. These are volume holograms with a sinusoidal modulation of the refractive index, which is recorded in a photo-thermo-reflective glass through UV interferences. The wavelength selectivity is proportional

Table 14.1 Characteristics of the Rayleigh filtering setups used in Raman spectroscopy.

Filtration device	Cut-off (cm^{-1})	Technology	Comments
Double fore monochromator	~ 3	Two gratings arranged in subtractive configuration	Strong reduction of Raman intensity
Notch filter	~ 120	Organic multilayer with sine modulation of the refractive index	Degrades over time (light and moisture sensitive)
Edge filter	~ 80	Dielectric multilayer with step modulation of the refractive index	Adds ripples to the spectra and suppresses the anti-stokes side
Volume Bragg Gratings (VBGs)	$\sim 5\text{--}10$	Volume holograms recorded in a photo-thermo-reflective glass	Maximum optical density is 4; several filters must be used in series

Table 14.2 The low-wavenumber Raman contributions made easily accessible using Volume Bragg Gratings (VBGs).

Denomination	Physical origin
Soft modes	The restoring force associated with a specific mode may weaken during a phase transition. The corresponding frequency drops to zero, which may be extrapolated from a Raman wavenumber versus thermodynamic variable profile recorded down to the filter cut-off [30,31].
Lamb modes	Particles of diameter D smaller than the laser wavelength seem homogeneous. The laws of elastodynamics then apply and predict a low-wavenumber contribution at $\sigma \propto 1/D$ (see text).
Folded acoustic modes	Acoustic modes away from Brillouin zone center may be activated by “zone folding” in periodic stackings, allowing for the characterization/control of superlattices [32–34].
External modes (intermolecular and lattice modes)	Weakly interacting and/or “heavy” entities tend to vibrate at low frequencies. The corresponding peaks are used to characterize semicrystalline chains in natural and synthetic polymers [35,36], 2D-materials (interlayer shear and breathing modes in multilayered graphene, hBN, bilayered MoS_2 , . . .) [37–39] and polymorphism (in organic semiconductors [40], pharmaceutical products [41–46], iron corrosion products [47], metal halide perovskites [48], 1,1'-binaphthyl microcrystals [49], . . .).
Boson peak	This contribution is a few tens of cm^{-1} -wide and comes in addition to the density of vibrational states predicted by Debye model. Its long-debated origin is somewhat related to local density fluctuations in amorphous (glassy) versus crystalline materials [50].
Miscellaneous	VBGs also make Raman spectroscopy sensitive to: • the structure of self-assembled peptides [51]; • self-organized surface structures induced by metal adsorbates on semiconductors [52];

(Continued)

Table 14.2 (Continued)

Denomination	Physical origin
	• sulfur allotropy [53]; • the effect of CrI_3 magnetic order on scattered light polarization [54]; • rotational transitions in O_2 and N_2 [55]; • the specific electronic properties of metals intercalated in 2D-materials [56]; • grain orientation in 2D metal halide perovskites [57] and barium nitrilotriacetate [58] (polarized low-frequency Raman analysis); • low-frequency Raman-active magnons in Sr_2IrO_4 [59]; • the adsorption of sugar by model biological membranes [60]; • amino-acids enantiomery [61].

to the ratio of the modulation period divided by the total thickness [26–29] and current technology makes it possible to lower the Raman cut-off down to about $5\text{--}10\text{ cm}^{-1}$, with as much throughput as with old generation notch and edge filters (Fig. 14.5). Most Raman spectrometers manufacturing companies now offer VBGs as quite an affordable option and it is also relatively easy to upgrade old spectrometers (all it takes is to buy two or three VBGs and place them on the optical pathway at angles cutting the laser wavelength—see Fig. 14.5B). The lower the Raman wavenumber, the higher the relative error induced by the spectral resolution limit (usually in the range of $\sim 1\text{ cm}^{-1}$) or a shifted zero-wavenumber calibration (following temperature variations or actions such as a grating or laser change). The calibration should therefore be carefully controlled before any low-frequency measurement, for instance by making the triply degenerate optical mode of a silicon wafer appear at perfectly symmetric $\pm 520.7\text{ cm}^{-1}$ position on the Stokes and Anti-Stokes sides.

No specific treatment of the raw data is necessary for the simple detection of low-frequency peaks but it goes otherwise if a mathematical line-shaped fitting is needed. Let us note $N(\sigma_{vib})$ the number of objects that vibrate at wavenumber σ_{vib} in the probed volume and $I_0(\sigma_{vib})$ their individual contribution:

$$I_{measured}(\sigma_{vib}) = N(\sigma_{vib})I_0(\sigma_{vib}) \quad (14.2)$$

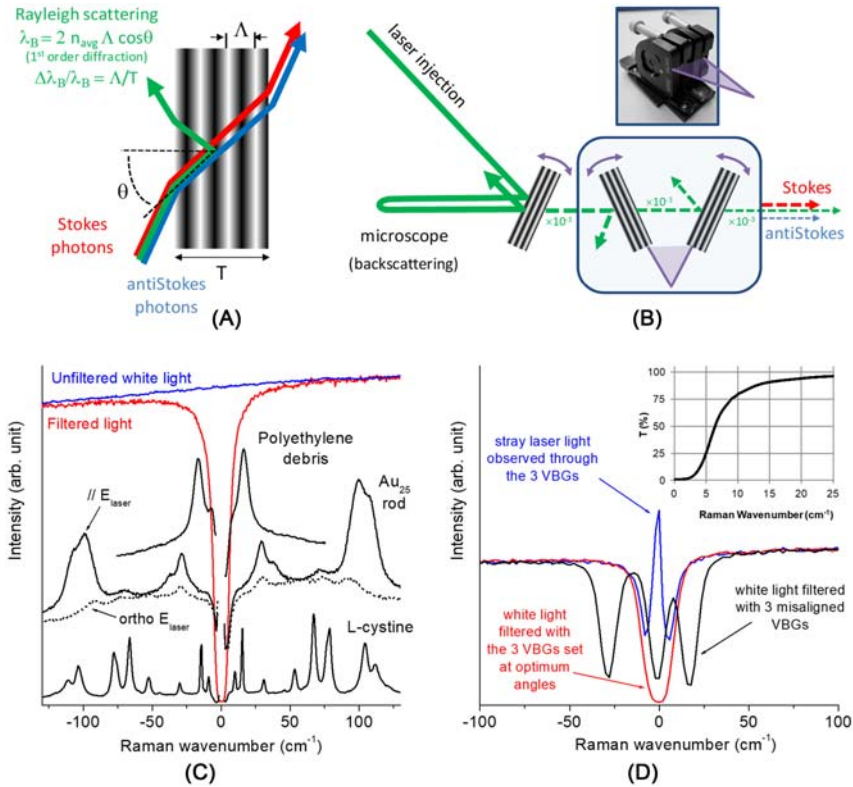


Figure 14.5 Schematics of a reflective VBG (period Λ , thickness T , average refractive index n_{avg}) used to reject laser wavelength λ_{las} . The wavelength selectivity is proportional to Λ/T (A) Rejection setup combining 3 VBGs [25]. The 1st one serves as a mirror on the way to the microscope and the picture shows the mount used for the other two on a Labram HR (Horiba), with angle-adjustment knobs (B) Low-frequency spectra recorded with 1800 g/mm grating and 514.5 nm excitation; the lowest band of L-cystine peaks at 9 cm^{-1} ; the Au_{25} rod (self-organized Au_{25} nanoclusters) is observed with the laser polarized either parallel or perpendicular to its length; the polyethylene debris was collected from the North Atlantic subtropical gyre (C) Rayleigh filtration is highly dependent on the VBGs tilt angle; the insert shows the % of transmitted light when the 3 VBGs are set correctly (D).

According to Placzek's theory of the Raman effect [62]:

$$I_0(\sigma_{vib}) \propto \frac{\nu_{scat}^4 \cdot P_{BE}(\sigma_{vib}) \cdot S(\sigma_{vib})}{\sigma_{vib}} \quad (14.3)$$

- The scattering is proportional to the fourth power of the scattered light frequency but exponent 4 should be replaced by 3 if a CCD is used to count the scattered photons (rather than measure their energy) [62].

- $P_{BE}(\sigma_{vib})$ accounts for the fact that vibrations are equivalent to bosonic harmonic oscillators; The probability of a Stokes event occurring at σ_{vib} is proportional to $n_{BE}(\sigma_{vib}) + 1$ (creation operator) and that for the anti-Stokes counterpart is proportional to $n_{BE}(\sigma_{vib})$ (annihilation operator), where $n_{BE}(\sigma_{vib}) = \frac{1}{e^{\frac{hc}{kT}\sigma_{vib}} - 1}$ is Bose–Einstein thermal occupation number.
- $S(\sigma_{vib})$ is a generalized wavenumber-dependent parameter associated with polarizability variations. For molecules, it is called the “Raman scattering activity” while in solids it corresponds to the product of the “Vibrational Density Of States (VDOS)” by the so-called “light-VDOS coupling coefficient.” All things considered, the last two equations yield:

$$\left\{ \begin{array}{l} I_{Stokes}(\sigma_{vib}) \propto \frac{(\sigma_{las} - \sigma_{vib})^3}{\sigma_{vib} \left(1 - e^{-\frac{hc}{kT}\sigma_{vib}} \right)} N(\sigma_{vib}) S(\sigma_{vib}) \\ I_{Anti-Stokes}(\sigma_{vib}) \propto \frac{(\sigma_{las} + \sigma_{vib})^3}{\sigma_{vib} \left(e^{\frac{hc}{kT}\sigma_{vib}} - 1 \right)} N(\sigma_{vib}) S(\sigma_{vib}) \end{array} \right. \quad (14.4)$$

Note that we assumed a CCD is used for detection (as indicated by the three exponent) and neglected its quantum efficiency dependency on the detected wavelength. A common practice to make Raman intensity reflect the density of scatterers is to correct the experimental spectra as follows:

$$\left\{ \begin{array}{l} I_{Stokes}(\sigma_{vib}) = I_{expS}(\sigma_{vib}) \sigma_{vib} (\sigma_{las} - \sigma_{vib})^{-3} \left(1 - e^{-\frac{hc}{kT}\sigma_{vib}} \right) \propto N(\sigma_{vib}) S(\sigma_{vib}) \\ I_{Anti-Stokes}(\sigma_{vib}) = I_{expAS}(\sigma_{vib}) \sigma_{vib} (\sigma_{las} + \sigma_{vib})^{-3} \left(e^{\frac{hc}{kT}\sigma_{vib}} - 1 \right) \propto N(\sigma_{vib}) S(\sigma_{vib}) \end{array} \right. \quad (14.5)$$

The proportionality factors appearing in this equation are plotted in Fig. 14.6A after normalization at 4000 cm^{-1} , which is the standard upper limit for 1st order Raman spectroscopy (C-H, OH and NH stretching modes). The Bose–Einstein correction soars on the Anti-Stokes side to compensate for plummeting experimental intensities. This is the reason why Raman spectra are usually recorded on the Stokes side. There, from $\sim 400 \text{ cm}^{-1}$ and above, the variations of all coefficients are sufficiently

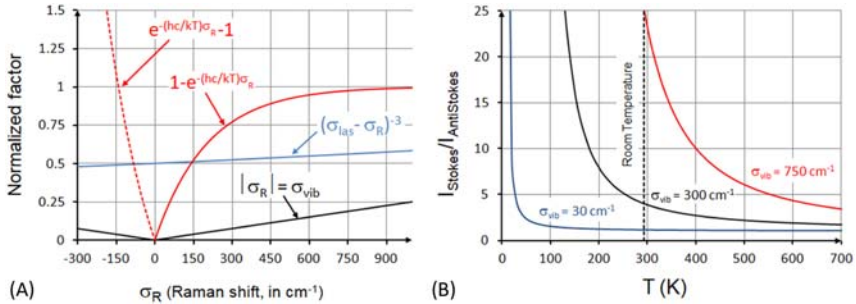


Figure 14.6 The proportionality factors used to correct experimental Raman intensities were normalized at $\sigma_{\text{vib}} = 4000 \text{ cm}^{-1}$ for $\lambda_{\text{laser}} = 514.5 \text{ nm}$ (see text) (A) Predicted “Stokes/Anti-Stokes intensity ratio versus sample temperature” curves for Raman bands peaking at 30, 300, and 750 cm^{-1} . Only limited portions of these curves are of practical interest (see text) (B).

limited and steady over a few tens of cm^{-1} to assume Raman bands are hardly deformed if fitted without prior correction. In the low wavenumber range, however, the Bose–Einstein correction becomes mandatory.

Note that $\frac{I_{\text{Stokes}}}{I_{\text{Anti-Stokes}}} = \left(\frac{\sigma_{\text{las}} - \sigma_{\text{vib}}}{\sigma_{\text{las}} + \sigma_{\text{vib}}} \right) \frac{hc}{kT} \sigma_{\text{vib}}$ and, because $\sigma_{\text{la}} \gg \sigma_{\text{vib}}$, this is equivalent to $T(\text{K}) \sim \frac{1.44\sigma_{\text{vib}}(\text{cm}^{-1})}{\ln\left(\frac{I_{\text{S}}}{I_{\text{AS}}}\right)}$

The measured Stokes/Anti-Stokes intensity ratio may therefore be used as an embedded sample thermometer. Yet, precise measurements require a good enough signal-to-noise ratio on both sides, which is usually achieved only for small σ_{vib} values. Then, for a given σ_{vib} , there is an upper limit to the temperature range where the intensity ratio varies significantly (Fig. 14.6B).

14.2.3.1 Low-frequency vibrations in nanoparticles

In crystals, only optical phonons of nearly infinite wavelength (Brillouin zone center) are observed by Raman spectroscopy. Size confinement most often results in a redshift of these modes (as depicted by the more or less sophisticated versions of the original “phonon confinement model” [63]) and the activation of acoustic contributions. When they are confined in spheres having a diameter smaller than the laser wavelength, the latter becomes the so-called Lamb modes of a free elastic sphere [64]. For symmetry reasons, only two of these “non-propagating acoustic modes” are Raman-active [65], namely the breathing mode (a spheroid mode of angular momentum $\ell = 0$) and the quadrupolar mode (a torsional mode

of angular momentum $\ell = 2$). These modes can be observed from a very small amount of matter (if the laser wavelength matches the surface plasmon resonance), discriminated through polarization selection and their wavenumber is inversely proportional to diameter D [65]:

$$\begin{cases} \sigma_B = S_B^n \frac{V_L}{c} \frac{1}{D} \\ \sigma_Q = S_Q^n \frac{V_T}{c} \frac{1}{D} \end{cases} \quad (14.6)$$

In this equation, c is the speed of light, $S_{B,Q}^n$ is a proportionality factor for the n^{th} -order mode and V_L (resp. V_T) is the longitudinal (resp. transverse) sound velocity in the bulk crystal. There is a maximum particle size to have at least σ_B remain above the $\sim 10 \text{ cm}^{-1}$ VBGs cut-off, which falls somewhere in the 10–25 nm range for most nanocrystals of interest (a Lamb modes calculator for Ag, Au, Co, Cu, CdS, CdSe, Si, ZnO, silica, anatase and monoclinic ZrO_2 is available on Lucien Saviot's professional webpage (Univ. de Bourgogne/CNRS—<https://saviot.cnrs.fr/index.en.html>), together with other calculation applets). Note that Lamb modes can also be observed by Brillouin scattering, THz spectroscopy, and pump-probe transient absorption spectroscopy, with specific resolutions and particle size limits. Lamb's model has been successfully used down to D values in the order of 2 nm [66] although shifts, lifted degeneracy and modified selection rules are expected in case of nonsphericity [67,68] and crystalline anisotropy [67–69] or due to environmental effects (ligand-capped nanoparticles [66] or/and supracrystalline organization [67,70–72] or/and dispersion in a matrix [69] or solvent [73]). Below a certain size, no cluster can be reasonably approximated by a homogeneous medium and numerical simulations (DFT [66], molecular dynamics [74],...) become necessary to get a correct band assignment. Fig. 14.5C shows two spectra recorded on a several mm-long, $\sim 20 \mu\text{m}$ thick, and $\sim 55 \mu\text{m}$ wide rod formed by self-assembled $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_4\text{Ph})_5\text{Cl}_2]^{2+}$ nanoclusters (unpublished results—a collaboration with Pr. C. Klinké and Dr. M. Galchenko [75]; The incoming laser power had to be lowered down to $\sim 25 \mu\text{W}$ (as measured below the microscope objective) not to damage the sample). The gold cores (two icosahedral Au_{13} units sharing one vertex) are roughly equivalent to 1.1 nm long cylinders of $\sim 0.5 \text{ nm}$ diameter [76]. For gold spheres having a diameter in the 0.5–1.1 nm range, Lamb's model predicts σ_Q in the $30\text{--}66 \text{ cm}^{-1}$ range and σ_B in the $94\text{--}208 \text{ cm}^{-1}$ range. The contributions visible at $29\text{--}38$ and $100\text{--}108 \text{ cm}^{-1}$ in Fig. 14.5C

certainly relate to these values but should obviously be considered with great care, as discussed above. One point to note with the rod sample in Fig. 14.5C is that because of the long-range 3D self-assembly, a large number of nanocrystals sharing the same orientation is observed at once. Hence the strong effect of the laser polarization on the peaks' intensity.

14.2.3.2 The low-frequency acoustic mode to study polyethylene weathering in oceanic gyres

In semicrystalline polymers such as polyethylene, the Straight Chain Segments length can be approximated from the profile of Raman first-order Longitudinal Acoustic Mode (LAM) using the Mizushima–Shimanouchi equation [77]:

$$L_{SCS} = \frac{1}{2c\sigma_{LAM}} \sqrt{\frac{E}{\rho}} \quad (14.7)$$

In this equation, ρ is the density of the crystallites, E their Young's modulus and c the speed of light. The chain segments may be at an angle with the normal to the crystalline lamellae but the average tilt is usually low enough in polyethylene (~ 35 degrees) to consider L_{SCS} a good estimate for the lamellar thickness. Fig. 14.7A shows the low-frequency spectrum from a polyethylene bit that was collected in the accumulation area of the North Atlantic subtropical gyre, in the course of a study that combined SEC, DSC, XRD, WAWS, 2D-SAXS, and low-frequency Raman spectroscopy to characterize the embrittlement of weathered polyethylene [36]. VBGs makes it possible to detect Raman peaks as low as $\sim 10 \text{ cm}^{-1}$ (Fig. 14.5C) but the profiles will be deformed at least up to $15\text{--}20 \text{ cm}^{-1}$ (Fig. 14.5D). Fig. 14.7A and B shows how this effect was corrected by a simple rule of three. The $I_{fit}(\sigma_{LAM})$ profiles were eventually converted into Lamellar Thickness Distributions (LTDs) using the following equation, which assumes that $S(\sigma_{LAM})$ is inversely proportional to L_{SCS} [77]:

$$N\left(L_{SCS} = \frac{\sqrt{E}}{2c\sigma\sqrt{\rho}}\right) = I_{fit}(\sigma)\sigma^2\left(1 - e^{-\frac{hc}{kT}\sigma}\right) \quad (14.8)$$

According to Garvey et al. [36], all the most probable L_{SCS} values were found to be about 2 nm shorter than the average ones, as a consequence of the distribution asymmetry (Fig. 14.7C). The small probing dimensions in Raman microscopy allow us to accurately study heterogeneous phenomena such as polymer weathering and metal corrosion (metals do not scatter but

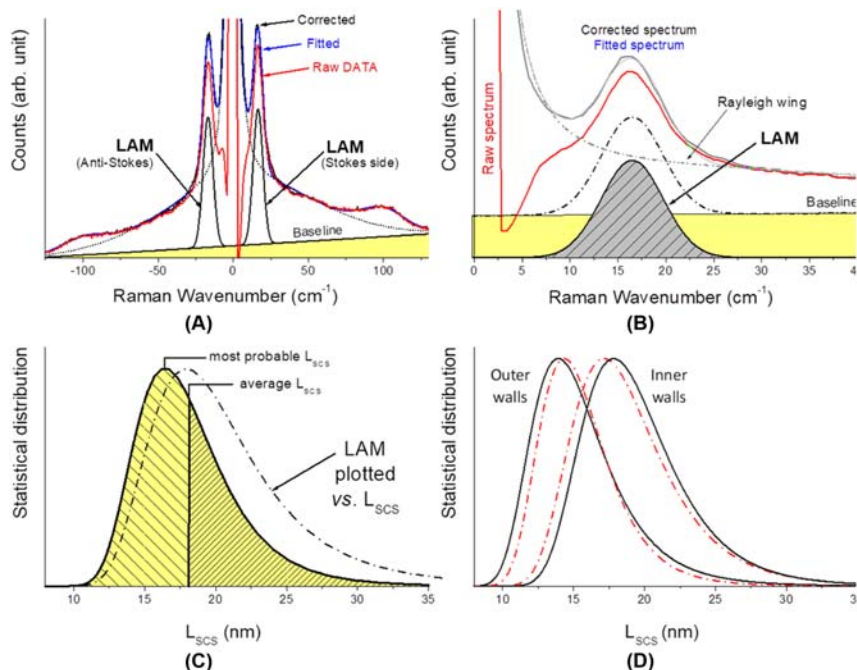


Figure 14.7 Lamellar Thickness Distributions (LTDs) can be obtained from the Low-frequency Acoustic Mode (LAM) of polyethylene—(A). A spectrum is fitted after correction of the Rayleigh filtering distortion (B, see text)—The adjusted LAM profile is converted into an LTD (C), note that plotting the LAM intensity as a function of the L_{SCS} associated with each Raman wavenumber does not give the correct LTD—There is more structural difference between the inner and outer walls from the red packaging of a famous instant coffee maker than between a brand-new packaging (black solid curves) and a weathered sample collected in the ocean (red dotted curves) (D). Adapted from C.J. Garvey, M. Imp  rator-Clerc, S. Rouzi  re, G. Gouadec, O. Boyron, L. Rowenczyk, A.F. Mingotaud, A. Ter Halle, *Molecular-scale understanding of the embrittlement in polyethylene ocean debris*, *Environ. Sci. Technol.* 54 (18) (2020) 11173–11181. <https://doi.org/10.1021/acs.est.0c02095>.

their degradation products do), and specifically interfaces. The calculated diffraction limits for the spot diameter and probing depth were respectively $D_{spot} \sim 0.75 \mu\text{m}$ and $d_z \sim 1.5 \mu\text{m}$ [36], which made it possible to evidence structural differences between the inner and outer walls of polyethylene packaging (Fig. 14.7D). The LTD was systematically upshifted by about 4 nm in the inner wall compared with the outer one. This difference most probably results from a temperature gradient during the blow-molding process and shows that even a pristine (unweathered) sample does not have a single reference state.

14.3 Raman imaging

This part of Raman spectroscopy consists in carrying out spectroscopic measurements over a given surface, a Raman spectrum is attached to each measuring point. A hyperspectral image is then generated and it is then possible to identify the spatial dispersion of some specific peaks over the surface and to generate a map of its chemistry and/or its microstructure. Nevertheless, before elaborating a hyperspectral image consistent with objectives, several challenges have to be overcome. These challenges are common to any Raman measurement such as signal-to-noise ratio, or ambient light. But some are specific to the elaboration of the map, among which surface roughness or topography, its contamination, the material heterogeneity, mapping accuracy, and duration, or the way a reconstructed image is elaborated. Different examples will illustrate the benefits of Raman imaging in the non-destructive characterization of a surface.

14.3.1 Raman spectroscopy and human health

Since it was first observed in 1928 [78], Raman spectroscopy has been broadly used as an analytical technique in various fields. As already indicated in the introduction part, inelastically scattered Raman photons from the sample include the “finger print” information about the sample. By analyzing Raman photons, the chemical composition of the sample can be obtained qualitatively and quantitatively. Confocal microscopy has been utilized to obtain 3-D structural information from cells [79]. The confocal pinhole only accepts the light from the focus resulting in high axial resolution. Confocal microscopy was implemented with reflectance, fluorescence, or even with inelastically scattered photons including Raman [80] or Brillouin [81]. Combining confocal microscopy and Raman spectroscopy provides the three-dimensional chemical mapping of biological samples with high spatial resolution.

Puppels et al. first used confocal Raman microscopy for cell study in 1990 [80]. Although it showed promising results, confocal Raman microscopy has not been widely used for biomedical research, compared to fluorescence microscopy, due to the small Raman conversion efficiency. For example, bright-field imaging and quantitative phase microscopy is the fastest as the imaging speed is the same as the frame rate of the camera. With advanced camera technology, more than 1000 frames per second (fps) is not uncommon. High-speed confocal fluorescence microscopy is about 10 fps. High-speed confocal Raman microscopy takes about one

minute per frame. In order to increase the imaging speed of Raman microscopy, line-scanning, and multifocal Raman systems were developed [82,83]. Rather than mapping the whole cell, which can be highly time-consuming, researchers first identified morphologically relevant features of a cell under bright-field imaging and subsequently measured the Raman spectra from the selected regions of interest [84]. Raman basis spectra were collected from this process and successfully utilized to develop clinical Raman devices and diagnosis software [85]. This two-step approach was very successful to balance high-resolution and high-speed data acquisitions.

According to Kang et al. [86], the live HeLa cell was imaged and analyzed using single peak analysis. Raman images were reconstructed from different Raman bands between 613 and 1825 cm^{-1} (Fig. 14.8A). Images reconstructed from single Raman bands with 15 cm^{-1} bandwidth reveal high-resolution images and biochemical maps. Specifically, the 720, 785, 1004, and 1450 cm^{-1} peak correlate to the cytoplasm, DNA, protein, and lipid distributions, respectively. This information is well correlated to the bright-field image in Fig. 14.8C. Since the protein signal is uniformly spread over the entire cell volume, this signal was excluded and a pseudo-color image was generated from three other Raman bands corresponding to the cytoplasm, DNA, and lipid Raman signals. In Fig. 14.8E, the red color represents 785 cm^{-1} (DNA) and is localized to the cell nucleus. Green and blue represents 720 cm^{-1} (cytoplasm) and 1450 cm^{-1} (lipids), respectively. Although Raman imaging cannot compete with the imaging speed and resolution of fluorescence imaging, Raman imaging can be performed without any staining, sample preparation, or external perturbation to the cell. In summary, Raman imaging and mapping can simultaneously track multiple chemical components of the live cell in-vitro.

Confocal Raman imaging can become a powerful method for monitoring the status of the cell and associated chemical changes in real-time. Since the cells do not need to be stained or altered for Raman imaging, live cell dynamics can be observed with minimal or no external perturbation. Many biological applications will benefit from this label-free quantitative chemical imaging capabilities. A few ongoing examples include studying the effects of cellular uptake of particles [87,88], the effects of drugs/UV radiations [89,90], and cellular growth and development.

Most cancer chemotherapies are administered in cycles lasting several weeks to months. The response rates vary greatly and robust biomarkers to predict drug-specific responders in most cases are elusive. The traditional

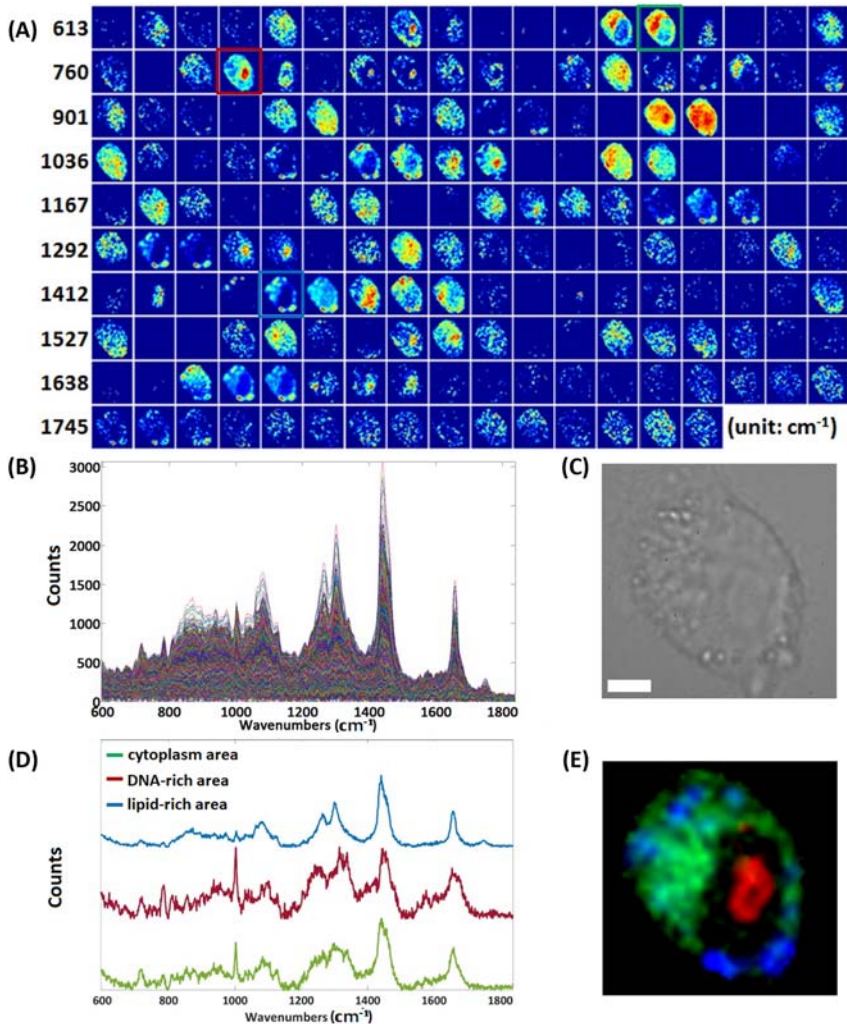


Figure 14.8 Raman images of a live HeLa cell from various Raman bands between 613 and 1825 cm^{-1} (A). Different Raman bands show different distributions throughout the cell. 1600 overlaid Raman spectra (40×40 spectra) from a single cell (B). Bright-field image of live HeLa cell used in the experiment (C) (scale bar: 5 μm). Representative spectra from the cytoplasm, nucleolus, and lipid droplets (D). Pseudo-color image reconstructed from (A) with data at 785 cm^{-1} (red), 720 cm^{-1} (green), and 1412 cm^{-1} (blue) Raman bands (E).

clinical efficacy measurements of a therapy regimen consist of noninvasive imaging of tumor shrinkage. Magnetic Resonance Imaging (MRI), for example, is often used. However, discernible differences in tumor mass by

MRI often require weeks to months of treatment to appear, which leads to a loss of valuable treatment time for nonresponders in which other therapies could be tried. Thus, methods to reliably detect drug efficacy earlier in the treatment cycle would have a significant clinical impact.

Raman spectroscopy has been widely used in various facets of biological research ranging from disease diagnostics to diabetes monitoring [2,91,92]. In contrast to conventional imaging techniques, it offers the advantages of being rapid, noninvasive, and label-free. In vivo identification of healthy and cancerous conditions has become feasible with the advent of fiberoptic probes [91–94]. This method has recently been applied to analyze and image live cells to determine cellular states such as apoptosis, division, or differentiation [95–98]. Molecular level changes under exposure to antibiotics or chemotherapeutic agents at the single cell level have been studied in detail using Raman spectroscopy [96–103]. Clinical applicability to examine the treatment response in cancer, however, requires direct monitoring of the Raman signal within a tissue because tumors are heterogeneous and is composed of varied cell types including not only tumor cells but stromal, immune, and other cell types [104,105]. The varied effects of the tumor microenvironment have a significant effect on actual drug response [106–108].

Raman spectroscopy could measure and identify an apoptotic response that is present only within the drug-treated tumor regions [109]. The results of this proof-of-concept study are relevant for the development of methods to optimize and monitor chemotherapy. The ability to obtain serial measurements in a minimally invasive manner will allow the determination of drug pharmacodynamics and assessment of intra-tumor response to therapy to enable more rapid and accurate clinical decision-making.

The most striking change in the Raman signal observed during apoptosis induced by doxorubicin occurs at wavenumbers that are characteristic of DNA (Fig. 14.9). Doxorubicin is a DNA-intercalating agent and induces apoptosis through either structural damage to DNA directly or by interfering with the replication machinery. Consistent differences at 785 cm^{-1} were observed in 300 measurements across three tumors. These findings were further verified by immunohistochemistry (IHC). Tumor sections were stained using cleaved-caspase-3 antibodies. Near-perfect spatial overlap is observed between the tumor regions that display reduced DNA Raman signal and the IHC antibody staining for apoptosis (Fig. 14.9). The reduction in DNA is thus congruent with the known biochemical mode of action of the drug.

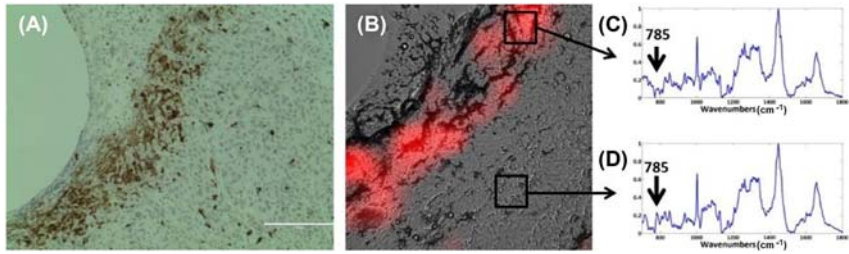


Figure 14.9 IHC image of an adjacent section of same drug & tumor model (A375 melanoma) (A). Brown cells depict apoptosis as measured by Cleaved-caspase-3 expression. Red color represents lower DNA Raman signal (785 cm^{-1}) (B). Raman image is overlaid with bright-field image. Representative spectra from lower DNA (red) and normal DNA areas (C and D).

Raman spectroscopic methods can be employed for *in vivo* detection of apoptosis. This might open a new avenue of label-free measurement of drug effect inside the tumor during chemotherapy. Such information could be used to guide further therapy for patients. Alternatively, this technology could be integrated with existing implantable devices for drug delivery. For instance, drug-eluting wafers could be equipped with Raman capabilities to directly feedback data on the released drug's effectiveness [110,111]. In the diagnostic realm, microdevices for drug sensitivity testing equipped with Raman sensing can provide efficacy information for multiple drugs in real-time to enable rapid selection of optimal personalized drug therapies [112,113].

14.3.2 Identification of mortar composition in an archeological sample

In previous examples, if monitored chemical species or specific Raman peaks were clearly identified, some situations are sometimes slightly more complicated than the ones described above. To the challenges indicated in Raman Imaging comes one of the search for unknown and specific chemicals. This can be illustrated in the specific case of an archeological tessellated tile to identify the mortar composition. The sample presented a rough surface, needing the implementation of an autofocus device to perform the monitoring. The area with mortar is located in the middle of the sample, though the frontiers between the stone (sandy chalk) to which the tessellated tile is attached to are clearly not easily identified. The sample being large ($5\text{ mm} \times 5\text{ mm}$), a compromise had to be found to obtain a Raman image accurate enough, though avoiding a long experiment duration. Raman

mapping was then performed using a LabRam Evolution HR with a 785 nm-laser wavelength (25 mW at the sample), using an integration-averaging time of 2×5 seconds on the $50\text{--}3200\text{ cm}^{-1}$ spectral range, with a spatial step of $50\text{ }\mu\text{m}$, a $\times 50$ objective and an autofocus of $50\text{ }\mu\text{m}$ with a $5\text{ }\mu\text{m}$ step. A total of over 400 Raman spectra were then collected, for data collection over half a day.

A principal components analysis (PCA) with 20 principal components was conducted on these Raman spectra, after a baseline correction based on a polynomial curve, and a standard normal variate (SNV), considering the $200\text{--}2000\text{ cm}^{-1}$ spectral range. Over 99% of the variance was explained with these 20 components, and over 80% with the first ten components (Fig. 14.10A). Chemometrics revealed the presence of a structure within collected data. On the scores plot, most Raman spectra are gathered together (black circles in Fig. 14.10B) while some others are clearly apart (*red circles right*). Using the X and Y coordinates of the motorized stage, among the Raman spectra represented by red circles, four corresponded to locations in the mortar area (X|Y corresponding to $1000|0$, $-500|2500$, $2000|0$ and $5000|1000$ [in μm]) (Fig. 14.11). Thus, the association of chemometrics and of Raman imaging provided a fast and non-destructive characterization of the sample.

Concerning spectra in Fig. 14.11, peaks at 266 , et 1072 cm^{-1} are present in all four. There are characteristics of vaterite in fish bones [114,115]. These peaks are different than the ones usually present in calcite Raman spectra [116], due to the substitution of calcium atoms for magnesium

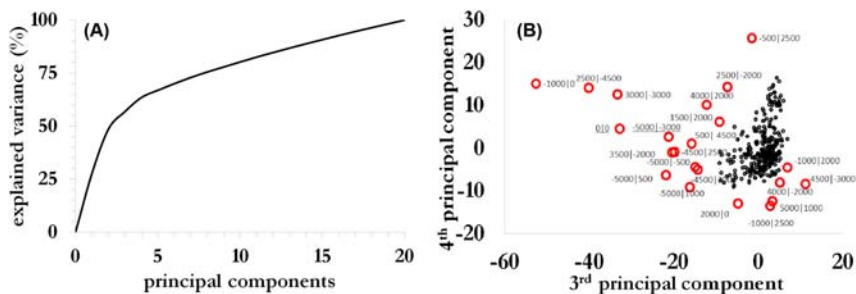


Figure 14.10 Explained variance (A) and scores plot (3rd and 4th principal components) (B) of PCA conducted on over 400 Raman spectra (785 nm-laser wavelength, integration-averaging time of 2×5 , spatial step of $50\text{ }\mu\text{m}$, $\times 50$ objective) collected during the mapping of an archeological sample made of a tessellated stone and a mortar, after a baseline correction based on a polynomial curve, and a SNV, to identify locations where the composition of the mortar is specific (*red circles*, figure on the (B)).

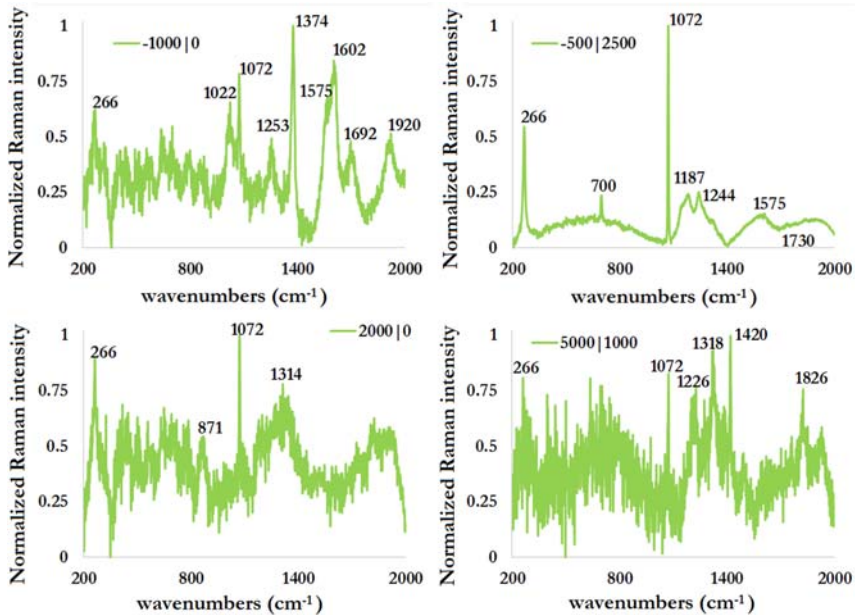


Figure 14.11 Raman spectra of mortar from an archeological sample of a tessellated tile, showing specificities, and considered as outliers after PCA calculations over the whole mapping (785 nm-laser wavelength, integration-averaging time of 2×5 , spatial step of $50 \mu\text{m}$, $\times 50$ objective) after a baseline correction based on a polynomial curve, and a SNV, considering the $200\text{--}2000 \text{ cm}^{-1}$ spectral range.

ones in the materials having an animal origin. Magnesium generates shorter chemical bonds than calcium, and therefore different vibration frequencies [117]. Other peaks are more specific. The one at 1022 cm^{-1} is attributed to a carotenoid pigment present in coral [114]. The presence of biogenic materials raises questions about the composition of this mortar. According to Dallongeville [118] (page 141), animal glues have been used for many centuries. Daher [119] presented some Raman characterizations of these materials but in the spectral range over 2000 cm^{-1} , where no significant Raman signature was observed in the case of the studied sample. Dallongeville [118] indicated these glues do contain collagen. When specifically considering fish collagen, consistent with peaks at 266 , 1022 and 1072 cm^{-1} , peaks at 1602 cm^{-1} (tyrosine and phenylalanine), 1244 cm^{-1} (NH_2 amide III twist), 1314 and 871 cm^{-1} (close to the Raman shift of a C–C bond present in hydroxyproline cycle), 1420 and 1318 cm^{-1} do correspond to type I fish collagen according to Ikoma et al. [120], although obtained with a 1064 nm laser but still in the NIR spectral region.

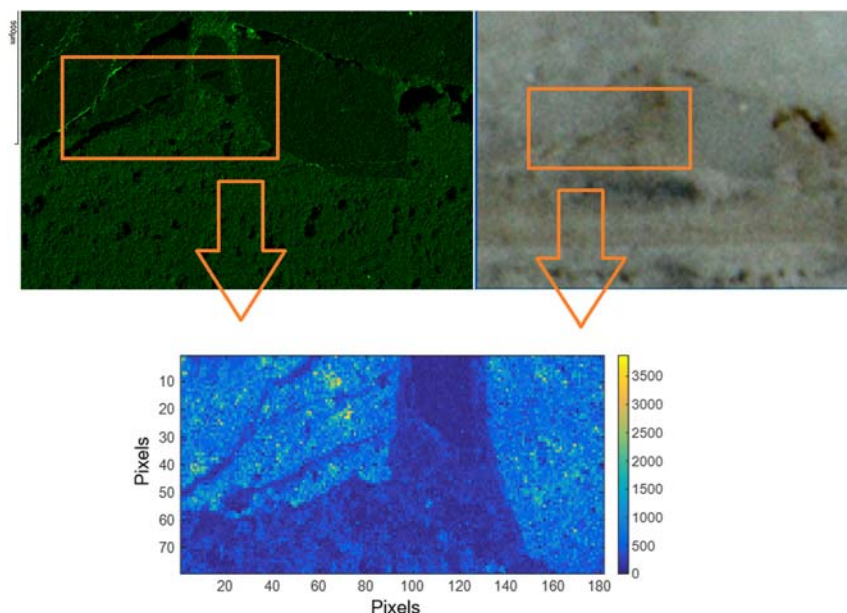


Figure 14.12 X-ray microanalysis (*upper part, left*) and Raman image of a pure component obtained from MCR calculation conducted on Raman spectra (*lower part*) (785 nm-laser wavelength (25 mW at the sample), integration-averaging time of 2×5 s, with a spatial step of $50 \mu\text{m}$, a $\times 50$ objective, and a $5 \mu\text{m}$ step) collected over a specific zone of the archeological sample (*upper part, right*) corresponding to the orange rectangle.

These results were encouraging enough to perform an accurate mapping of a more restricted area ($\sim 400 \times 900 \mu\text{m}^2$) where some biogenic material was detected. The analysis combined X-ray microanalysis for magnesium with a scanning electronic microscope (SEM), and Raman spectroscopy associated with multivariate curve resolution—alternate least-square (MCR-ALS). Results in [Fig. 14.12](#) confirmed previous ones of the spatial occurrence of specific biogenic material in the mortar of this archeological tessell, again preserving the sample.

14.4 Field measurements

The benefits of Raman spectroscopy have been extensively illustrated in the previous paragraphs, but mainly in controlled conditions and in a laboratory environment. In most of the situations described above, samples were collected and then brought to the spectrometer, or to any other

analytical instruments (SEM, X-ray diffractometer. . .). In some situations, sample collection is sometimes possible, though neither easy nor practical. Therefore, the main idea is then to bring the instrument to the material and its environment to perform spectroscopic measurements along with optical adaptations to cope with a context sometimes unadapted or poorly adapted to Raman measurements. Raman probe protections, how to cope with ambient light, improving the signal-to-noise ratio, identifying the most appropriate compromise of integration time with respect to sampling, the detection thresholds, and fluorescence are among the nonexhaustive challenges to overcome in the case of field measurements. This paragraph will present how Raman spectroscopy was implemented in some specific conditions and will provide details on the methods and the means to obtain an appropriate Raman signal. Presented situations will be extremely different in terms of contexts, sensibility, of experiment durations but Raman spectroscopy appeared as an appropriate non-destructive testing method.

14.4.1 De-icer monitoring

In spite of many techniques to fight against winter conditions, the use of chemicals is one the cornerstone of winter maintenance on highways, roads, airports (runways/taxiways), and also aircraft. They prevent ice accretion, and snow accumulation on circulated lanes and on specific parts either on airplanes or infrastructures surfaces lowering the freezing point of water once dissolved into it to maintain a proper grip level. Ice occurrence and snow accumulation are generating transportation hazards and traffic disruptions. Nevertheless, current technical solutions to detect the residual amount of these chemicals are either not efficient enough or not accurate enough to determine whether or not additional chemicals have to be spread on roads [121–124]. Such additional operations raise economic and environmental concerns [125], firstly because of millions of euros spent on winter maintenance operations, but also because these chemicals ultimately end up in soils and water, causing a threat to fauna and flora. As an example, deicing an aircraft weighing over 50 tons will use between 160 and 650 L, with specific instructions and standards [126]. Back in the early years of 2000, Raman spectroscopy appeared as an efficient technique to characterize these chemicals used in winter maintenance and recently improved with the implementation of chemometrics methods [1], and therefore as a non-destructive technique for their

detection and their quantification onto transportation infrastructures. The idea was then to track these chemicals, not in their crystal states, but once dissolved into water present at the surface where they were applied (pavements, runways. . .). The challenge is then to track this residual amount over a whole network, and not at a specific location. The measurement has to be performed with a Raman spectrometer installed in a circulating vehicle, whose speed is adapted to the traffic, and measurements triggered to obtain information at a regular spatial frequency.

In this specific case, measurements do need specific protection of the Raman probe from both ambient light and projections. The vehicle circulates at a given speed and because a regular spatial frequency was required, each collected Raman spectrum is obtained with an external trigger signal sent to the instrument. The vehicle moving speed implies collected Raman signal corresponds to information over a given length. Therefore, integration time has to be short enough to avoid a large spatial dispersion. The instrument must also stand requests to perform measurements with a spatial frequency enabling a proper mapping of residual amounts of a chemical. Considering an average speed of 50 km/h, a maximum spatial frequency of 25 m, and measurement over a distance close to half of this distance, the integration time cannot exceed 1 second, and the duration between two measurements as short as 10 ms. A comparison of the results for an integration time of 400 ms and 1 second is provided in Fig. 14.13, with a 532 nm laser and 100 mW output. Thus, such a field measurement is a compromise between the constraints and requirements of winter maintenance and the performance of the spectrometer that must remain cost effective. As illustrated in Fig. 14.13, the signal to noise ratio is too weak with an integration time below 1 seconds. Some tests were then performed with a vehicle circulating on a wet pavement, the Raman spectrometer collecting data continuously. Results are illustrated in Fig. 14.14, enabling the identification of chemicals present in the pavement.

14.4.2 Water quality appreciation and pollution mapping

Still within the frame of field measurements, Raman spectroscopy has been involved in the appreciation of anthropogenic transportation activities on water quality. Investigations started in the early years 2000 with single measurements on water samples, up to the coupling of with the determination of quantitative uncertainties [1,127]. The idea is then to reach the information on water quality by switching from a measurement in a laboratory

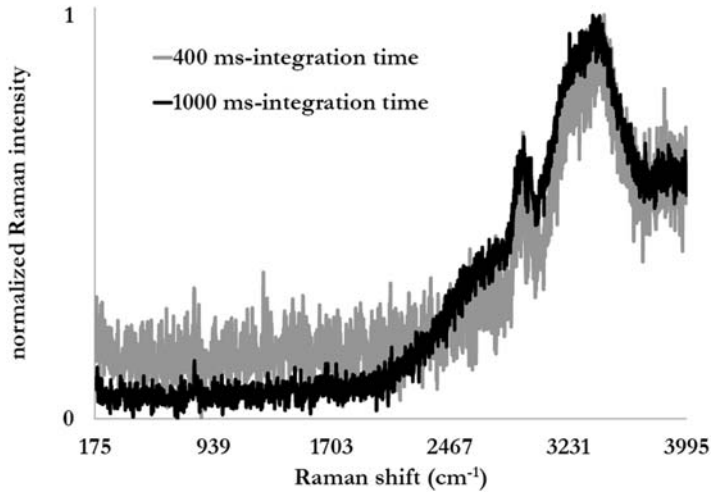


Figure 14.13 Raman spectra of a deicing solution obtained with integration time of respectively 400 and 1000 ms to identify the most appropriate integration time to perform Raman measurements at 50 km/h with a spectrometer on board of a circulating vehicle.

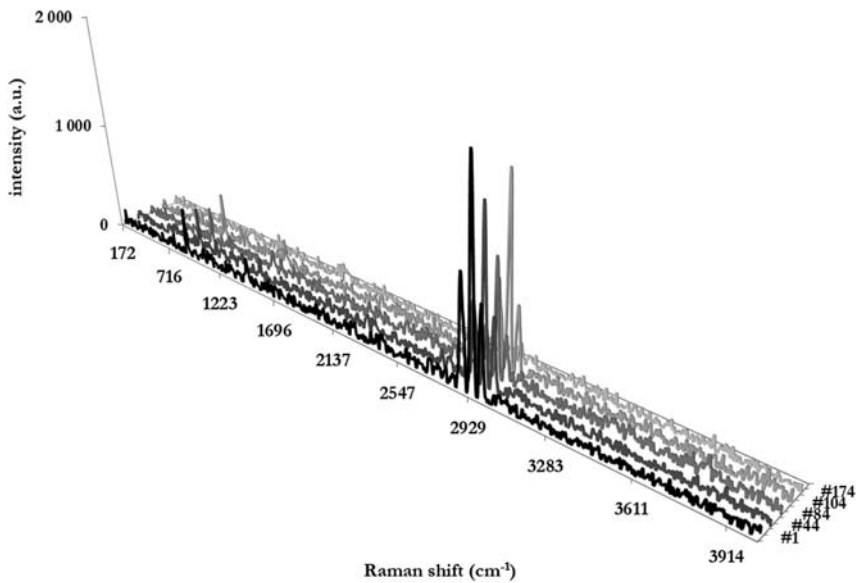


Figure 14.14 Raman spectra of a fluid present on a pavement at different locations (integration time 1 s, laser at 532 nm, 100 mW) obtained with a spectrometer on board a vehicle circulating at 50 km/h on a road during the winter season.



Figure 14.15 Evolution of Raman spectrometers used to identify water quality, from a laboratory instrument to an on-board one.

context on a high-performance spectrometer to cost-effective and immediate measurement (Fig. 14.15). Such an endeavor was then applied to obtain qualitative and quantitative information on water quality variations, and monitoring of a river from the spring to the confluence with another river. Measurements were performed on seven locations, every month, over 2 years. Two sets of comparisons were then done. A first one will be dedicated to the evolution of water quality with time at each location, and a second one related to the comparison of Raman spectra between each location, this one providing its evolution along the water course and thus an insight into anthropogenic effects on water quality.

The evolution with time of water quality at each location is estimated through a comparison of Raman collected spectra and their intrinsic changes. This comparison is performed on Raman spectra collected from 2012 to 2014, with an integration time of a few seconds, with a 532 nm-laser with a 100 mW-power output (Fig. 14.16). Raman spectroscopy indicates that the farther from the spring, the greater the fluorescence. When combined with chemometrics, it revealed some evolution in water quality, including at the spring of the river. Changes were identified in the $800\text{--}1700\text{ cm}^{-1}$, and $2800\text{--}3600\text{ cm}^{-1}$ spectral range. These changes can be either attributed to the presence of specific chemicals, or to the presence of dissolved ions generating a deformation of the Raman signature of water. First, a PCA was specifically conducted on Raman spectra of location 1 (spring) and 7 (confluence) for the years 2012, 2013, and 2014, with a specific focus on the third loading. No significant difference was observed for the years 2012 and 2014 between the source and the confluence, but not for the year 2013. The analysis of loadings (Fig. 14.17) does reveal the specificity of the year 2013 with a peak in the $1200\text{--}1300\text{ cm}^{-1}$ spectral range. The second step consists in spectroscopically detecting the location from which this peak is appearing, performing PCA on Raman spectra obtained at each location during the years 2012, 2013, and 2014, starting from location 1, till the peak in the $1200\text{--}1300\text{ cm}^{-1}$ spectral range appears. This peak does appear in loadings at location three, as illustrated in Fig. 14.18, which corresponds to an increase

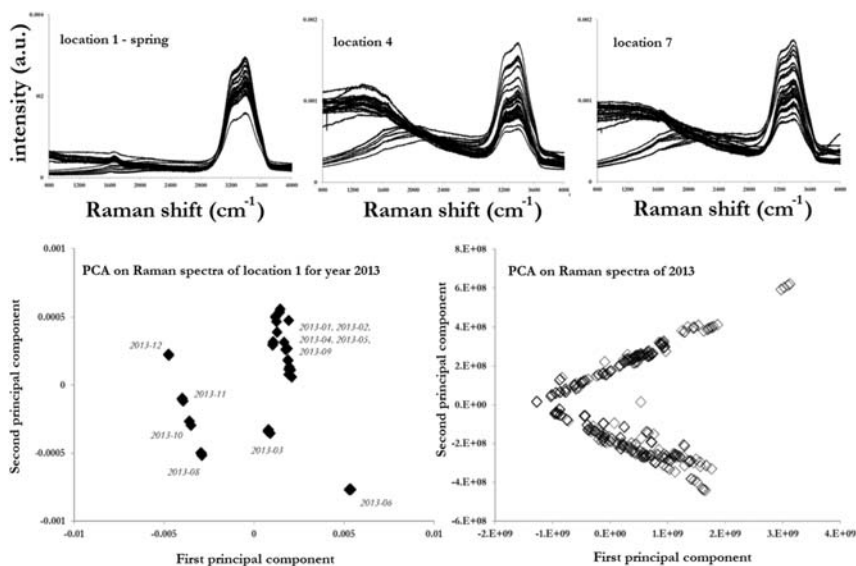


Figure 14.16 Raman spectra for years 2012, 2013, and 2014 on three distinct locations along the Moselle river (France), and scores plot of PCA conducted on Raman spectra of the location 1 (spring of the river) for the year 2013 (*lower part, left*) and scores plot of PCA conducted on all Raman spectra for the year 2013 (*lower part, right*).

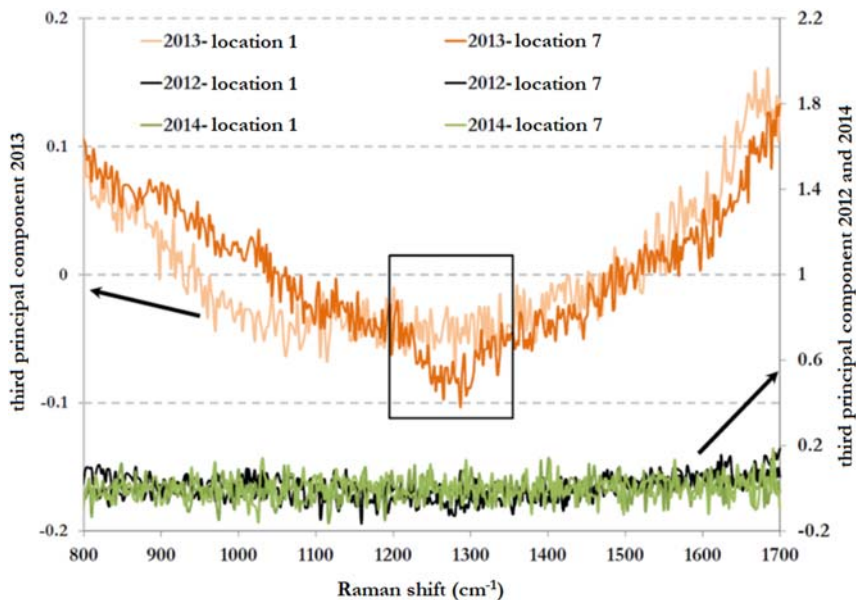


Figure 14.17 Third principal component obtained after a principal component analysis on Raman spectra of water samples collected along the Moselle river (France) on first (spring of the river) and seventh (confluence with another river) locations for years 2012, 2013, and 2014.

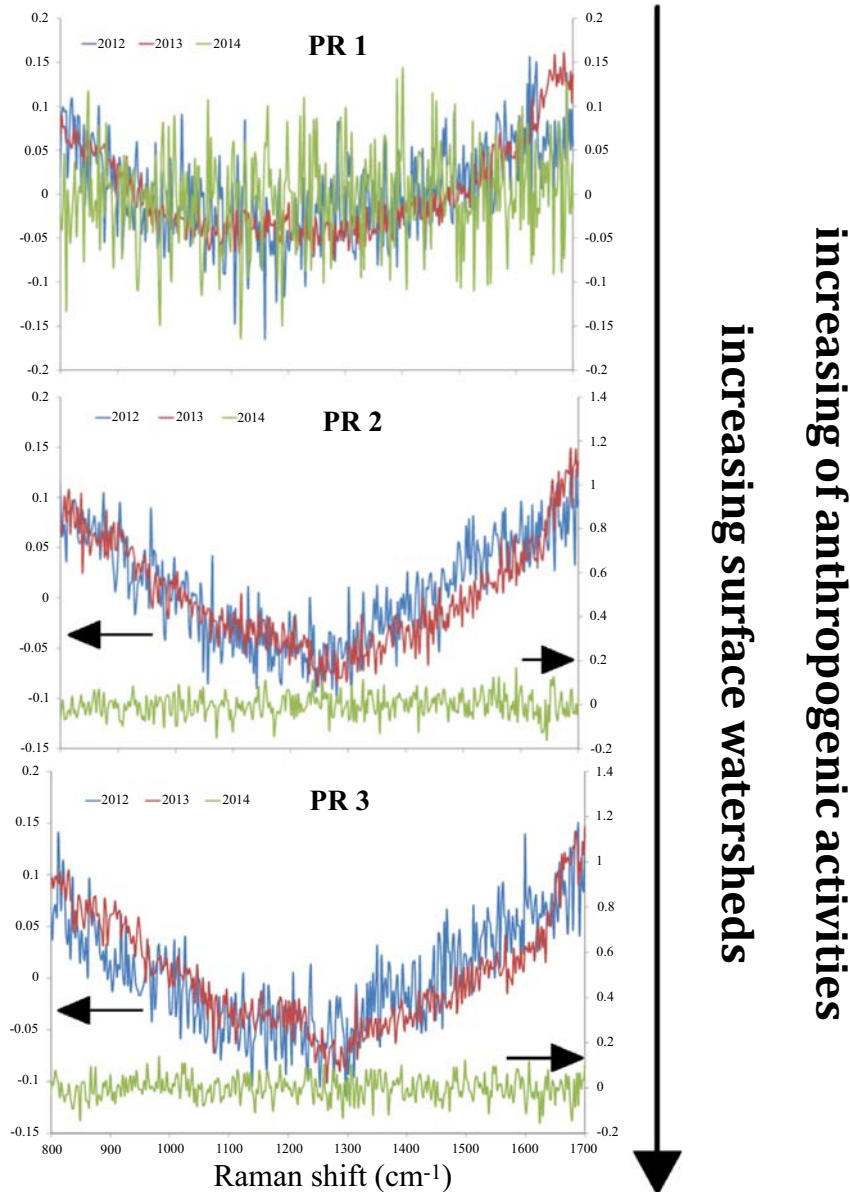


Figure 14.18 Principal components obtained after a principal component analysis on Raman spectra of water samples collected along the Moselle river (France) on the first (spring of the river) (*top*), second (*middle*), and third (*bottom*) locations for years 2012, 2013, and 2014.

in both watershed surfaces and anthropogenic activities. Such a non-destructive approach eases the detection of locations where water quality is at stake, and the implementation of specific analysis to identify the pollutants types and their concentrations.

14.5 Conclusion

Recent innovations have allowed to implementation of Raman spectroscopy in increasing monitoring processes where in situ non-destructive characterization was before not possible. Here again, Raman spectroscopy demonstrated its ability to provide answers in a large scope of scientific domains, such as human health and the environment. This chapter described the monitoring of a specific physical characteristic of a material through one of its Raman spectral responses, or Raman imaging. This non-destructive spectroscopic approach was also transposed to field measurements when collecting samples is either impossible, or cost effective, or simply poorly adapted to the hope of obtaining a characterization of the material. The development of specific Raman probes has allowed applications such as embedded instruments into moving vehicles. Some precisions on instrumental specifications are also provided, allowing a non-destructive approach in very particular and different configurations and contexts. Many instrumental obstacles were overtaken, such as triggering data collection at high frequency, not accessible by conventional analytical techniques, and thus obtaining an appropriate compromise between instruments limits and constraints of some specific contexts (measurements performed outside, patient health at stake) still without affecting the material during its spectroscopic characterization. Elements presented in this chapter confirmed the clear and obvious benefits of chemometrics inputs in Raman data processing. As in the previous conclusion, Raman spectroscopy confirmed its ability to perform accurate and efficient non-destructive characterization of materials.

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CHAPTER 15

UV–Vis spectroscopy in non-destructive testing

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15.1 Preface

Non-destructive testing (NDT) is an analysis technique used by industry to evaluate the properties of a material, component, structure, or system for characteristic differences or defects without causing damage to the original matrix. In this chapter, UV–Vis spectroscopy or spectrophotometry (UV–Vis) as an NDT tool is well described. As its name implies, UV–Vis quantifies the properties of samples in the UV–Vis wavelength ranges of light (typically 190–900/1100 nm) without destroying the matrix. Specifically, UV–Vis visible spectroscopy determines how much light of a given wavelength passes through a sample, and how much is absorbed. Such information can be diagnostic of molecular identity, concentration, structure, or activity, whether of organic species such as porphyrins, benzenes, and naphthalenes or of biomolecules like nucleic acids and proteins. Spectrophotometers can scan either fixed (i.e., predefined) or variable wavelengths, and come in both single- and double-beam configurations. Its simple operating system and robustness have enthralled the attention of users. Thus this technology is widely used in various applications especially in the environment, pharmaceutical, and agriculture. In this chapter, the principle, significant applications, and future potential of UV–Vis spectroscopy as an NDT tool will be well described.

15.2 Introduction

UV–Vis spectroscopy is a common and well-known technique used in many areas of science ranging from biology, chemistry, physics, and

engineering. The application includes drug identification, bacterial culturing, and nucleic acid purity assay for non-destructive testing [1–3]. It is an analytical tool that compares a sample to a blank to see how many distinct wavelengths of UV or Vis light it absorbs or transmits. This feature is influenced by the sample's composition and reveals information on the concentration of the sample [4–6]. The UV–Vis spectroscopy approach is based on the interaction of matter and light where the absorption of UV light or visible light is influenced by chemical compounds. The amount of energy contained in light is conversely relative to its wavelength. As a result, shorter wavelengths have more energy than longer wavelengths. Moving electrons in a substance to a better energy state require a certain amount of energy, which we will perceive as assimilation. To put electrons in a higher energy state, they need a varying amount of energy in different binding conditions of a substance. This is why light absorption in different substances happens at different wavelengths. People can see the distinctive light range from around 380 nm, which also be seen as violet, to 780 nm, which can be sensed as ruddy. This spectrophotometric procedure is a quantitative explanatory method is concerned with the assimilation of near UV–Vis (180–390 nm) or unique (390–780 nm) radiation by chemical species in the arrangement. UV–Vis light includes a wavelength of generally 100 nm, which is shorter than apparent light.

As a result, the wavelength of light can be used to examine or identify distinct compounds in UV–Vis spectroscopy by determining the exact wavelengths that correlate to maximum absorption [7,8]. These districts of electromagnetic range give energy that leads to electronic moves the diverse colors of obvious light and the complementary colors of arrangements are retained at a particular wavelength. Due to the superposition of vibrational and rotational moves, the UV–Vis range of analytes in the arrangement has a small fine structure. UV–Vis spectrophotometer is also one of the foremost commonly utilized procedures for quantitative investigation [9–11]. Under the controlled test conditions, the sum of radiation ingested can be straightforwardly related to the concentration of the analyte in arrangement (Beer's law). It can evaluate both organic (basically within the close UV–Vis range) and inorganic species.

UV–Vis spectrophotometric strategies are better than fluorimetric analysis, which is able to distinguish concentrations of some nanomoles per milliliter. In some cases, the application is much broader, including inorganic species, organic compounds, and proteins because absorption

within the UV–Vis spectrum, because of the spectra, is wider than fluorescence [12–15]. Spectrophotometry is valuable for observing enzymatic responses, either to decide the response items straightforwardly or to the degree of response rate [16,17].

15.3 Principles

While there are many different types of UV–Vis spectrophotometers, we could have a look at the major components in Fig. 15.1 to get a better understanding of how they work.

Basically, spectroscopy is essentially concerned with the interaction of light and matter. When light is absorbed by matter, it increases the energy content of the atoms or molecules. When bright radiation is retained, the molecules excite the electrons from the ground state to a higher level. Particles containing π -electrons or nonbonding electrons (n -electrons) can retain energy within the frame of bright light to energize these electrons to higher, nonbonding atomic orbitals [18–20].

The more effortlessly the electrons are energized, the longer the wavelength of light they can assimilate. There are four conceivable sorts of moves ($\pi-\pi^*$, $n-\pi^*$, $\sigma-\sigma^*$, and $n-\sigma^*$), which can be rearranged as the following flows: $\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$. A chemical compound's assimilation of bright light produces a unique range that makes a difference within the distinguishing proof of the compound [21–25].

15.3.1 Component analysis

15.3.1.1 Light source

A consistent light source capable of generating light over a wide variety of wavelengths is required in UV–Vis spectroscopy because the present technique is a light-based approach. A single xenon lamp is typically utilized as a high-intensity light source in both the UV and visible areas.

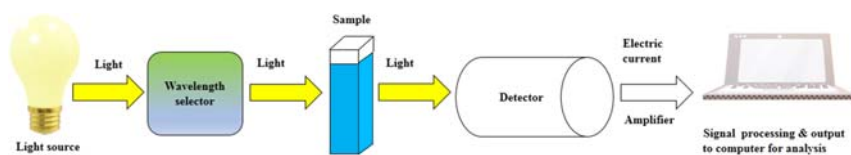


Figure 15.1 A schematic diagram of major components in a UV–Vis spectrophotometer. UV–Vis, Ultraviolet–visible.

On the other hand, xenon lamps are more expensive and less stable than tungsten and halogen bulbs [26–28].

A tungsten or halogen light is regularly utilized for unique light in dual-lamp gadgets, while a deuterium lamp is typically used for UV–Vis light. These two lamps are the most popular and suitable light sources because they span the whole UV–Vis range. Tungsten filament lamps emit a lot of red light, notably at 375 nm and above, whereas deuterium lamps emit light at a wavelength below 375 nm. The light source within the instrument must be swapped amid the estimation since two distinctive light sources are required to cover both the UV–Vis and visible wavelength ranges. This exchange happens between 300 and 350 nm wavelength when the light outflow from both light sources is comparative and flow is refined [29,30].

15.3.1.2 Selection of the wavelength

From the wide wavelengths transmitted by the light source for test review, specific light wavelengths suited for the sample type and analyte to be detected must be selected. The following are some of the methods that can be used for this:

- If more than an absorption maximum is available in the absorption spectrum, the wavelength far from the instrument extremes should be preferred
- A wavelength at the maximum of a broad peak should be preferred to another of a sharp peak
- The peak with a maximum peak height is preferred
- If interferences are present, the wavelength that is far away from interferences should be selected
- Working in the visible region should be preferred

15.3.1.2.1 Monochromators

A monochromator separates light into a focal wavelength band. It is primarily based on diffraction gratings which will be pivoted at the specified point of focus and reflected angles the selection of unique wavelength. The channel recurrence of the grafted diffraction is frequently measured in terms of the number of grooves per millimeter [31–33]. In spite of the fact that the prominent groove recurrence gives progressed optical determination, it moreover limits the wavelength extent that can be utilized. A lower groove recurrence permits for a bigger wavelength run to be utilized but at the fetch of second-rate optical determination [34,35].

UV–Vis spectroscopy requires 300–2000 grooves per mm, with a minimum of 1200 grooves per mm at normal state. Physical defects in the diffraction grating and optical arrangement affect the quality of spectroscopic observations [36,37]. As a result, line-shaped diffraction gratings are more likely to have issues than holographic diffraction gratings. Holographic diffraction gratings frequently give much prevalent estimation quality [38–40].

15.3.1.2.2 Absorption filters

Retention channels are ordinarily made of colored glass or plastic and are outlined to assimilate particular wavelengths of light.

15.3.1.2.3 Interference filters

Moreover known as dichroic channels, these commonly utilized channels are made up of different layers of dielectric fabric with impedances happening between the lean layers of fabric. These channels can be utilized as a wavelength selector by expelling undesirable wavelengths by damaging interference.

15.3.1.2.4 Cut-off filters

Cut-off filters allow light to pass that is either below (short pass) or above (long pass) a specified wavelength. These are usually implemented with interference filters.

15.3.1.2.5 Bandpass filters

Bandpass filters combine shortpass and longpass filters to pass a wide range of wavelengths. Monochromators are the most widely utilized for this technique due to their versatility. On the other hand, filters are habitually utilized in conjunction with monochromators to diminish the wavelengths of light chosen for more correct estimations and extend the signal-to-noise proportion.

15.3.1.3 Sample and reference cells

Both the sample and reference cell arrangements are found within the UV–Vis spectroscopy compartment. These cells are made of either silica or quartz. Glass cannot be used for the cells because it assimilates light within the UV–Vis range.

15.3.1.4 Detector

In common, two photocells serve as locators in UV–Vis spectroscopy. One of the photocells gets radiation from the test cell, and the moment finder gets radiation from the reference. The escalation of the radiation from the reference cell is more grounded than the radiation from the test cell. This comes about within the era of pulsating or substituting streams within the photocells.

15.3.1.5 Amplifier

The substituting current created within the photocells is passed to the amplifier. The amplifier is coupled to a little servo meter. In general, the current produced within the photocells is exceptionally escalated. The reason for the amplifier is to increase the signals numerous times so that they are ready to capture clear and recordable signals.

15.3.1.6 Recording and processing equipment (computer)

In most cases, the amplifier is coupled with a recorder which is associated with the computer. The computer stores all the information produced and makes the range of the required connection.

15.3.2 Analysis of the samples

Light passes through a sample regardless of which wavelength selector is used in the spectrophotometer. A reference sample, frequently known as a “blank,” such as a cuvette filled with the same dissolvable utilized to form the sample, is required for all examinations. In case the estimations are done with a watery buffered arrangement containing the sample, the reference is water. The sterile culture medium is used as a reference while analyzing bacterial cultures. The equipment then uses the signal from the reference sample to calculate the actual absorbance values of the analytes [41–43].

The materials and circumstances used in UV–Vis spectroscopy tests must be concerned. Most plastic cuvettes, for instance, are unacceptable for UV–Vis retention ponders since plastic retains UV light. Glass can work as a channel, retaining the larger part of the bands namely UVC for short wavelength (100–280 nm), and UVB for medium wavelength (280–315 nm) light whereas permitting a few UVA long wavelength (315–400 nm) light to pass through [44,45].

Since quartz is permeable to most UV–Vis light, sample holders developed of quartz are fundamental for UV–Vis investigation. Since

light wavelengths underneath 200 nm are ingested by atomic oxygen within the discussion, it can be called a channel. A more advanced and costly setup, as a rule consolidating an optical framework filled with immaculate argon gas, is fundamental for the estimations of sample wavelengths below 200 nm [46–48].

15.3.3 Detection

After the light passes through the sample, a locator changes over the light into an electronic flag that can be examined. Finders are regularly made of photoelectric coatings or semiconductors. When light strikes a photoelectric film, contrarily charged electrons are shot out. When electrons are removed, an electric current proportionate to the light escalated is created.

In UV–Vis spectroscopy, a photomultiplier tube (PMT) is one of the foremost utilized detectors. When light is experienced, a PMT employs the photoelectric impact to discharge electrons, which are consecutively increased to create a more prominent electric current. PMT locators are particularly valuable for identifying exceptionally moo light levels. When light is shone on semiconductors, it causes an electric current to stream corresponding to the concentrated light. Photodiodes and charge-coupled detectors are two of the foremost common finders based on semiconductor technology. The signal is recognized and yielded to a computer or shown once the specific locator produces the electric current utilized [49,50].

15.4 UV–Vis spectroscopy analysis, absorption spectrum, and data analysis

UV–Vis spectroscopy information may be presented as a graph of absorbance, optical density or transmittance as a function of wavelength. However, the information is more often presented as a graph of absorbance on the vertical y axis and wavelength on the horizontal x axis (Fig. 15.2). Absorbance (on the vertical axis) is just a measure of the amount of light absorbed and the higher the value, the more of a particular wavelength absorbed. This graph is typically referred to as an absorption spectrum; an example is shown in Fig. 15.3 represents a simple UV–Vis absorption spectrum for buta-1,3-diene—molecule [51–53].

The assimilation crests can be seen at an esteem peak of 217 nm. This esteem is within the UV extent, so there's no unmistakable sign of

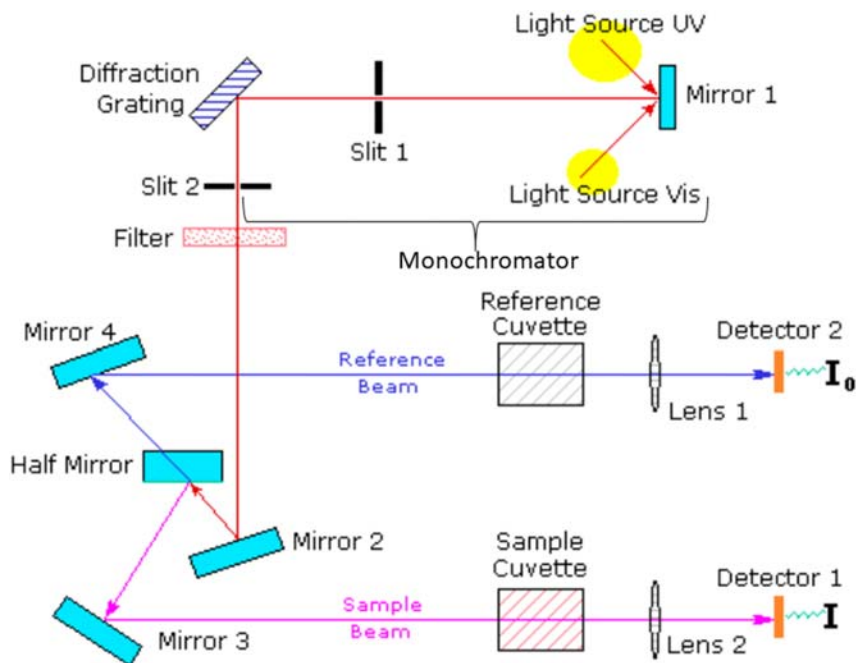


Figure 15.2 Schematic diagrams of UV–Vis spectrophotometers in simple form. UV–Vis, Ultraviolet–visible.

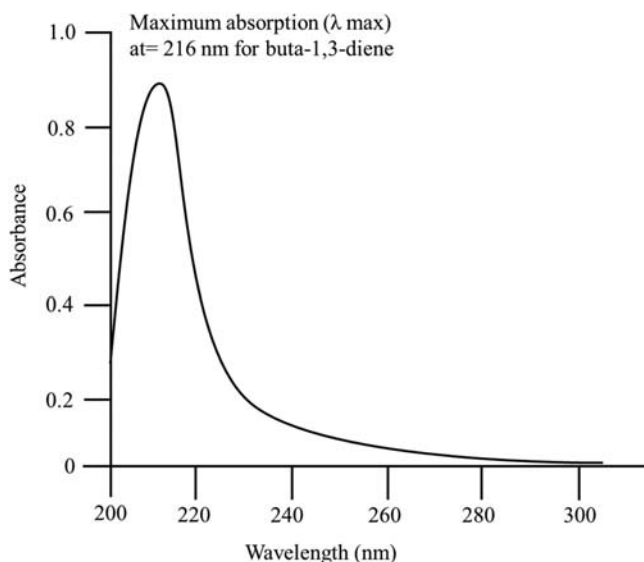


Figure 15.3 An assimilation range captured by a UV–Vis spectrophotometer. Buta-1,3-diene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$, was the test investigated. UV–Vis, Ultraviolet–visible.

assimilation of light—buta-1,3-diene is colorless. There are no nonbonding electrons in buta-1,3-diene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$. This implies that, as it were, electron hops that take out (inside the extent that the spectrometer can provide degree) are from pi-bonding to pi-antibonding orbitals.

The absorbance (A) is equal to the logarithm of a fraction involving the intensity of light before passing through the sample (I_0) divided by the intensity of light after passing through the sample (I). The fraction I divided by I_0 is also called transmittance (T), which expresses how much light has passed through a sample. However, Beer–Lambert’s law is often applied to obtain the concentration of sample (c) after measuring the absorbance (A) when the molar absorptivity (ε) and the path length (L) are known. Typically, ε is expressed with units of $L / \text{mol}/\text{cm}$, L has units of cm, and c is expressed with units of mol/L . As a consequence, A has no units [1,54].

Beer–Lambert’s law is especially useful for obtaining the concentration of a substance if a linear relationship exists using a measured set of standard solutions containing the same substance. Eq. (15.1) shows the mathematical relationships between absorbance, Beer–Lambert’s law, the light intensities measured in the instrument, and transmittance (Eq. 15.1)

$$A = \varepsilon Lc = \log_{10} \left(\frac{I_0}{I} \right) = \log_{10} \left(\frac{1}{T} \right) = -\log_{10}(T) \quad (15.1)$$

Eq. (15.1): A collection of conditions outlining the connections between assimilation A , Beer-law, Lambert’s light force measured within the instrument, and transmittance.

The word optical density (OD) is retention confounded with the term retention as often as possible. Both OD and retention measure the sum of light escalated misplaced in an optical component, even though OD accounts for light scrambling misfortunes whereas assimilation does not. The light scrambling in estimation is moderately minor, OD can be specifically calculated utilizing assimilation and the Beer–Lambert law.

During measurements, it’s critical to be aware of the experimental conditions. The conventional and most often used cuvettes have a layer thickness of 1 cm. When there is a limited amount of sample available for testing, thinner slice thicknesses of less than 1 mm are required. Within the instrument’s dynamic range, absorbance levels should be kept below 1 when quantification is required. An absorbance of 1 demonstrates that the test has retained 90% of the occurrence light or that 10% of the occurrence

light has been transmitted through the test, usually the case. A few UV–Vis spectrophotometers aren't touchy sufficient to accurately evaluate little sums of light since so small light comes to the locator. Weakening the test or shortening the travel are two direct arrangements for this problem [54,55]

As said prior, recording a pattern range with a “purge” reference arrangement is basic. The instrument has culminated in each way, the pattern would have zero absorbance at each wavelength inspected. In any case, in a genuine circumstance, the standard range will as a rule have a few exceptionally few positive and negative absorbance values. At home, these little absorbance values are regularly naturally subtracted by the computer program from the absorbance values of the test for each wavelength of light to get the genuine absorbance values [56,57].

The foundation of a calibration bend may be supportive depending on the objective of the investigation. Creating a calibration bend requires a little information investigation and extra exertion, but it is greatly valuable for calculating the concentration of a certain medicate in a test utilizing absorbance estimations. In any case, in numerous applications, such as OD estimations for bacterial culture, measuring absorbance proportions at certain wavelengths to decide the virtue of nucleic acids, or distinguishing particular solutions, a calibration bend is not required [58].

15.5 Major applications of UV–Vis spectroscopy

1. Discovery of impurities
 - a. It is one of the finest strategies for ensuring pollutions in natural molecules.
 - b. Extra peaks can be watched due to debasements within the test and compared with those of a standard crude material.
 - c. The debasements can be detected by measuring the absorbance at a specific wavelength [59–61].
2. Structure explanation of natural compounds
 - d. UV–Vis assimilation spectroscopy is valuable for natural atoms' basic illustration, such as identifying the nearness or nonattendance of unsaturation and heteroatoms [62,63].
3. UV–Vis absorption spectroscopy can be used to quantitatively determine compounds that absorb UV–Vis radiation [41,64].
4. UV–Vis absorption spectroscopy can characterize compounds that absorb UV–Vis radiation, thus used in the qualitative determination

of compounds. Identification is made by comparing the absorption spectrum with the spectra of known compounds [65,66].

5. This technique is used to detect the presence or absence of a functional group in the compound. The absence of a band at a particular wavelength is regarded as a piece of evidence for the absence of a particular group [67,68].
6. Kinetics of the reaction can also be studied using UV–Vis spectroscopy. The UV–Vis radiation is passed through the reaction cell and the absorbance changes can be observed [69,70].
7. Many drugs are either in the form of raw material or in form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at a specific wavelength [71,72].
8. Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds [73,74].
9. UV–Vis spectrophotometer may be used as a detector for HPLC [75,76].

15.6 UV–Vis spectroscopy as non-destructive testing tools

UV–Vis spectrophotometry has been widely used to identify and quantify organic compounds, both UV–Vis qualitative and quantitative analysis has the potential to analyze sample at very low concentrations with required pretreatment sample techniques. This section will describe the applications of UV–Vis spectrophotometers in selected areas as NDT tools [77,78].

15.6.1 Application UV–Vis spectrophotometer in the food and agriculture sector

In agriculture, UV–Vis spectroscopy offers a sophisticated way to control the quality of food, investigate the chemical purity level in soil, maximize crop yields, analyze the properties of fertilizers, and more. In this section, the current agricultural applications of UV–Vis spectroscopy as an NDT tool are discussed in more detail [79,80].

15.6.1.1 Assurance of soil quality with spectroscopy

The quality of soil utilized in both agribusiness and rural applications plays a critical part in deciding the by and large rate of food generation at in these areas. Since mass food generation and long gathering times

can influence soil quality, agriculturists and agrarian directors regularly got to include supplemental supplements, such as fertilizers, in their soils to advance ideal conditions and proceed development of their crops. Whereas these supplement augmentations are valuable in advancing plant growth, they must be closely observed to guarantee that the right supplement levels are included in the soil. Most agricultural fertilizers contain intemperate levels of nitrogen and phosphorus, both of which have to be closely analyzed to guarantee that solid crops are developed with higher yields.

Both phosphorus and nitrogen are basic components that advance plant development and maintainability. One explanatory method that has demonstrated fruitful in later think about to deciding phosphorus concentration in sugarcane juice, water, fertilizer, and cleanser tests may be a UV–Vis spectrophotometer. Molybdenum blue may be a common strategy utilized to precisely decide the concentrations of inorganic phosphate in a test. In this specific test, the absorbance of phosphor-molybdenum blue, which comes about from the response between molybdenum blue and the inorganic phosphates shown within the test, was measured between 800 and 900 nm to decide the λ max esteem. The response takes around 35 minutes to total. By utilizing this UV–Vis test, ranchers can rapidly decide the nearness of phosphates in their tests without the requirement for analyte extraction [81–83].

15.6.1.2 UV–Vis spectroscopy to control the quality of edible oils

There are two perspectives of the oil that can be tried: fat oxidation and general color.

1. Fat oxidation: the anisidine esteem (AV) is utilized as a marker of fat oxidation. AV measures the sum of aldehydes created when fats are oxidized, which is activated by light, oxygen, and high temperatures. Oxidation is not alluring because it decreases the quality of oils; subsequently, oils ought to have an AV of no more than 8.
2. Color of the oil: Plant colors such as chlorophyll or carotenoids can color the oil, particularly if it has been cold squeezed. Refined oils contain exceptionally few shades since they are evacuated amid the refining preparation. Carotenoids are a gathering of sound cancer prevention agents; hence, food producers point to higher levels of them in oils. On the other hand, chlorophyll an advanced oxidation and gives a biting note to the oil. To guarantee customer fulfillment, chlorophyll levels must be kept low [84,85].

15.6.1.3 UV–Vis spectra of chitin and chitosan

Chitin and chitosan contain diverse proportions of two chromophoric far-UV–Vis bunches, N-acetylglucosamine (GlcNAc) and glucosamine (GlcN); hence, their termination coefficients are non-zero for wavelengths shorter than almost 225 nm. Since the GlcNAc and GlcN buildups appear to have no proof of interaction inside the chitin/chitosan chain, the monomer units contribute in a straightforward, added substance way to the full absorbance of these polymers at a given wavelength [86,87]. The UV–Vis spectra of blends of N-acetyl glucosamine and glucosamine hydrochloride are very comparative to the spectra of chitosan, and the λ_{max} is 201 nm in 0.1 M HCl arrangement (Fig. 15.4).

UV–Vis spectroscopy can be used for the optical characterization of the chitin source [88,89]. The optical spectra of two dark coral species, *Antipathes caribbeana* and *Antipathes pennacea*, uncovered a wide band between 300 and 500 nm, with minor changes depending on the species.

Furthermore, the spectra revealed that *A. caribbeana* has Fe^{+3} , and both species have Mn^{+3} . To evaluate the degree of N-acetylation of chitin and chitosan, UV–Vis spectroscopy can be employed as an NDT technique. The researchers proposed the first derived UV–Vis method for determining the degree of deacetylation (DA) in 1985 [90,91]. The assimilation of the N-acetyl concentration gather in chitin or chitosan was

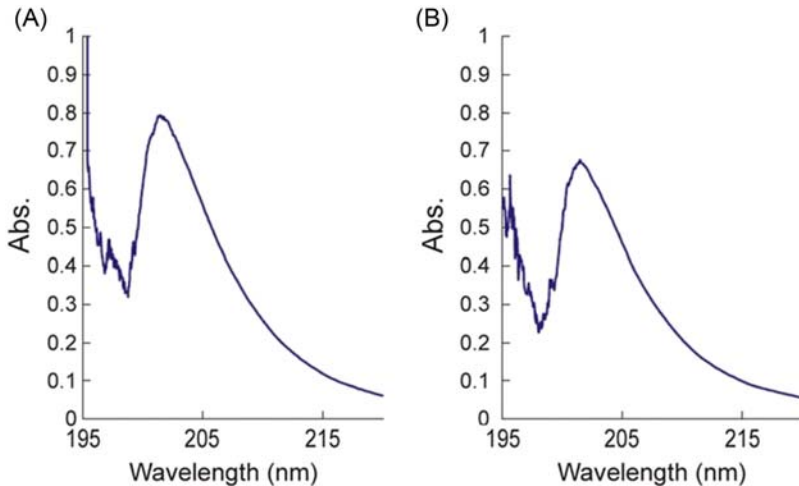


Figure 15.4 UV–Vis spectra: (A) a blend of N-acetyl glucosamine and glucosamine hydrochloride in 0.1 M hydrochloric corrosive arrangement; (B) chitosan in 0.1 M hydrochloric corrosive arrangement. UV–Vis, Ultraviolet–visible.

the premise for this approach. The absorbance of acetylglucosamine (at maximum wavelength) was directly proportional to its concentration in the range of 0.50–5.0 mg/L. GlcNAc was found to have a detection limit of 0.5 mg/L in 0.01 M acetic acid. The DA levels were measured at 199 nm in acetic acid solutions [92,93]. Since it required amazingly little sums of tests and did not require costly hardware, this strategy was foremost straightforward and helpful of the accessible methods.

Furthermore, background noise and contaminants were less of an issue in the first spectra derivation. A few made strides in UV–Vis to begin with induction strategies have been created to extend estimation comfort and exactness [94].

15.6.2 UV–Vis spectrophotometer in the surfactant and detergent industry

UV–Vis spectroscopy has been used to determine the counterion binding constant of individual surfactant molecules (micelles). This study provides information on the micellar transformation from a single molecule to a spherical, wormlike, or vesicular structure under the influence of salt concentration, temperature, pH, and shelf life (Fig. 15.5) [95,96].

15.6.2.1 The analysis of counterion-induced cationic flexible nanoparticle catalytic piperidinolysis of phenyl salicylate

The importance of counterions as nutrients and bioactive species has drawn the attention of scientists to determine the reaction kinetics and mechanism of the aqueous system. The spectrophotometric thought of piperidinolysis of ionized phenyl salicylate (PSa^-) was carried out by measuring the decrease in absorbance at 370 nm and 35°C as a work of response time (t). Active estimations were carried out by employing a Perkin Elmer UV–Vis Lambda 25 with an electronically temperature-controlled cell compartment and a temperature-regulating water shower

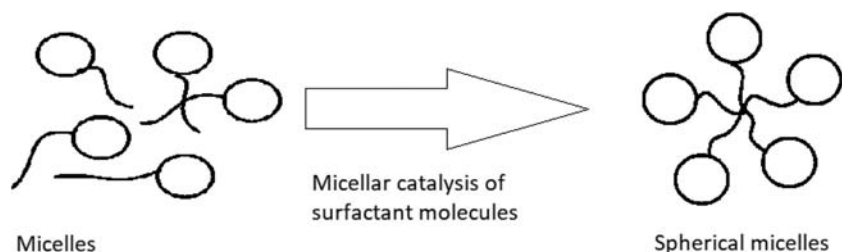


Figure 15.5 Micellar catalysis of molecules of surfactant to spherical micelles.

to keep the temperature steady. PSaH, Pip, and NaOH concentrations were kept consistent at 0.2 mM, 0.1 M, and 30 mM, separately, for each active trial. MX (MX = 2-FBzNa, 4-FBzNa, 2-ClBzNa, 4-ClBzNa, 2-BrBzNa, 4-BrBzNa, 2-IBzNa, or 4-IBzNa) concentrations were modified as required [97].

The responses were carried out for 6–8 half-lives. The watched dynamic information (A_{obs} vs t , where A_{obs} signifies the absorbance esteem at response time t) was dealt with a nonlinear slightest squares strategy.

$$A_{obs} = [R_0]\delta_{app}e^{(-k_{obs}t)} + A\infty \quad (15.2)$$

where $[R_0]$ is the introductory PSaH concentration, δ_{app} is the response mixture's clear molar absorptivity, k_{obs} are the first-order pseudo rate steady, and $A = A_{obs}$ at $t = \infty$. The information examination handle is clarified in detail somewhere else [97]. The catalytic impact of TTABr/MX/ H_2O nanoparticles (with MX = 2- and 4-halo benzoate salts) on the nucleophilic substitution response between PSa^- and Pip shows a monotonic increment in jobs with expanding $[MX]$ at steady $[TTABr]_T$, concurring to the discoveries. The catalytic consistent $^Xk_{cat}$ can moreover be utilized to compute the values of the particle trade constants K_X^{Br} or R_X^{Br} for $X = 2$ - and 4-halobenzoates (Fig. 15.5).

The K_X^{Br} or R_X^{Br} values for $X = 4$ -halobenzoates are higher than those for $X = 2$ -halobenzoates, which is due to the 4-halo benzoate ions' superior solubilization in micellar totals than the 2-halobenzoate particles. The expanding values of K_X^{Br} or R_X^{Br} from FBzNa to IBzNa are due to electronegativity and polarizability contrasts. The bigger counterion officially consistent within the nearness of CTABr nanoparticles than within the nearness of TTABr nanoparticles may be a conceivable explanation for the bigger values of K_X^{Br} or R_X^{Br} for $X = 2$ - and 4-halobenzoates within the nearness of CTABr nanoparticles than within the nearness of TTABr nanoparticles.

15.6.3 UV–Vis spectrophotometer in pharmaceuticals analysis

Qualitative examination utilizing spectrophotometric strategies gives fast and exact comes about with as it were little test volumes. These quick and robust machines have been a successful essential apparatus in the pharmaceutical industry due to their versatility and financial benefits. The

subjective investigation has demonstrated amazingly valuable for numerous vital shapes of natural compounds and makes a difference to guarantee quiet well-being and safety [98–100].

15.6.3.1 Examination for the control of paracetamol quality

One of the foremost commonly utilized drugs in the world is paracetamol. Paracetamol or acetaminophen may be common in the medicinal industry and found in numerous medical solutions. This painkilling operator, way better known as Tylenol, is by and large secure when taken as endorsed. Be that as it may, an intense overdose of acetaminophen can be possibly deadly, and its harmfulness is the driving cause of liver disappointment in most nations within the Western world. Subjective investigation guarantees that the estimation of dynamic fixings is exact and free of tainted compounds. The outcomes of these strategies give information that can be utilized for quality control and consistency of item detailing. Exact and precise comes about guarantee that the right measurement and estimation being utilized for the expected applications [101,102].

15.6.3.2 Analysis of bioactive compounds

The applications of quantitative investigation through spectroscopy permit pharmaceutical analysts to extraordinarily distinguish and compare natural compounds to guarantee that sedate atoms are legitimately ingested by the body and dispersed to the proper locales. Whether recognizing dynamic fixings or analyzing proteins, each component of pharmaceutical inquiry depends on spectrophotometers to empower subjective examination and exact sedate formulations [103,104].

15.6.4 UV–Vis spectrophotometer in environmental analysis

Water examination may be a hot point in our ecologically inviting world, and it is genuine that water defilement is central to natural security. UV–Vis spectroscopy is not as it were an affordable method of water investigation, but moreover has numerous applications within the world of natural science. Compared to other methods of spectrophotometry, UV–Vis spectroscopy is more adaptable and versatile than many scientists previously believed [105,106].

15.6.4.1 Bacterial-water contaminants

Bacteria is one of the most serious issues linked with water contamination. While standard bacterial tests are successful, they are also time-intensive, taking nearly two days to complete. New breakthroughs in UV–Vis

spectroscopy, are now able to correctly quantify the concentration of bacteria in water samples by measuring light absorption. This procedure is ready-to-use, versatile, and cost-effective, making it a well-known choice for water security investigations explanatory device [107,108].

The internet site The Environmental Protection Agency is always on the lookout for novel technologies to assess pollutants in drinking water. New breakthroughs in UV–Vis technology, which were previously overlooked, now provide more information and data on water quality and safety. Spectrophotometers that degree light within the UV–Vis and near-infrared groups are outlined to be convenient and long-lasting, making them perfect for natural fieldwork.

15.6.4.2 Chlorine and fluoride quantification

Chlorine is frequently added to water sources because it has a disinfecting effect. The water must be persistently checked to confirm that it is secure for human utilization since this strategy produces a little amount of left-over chlorine.

There are two types of residual chlorine, referred to as “free chlorine” and “mixed chlorine”, respectively. UV–Vis spectroscopy is a good way to tell the difference between these two types. This qualification is noteworthy since free remaining chlorine is regularly respected as a more compelling disinfectant and, in case appropriately found, can be used more successfully in drinking water. Another normal fixing in our drinking water is fluoride [109–111].

15.6.4.3 Geological studies

Geologists are also using these tools for analyzing the unique data spectrum from mineral samples. The data will be used to determine the geological element mapping that provides the mineral profiles and contamination information for further necessary actions. UV–Vis is also a powerful tool to quantify the residual polymer concentration in water and environmental samples. The polymers that exhibited a specific range of UV between 200 and 300 nm were analyzed. The results of the analysis showed that incremental increases in polymer concentrations corresponded to incremental increases in absorbance measurements, and a strong linear relationship was established between the polymer concentration and the absorbance values. The method was successfully used in the determination of polymer concentrations in water samples, as well as in concentrate samples collected from a wastewater treatment plant [112,113].

15.7 Advantages of UV–Vis spectrophotometry as non-destructive testing tool

Over the last few decades, UV–Vis spectrophotometry has advanced by leaps and bounds. Scientists now have a tool that may be used for a wide spectrum of analytical studies due to technological advancements. These approaches have been developed for use in a variety of scientific fields, and they are now widely used in biomedical and environmental research. Spectrophotometers' advantages are particularly useful in environmental science. These light meters are extremely adjustable to specific requirements and provide a long-lasting, portable, and ready-to-use technique of examination. A strategic collaboration with noticeable researchers and analysts from over the world is needed to create imaginative UV–Vis spectroscopy strategies and applications, and we are enthusiastic approximately making colorimeters that have a positive effect on the world [114–116].

15.8 Future potentials

The future of UV–Vis spectrophotometer is bright and promising. This technology will be developed to a more advanced integration with other instrumentation, easy-to-use, portable with specific applications. The evolution of LED as the light source will bring a new future for this remarkable technique. The LED light source will be a trendsetter for new applications for analysis and improving the traditional UV–Vis spectrophotometer.

15.9 Conclusion

UV–Vis spectroscopy is a cost-effective, simple, versatile, non-destructive, and analytical technique, which is suitable for a large spectrum of organic compounds and some inorganic species. As a function of wavelength, UV–Vis spectrophotometers measure the absorption or transmission of light that passes through a medium. UV–Vis spectrophotometer techniques are applicable to a wide range of research disciplines, namely agriculture, food, pharmaceutical, environment, and many others. Inevitably, this technique has contributed to significant finds for the researcher worldwide.

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CHAPTER 16

Hard X-ray photoelectron spectroscopy and X-ray diffraction techniques: non-destructive compositional, electronic, chemical and structural in-depth characterization in the tens-of-nanometer scale

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16.1 Introduction

X-ray diffraction has been and is still one of the most successful techniques for the structural characterization of solid materials. Its application to the study of bulks, thin films, surfaces, and interfaces in materials science has reached a high degree of sophistication and development. Thus, it constitutes nowadays one of the preferred techniques to investigate structural problems of bulks, heterostructures, surfaces, and interfaces [1–7]. This is due, first, to the high penetration of the X-rays, which facilitates the investigation of surfaces, buried interfaces, and bulks in conditions otherwise impossible, and in some cases close to real industrial processes (e.g., high pressures, presence of liquids, etc.) [8,9]. Second, the well-known theoretical background coming from the experience accumulated in the research of bulk materials makes the data analysis relatively straightforward. Finally, the availability of high fluxes (such as the EBS (Extremely Brilliant Source) at ESRF—The European Synchrotron) makes it possible to analyze dynamic processes at surfaces and interfaces on a real-time scale. A wide variety of techniques are suitable for structural and morphological characterization of materials, such as X-ray

reflectivity (XRR) at low and high angles, grazing-incidence X-ray diffraction (GI-XRD), surface X-ray diffraction (SXD), reciprocal space maps (RSM), high resolution powder diffraction (HRPD), etc.

The photoemission and the Auger electron spectroscopies play a preponderant role in the study of the composition and the electronic properties of solids [10,11]. These techniques have been used extensively for decades and have reached a high degree of sophistication. Electron spectroscopies, like X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES), are the most powerful techniques for the chemical, compositional, and electronic characterization of solid materials. The basis for quantitative composition analysis of homogeneous and/or heterogeneous materials is the fact that the photoemission cross-section of a core level is nearly independent of the valence state of the excited element so that the photoemission signal intensity can be considered to be proportional to the number of atoms in the analyzed volume. This intensity is also dependent on the incident X-rays flux, the photoionization cross-section, the angular anisotropy, the electron effective attenuation length (related to the electron inelastic mean path) of the photoelectrons and the detector efficiency and detector transmission function. The last two depend on the kinetic energy of the photoelectrons and the operation mode of the electron analyzer [12,13]. Special attention should be paid to the analyzer's mode of operation. The analyzer setting should be selected to ensure a linear response over the energy range in which it operates. Inappropriate settings can lead to large errors in determining the sample composition. Quantification accuracy implies than accurate knowledge of the effective attenuation length, the ionization subshell cross-section, the angular anisotropy dependence with X-ray energy, and, of course, of the detector efficiency and transmission function.

Overall, their application has been limited to the investigation of surface phenomena by using energies between 40 and 2000 eV for both, the excitation sources and detected electrons. The low electron inelastic-mean-free path (IMFP) and/or the effective attenuation length (EAL) [14–19] in solid materials, at the energies used with these techniques, are responsible for their surface sensitivity. Particularly, buried interfaces are not accessible for the great majority of the techniques of surface physics. However, using hard X-rays as an excitation source, which has a macroscopic penetration depth in the materials, high kinetic energy photoelectrons can be produced [20,21]. Consequently, Hard X-ray photoelectron spectroscopy (HAXPES) benefits from the exceptionally large escape

depth of high kinetic energy photoelectrons enabling the study of bulk and buried interfaces up to several tens of nanometers in depth [14,22,23]. Using hard X-rays as an excitation source also makes possible access to deeper orbitals that cannot be reached with conventional XPS. Fig. 16.1 shows two HAXPES spectra recorded at 15 keV (Fig. 16.1A) and 22 keV (Fig. 16.1B) on a polycrystalline Au sample, measured on the CRG-BM25 SpLine beamline at the ESRF [20,24,25]. It is important to note that with the exception of the Au-1s orbital with a binding energy of 80.7 keV, all other core levels are accessible and emitted with relatively high kinetic energy. For example, the photoelectron corresponding to the Au-2s level with a binding energy of 14.3 keV, when it is excited with a photon energy of 22 keV, is emitted with a kinetic energy of 7.7 keV. The advantages of HAXPES over XPS are its greater information depth, which can also be changed and/or tuned, and its accessibility to deeper core levels. The information depth can reach several tens of nanometers for 15 keV electron kinetic energy [14,26,27]. Using the advantage of tunable X-ray radiation provided by the synchrotron, the photoelectron

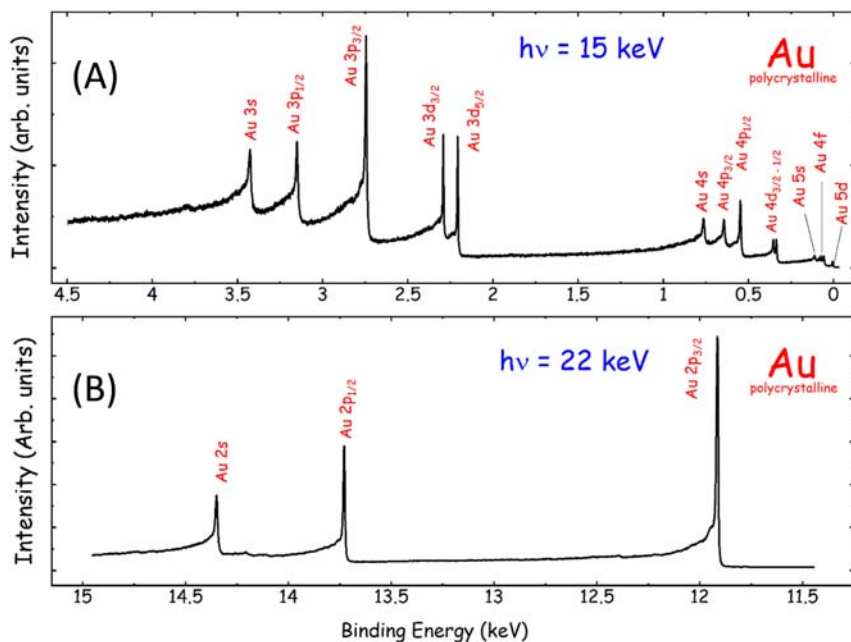


Figure 16.1 HAXPES spectra recorded at 15 keV (A) and 22 keV (B) photon energy on a polycrystalline Au sample, measured on the CRG BM25 SpLine beamline at the ESRF.

kinetic energy, that is the information depth can be changed and consequently, non-destructive electronic, chemical, and compositional depth profiles can be obtained [21–23,26–28]. HAXPES is becoming a well-established technique available in many third-generation synchrotron beamlines [29–31]. Recently the commercialization of a significant number of laboratory systems has appeared, which use monoenergetic X-ray sources [30,32–34].

The complementation of HAXPES with an atomic structure sensitive technique such as GI-XRD, XRR, SXD, RSM, X-ray Standing Waves (XSW), etc. [29,35–39] enhances research capabilities and performances with major applications for materials science. The knowledge of the layer thicknesses obtained from XRR measurements [40–43], is extremely valuable information to enhance the accuracy of the compositional depth profile determined from the HAXPES signal intensities analysis. Hence, it will be possible to access directly the fundamental information necessary for the understanding of the interplay between geometric structure, electronic structure, composition profile, electrical conductivity, and magnetic properties.

Due to the macroscopic X-ray penetration depth in the materials, the surfaces and the interfaces give rise to particular processes of diffraction throughout the perpendicular direction of the surface and/or to the crystal interfaces (Crystal Truncation Rods, CTR). On the other hand, the electron mean-free-path and/or the effective attenuation length in solid materials can achieve values in the several tens of nanometers at photoelectron kinetic energies ranging between 5 to 15 keV [16–19,44,45]. The combination of HAXPES with X-ray diffraction techniques thus leads to a fundamentally important technique for the characterization of solids. Today there are several synchrotron beamlines [20,37,38,46–48] that exploit the combination of both techniques.

16.2 Physical principles

16.2.1 Photoemission process

The origin of photoemission spectroscopy is based on Einstein's famous 1905 paper [49], which postulates the quantum hypothesis of light by means of the fundamental relation

$$E_{kin} = h\nu - E_B^V \quad (16.1)$$

where E_{kin} is the photoelectron kinetic energy, $h\nu$ the photon energy and E_B^V the binding energy with respect to the vacuum level, respectively.

Thus, if the photon energy increases, the kinetic energy of the photoelectron increases proportionally to that of the photon, which constitutes the very principle of HAXPES. The basic principle of photoelectron spectroscopy is the following: the difference between the energy of this excited state and the energy of the fundamental state of the sample before the photon is absorbed, must be equal to the energy of the absorbed photon. This viewpoint, although simple, is rigorous and in practice is difficult to handle. However, in many cases, it is possible to treat the photoemission process in the single-particle framework (one-electron picture). Consider a system containing N electrons, which is ionized by a photon of energy $h\nu$. After ionization, the system remains with $N - 1$ electrons and the photoelectron leaves with kinetic energy E_{kin} (which is measurable). According to the conservation of energy:

$$E_{kin} = h\nu - [E(N - 1) - E(N)] = h\nu - E_B^V \quad (16.2)$$

Here $E(N)$ represents the energy of the system with N electrons, $E(N - 1)$ is the energy of the system with $N - 1$ electrons and E_B^V is the binding energy with respect to the vacuum level of the photoemitted electron. This binding energy of a particular core level can be and in general is different, between different chemical forms (species) of the same atom. This energy difference is called chemical shift [10,50–53] and it is related to the different electronic configurations. However, care must be taken in its interpretation since the observed shifts may also be due to recoil effects [54,55], particularly when hard X-rays are used. The recoil effect is associated with the conservation momentum and, as a consequence, both the peak shift and the peak broadening depend on the photon energy. Recoil is routinely observed in HAXPES of gas-phase atoms and molecules, observations in solids are scarce. Recent publications, however, report that recoil-induced shifts can be observed at the core level and in valence band spectra, the effect being greater when the atom analyzed is lighter [55].

The photoelectron intensity $I_{A_\xi}(E_{kin})$ of the atomic level ξ from the component element A produced at a sample depth between Z_1 and Z_2 of a laterally homogeneous sample, within the observation area of the electron analyzer, is given by:

$$I_{A_\xi}(E_{kin}) = C \cdot f(E_{h\nu}) \cdot \Gamma(E_{kin}, E_p) \cdot \sigma_{A_\xi}(E_{h\nu}) \cdot P_{A_\xi}(E_{h\nu}, \theta_{pk}, \varphi_{pk}) \cdot \frac{\Omega}{4\pi} \cdot \int_{Z_1}^{Z_2} N_A(z') \cdot e^{-\left[\frac{Z'}{EAL(E_{kin}) \cdot \cos(\theta)} \right]} \cdot dz' \quad (16.3)$$

Where the proportionality constant C is the area ratio between the area collected/observed by the analyzer and the area irradiated by the X-rays; if the X-ray footprint is smaller than the analyzer collected area, the constant C is set to 1, $f(E_{h\nu})$ is the X-ray photon flux of energy $E_{h\nu}$, $\Gamma(E_{kin}, E_p)$ is the detector efficiency and transmission function that depends on the photoelectron kinetic energy E_{kin} and the analyzer pass energy E_p . Here $\sigma_{A\xi}(E_{h\nu})$ [56,57] is the subshell photoionization cross-section, $P_{A\xi}(E_{h\nu}, \theta_{pk}, \varphi_{pk})$ [57–60] is the angular asymmetry factor, θ_{pk} is the angle between the photoelectron propagation and the photon polarization vectors and φ_{pk} is the angle between the photon propagation vector and the plane passing through the photon polarization axis and the photoelectron propagation vector, respectively (see Fig. 16.2); Ω is the analyzer collection solid angle, $N_A(z)$ the atomic density of element A which is assumed to be laterally constant in the detection area and depends only on the depth, $EAL(E_{kin})$ is the effective attenuation length of the photoelectron at the kinetic energy E_{kin} and θ is the angle between photoelectron collection direction and the surface normal. Fig. 16.2 shows a schematic representation (isometric view) of a photoemission setup, where α_i is the incidence angle with respect to the surface of the X-ray (see Fig. 16.8) and θ the electron take-off angle respect to the surface normal vector of the sample.

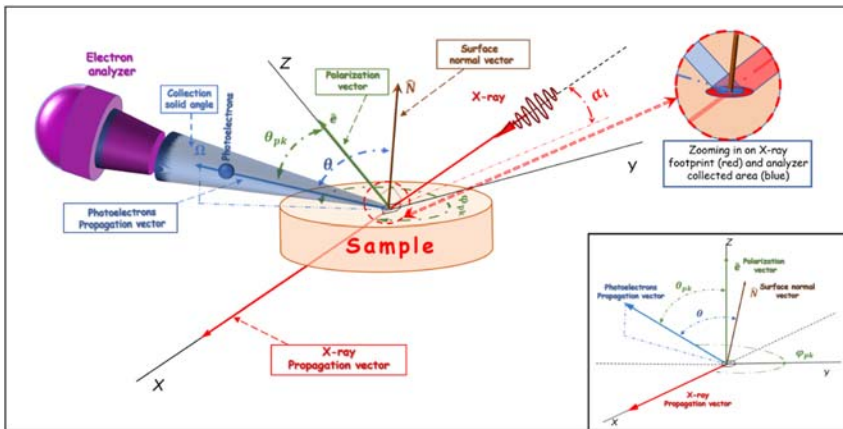


Figure 16.2 Schematic representation of a photoemission experimental setup (see text), where α_i is the X-ray incidence angle with respect to the surface (see Fig. 16.8) and θ the electron take-off angle with respect to the surface normal vector. The circle on the top right shows a zoom of the X-ray footprint and the analyzer collected area. The inset shows, for clarity, the angles and directions concerned. The figure shows the case of linear polarization, but the incident X-ray can be either linear or circular polarized or non-polarized.

The X-ray propagation vector is taken to be on the x-axis of a cartesian reference frame. The layout displayed corresponds to the case of linear polarization. It should be noted that the incoming radiation can be either non-polarized or linear or circular polarized; in the figure linear polarization has been supposed. The inset in Fig. 16.2 shows, for clarity, the angles and directions of the X-ray beam and the photoelectrons.

Accordingly, by following the intensity dependence and the line shape with the $EAL(E_{kin})$ it is possible to reconstruct or obtain the sample composition as a function of the depth and consequently the composition profile. The quantification accuracy implies an accurate knowledge of the effective attenuation length, the ionization subshell cross-section, the angular anisotropy dependence with X-ray energy, and, of course, the detector efficiency and transmission function. In the literature, there are abundant ways to obtain data for the cross-sections [56,57,60] and the effective attenuation lengths [14,16–19,44,45,61,62], although the detector efficiency and transmission function are specific to each experimental system and operation mode. One way to overcome this problem is to use suitable standards acquired under identical conditions in the same experimental system in order to reduce the number of unknowns in obtaining the composition.

Thus, for example, in the case of a homogeneous semi-infinite solid ($N_A(z) = N_A^\infty = \text{const}$), that is, with constant atomic density, the intensity of the photoemission signal is reduced to:

$$I_{A\xi}^{Std}(E_{kin}) = C \cdot f(E_{hv}) \cdot \Gamma(E_{kin}, E_p) \cdot \sigma_{A\xi}(E_{hv}) \cdot P_{A\xi}(E_{hv}, \theta_{pk}, \varphi_{pk}) \cdot N_A^\infty \cdot EAL_{Std}(E_{kin}) \cdot \cos(\theta) \quad (16.4)$$

This can be used as a normalization standard and consequently the photoelectron intensity [Eq. (16.3)] $I_{A\xi}(E_{kin})$ of the atomic level ξ from the component element A is reduced to a function of only two variables, the EAL, and the atomic density $N_A(z)$:

$$I_{A\xi}(E_{kin}) = \frac{I_{A\xi}^{Std}}{N_A^\infty \cdot EAL(E_{kin}) \cdot \cos(\theta)} \cdot \int_{Z_1}^{Z_2} N_A(Z') \cdot e^{-(Z'/EAL(E_{kin}) \cdot \cos(\theta))} dZ' \quad (16.5)$$

In almost all of the literature related to the photoemission cross-sections, only data for excitation photon energies below 10 keV and consequently for core levels with small binding energy are given. The tables of Scofield [56] contain data for excitation energies from 1 to 1500 keV and for all the elements and all their core levels. The photoemission cross-section of a core

level is nearly independent of the chemical state of the element excited but decreases considerably with the excitation photon energy. Fig. 16.3 shows this dependence for three elements, carbon (C), aluminum (Al), and iron (Fe) for photon energies between 1 and 30 keV; the data are taken from the Scofield [56] tables. Its decrease is more important for elements of low atomic number. The decrease can reach up to 8 or more orders of magnitude. It is more accentuated as the core level binding energy is lower. The higher the atomic number, the higher the photoemission cross-section. Fourth-generation synchrotron radiation sources, such as the Extremely Brilliant Source ESRF-EBS, produce sufficient photon flux to compensate for the decrease in the cross-section. This flux can reach values more than 10^{12} times higher than that produced by conventional sources (see Fig. 16.11), which allows for compensating for the decrease in cross-section.

16.2.2 Effective attenuation length

The IMFP and the EAL are the most relevant parameters for XPS and AES related to electron transport through the solid. The IMFP [63], defined as the average distance that an electron with a given energy travels between successive inelastic collisions, has been widely used since the early beginning

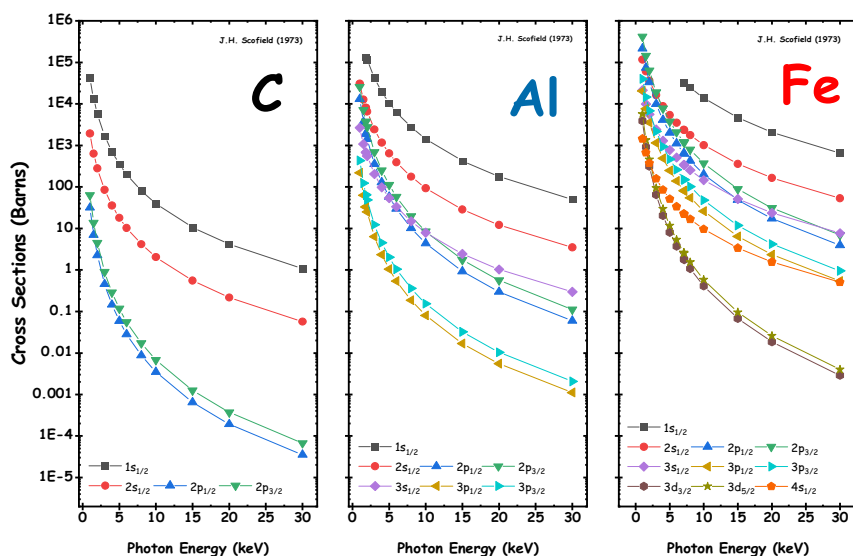


Figure 16.3 Subshell cross-section according to Scofield [56] in the photon energy range from 1 to 30 keV. The graph on the left corresponds to the core levels of carbon, in the middle to aluminum, and on the right to iron.

of electron spectroscopies. Due to elastic collisions, the electron path length can be seen as a zigzag path consisting of linear trajectories from the electron creation point to the solid surface. For quantification, the distance traveled by the electron from its point of creation to the surface without loss of energy is the important parameter. Hence, the apparent controversy of considering IMPF as the distance between two elastic collisions or the distance from the point of creation to the surface can be resolved by introducing a new parameter: the effective attenuation length, EAL [63] in order to account for the elastic-scattering events present during the electron transport. The EAL parameter which, when introduced in place of the IMFP into an expression derived for AES and XPS (Eqs. 16.3–16.5) and on the assumption that elastic scattering effects are negligible for a given quantitative application, will correct that expression for elastic scattering effects.

The EAL has a strong dependence on the experimental configuration and type of solid, so it depends on the electron emission angle with respect to the surface normal, on the angle between the incident photon direction and the electron emission direction, on the photoelectron angular asymmetry parameter, on the overlayer thickness, and the sample characteristics. The use of EAL for XPS and AES quantification applications is, for sure, a suitable option because it includes the effects of the elastic and inelastic scattering of the electrons occurring in the transport process from the solid to the detector. A large number of empirical formulas, practical guidelines, and databases for the calculation of both IMPF and EAL, as well as abundant experimental data, can be found in the literature [14,16–19,44,45,61,62]. The most practical and widely used formulas are those from Tanuma et al. [18,61,62], denoted by TPP-1 and TPP-2, and the NIST-71 database [64] for the IMFP prediction. Although the mean free path of electrons in a solid differs depending on the material, their behavior is universal.

Fig. 16.4 shows EALs values of different materials and at different energies; on the left are the theoretical values obtained with the TPP-2 formula and on the right are different experimental data taken from the literature. The references for the experimental data are in the legend. It is important to note that the EAL at 10 keV can reach values between 6 and 10 nm and at 15 keV in some cases it can reach a value of 25 nm. As noted above, it is precisely this effect that confers exceptional capabilities to hard X-ray photoemission spectroscopy and suitability for studying heterostructures, thin films, buried interfaces, and bulk materials. In growth processes, for example, it is possible to follow the evolution of the volume electronic structure as a function of the layer thickness.

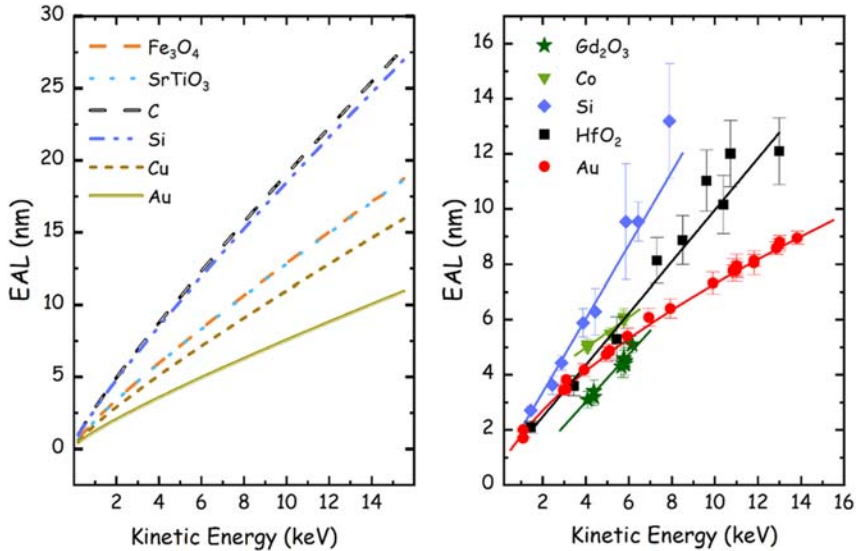


Figure 16.4 Effective attenuation length of different materials: in the left graph values calculated with the TPP 2 formula [61,62,64] for Fe₃O₄, SrTiO₃, C, Si, Cu and Au and in the right graph, experimental values obtained from the literature: Gd₂O₃, [65] Co, [65], Si, [66] HfO₂, [43,67] and Au [16].

More recently, Rubio et al. [65] proposed a simple practical equation for the evaluation of the EAL of solids in the electron kinetic energy range between 1 and 14 keV. The proposed equation is based on a fitting the expression $EAL = a \times (E_{kin})^b$ to the EAL experimental data obtained for Cu, Au, Ti, Si, Ge, TiN, SiO₂, HfO₂, Fe₃O₄, SrTiO₃.

For each experimental data (sample) different a and b parameters have been obtained. The dependence of these parameters on the material's effective atomic number Z_{eff} have been evaluated. The parameter a shows a polynomial dependence with Z_{eff} , while b presents a linear dependence. Thus, the proposed equation is only dependent on the compound effective atomic number eliminating tedious calculations based on electron IMFPs and transport mean free paths. The results of the corresponding adjustments/analyses lead to the following expressions:

$$\begin{aligned}
 a &= 0.0044 + 10^{-7} \times (Z_{eff})^{2.7} \\
 b &= 0.927 - 0.0037 \times Z_{eff} \\
 EAL &= \left(0.0044 + 10^{-7} \times (Z_{eff})^{2.7}\right) \times (E_{kin})^{(0.927 - 0.0037 \times Z_{eff})}
 \end{aligned} \tag{16.6}$$

Where E_{kin} is in eV and EAL in nm, respectively.

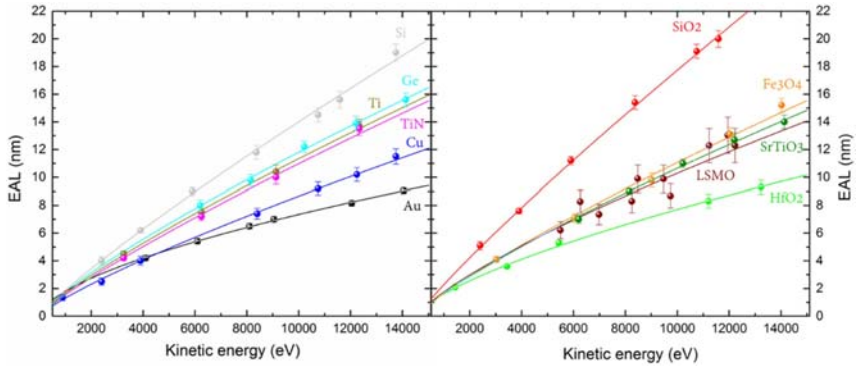


Figure 16.5 Experimental EALs obtained in the electron kinetic energy range between 1 and 14 keV for several metal (*left*) and oxide (*right*) compounds. Solid lines correspond to an individual fitting using the expression $EAL = a \times (E_{kin})^b$. Reprint from J. Rubio-Zuazo, G. R. Castro, *Experimental effective attenuation length on solids for electron kinetic energies between 1 and 14 keV: determination of a simple practical equation*, *Appl. Surf. Sci.* 599 (2022) 153918. <https://doi.org/10.1016/j.apsusc.2022.153918> with permission from Elsevier.

Fig. 16.5 shows the experimental data (fat points) used to obtain the simple practical equation, the solid line corresponds to the derived equation. The accuracy of the proposed practical equation reproduces within the experimental errors the experimental EALs presented in their work and the data available in the literature.

16.2.3 X-ray diffraction and reflectivity

X-ray diffraction is the most wide technique used for the structural analysis of bulk materials [66–68]. For many decades, the application of X-ray diffraction to material science problems has been developed to a high degree [1–5,8,9,40,69,70]. Therefore, X-ray scattering techniques are nowadays probably the preferred methods for the structural characterization of bulks, heterostructures, thin films, surfaces, and interfaces. This is certainly primarily due to the high penetration depth of X-rays, which facilitates the study of thin films, surfaces, and interfaces under conditions that are difficult to access with other structural characterization techniques, such as studies at very high pressure/high temperature or in complex reactive environments, and secondly, to the well-known theoretical basis resulting from the accumulated experience of more than 100 years of research on the interaction of X-rays with the matter, which makes interpretation and analysis of X-ray scattering data straightforward. Furthermore, with the advent of high flux X-ray sources such as third or

fourth generation synchrotrons (e.g., ESRF-EBS), dynamical processes at surfaces, interlayers, and solids can be addressed in real time.

There is a variety of X-ray techniques that when used in combination with photoemission contribute to a better comprehension of the macroscopic behavior of the studied material by correlating electronic, compositional, and crystalline structure. Thus, the most commonly used X-ray techniques are XSW, XRR, SXD, Single Crystal Diffraction, RSM, GI-XRD and Grazing Incidence HRPD.

The elastic X-ray scattering is described according to the following expression:

$$\vec{K}_f - \vec{K}_i = \vec{Q} \quad (16.7)$$

Here $\vec{K}_f$ and $\vec{K}_i$ are the wave vectors of the diffracted and incident monochromatic plane wave, respectively. $\vec{Q}$ is the scattering vector and it is called the momentum transfer vector. In a crystalline sample X-ray diffraction occurs when $\vec{Q} \equiv \vec{G}_{hkl} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$, where $\vec{G}$ is a reciprocal space vector and h , k , and l and $\vec{a}_1^*$, $\vec{a}_2^*$ and $\vec{a}_3^*$ are the Miller indices and the primitive reciprocal basis vectors, respectively. The primitive reciprocal basis vectors are related to the primitive basis vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ of the crystal lattice by:

$$\vec{a}_i \cdot \vec{a}_j^* = 2\pi\delta_{ij} \quad (16.8)$$

where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$. The momentum transfer plays a fundamental role in the study of condensed matter. For elastic scattering $|\vec{K}_f| = |\vec{K}_i| = K = 2\pi/\lambda = 5.08 \times E$, where λ and E are given in nm and keV, respectively, and $\vec{Q}$ is related to the scattering angle θ by $|\vec{Q}| = 4\pi/\lambda \sin\theta$. $\vec{G}_{hkl}$ is a vector of the reciprocal lattice which is perpendicular to the planes with Miller indices (h, k, l) . The interplanar adjacent plane distance d_{hkl} ¹ which is normal for the vector $\vec{G}_{hkl}$ is given by:

$$d_{hkl} = \frac{2\pi}{|\vec{G}_{hkl}|} \quad (16.9)$$

¹ The general formula to obtain the spacing between the adjacent crystal planes is:

$$d_{hkl} = \sqrt{\frac{(1 - \cos^2(\alpha_1) - \cos^2(\alpha_2) - \cos^2(\alpha_3) + 2\cos(\alpha_1)\cos(\alpha_2)\cos(\alpha_3))}{\left\{ \frac{h^2 \sin^2(\alpha_1)}{(a_1)^2} + \frac{k^2 \sin^2(\alpha_2)}{(a_2)^2} + \frac{l^2 \sin^2(\alpha_3)}{(a_3)^2} + \frac{2hl}{a_1 a_2} [\cos(\alpha_1)\cos(\alpha_2) - \cos(\alpha_3)] + \frac{2hl}{a_2 a_3} [\cos(\alpha_2)\cos(\alpha_3) - \cos(\alpha_1)] + \frac{2hl}{a_1 a_3} [\cos(\alpha_3)\cos(\alpha_1) - \cos(\alpha_2)] \right\}}}$$

Where α_1 , α_2 , and α_3 are the angles between the primitive lattice vectors $\alpha_1 \angle (\vec{a}_2, \vec{a}_3)$, $\alpha_2 \angle (\vec{a}_3, \vec{a}_1)$, and $\alpha_3 \angle (\vec{a}_1, \vec{a}_2)$, respectively

Therefore, the diffraction condition expressed in Eq. (16.7) can be transformed into the usual form of Bragg's law:

$$\begin{aligned} K_f^2 + K_i^2 - 2K_f K_i \cos(2\theta) &= |\vec{G}_{hkl}|^2 \Rightarrow 2K^2[1 + \cos(2\theta)] = \left(\frac{2\pi}{d_{hkl}}\right)^2 \\ 2d_{hkl}\sin(\theta) &= \lambda \end{aligned} \quad (16.10)$$

But the (h, k, l) indices that define $\vec{G}_{hkl}$ are not necessarily identical to the indices of an actual crystal plane, since the Miller indices are the three smallest integers that have the same ratio as the intersection points of the plane with the crystallographic axes. Thus (h, k, l) indices may contain a common factor n . Hence, Eq. (16.10) can be transformed into the well-known Bragg law expression:

$$2d\sin(\theta) = n\lambda \quad (16.11)$$

Fig. 16.6 shows the general X-ray scattering geometry. The top left panel (Fig. 16.6A) shows an isometric view and the right panel (Fig. 16.6B) shows a top view.

The momentum transfer $\vec{Q}$ -vector in-plane (x, y) and perpendicular (z) components depends on the four angles $\alpha_i, \varphi_i, \alpha_f$ and φ_f from the laboratory frame-system as follows:

$$\begin{aligned} Q_x &= K \left[\cos(\alpha_f) \times \cos(\varphi_f) - \cos(\alpha_i) \times \cos(\varphi_i) \right] \\ Q_y &= K \left[\cos(\alpha_f) \times \sin(\varphi_f) - \cos(\alpha_i) \times \sin(\varphi_i) \right] \\ Q_z &= K \left[\sin(\alpha_f) + \sin(\alpha_i) \right] \end{aligned} \quad (16.12)$$

The incident and diffracted beams directions are described in the laboratory frame system by means of $\alpha_i, \varphi_i, \alpha_f$ and φ_f angles, and are related to the reciprocal space system by the $\vec{Q}$ -vector or the $\vec{G}_{hkl}$ direction. If one of the four angles is kept fixed, it is possible to scan across the reciprocal space in three dimensions by varying the other three. Thus, it is possible to obtain RSM in different scattering plane projections. The α_i, φ_i angles correspond to the sample orientation with respect to the incoming X-ray beam and α_f and φ_f correspond to the detector orientation/position in the reciprocal space. The relationship between the crystallographic axes and the laboratory coordinate system is obtained by means of the so-called orientation matrix, which defines the relationship between the two systems.

In the case of SXD and/or GI-XRD, the incidence angle α_i is kept fixed at low values. The information depth or the X-ray penetration can be

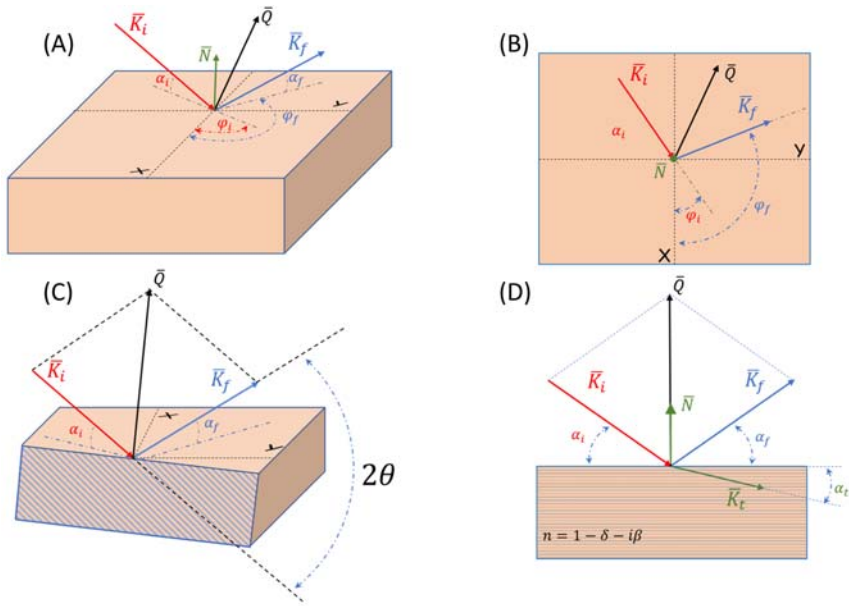


Figure 16.6 X-ray scattering geometric, where $\vec{K}_i$, $\vec{K}_f$ and $\vec{K}_t$ are the wave vectors of the incident, diffracted and transmitted X-ray beam, respectively; $\vec{Q}$ is the scattering vector called the momentum transfer and $\vec{N}$ is the surface normal vector; α_i , α_f and α_t are the incident, diffracted, and transmitted angles of the wave vectors with respect to the sample surface; φ_i and φ_f are the corresponding azimuthal angles, respectively. (A) isometric view of the scattering. (B) top view. (C) non-coplanar scattering plane and (D) coplanar scattering plane.

varied by changing the incidence angle value. The diffraction plane is in the X-Y plane (sample surface) when the angles α_i and α_f are zero and the perpendicular component Q_z of momentum transfer vector is zero. CTRs can be obtained by varying or changing the other three angles (φ_i , α_f and φ_f) by keeping the in-plane momentum transfer component constant [see Eq. (16.12)]. In the case that the wave vectors $\vec{K}_f$ and $\vec{K}_i$ and the surface normal vector $\vec{N}$ lie in the same plane (scattering plane) and the angles α_i , and α_f are the same ($\alpha_i = \alpha_f$) (see Fig. 16.6D), the parallel component $\vec{Q}_{\parallel}$ of momentum transfer vector is zero. Thus, Eq. (16.12) is reduced to:

$$Q_z = K [\sin(\alpha_f) + \sin(\alpha_i)] \quad (16.13)$$

with $\alpha_i + \alpha_f = 2\theta$, and Q_z describes the lattice crystal periodicity parallel to the sample surface.

In addition to the X-ray diffraction techniques described above, a more specific technique can be used: XRR. XRR in the range of total reflection is a non-destructive technique to obtain the electron density

profile [40–42,66,71–73]. It is a well-established method for several decades as it is useful to investigate the thickness and roughness of thin layers [74–76]. It is extremely sensitive to the actual interface roughness profile of buried interfaces. In the case of grazing incidence angles, the X-ray reflection and refraction at a flat surface between two media of different refraction indices (see Fig. 16.6D) can be understood in the framework of a phenomenological model. The complex index of refraction for X-ray radiation is related to medium scattering properties of density of electrons ρ , scattering amplitude per electron r_e (classical electron radius) and the absorption coefficient μ by the relation:

$$n = 1 - \delta - i\beta \quad (16.14)$$

where $\delta = \frac{r_e}{2\pi} \lambda^2 \rho \approx 10^{-4} \dots 10^{-6}$ and $\beta = \frac{\lambda}{4\pi} \mu \approx 10^{-6} \dots 10^{-9}$. For the energy-dependent optical constants, it should be noted that δ is the decrease in refractive index and β is the absorption index. Therefore $\alpha_t < \alpha_i$ and $|n| \lesssim 1$ but in any case, it will always be less than 1. Since $|n| \lesssim 1$, the angle α_t , between the X-ray beam and the sample surface will always be less than the X-ray incidence angle ($\alpha_t < \alpha_i$). Consequently, the condition for observing total external reflection ($\alpha_t = 0$) is that the incidence angle α_i has to be less than a critical angle α_C . By applying Snell's law $\cos(\alpha_i) = n \cos(\alpha_t)$ with the condition that $\cos(\alpha_t) = 1$, it is possible to obtain an expression for the critical angle α_C as a function of the medium scattering properties. Since the refractive index is slightly less than 1, the critical angle is clearly very small; hence $\cos(\alpha_C)$ can be approximated as $1 - \frac{(\alpha_C)^2}{2}$ yielding to:

$$\alpha_C = \sqrt{2\delta} = \lambda \sqrt{\frac{r_e}{\pi} \rho} = \frac{\sqrt{4\pi r_e \rho}}{K} \quad (16.15)$$

Applying the boundary conditions (normal and tangential components are continuous at the interface) for the electric and magnetic field at the interface between two media, it is possible to deduce the amplitude reflectivity ($r = A_r/A_i$) and transmittivity ($t = A_t/A_i$), where coefficients A_i, A_r and A_t are the amplitude of the incident, reflected and transmitted fields and considering that $1 + r = t$. For the case of small grazing angles of incidence, Fresnel reflectivity and transmitted intensity become:

$$\begin{aligned} R(\alpha_i) &= r.r^* = \left| \frac{\alpha_i - \sqrt{(\alpha_i)^2 - (\alpha_C)^2 - 2i\beta}}{\alpha_i + \sqrt{(\alpha_i)^2 - (\alpha_C)^2 - 2i\beta}} \right|^2 \\ T(\alpha_i) &= t.t^* = \left| \frac{2\alpha_i}{\alpha_i + \sqrt{(\alpha_i)^2 - (\alpha_C)^2 - 2i\beta}} \right|^2 \end{aligned} \quad (16.16)$$

Here it was assumed that the reflectivity (r) and transmissivity (t) coefficients are the same for S polarization (electrical field perpendicular to the scattering plane) and P polarization (electrical field parallel to the scattering plane), that is, $r^{(s)} \approx r^{(p)}$.

The reflectivity $R(\alpha_i)$ (see Fig. 16.7A) exhibits three different behaviors: first it describes a plateau close to one ($R(\alpha_i) \approx 1$) (depending on the absorption or roughness), when $\alpha_i < \alpha_C$ or $Q_z < Q_C$, secondly it shows an abrupt step at $\alpha_i = \alpha_C$, or $Q_z = Q_C$ and thirdly, it decreases as α_i^{-4} or Q_z^{-4} when $\alpha_i \gg \alpha_C$ or $Q_z \gg Q_C$. The transmitted intensity $T(\alpha_i)$ (see Fig. 16.7B) has its maximum at $\alpha_i = \alpha_C$. At very low incidence angles the intensity is close to zero and at large incidence angles it decreases asymptotically to one. The depth of penetration $D(\alpha_i/\alpha_C)$ (see Fig. 16.7C) is a function of the angle of incidence (α_i) and depends on the absorption of the X-rays by the medium, and is directly related to the imaginary part (β) of the refractive index. For angles of incidence less than the critical angle ($\alpha_i < \alpha_C$), the penetration depth is only a few angstroms and increases sharply at the critical angle; finally, at higher angles, it grows progressively. Thus, it is this behavior that gives rise to SXD and allows to the achievement of surface sensitivity in both X-ray diffraction and hard X-ray photoemission. Regardless of the X-ray energy used and/or the kinetic energy of the photoelectron excited, it is sufficient to work at angles of incidence less than the critical angle.

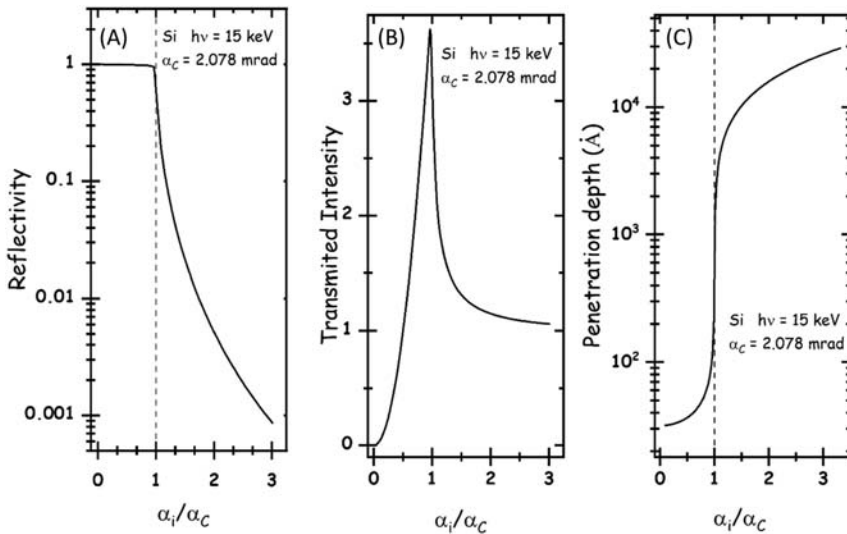


Figure 16.7 Calculated reflectivity (A), transmitted intensity (B), and penetration depth (C) of a semi-infinite flat silicon sample as a function of the ratio between incidence angle and critical angle (α_i/α_C) for the case of a photon energy of 15 keV.

Fig. 16.7 shows the calculated reflectivity $R(\alpha_i/\alpha_C)$, transmitted intensity $T(\alpha_i/\alpha_C)$ and the penetration depth $D(\alpha_i/\alpha_C)$ as a function of the ratio α_i/α_C with an X-ray energy of 15 keV for the case of a semi-infinity flat silicon sample. Fig. 16.7 provides a good understanding of the behavior below and near the critical angle, in particular the high surface sensitivity.

XRR is commonly used to determine the thickness and mean electron density of thin layers. For the case of a single layer deposited on a semi-infinite substrate, the reflectivity and the transmitted intensity are given by:

$$\begin{aligned} R(\alpha_i) = r.r^* &= \left| \frac{r_{0,1} + r_{1,2}e^{-2iK_1^z d}}{1 + r_{0,1}r_{1,2}e^{-2iK_1^z d}} \right|^2 \\ T(\alpha_i) = t.t^* &= \left| \frac{t_{0,1}t_{1,2}e^{-2iK_1^z d}}{1 + r_{0,1}r_{1,2}e^{-2iK_1^z d}} \right|^2 \end{aligned} \quad (16.17)$$

Here $r_{0,1}$ and $t_{0,1}$ are the Fresnel reflection and transmission coefficients (see Eq. 16.16) corresponding to the interface between vacuum (0) and overlayer, $r_{1,2}$ and $t_{1,2}$ are the ones corresponding to the interface between overlayer (1) and substrate (2), respectively, K_1^z is the wave vector vertical component of the transmitted X-ray beam, and d is the overlayer thickness.

A schematic representation of the XRR geometry for the case of an overlayer of thickness d is shown in Fig. 16.8. At each boundary between two media, an incident, reflected and transmitted X-ray beam is present. The medium 0, 1, and 2 correspond to the vacuum, the overlayer and the substrate, respectively. The reflectivity (Eq. 16.17) exhibits an oscillatory behavior with maxima each time that the condition $e^{-2iK_1^z d} = 1$ is met. This condition $e^{-2iK_1^z d} = 1$ is fulfilled when the exponent is a multiple of 2π , for example, $2iK_1^z d = m2\pi$, where m is an integer. The observed maxima are called Kiessig fringes and the incidence angles $\alpha_{1,m}$ at which that reflectivity maxima occur are given by:

$$m\lambda = 2d\sqrt{\sin^2(\alpha_{i,m}) - \sin^2(\alpha_C)} \approx 2d\sqrt{(\alpha_{i,m})^2 - (\alpha_C)^2} \quad (16.18)$$

As the incidence angle is rather small in most cases, $\sin(\alpha)$ can be approximated to α ; consequently, the expression (16.18) can be reduced to:

$$(\alpha_{i,m})^2 = (\alpha_C)^2 + \left(\frac{\lambda}{2d}\right)^2 m^2 \quad (16.19)$$

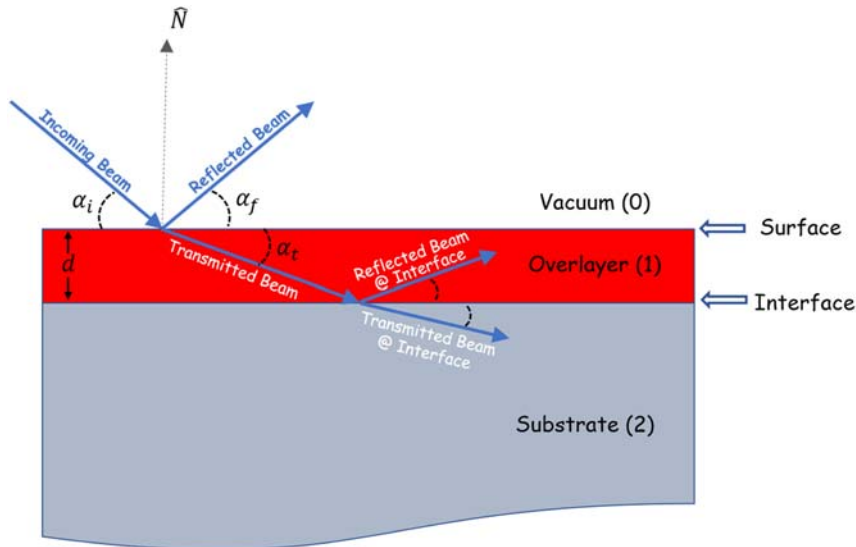


Figure 16.8 Schematic representation of the x-ray reflectivity geometry for an overlayer of thickness d .

Thus, if the square of the angular position where the maxima appear $(\alpha_{i,m})^2$ is plotted against the square of Kiessig fringes' order m^2 , the overlayer thickness is obtained from the straight-line slope.

The obtained oscillations are the consequence of the constructive interference between the X-ray beam reflected at the interfaces between vacuum and overlayer and between overlayer and substrate. Surface and interface roughness lead to a more significant decrease in the reflected intensity and in the amplitude of oscillations. The effect of roughness on the reflectivity is generally accounted for using a diminution factor $e^{-2K_z^0 K_z^1 \sigma^2}$ [42], which contains in the exponent the root mean square (r.m.s) roughness (σ), and the product of the perpendicular components of the scattering vectors on both sides of the interface/surface. Fig. 16.9 shows the calculation of the reflectivity of a 3 nm thick silicon layer deposited on a MgO substrate [71]. In this case, both, the surface and the interface have an r.m.s roughness of 0.1 nm. The inset displays the square of the incidence angle $(\alpha_{i,m})^2$ against the square of Kiessig fringes order m^2 . From the slope value, the layer thickness can be obtained as shown in the figure inset.

To obtain the reflectivity of a multilayer sample it is necessary to consider that the X-ray beam traveling through the sample will be transmitted and reflected at each interface. Each layer is described by their thickness d_i , index of refraction n_i and vertical component of their wave vector K_i^z .

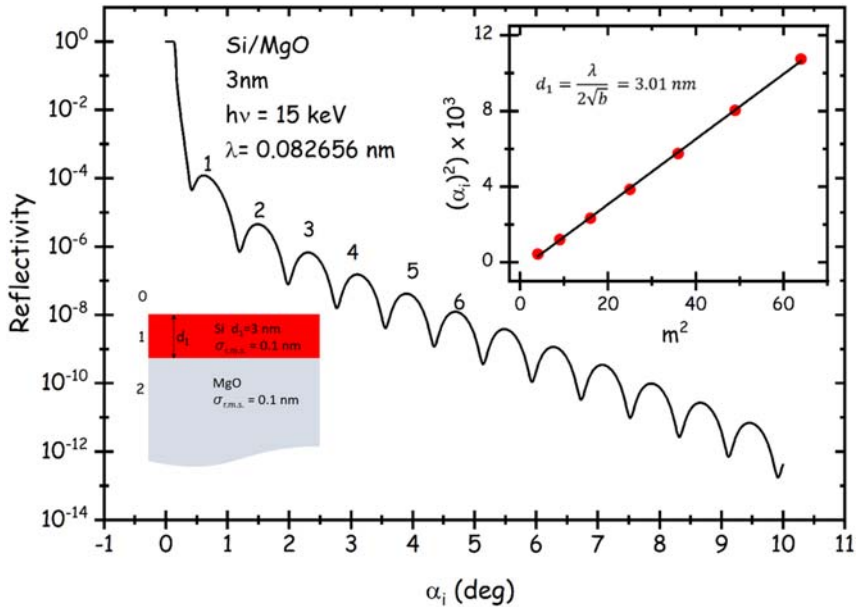


Figure 16.9 Calculation of the reflectivity of a 3 nm thick silicon layer deposited on a MgO substrate; both, the surface and the interface, have an r.m.s roughness of 0.1 nm. In the inset a plot of $(\alpha_{i,m})^2$ against m^2 is presented, from which the layer thickness is obtained.

For the case of a pseudomorph multilayer formed by N layers and $N + 1$ interfaces, $N + 1$ is the substrate, and defining the reflection and transmission coefficients between a generic interface i based on Eq. (16.17), a recursive formula can be deduced and thus the reflectivity and transmitted intensity for the multilayer can be obtained.

Fig. 16.10 shows an XRR calculation [71] as an example for a bilayer formed by a 3 nm Si film on a 25 nm HfO_2 film deposited on a MgO substrate. Clearly, two oscillation frequencies are observed. The high frequency is a measure of the HfO_2 layer thickness, and the low frequency is that of the Si top layer. An r.m.s roughness of 0.1 nm has been used for the top surface and for the two interfaces, and the X-ray beam energy was 15 keV.

16.3 Excitation sources and instrumentation

The first criterion for the selection of the excitation X-ray source for hard X-ray photoemission experiments is to select high-energy photons in adequacy with the desired photoelectron kinetic energy and detection capabilities of the

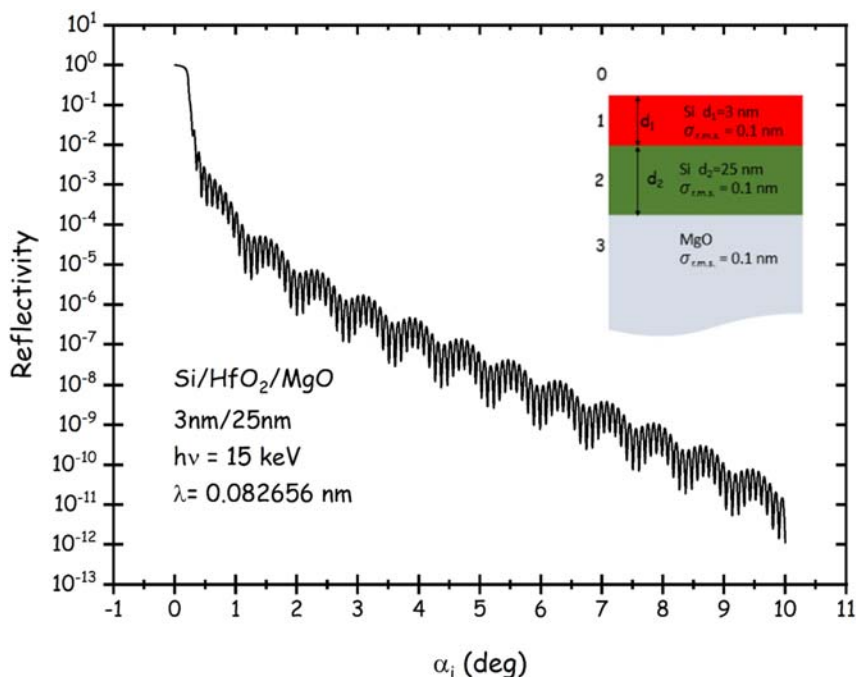


Figure 16.10 Calculation of the reflectivity of a bi-layer formed by 3 nm thick Si layer deposited on 25 nm thick HfO₂ layer on a MgO substrate. Both interfaces and the surface have an r.m.s roughness of 0.1 nm.

analyzer, but also that the source energy bandwidth has to be as small as possible, depending on the objectives pursued, for example, to be able to detect recoil effects or possible chemical shifts produced at different depths/environments and it should have sufficient intensity to compensate for the decrease of the photoemission cross-section with the excitation photon energy.

The dependence of the cross-section on the photon energy of the orbital to be chosen must also be considered in order to select the most suitable orbital in accordance with the objective pursued. If, for example, one is only interested in the composition regardless of the chemical state, one should choose the orbital with the highest effective cross section independent of the FWHM, but if the chemical state is important, the orbital with the lowest FWHM is the most suitable.

16.3.1 Synchrotron radiation/home laboratory sources

From the very beginning of the photoemission technique in the 1960s, K. Siegbahn's group conducted a series of experiments using different

radiation sources [77]. The first published results actually used hard X-ray radiation [78], using Mo $K_{\alpha 1}$ (17.479 keV) and $K_{\alpha 2}$ (17.374 keV) radiation on a 50 nm Cu films sample, where two Cu-1s photoemission signals, corresponding to the two excitation energies, were obtained. Later, Mg-1s, -2p and O-1s spectra were reported using Cu K_{α} (8.047 keV) and K_{β} (8.905 keV) radiation as the excitation source. Other sources (e.g., Cr K_{β}) were tested and finally, Al K_{α} (1.4867 keV) and Mg K_{α} (1.2536 keV) were preferred as they offered a better signal/background ratio and were relatively easy to focus. These pioneering works demonstrated proof of fact that deep atomic core levels can be reached if sufficiently high energy is used, as well as the great sensitivity of the technique to the chemical state of the studied element (chemical shift). This opened the way for wide use of the technique in non-destructive chemical analysis.

Lindau et al. [79] made 1974 the first HAXPES experiment measuring the Au-4f subshell at a photon energy of 8 keV. However, no other group followed this pioneering work as has been the case for lab-based X-ray sources, certainly because of the strong drop of the photoemission cross-section at higher photon energies. Even more so due to the fact that, at that time and up to about 20 years ago, there was a lack of commercial analyzers available to handle high electron energies. For low-Z elements and low binding energy core levels, a drop of more than 8 orders of magnitude is observed when the photon energy is increased from 2 to 15 keV (see Fig. 16.3).

Very high photon fluxes requested by HAXPES became available with the fourth and third-generation synchrotron sources. Fig. 16.11 shows the evolution over time of the brilliance of different X-ray sources. Synchrotron radiation is undoubtedly more suitable for HAXPES experiments, and even first or second-generation synchrotrons offer higher brilliance than the best laboratory-based sources.

Although there has been an ongoing interest in the development of the HAXPES technique, at least two factors have been limiting its wider use. Conventional X-ray sources (X-ray tubes) have the disadvantage of being low intensity sources and the higher their characteristic energy the wider their natural energy width (full width at half maximum, FWHM), but also greater the number of coexisting lower energy characteristic lines. Therefore, using laboratory-based sources makes the use of a monochromator unavoidable, which results in an ever-greater photon flux decrease, while simultaneously the effective photoemission cross-section decreases as the excitation energy increases. High brilliance, synchrotron radiation

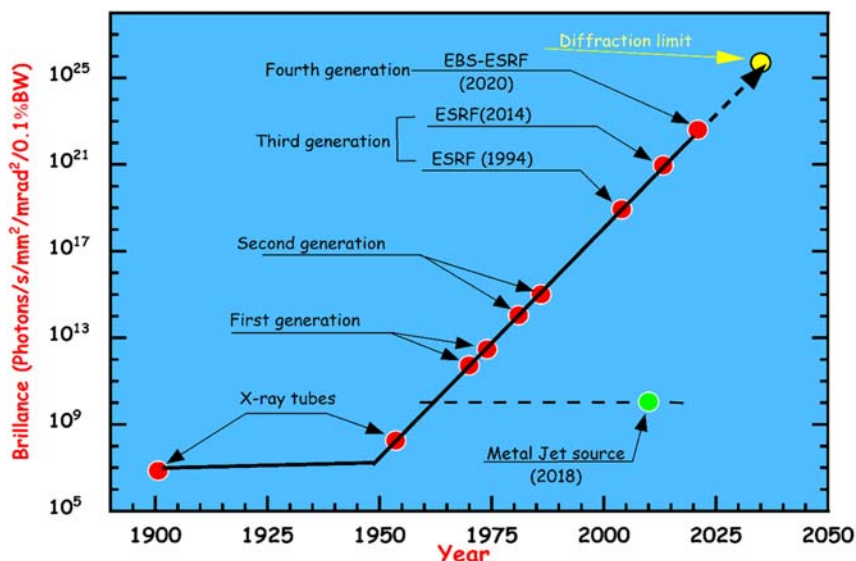


Figure 16.11 Brilliance development of x-ray radiation sources [80]. The figure is inspired/taken from the ESRF webpage. The green dot corresponds to the lab-based liquid-metal jet sources that have been developed recently.

sources such as the ESRF-EBS, produce a much higher photon flux than any laboratory-based X-ray sources. Synchrotron brightness is more than 10 orders more intense than the best laboratory-based source (see Fig. 16.11), which is most likely to be the one using metal-jet anode technology [81,82].

16.3.2 Experimental stations

Despite the disadvantages in terms of energy tunability and intensity of a laboratory source compared to synchrotron radiation, in recent years there has been a great effort performed in the implementation of commercial and home-made laboratory HAXPES systems. The emergence of these systems contributes to the spreading of the technique to a much broader public, with a widespread range of interests crossing very different scientific and industrial research areas. Commercially there are at least four suppliers of laboratory HAXPES systems [32–34], some of them offering a dual-source possibility combining standard Al K_{α} with high energy X-ray sources. There are also some home-made laboratory systems [83,84] based on the same principles as the commercially available ones. The sources commonly offered are Ag L_{α} (2.984 keV), Cr K_{α} (5.414 keV) and Ga K_{α}

(9.251 keV), although other sources are possible. The sources shortage is mainly due to the availability of suitable or adapted monochromators. Certainly, the achieved information depth is higher than that obtained with Mg K_{α} (1.2536 keV) and/or Al K_{α} (1.4866 keV) sources, which are standard in XPS, but an important drawback arises from the limited deep core levels accessible at relatively low X-ray energies. The higher the core levels binding energy, the lower the corresponding photoelectron kinetic energy and, consequently, the lower the information depth. This is not only a drawback of laboratory HAXPES systems but also of synchrotron stations using lower photon energies.

An overview of the current state of the art of the HAXPES technique has been reported in several articles, proceedings, and books [29–31], and according to the last reported data [30] there are around 25 synchrotron stations in operation worldwide, with Japan having the largest number, although Europe is close behind. The most widely used electron analyzer in both laboratory systems and synchrotron facilities is the hemispherical deflection electron analyzer [85–88], but this is not the only one [13,89–92] coupled to a 2D detector and retarding lens system [89,93,94]. The retarding lens has the function of retarding/braking electrons with kinetic energies up to 15 keV at the value of the pass energy of the analyzer while maintaining constant spatial magnification and accepting a large volume of the phase space. Most HAXPES stations are UHV vacuum chambers with standard auxiliary techniques for sample growth and/or preparation. Furthermore, several of these chambers are equipped with a high-precision sample holder with five or more degrees of freedom. Some also have piezo-translations for accurately aligning single crystals, but the common configuration includes only four degrees of freedom: X, Y, Z, and rotation. Most of them have cooling and heating capabilities. The 5-degree manipulator configuration is suitable for (near) total reflection-HAXPES [95,96] and X-ray standing wave experiments [48,97].

By choosing the X-ray incidence angle below and above the total reflection critical angle, it is possible to modulate the HAXPES information depth due to a huge variation of the X-ray penetration depth (see Fig. 16.7), in which below the critical angle is less than the EAL of the photoelectrons. Thus, using the same experimental setup it is possible to obtain surface and bulk information, but above the critical angle the X-ray penetration varies abruptly and quickly reaches values much higher than the IMFP, making it very difficult to obtain accurate compositional

profiles [95,96]. However, by rocking through a Bragg diffraction peak, it is possible to obtain an accurate spatial distribution down to the picometer/nanometer scale, as is the case of XSW [48,97]. The interference between the incident and reflected X-ray beams creates an XSW field when diffraction occurs. The diffraction/reflection can be produced under the Bragg condition for a crystalline lattice or a multilayer superlattice; thus, the period of the XSW is equal to the periodicity of the reflecting planes. Hence, a spatial modulation of the standing electrical field is produced when an angular sweeping is performed around the Bragg peak. Because of the relative phase variation between the incoming and the reflected beam, the nodal planes of the XSW field shift by a half distance of the diffracting planes. Consequently, depending on the atoms position in the standing wave field, the element-specific X-rays absorption changes in a distinctive way. Hence, by measuring the element-specific photoemission and/or the X-ray fluorescence signal it is possible to obtain the position of the corresponding element [39,48,86,98–102]. However, the XSW technique leads to some important constraints. Thus, the sample to be studied must have either a crystalline structure or a periodic heterostructure (superlattice), or grown on a crystalline substrate (single crystal or superlattice). If necessary, the standing wave amplitude could be increased and, consequently, the spatial range analyzed by using superlattice substrates, which is not always possible.

The majority of synchrotron-based HAXPES facilities are located at insertion device sources, while a few are located on bending magnets, which is not necessarily a disadvantage when compared to home-laboratory stations. Most synchrotron-based HAXPES facilities are equipped with Si(111) double crystal monochromators (DCMs), although some use Si(311) or Si(220) and a majority of them add higher-index channel-cut or pseudo-channel-cut post-monochromators to the optical configuration in order to achieve high-resolution. The X-ray energy range is quite wide, but in many stations, the upper limit is close to 10 keV, and the lower limit depends on the crystals used. For Si(111) it can go down to the theoretical minimum of 1.977 keV, but it is higher when using higher-index crystals. The upper limit of 10 keV is in general due to restrictions imposed by the electron analyzer used.

At the current time, only two HAXPES stations [20,25,37,38] are known, at least for the authors, to be installed directly on a diffractometer, enabling the realization of simultaneous X-ray diffraction and HAXPES measurements. One is located on the beamline 33-ID-D at the Advanced

Photon Source (APS) in the United States [38] and the other is on the CRG BM25 SpLine beamline at the ESRF in France [25,35,103,104].

The 33-ID-D HAXPES end-station is generally operated at 10 keV photon energy and is devoted to the in-situ structural and spectroscopic characterization of the growth process of thin films and heterostructures by pulsed laser deposition (PLD) [38,105]. The X-ray energy range there goes from 4 to 12 keV and the photon beam is delivered by an APS undulator type A. The station is intended to operate both online and off-line. The cylindrical vacuum chamber is installed on an S2 + D2 [106] diffractometer and it is equipped with two removable, O-ring sealed beryllium (Be) windows. The diffractometer provides two degrees of freedom for the sample motion (2S) and two for the detector (2D). The movements of the sample and detector circles are mechanically decoupled, making this geometry suitable for both surface and GI-XRD. The incident X-ray beam arrives at the sample through a Be flat strip of $19 \times 1 \text{ cm}^2$ and the diffracted beam reaches the detector through a cylindrical Be window with an angular aperture ranging from -3.6 to 122 degrees and from 0 to 50 degrees in the vertical and horizontal planes, respectively.

The base pressure in the system is about 10^{-8} mbar, which is typical for PLD systems. The vacuum chamber is also equipped with a Scienta-Omicron EW4000 [32] electron spectrometer mounted at a fixed angle, perpendicular to the sample surface, and at a working distance of 40 mm; the kinetic energy can go up to 10,000 eV. In addition, the vacuum chamber is equipped with a sample holder with sample heating capabilities up to 800°C , a differential pumped RHEED (Reflection high-energy electron diffraction) [107] gun and its corresponding RHEED screen, a leak valve, a flood gun, a quartz window, a laser mirror, and a motorized shutter to protect the electron analyzer entrance/retarding lens, which serves also as a support for up to three targets. PLD is performed using a pulsed excimer laser with a wavelength of 248 nm, which enters the chamber through a quartz window.

The CRG BM25-SpLine beamline is located at port D25 of the ESRF [104]. The end-station (see Fig. 16.12) is devoted to surface and interface X-Ray diffraction (SXRD), XRR, and HAXPES. The available X-ray energy range goes from 5 to 45 keV and is generated by a 2-pole wiggler (2PWA) in configuration A of the upgraded ESRF-EBS. The end-station hosts a state-of-the-art set-up dedicated to the simultaneous combination of X-ray diffraction and hard/soft X-ray photoelectron spectroscopy. The experimental set-up includes a heavy 2S + 3D [108] diffractometer, a UHV chamber, and an electrostatic analyzer. The diffractometer provides two degrees of freedom for the sample motion (2S) and three for the detector (3D). The addition of

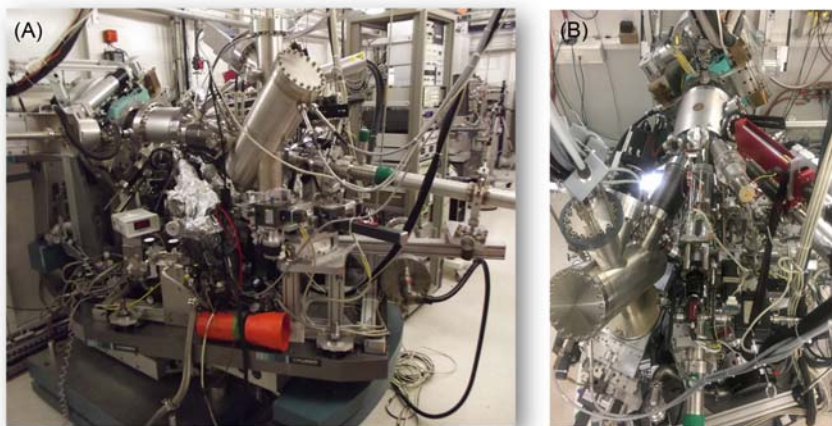


Figure 16.12 Pictures of the CRG BM25-SpLine SRD-HAXPES end station (A) side view and (B) top view.

an azimuthal detector rotation to a 2S + 2D-type diffractometer makes it fully equivalent to a z-axis type. This geometry combines the optimal resolution characteristics of a z-axis diffractometer, which is ideal for surface and grazing-incidence diffraction while maintaining the simplicity and angular accessibility of a 2S + 2D circle diffractometer. The vacuum chamber has two welded Be windows so that the incoming and outgoing X-ray beams can hit the sample and the X-ray detector, respectively. The exit Be-window allows the out-going diffracted X-ray beam to cover 120 degrees in-plane and 50 degrees out-of-plane. The in-coming Be-window is wide enough to reach up to a 50 degrees X-ray incidence angle. A wide portion of the reciprocal space ($Q_{max} = 10 \text{ \AA}^{-1}$ at 12 keV) is therefore accessible. The UHV chamber ($P < 10^{-10}$ mbar) is equipped with a Focus HV-CSA 300/15 [13] electron spectrometer able to handle electrons with kinetic energies from a few eV up to 15 keV. The retarding-lens system is operated at fixed high spatial magnification so that maximal transmission is achieved by appropriately imaging at the entrance slit of the small X-ray synchrotron beam on the sample. The sample-lens distance is maximized to 50 mm, allowing the simultaneous accomplishment of photoemission and diffraction experiments. The electron analyzer is mounted on a 3-degrees-of-freedom motorized alignment base so that the analyzer focal point position can be changed/swept on the sample enabling to optimization of the detection geometry. This configuration allows considering the fact that the maximum of angular distribution

of the photoelectrons shifts towards the forward incident beam direction when the excitation energy is increased.

The XRD-HAXPES end-station (see Fig. 16.12) also hosts several MBE (Molecular-beam epitaxy) [109] evaporation sources, an ion gun, an electron gun (up to 15 keV), an X-ray tube (Mg K_α and Ti K_α anodes), Low-energy electron diffraction [110] optics, sample heating (up to 1800K) and a cooling device (down to 20K on the sample), leak valves, a mass spectrometer and a load-lock for in-vacuum sample transfer. Such a set-up offers the unique possibility to correlate the atomic structure with the compositional, chemical, and electronic properties under the same experimental conditions. The combination of XRR with hard and soft X-ray photoelectron spectroscopy is crucial for retrieving an accurate non-destructive compositional and electronic depth profile in the tens of nanometers depth-scale with nanometer resolution in amorphous, polycrystalline, single crystalline samples or heterostructures. Such a combination of techniques finds its optimal use in in-situ experiments, that is, in-situ growth or in-situ treatment, as it is the only possibility to guaranty an accurate correlation between structural, compositional, chemical, and electronic properties.

16.4 Experimental methodology and selected application examples

In photoemission, three methods are commonly used to change the information depth, that is, the EAL value, and consequently be able to reconstruct the composition profile:

1. varying the kinetic energy of the photoelectron by changing the photon energy (see Fig. 16.13 and caption);
2. measuring different orbitals or signals of the same element at a fixed photon energy (see Fig. 16.1),
3. changing the detection geometry either by changing the X-ray incident angle or changing the photoelectrons detection angle, for the same or several signals of the same element (see Fig. 16.14 and caption).

16.4.1 Experimental methodology

The methodology consists in collecting/measuring a series of photoemission signals with different information depths for the same element, independently of the excited orbital. The experimental signal obtained is then normalized with the detector efficiency and transmission function ($\Gamma(E_{kin}, E_P)$), cross-section ($\sigma_{A_\xi}(E_{h\nu})$), photon flux ($f(E_{h\nu})$) corresponding to the experimental

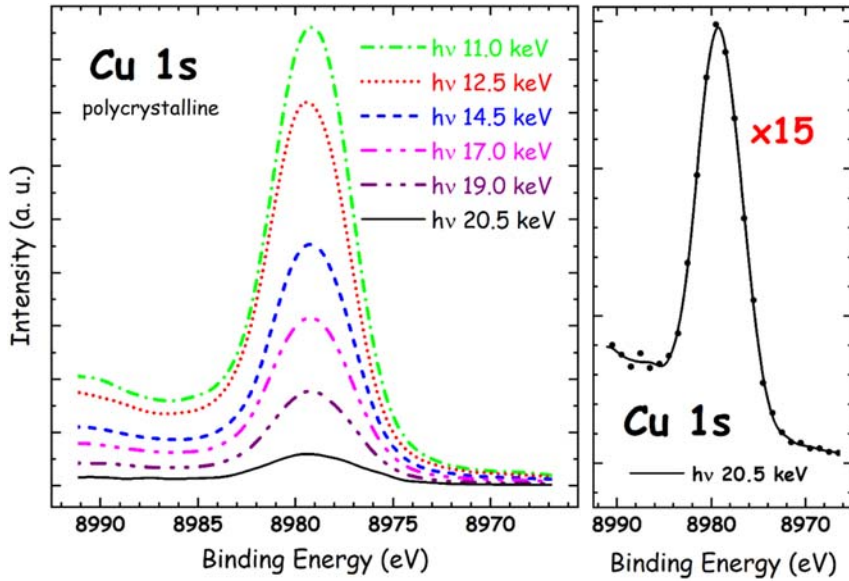


Figure 16.13 Cu-1s HAXPES spectra from a polycrystalline Cu sample. *Left-panel:* recorded at 11.0, 12.5, 14.5, 17.0, 19.0, and 20.5 keV from top to bottom; *right-panel:* recorded at 20.5 keV multiplied by 15. Data measured on the CRG BM25 SpLine beamline at the European Synchrotron. Note the decrease in intensity as the photon energy increases due to the decrease in cross-section.

setup and to the X-ray photon energy used, and the orbital excited, respectively [14,25,37,44,111–115]. Therefore, the signal thus obtained will depend exclusively on the atomic density $N_A^x(z)$, the effective attenuation length $EAL^x(E_{kin})$ and the photoelectrons collection angle $\cos(\theta)$. The superscript x labels the region where the signal is coming from.

As the EAL is reasonably well known either because it has been measured or because it has been calculated (see Section 16.2.2), the only unknown variable or parameter is the atomic density dependence with depth. Thus, the composition profile can be obtained by fitting Eq. (16.3) to experimental data using a suitable atomic density model. Using the normalization described above Eq. (16.3) is reduced to:

$$\begin{aligned}
 I_A^x(E_{kin}) &= \frac{F_{A_\xi}^x(E_{kin})}{C \cdot f(E_{h\nu}) \cdot \Gamma(E_{kin}, E_p) \cdot \sigma_{A_\xi}(E_{h\nu}) \cdot P_{A_\xi}(E_{h\nu}, \theta_{pk}, \varphi_{pk}) \cdot \frac{\Omega}{4\pi}} \\
 &= K_A \cdot \int_{Z_1}^{Z_2} N_A^x(z') \cdot e^{-\left[\frac{Z'}{EAL^x(E_{kin}) \cdot \cos(\theta)} \right]} \cdot dz'
 \end{aligned} \quad (16.20)$$

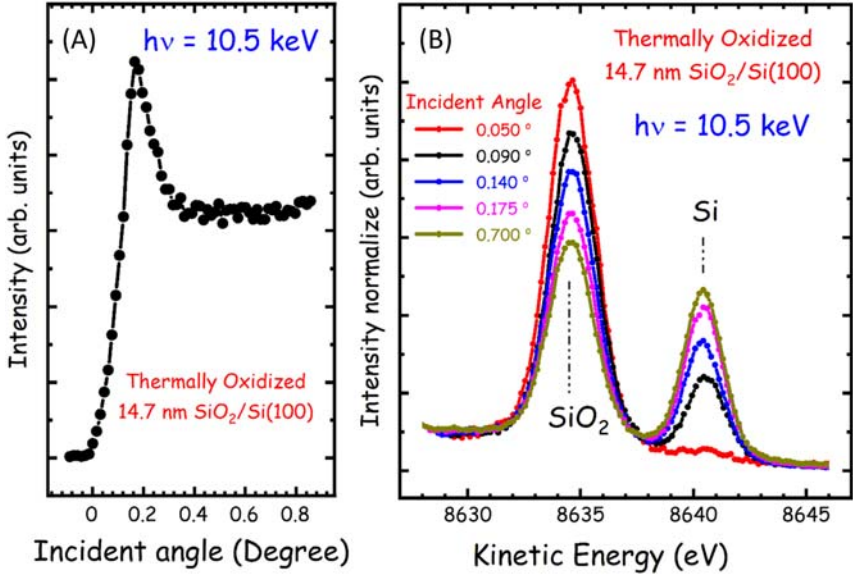


Figure 16.14 (A) Low-angle reflectivity curve of a 14.7 nm SiO₂ layer obtained by thermal oxidation of the Si(100) substrate. (B) Si-1s HAXPES spectra recorded (*top to bottom*) at incidence angles of 0.05 degrees (red), 0.09 degrees (black), 0.140 degrees (blue), 0.175 degrees (magenta) and 0.7 degrees (dark yellow), respectively. Data measured with a photon energy of 10.5 keV on the CRG BM25 Spline beamline at the European Synchrotron. Note the intensity decrease of the signal corresponding to metallic Si as the incidence angle decreases, until it practically disappears at an angle of 0.05 degrees; while the signal of SiO₂ increases simultaneously with the decrease of that of Si.

Henceforth, using the following notation $EAL^x(E_{kin}).\cos(\theta) = \lambda_k^x$, Eq. (16.1) becomes:

$$I_A^x(E_{kin}) = K_A \cdot \int_{Z_1}^{Z_2} N_A^x(z') \cdot e^{-(z'/\lambda_k^x)} \cdot dz' \quad (16.21)$$

For a sample with, for example, three layers or regions (model 1 in Fig. 16.15), the measured intensity coming from element A will correspond to the sum of the contributions of each region:

$$I_A(E_{kin}) = I_A^1(E_{kin}) + I_A^2(E_{kin}) + I_A^3(E_{kin}) \quad (16.22)$$

To illustrate the methodology, different concentration profile models will be used to calculate the dependence of the photoemission signal on the EAL. Fig. 16.15 shows schematically three concentration profile models: model 1 represents a three-layer heterostructure. Here region 1 is representing an

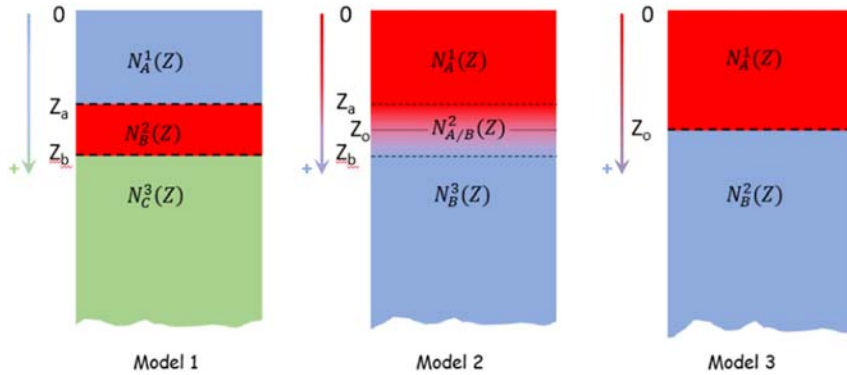


Figure 16.15 Schematic models of concentration profiles. Model 1 represents a tri-layer with abrupt boundaries, region 1 corresponds to the overlayer ($0-Z_a$), region 2 to a buried-layer (Z_a-Z_b), and Region 3 to the substrate ($Z_b-\infty$), respectively. Model 2 corresponds to a bi-layer, with an interdiffusion zone (Z_a-Z_b), and Model 3, represents an abrupt bi-layer where the overlayer has a constant composition profile. More details in the text.

overlayer that extends from the sample surface to depth Z_a ; region 2 is representing a buried layer that extends from Z_a to depth Z_b and, finally, region 3 is representing the substrate which goes from depth Z_b to infinity. Model 2 corresponds to a bi-layer, with an interdiffusion region that extends from Z_a to Z_b , where $Z_b > Z_a$ and model 3, representing an abrupt bi-layer where the overlayer extends from the surface to depth Z_0 .

For the models 1 and 2 it is supposed that the atomic density of components A, B and C in the regions 1 and 3, respectively, are constant ($N_A^1(z) = N_A^1 = \text{constant}$, $N_B^3(z) = N_B^3 = \text{constant}$ and $N_C^3(z) = N_C^3 = \text{constant}$). Hence, by performing the integral in Eq. (16.20) the contribution to the total intensity coming from region 1 for both models is given by:

$$I_A^1(E_{kin}) = K_A \cdot \lambda_k^1 \cdot N_A^1 \cdot (1 - e^{-(Z_a/\lambda_k^1)}) \quad (16.23)$$

For the one coming from region 3 for model 1 and model 2,

$$I_C^3(E_{kin}) = K_C \cdot \lambda_k^3 \cdot N_C^3 \cdot e^{-Z_b/\lambda_k^3} \cdot e^{-(Z_b-Z_a)/\lambda_k^2} \cdot e^{-Z_a/\lambda_k^1} \quad (16.24)$$

and

$$I_B^3(E_{kin}) = K_B \cdot \lambda_k^3 \cdot N_B^3 \cdot e^{-Z_b/\lambda_k^3} \cdot e^{-(Z_b-Z_a)/\lambda_k^2} \cdot e^{-Z_a/\lambda_k^1} \quad (16.25)$$

respectively. The last two exponential terms in Eqs. (16.24) and (16.25) correspond to the attenuation produced by the buried layer $e^{-(Z_b-Z_a)/\lambda_k^2}$ and the overlayer e^{-Z_a/λ_k^1} , respectively.

In the second region (2) delimited between Z_a and Z_b , ($Z_a < Z_b$) two different cases can be considered: constant atomic density that is $N_B^2(z) = N_B^2 = \text{constant}$ (model 1), or variable atomic density that is $N_B^2(z) = f(z)$ (model 2), which can be originated either by the interdiffusion of the overlayer and the substrate in the buried layer, or mismatch stress release, or other effects. In this case, different composition profiles may occur or be conceivable (e.g., linear, exponential, error function, etc.). For the case of constant composition in the region between Z_a and Z_b , the intensity signal coming from region 2 is given by:

$$I_B^2(E_{kin}) = K_B \cdot \lambda_k^2 \cdot N_B^2 \cdot \left(e^{-(Z_a/\lambda_k^2)} - e^{-(Z_b/\lambda_k^2)} \right) \cdot e^{-Z_a/\lambda_k^1} \quad (16.26)$$

The last exponential factor e^{-Z_a/λ_k^1} corresponds to the attenuation produced by the overlayer of thickness Z_a .

Fig. 16.16 shows a simulation of the behavior/dependence of the photoemission intensity with the photoelectron kinetic energy for a

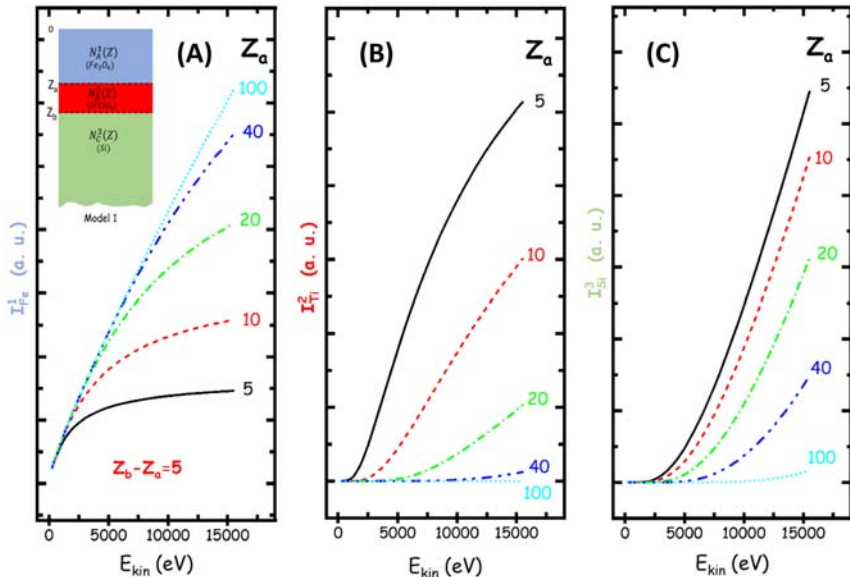


Figure 16.16 Calculation of the photoemission intensity dependence on the photoelectron kinetic energy of the overlayer (A), the buried layer (B), and the substrate (C) for a three-layer heterostructure model system consisting of a Fe_3O_4 overlayer of different thicknesses, a 5 nm thick SrTiO_3 buried layer and a Si substrate. The solid black, dash-dash red, dash-point-dash green, dash-point-point blue, and points cyan lines correspond to 5, 10, 20, 40, and 100 nm overlayer thickness, respectively.

three-layer heterostructure. The heterostructure model used is formed by an Fe_3O_4 overlayer of different thicknesses (5, 10, 20, 40, and 100 nm), a 5 nm thickness SrTiO_3 buried layer, and a Si substrate. The intensity dependence with increasing photoelectron kinetic energy is shown in Fig. 16.16, where panels (A), (B) and (C) correspond to the signal coming from the overlayer, buried layer, and substrate, respectively. The solid black line, dash-dash red line, dash-point-dash green line, dash-point-point blue line, and points cyan line correspond to 5, 10, 20, 40, and 100 nm overlayer thickness, respectively. For the calculation, abrupt (non-interdiffusion) overlayer/buried and buried/substrate interfaces, and constant composition profile [Eqs. (16.24)–(16.26)] in each sample region, have been considered. The maximum photoelectron kinetic energy was set to 15 keV, which is the maximum kinetic energy achievable with the CRG BM25 Spline HAXPES setup. The signals coming from the three zones (overlayer, buried layer and substrate) show a clear difference with the overlayer thickness, but all intensity signals, regardless of where they come from, increase when the photoelectron kinetic energy increases. For the case of signals coming from the buried layer (Fig. 16.16B) and the substrate (Fig. 16.16C), at low kinetic energies, a weak intensity or non-intensity is obtained as the EAL is much less than the overlayer thickness but increases as the photoelectron kinetic energy rises due to the fact that the information depth increases, and consequently reaching the buried and substrate regions. The overlayer intensity (Fig. 16.16A) also increases with increasing photoelectron kinetic energy but tends to saturate especially at small overlayer thickness when the information depth exceeds or is comparable to the overlayer thickness. These results clearly show the suitability of HAXPES to model and obtain composition profiles in solid samples at depths of tens of nanometers. Models 2 and 3 schematized in Fig. 16.15 are well suited to further illustrate the HAXPES suitability to obtain non-destructive compositional profiles.

Model 2 corresponds to a bi-layer, with a graded interdiffusion zone ($Z_a - Z_b$) centered at Z_0 and Model 3, representing the same bi-layer model but with an abrupt interface. The concentration profile in regions from 0 to Z_a and from Z_b to ∞ are assumed as constant, and in model 3, an abrupt interface is supposed, that is there is no graded interface or interdiffusion zone and consequently $Z_a = Z_b = Z_0$. For model 2, the graded zone width is 2δ centered at Z_0 that is delimited between $Z_a = Z_0 - \delta$ and $Z_b = Z_0 + \delta$, respectively. Five different interface concentration profiles (graded zone) will be considered: error function,

exponential, linear, sinusoidal, and abrupt. The model used in the calculation consists of a Fe_3O_4 overlayer, and a SrTiO_3 substrate, and the width of the graded/diffusion zone is 2 nm centered at 12.5 nm.

Therefore, the model comprises a constant overlayer 10.5 nm thick, that is $Z_a = 10.5$ nm, $Z_0 = 12.5$ nm and $Z_b = 14.5$ nm. Fig. 16.17 shows the XRR calculation (see Section 16.2.3) for the $\text{Fe}_3\text{O}_4/\text{SrTiO}_3$ bilayer model using an incoming X-ray beam energy of 15 keV. For the calculation, the IMD software for modeling the optical properties on multilayers has been used [71]. Fig. 16.17A represents the reflectivity as a function of the incidence angle in the model including a 2 nm graded zone, where a gradual variation of optical properties between the values of Fe_3O_4 and SrTiO_3 has been adopted. Clearly, two oscillation frequencies are

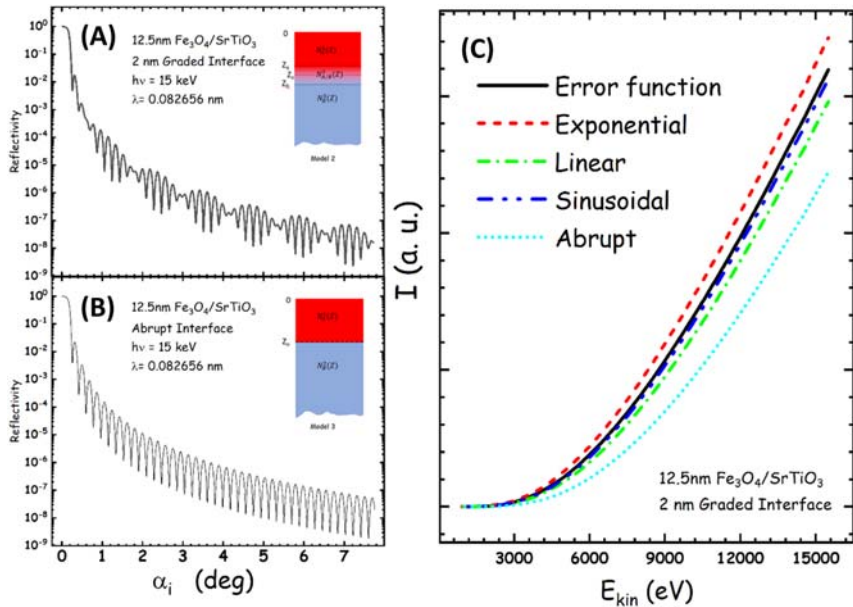


Figure 16.17 XRR and substrate photoemission intensity calculation for a $\text{Fe}_3\text{O}_4/\text{SrTiO}_3$ bilayer model. Panel (A) XRR for the case of a graded zone of 2 nm width at the interface and panel (B) For the case of an abrupt interface, in both cases using an incoming X-ray energy of 15 keV. Panel (C) Dependence of the substrate photoemission intensity with the photoelectron kinetic energy of one component of the substrate, namely Ti. The solid black line, dash-dash red line, dash-point-dash green line, dash-point-point blue line, and points cyan line correspond to error function, exponential, linear, sinusoidal and abrupt composition profiles, respectively. The maximum photoelectron kinetic energy was set to 15 keV, which is the maximum kinetic energy achievable with the CRG BM25 Spline HAXPES setup.

observed reflecting the existence of two regions with different compositions and, consequently, different optical properties. The high-frequency oscillation originates from the 10.5 nm Fe_3O_4 overlayer of constant composition, while the low-frequency comes from the 2 nm graded zone. Fig. 16.17B shows equivalent XRR calculations but for the case of a bilayer with an (or almost) abrupt interface; in this case, only one oscillation is observed showing the fact that there is only one overlayer. It is very difficult to obtain the exact composition profile by XRR but it allows us to estimate and conclude the existence of several zones with different compositions, the combination of XRR with HAXPES allows us to sharpen a compositional model. Fig. 16.17C shows a simulation of the behavior/dependence of the substrate photoemission intensity with the photoelectron kinetic energy of one substrate component, namely Ti. The solid black line, dash-dash red line, dash-point-dash green line, dash-point-point blue line, and points cyan line correspond to error function, exponential, linear, sinusoidal, and abrupt composition profiles, respectively. In the calculations the expressions of Table 16.1 for the composition profiles, as well as Eqs. (16.20–16.22), were used. All intensity signals increase continuously as the electron kinetic energy rises, independently of the composition profile in the interdiffusion (graded) zone. However, differences are obtained depending on the composition profile. The differences for the case of the overlayer intensity signal are less important (not shown) and are observed only at high kinetic energies, since a large part of the overlayer ($Z < Z_a$) is the same for all profile models. It is only when the information depth starts to approach the diffusion zone that the differences may appear. The analytical expressions of the dependence with the photoelectron kinetic energy of photoemission signal from the overlayer [$I_A(E_{kin})$] and the substrate [$I_B(E_{kin})$] for the five different interface profiles are given in Table 16.2. For the error function profile, numerical integration is done.

The superscripts and subscripts 1 and 2, indicate the area to which the EAL corresponds and the area of origin of the photoemission signal; mixed subscripts correspond to equivalent values in the graded zone. Subscripts A and B indicate the element from the overlayer and substrate, respectively.

The required EAL values have been obtained/estimated (see Section 16.2.2) with the formula TPP2-2M [18,61,62,116], and λ_1 , λ_2 and λ_{12} are the values corresponding to the Fe_3O_4 overlayer, the SrTiO_3 substrate and the diffusion zone, respectively; λ_{12} is taken as the average value of the EALs of the substrate and the overlayer, respectively.

Table 16.1 Interface profile functions [44,72] used for the HAXPES intensity calculation shown in Fig. 16.17.

Error function		Linear	
$N_B^1(z) = 0$	$Z \leq Z_a$	$N_B^1(z) = 0$	$Z \leq Z_a$
$N_B^2(z) = \frac{N_B^2}{\sqrt{\pi}} \cdot \int_{-\infty}^Z e^{-\left(\frac{z'-Z_a}{2\sigma}\right)^2} dz'$	$Z_a \leq Z \leq Z_b$	$N_B^2(z) = \frac{1}{2} + \frac{(Z - Z_0)}{2\sqrt{3}\sigma}$	$Z_a \leq Z \leq Z_b$
$N_B^2(z) = 1$	$Z \geq Z_b$	$N_B^2(z) = 1$	$Z \geq Z_b$
$ Z_a - Z_0 = Z_b - Z_0 = \delta = \sigma$		$ Z_a - Z_0 = Z_b - Z_0 = \delta = \sqrt{3}\sigma$	
Exponential		Sinusoidal	
$N_B^1(z) = 0$	$Z \leq Z_a$	$N_B^1(z) = 0$	$Z \leq Z_a$
$N_B^2(z) = \frac{N_B^1}{2} \cdot \left(e^{\sqrt{2}(Z-Z_0)/\sigma} \right)$	$Z_a \leq Z \leq Z_0$	$N_B^2(z) = \frac{1}{2} + \frac{1}{2} \sin \left[\frac{\pi(Z - Z_0)}{2a\sigma} \right]$	$Z_a \leq Z \leq Z_b$
$N_B^2(z) = \frac{N_B^1}{2} \cdot \left(2 - e^{-\sqrt{2}(Z-Z_0)/\sigma} \right)$	$Z_0 < Z < Z_b$	$a = \pi / \sqrt{\pi - 8}$	
$N_B^2(z) = 1$	$Z > Z_b$	$N_B^2(z) = 1$	$Z \geq Z_b$
$ Z_a - Z_0 = Z_b - Z_0 = \delta = 2.5\sigma$		$ Z_a - Z_0 = Z_b - Z_0 = \delta = 2a\sigma$	

The width of the graded/diffusion zone is $Z_b - Z_a = 2\delta$ and it is centered at $Z_0 = 12.5$ nm. The σ value is 2 nm.

Table 16.2 The analytical expressions of the dependence with the photoelectron kinetic energy of photoemission signal of the overlayer $I_A(E_{kin})$ and the substrate $I_B(E_{kin})$ for the five different interface profiles (see Table 16.1).

Error function

$$I_B(E_{kin}) \propto N_B^2 \left[\int_{Z_a}^{Z_b} \frac{1}{\sqrt{\pi}} \cdot \int_{-\infty}^Z e^{-\left(\frac{Z'-Z_a}{2\sigma^2}\right)} \cdot dz' \times e^{-(Z/\lambda)} dZ + \lambda_2 e^{-(Z_0/\lambda_2)} e^{-(\delta/\lambda_2)} \right] e^{-(Z_0/\lambda_2)} e^{\delta/\lambda_2}$$

$$I_A(E_{kin}) \propto N_A^2 \left[\lambda_1 \left(1 - e^{-(Z_0/\lambda_1)} e^{\delta/\lambda_1} \right) + \lambda_{12} e^{-(Z_0/\lambda_{12})} \left(e^{\delta/\lambda_{12}} - e^{-(\delta/\lambda_{12})} \right) - \int_{Z_a}^{Z_b} \frac{1}{\sqrt{\pi}} \cdot \int_{-\infty}^Z e^{-\left(\frac{Z'-Z_a}{2\sigma^2}\right)} \cdot dz' \times e^{-(Z/\lambda)} dZ \right]$$

Exponential

$$I_B(E_{kin}) \propto N_B^2 \left\{ \frac{\sigma \lambda_{12} e^{-\frac{Z_a}{\lambda_{12}}}}{2 \left((\sqrt{2} \lambda_{12})^2 - \sigma^2 \right)} \left[\sqrt{2} \lambda_{12} \left(2 - e^{-\frac{\delta \sqrt{2}}{\sigma}} e^{\frac{\delta}{\lambda_{12}}} - e^{-\frac{\delta \sqrt{2}}{\sigma}} e^{-\frac{\delta}{\lambda_{12}}} \right) + \sigma \left(e^{-\frac{\delta \sqrt{2}}{\sigma}} e^{-\frac{\delta}{\lambda_{12}}} - e^{-\frac{\delta \sqrt{2}}{\sigma}} e^{\frac{\delta}{\lambda_{12}}} \right) \right] + \lambda_{12} e^{-\frac{Z_a}{\lambda_{12}}} \left[1 - e^{-\frac{\delta}{\lambda_{12}}} \right] + \lambda_2 e^{-\frac{Z_0}{\lambda_2}} e^{-\frac{\delta}{\lambda_2}} \right\} e^{-Z_0/\lambda_1} e^{\delta/\lambda_1}$$

$$I_A(E_{kin}) \propto N_A^2 \left\{ \lambda_1 \left[1 - e^{-\frac{Z_0}{\lambda_1}} e^{\frac{\delta}{\lambda_1}} \right] + \lambda_{12} e^{-\frac{Z_a}{\lambda_{12}}} \left[e^{\frac{\delta}{\lambda_{12}}} - 1 \right] + \frac{\lambda_{12} \sigma e^{-\frac{Z_a}{\lambda_{12}}}}{2 \left[\sigma^2 - (\sqrt{2} \lambda_{12})^2 \right]} \left\{ \sigma \left[2 - e^{\frac{\delta}{\lambda_{12}}} e^{-\frac{\delta \sqrt{2}}{\sigma}} - e^{-\frac{\delta}{\lambda_{12}}} e^{-\frac{\delta \sqrt{2}}{\sigma}} \right] + \sqrt{2} \lambda_{12} \left[e^{\frac{\delta}{\lambda_{12}}} e^{-\frac{\delta \sqrt{2}}{\sigma}} - e^{-\frac{\delta}{\lambda_{12}}} e^{-\frac{\delta \sqrt{2}}{\sigma}} \right] \right\} \right\}$$

Linear

$$I_B(E_{kin}) \propto N_B^2 \left\{ \frac{\lambda_{12} e^{-Z_0/\lambda_{12}}}{2} \left[\frac{\lambda_{12}}{\sqrt{3}\sigma} \left(e^{\sqrt{3}\sigma/\lambda_{12}} - e^{-\sqrt{3}\sigma/\lambda_{12}} \right) - 2e^{-\frac{\sqrt{3}\sigma}{\lambda_{12}}} \right] + \lambda_2 e^{-Z_0/\lambda_2} e^{-\sqrt{3}\sigma/\lambda_2} \right\} e^{-Z_0/\lambda_1} e^{\sqrt{3}\sigma/\lambda_1}$$

$$I_A(E_{kin}) \propto N_A^2 \left\{ \lambda_1 - \lambda_1 e^{-\frac{Z_0}{\lambda_1}} e^{\frac{\sqrt{3}\sigma}{\lambda_1}} + \frac{\lambda_{12} e^{-Z_0/\lambda_{12}}}{2\sqrt{3}\sigma} \left[\lambda_{12} \left(e^{-\frac{\sqrt{3}\sigma}{\lambda_{12}}} - e^{\frac{\sqrt{3}\sigma}{\lambda_{12}}} \right) + 2\sqrt{3}\sigma e^{\frac{\sqrt{3}\sigma}{\lambda_{12}}} \right] \right\}$$

Sinusoidal

$$I_B(E_{kin}) \propto N_B^2 \left\{ \frac{\lambda_1 e^{-Z_0/\lambda_1}}{2} \left(e^{\delta/\lambda_1} - e^{-\delta/\lambda_1} \right) + \frac{\lambda_{12} a \sigma e^{-\frac{Z_a}{\lambda_{12}}}}{(2a\sigma)^2 + (\pi \lambda_{12})^2} \left[\lambda_{12} \pi \cdot \cos\left(\frac{\pi \delta}{2a\sigma}\right) \left(e^{\frac{\delta}{\lambda_{12}}} - e^{-\frac{\delta}{\lambda_{12}}} \right) - 2a\sigma \cdot \sin\left(\frac{\pi \delta}{2a\sigma}\right) \left(e^{\frac{\delta}{\lambda_{12}}} + e^{\frac{\delta}{\lambda_{12}}} \right) \right] + \lambda_2 e^{-Z_0/\lambda_2} e^{-\delta/\lambda_2} \right\} e^{-Z_0/\lambda_1} e^{\delta/\lambda_1}$$

$$I_A(E_{kin}) \propto N_A^2 \left\{ \frac{\lambda_{12} e^{-Z_0/\lambda_{12}}}{2} \left(e^{\delta/\lambda_{12}} - e^{-\delta/\lambda_{12}} \right) - \frac{\lambda_{12} a \sigma e^{-\frac{Z_a}{\lambda_{12}}}}{(2a\sigma)^2 + (\pi \lambda_{12})^2} \left[\lambda_{12} \pi \cdot \cos\left(\frac{\pi \delta}{2a\sigma}\right) \left(e^{\frac{\delta}{\lambda_{12}}} - e^{-\frac{\delta}{\lambda_{12}}} \right) - 2a\sigma \cdot \sin\left(\frac{\pi \delta}{2a\sigma}\right) \left(e^{\frac{\delta}{\lambda_{12}}} + e^{\frac{\delta}{\lambda_{12}}} \right) \right] + \lambda_1 \left(1 - e^{-\frac{Z_0}{\lambda_1}} e^{\frac{\delta}{\lambda_1}} \right) \right\}$$

Abrupt

$$I_B(E_{kin}) \propto N_B^2 \left[\lambda_2 e^{-(Z_0/\lambda_2)} \right] e^{-(Z_0/\lambda_1)}$$

$$I_A(E_{kin}) \propto N_A^2 \left[\lambda_1 \left(1 - e^{-(Z_0/\lambda_1)} \right) \right]$$

16.4.2 Selected application examples

There is a wide variety of examples of HAXPES applications [29–31,97,117]. Here are presented only some examples where HAXPES is used in the determination of compositional depth profiles. The combination of X-ray spectroscopy techniques with X-ray diffraction and X-ray reflection allows a comprehensive characterization of morphology, atomic structure, chemical composition, and electronic properties.

16.4.2.1 *Iron-silicon interfaces*

The great challenge of materials science today is the incorporation of complex systems into the field of nanotechnologies. An essential aspect is the production of materials with specific and controlled properties. Many highly relevant systems in use today consist of multiple layers of various complex compounds (magnetic and non-magnetic). Many open questions require a clear distinction between surface, interfacial, and bulk properties.

16.4.2.2 *Role of the metal supply pathway on silicon patterning*

The bombardment of amorphous and crystalline surfaces with energetic ions is frequently used to grow self-organized nano-structures with different surface morphologies, such as ripple or dot patterns [118–123]. Often, the structures produced by ion beams extend into the range of tens of nanometers, and thus can potentially serve as templates for the fabrication of heterostructures, for example, through the subsequent deposition of magnetic materials, which are key for the emerging field of spintronics. A key aspect is to establish/study possible correlations between crystal structure and morphology with electronic, magnetic, and ferroelectric properties, which in general requires a multi-technique approach. Due to the unique physical properties of ferromagnetic metal/semiconductor nanostructures for spintronics applications, much work has been devoted to the growth and characterization of those structures. The diffusion and reaction of elements at the interfaces of nanostructured systems play an important role in controlling their physical and chemical properties for downstream applications.

Ion beam sputtering (IBS) is a suitable and low-cost technique for generating diverse nanopatterns on relatively large surfaces of a variety of materials, including semiconductors, metals, and dielectrics [123]. In recent years, the greatest efforts have focused on the study of IBS self-assembled patterning on silicon surfaces because of its flatness and

technological implication, although many aspects of the self-assembled patterning mechanism remain incompletely understood. Several experimental studies indicate that at normal and/or near-normal ion beam incidence, nanopatterning only above a certain threshold of the incidence angle occurs when metallic impurities such as Mo^+ or Fe^+ are present during the sputtering process. This suggests that the supply of metallic impurities is key in the nanopatterning of silicon surfaces by IBS. However, under impurity-free conditions (no metallic supply) it has also been shown [120] that IBS produces nanopatterning on Si only above a certain threshold of the ion beam incidence angle (in the range 45–50 degrees). A particular example is the role of metal ion co-deposition, for example, Fe^+ ions, in the morphology and composition of the induced self-organized nano-structures on silicon by bombardment with high energetic ions (~ 40 keV) [119,120,124]. Redondo-Cubero et al. [119,120] have studied the dynamics of nanostructure formation induced on a silicon surface by the oblique incidence of a Fe^+ ion beam of 40 keV. The results were compared with those obtained by bombarding the Si surface with a high-energy beam of noble-gas ions, without and with Fe co-deposition. The multi-technical approach includes Atomic Force Microscopy (AFM), Rutherford Backscattering Spectrometry, Transmission Electron Microscopy, XPS, and HAXPES, as well as Superconducting Quantum Interference Device measurements. Si (100) single crystals ($12 \times 12 \text{ mm}^2$) were irradiated at an angle of 60 degrees with respect to the surface normal in a Danfisik ion implanter; the operation base pressure was 1×10^{-6} mbar. The fluence varied from 10^{16} up to $4 \cdot 10^{18} \text{ cm}^{-2}$. Three sample sets were prepared using 40 keV Fe^+ ions (pure metal implantation), 40 keV Xe^+ ions (reference for non-metallic implantation/co-deposition), and 40 keV Ar^+ ions with Fe co-deposition (reference metal for co-deposition). For the last sample set a steel plate was placed close to the Si(100) target. The focalized ion beam was scanned over the Si surface to guarantee homogeneous irradiation and in the case of metal co-deposition the beam was also scanned over the steel plate.

The morphological evolution of the three sample sets was checked *ex-situ* by AFM, supported by using power spectral density (PSD) [125,126]. PSD analysis provides a more complete description of the surface topography both laterally and vertically by decomposing the surface profile into its spatial wavelengths and allows comparison of roughness measurements in different spatial frequency ranges. For all three sample sets a uniform patterning was observed. For the case of sample set (references) irradiated with Xe^+ and Ar^+ ions (with Fe co-deposition), the surface remains featureless

until a fluence of 10^{17} cm^{-2} is reached, where surface roughness starts to be evident. At a fluence up to 10^{18} cm^{-2} , a ripple pattern develops, which is more pronounced in the Xe^+ irradiated samples. Up to this fluence, the surface roughness increases for both sets, while the respective characteristic wavelength of the ripple pattern remains practically constant. Finally, at even higher fluences ($4 \times 10^{18} \text{ cm}^{-2}$), the pattern becomes more disordered, especially in the case of Ar^+ irradiated, where a pronounced sawtooth morphology develops along the ion beam direction. For Xe^+ irradiated samples, raised triangular regions appear in addition to the nanometer ripples. Up to intermediated fluences, samples irradiated with Fe^+ , exhibit small structures aligned along the ion beam direction, rather than vertically aligned ripples as in the case of Xe^+ irradiated ones. As Fe^+ fluence increases, a sawtooth morphology develops with short-range order, and with hexagonal symmetry. The patterning morphology is rather different and depends on the ions' fluences as well as showing a clear difference in whether or not there is metal incorporation. The Fe^+ -induced patterning differs from those of the two reference systems (Xe^+ and Ar^+) as it shows a short hexagonal ordering, although it shares some features between them. With respect to magnetic characterization, in the sample sets irradiated either with Fe^+ or Ar^+ with Fe co-deposition both, the saturation and remnant magnetization, increases with increasing ion fluence. However, all these values are systematically much higher for the Fe^+ irradiated samples than for the Ar^+ irradiated ones, pointing to a more efficient implantation process in the former case. Direct implantation of pure metal leads to a more robust magnetism of the implanted phase, which allows obtaining not only higher saturation and remanence values but also smaller coercive fields. A common feature observed in both samples is the non-monotonic dependence of coercivity on fluence.

To provide further insight into the mechanism of the metal incorporation pathway process, HAXPES was used for non-destructive compositional profiling, three different photon energies (9.0, 10.5 and 14.0 keV) were used and spectra were recorded for various energy levels: Fe 1s (7112.0 eV), Fe 2p_{1/2} (721.1 eV), Fe 2p_{3/2} (708.1 eV), Fe 3s (92.9 eV), Si 1s (1839.0 eV) and O 1s (543.1 eV). The acquisition geometry was 2 degrees respect to the sample surface for the incident X-ray beam and 15 degrees respect to the surface normal, for the photoelectrons. The energy resolution was in the range of between 1.6 and 2.8 eV, which is limited by the bandwidth of the Si(111) DCM monochromator ($\Delta E/E \cong 1.4 \times 10^{-4}$) and analyzer pass energy.

The photoelectron kinetic energy ranges from 1.9 to 13.3 keV, corresponding to an information depth of 5 to 50 nm, respectively. Fig. 16.18 shows the normalized with respect to cross-section, photon flux and analyzer response HAXPES spectra of the Fe-1s, Fe-2p (panels A and B) and Si-1s (panels C and D) core levels. Panels A and C correspond to the sample bombarded with 40 keV Fe⁺ ions (pure metal implantation) and panels B and D to the sample bombarded with 40 keV Ar⁺ ions with Fe co-deposition (reference system). For ease of comparison, the spectra of the Fe-1s and Fe-2p levels were aligned with respect to their respective binding energies as well as normalized in intensity. The Fe-1s, Fe-2p and

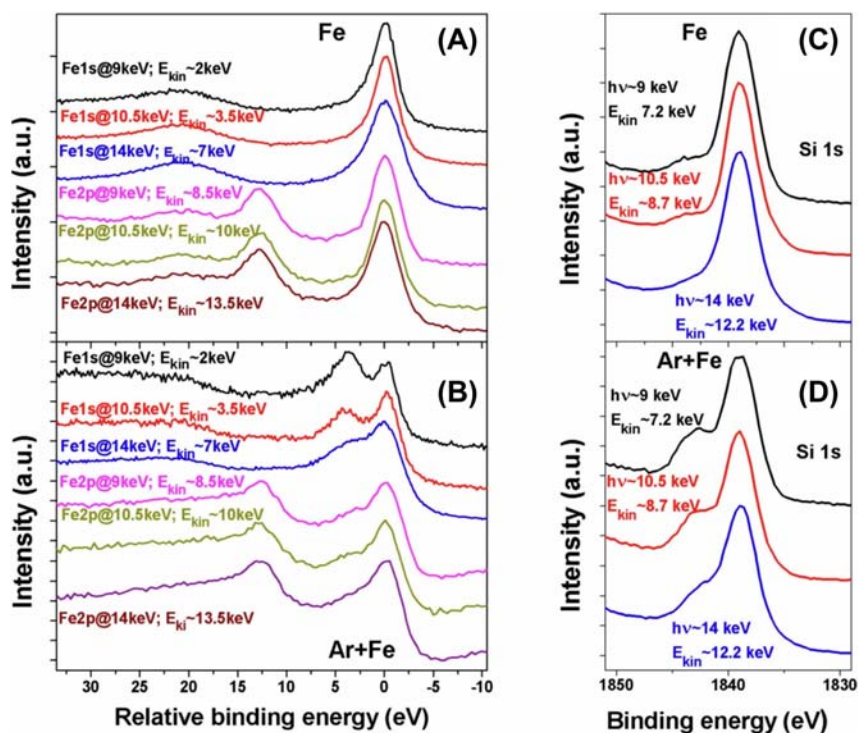


Figure 16.18 Normalized with respect to cross-section, photon flux and analyzer response HAXPES spectra of Fe-1s, Fe-2p [panels (A) and (B)] and Si-1s [panels (C) and (D)] core levels. Panels (A) and (C) correspond to the sample bombarded with 40 keV Fe⁺ ions (pure metal implantation) and panels (B) and (D) to the sample bombarded with 40 keV Ar⁺ ions with Fe co-deposition (reference). Reprinted from A. Redondo-Cubero, F.J. Palomares, K. Lorenz, J. Rubio-Zuazo, R. Hübner, F.J. Mompeán, et al., Role of the metal supply pathway on silicon patterning by oblique ion beam sputtering, *Appl. Surf. Sci.* 580 (2022). <https://doi.org/10.1016/j.apsusc.2021.152267>.

Si-1s core levels spectra corresponding to the samples irradiated with a 40 keV Fe^+ ion beam (pure metal implantation) show a single contribution, while for the case of samples irradiated with 40 keV Ar^+ ions with Fe-co-deposition, they show two contributions. The additional contribution, which is most clearly seen in the Fe-1s and Si-1s spectra, is shifted approximately by 3.6 eV towards higher binding energies and its intensity decreases with increasing photon energy or, equivalently, with increasing information depth. The Si-1s HAXPES spectrum line-shape, especially the one corresponding to the 9 keV photon energy (see Fig. 16.18D) shows features characteristic of Si/SiO₂. The contribution at 3.6 eV towards higher binding energy is characteristic of SiO₂ and it is associated with surface contamination. The intensity of the signal at 3.6 eV with respect to the main peak in the Fe-1s and Fe-2p spectra decreases, similarly as it is observed in the Si-1s spectra, with increasing photon energy. For comparison, Fig. 16.19B shows the evolution of the Fe-1s spectra with the photon energy of an air-exposed Fe reference sample. Therefore, the observed features are associated with surface contamination in the form of oxides. It should be noted that at high photon energy (15 keV) the signal at 3.6 eV with respect to the main peak is almost completely diminished. Comparison between the sample bombarded with 40 keV Fe^+ ions (pure metal implantation) and the sample bombarded with 40 keV Ar^+ ions, with Fe co-deposition (reference system), shows

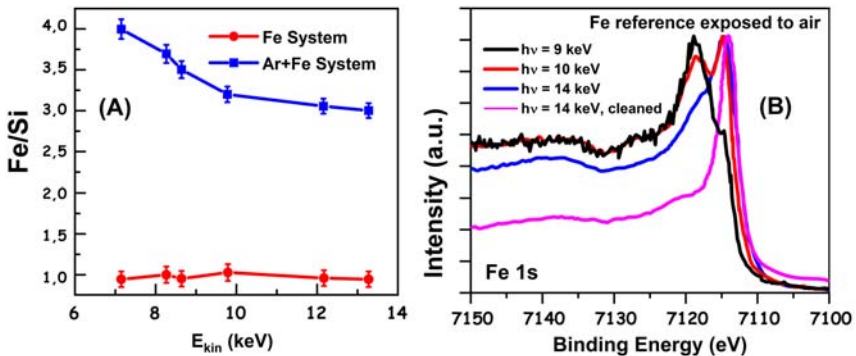


Figure 16.19 (A) HAXPES Fe-2p and Si-1s absolute intensity ratio $I_{\text{Fe}}^{2p}/I_{\text{Si}}^{1s} = \text{Fe/Si}$ as a function of the photoelectron kinetic energy. (B) Evolution of the Fe-1s spectra with the photon energy of an air-exposed Fe reference sample. Reprinted from A. Redondo-Cubero, F.J. Palomares, K. Lorenz, J. Rubio-Zuazo, R. Hübner, F.J. Mompeán, et al., *Role of the metal supply pathway on silicon patterning by oblique ion beam sputtering*, *Appl. Surf. Sci.* 580 (2022). <https://doi.org/10.1016/j.apsusc.2021.152267>.

that the samples that were Fe^+ irradiated have no surface contamination, while the sample that was Ar^+ sputtered with Fe co-deposition has an iron contaminated overlayer on the order of 20 nm. The Fe-1s HAXPES spectra for iron silicide compounds are dominated by the main Fe^0 contribution together with a second contribution shifted by 1.2 eV (less than the overall energy resolution). The stoichiometry depth profile as obtained by comparing the normalized (cross-section, photon flux and analyzer response) HAXPES Fe-2p and Si-1s absolute intensity ratio ($I_{\text{Fe}}^{2p}/I_{\text{Si}}^{1s} = \text{Fe/Si}$) as a function of the photoelectron kinetic energy is shown in Fig. 16.19A. For the samples irradiated with 40 keV Fe^+ ions a Fe:Si intensity ratio of 1:1 is obtained and it remains constant for all photon energies used, while for the Ar^+ irradiated (with Fe co-deposition) the ratio varies from about 4:1 to 3:1 as the photon energy or the information depth increases. It is important to stress that these results are indicating a trend but cannot be equated with the sample stoichiometry. In any case, the results show that under Ar^+ bombardment with Fe co-deposition, a silicide phase is formed with a compositional gradient from a Fe-rich silicide near the surface to a silicide with higher Si content in the deeper layers. Whereas in the case of Fe^+ irradiated samples, a homogeneous silicide layer is formed, which has a stoichiometry with less Fe than when it is irradiated with Ar^+ with Fe co-deposition.

The metal pathway has a marked influence on the patterns' morphological properties and on the spatial correlation between the chemical and morphological patterns. It also determines the iron silicide stoichiometry and the surface pattern magnetic properties that are better for the Fe^+ irradiated sample sets. The obtained results show that in ion-beam-induced silicon surface patterning with reactive metals, the metal supply pathway is critical to determine not only the morphological pattern properties but also the chemical and magnetic ones.

16.4.2.3 Morphological and compositional of Si/Fe interface

The growth of ferromagnetic thin films on semiconducting surfaces has attracted attention due to the fundamental interest in their magnetic properties, and, on the other hand, to potential applications for magnetoelectronic devices in silicon technology. Much attention has been paid to magnetic Fe/Si multilayer structures [118–120,127–130], as they are quite compatible with Si microchip technology. However, technical problems arise with such multilayers due to atomic diffusion and the formation of iron silicides at the Fe/Si interface. In fact, iron silicides at the

interfaces can influence their physical properties and potential applications. Thus, the characterization of Fe-Si interfaces, including morphology and formation of iron silicides during the deposition process, is of the greatest importance. For many years, multiple studies have pointed out the fact that the Fe/Si and Si/Fe interfaces are not equivalent with respect to the formation of iron silicides.

Driven by the desire to contribute to understanding the nature of differences of the iron silicides at the Si/Fe and Fe/Si interfaces Badía-Romano et al. [127,128] have conducted a research study of the morphology and composition of Fe-Si interfaces as a function of depth. Morphological characterization of the Si-on-Fe interface was performed on a bilayer (Si/Fe) grown on a Si(100) substrate with nominal thickness sequence Si(100)/SiO_x/Fe(18 nm)/Si(4.3 nm). Fe/Si interfaces were prepared by vacuum thermal deposition on a Si(100) substrate under ultra-high vacuum conditions (1×10^{-9} mbar). Morphological characterization of these films was performed by a combination of conversion electron Mössbauer spectroscopy (CEMS), scanning transmission electron microscopy (STEM), angle-resolved X-ray photoelectron spectroscopy (ARXPS), and HAXPES in combination with synchrotron XRR. The experimental XRR data and the corresponding fit (*solid line*) are shown in Fig. 16.20 *left*.

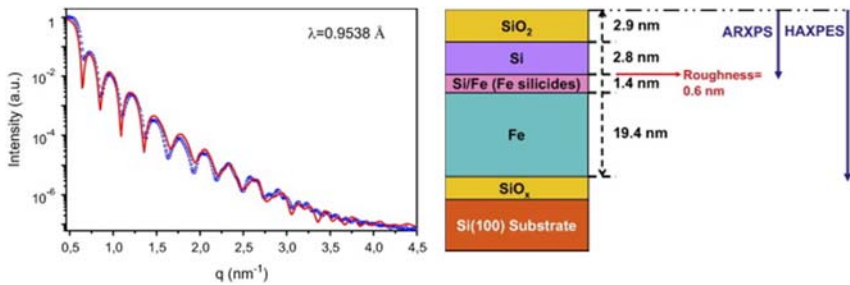


Figure 16.20 (*Left-panel*) XRR measurement on the Si/Fe bilayer. The experimental data are represented by the open blue circles while the solid red line represents the corresponding fit [127,128]. Fitted thickness and roughness of each layer are summarized in Table 16.3. (*Right-panel*) Schematic diagram of the (Si/Fe) bilayer structure. Taking into account the STEM, XRR, ARXPS, and HAXPES results. Arrows (*at the right*) indicate the information depth obtained by the different techniques. *Reprinted from L. Badía-Romano, J. Rubín, F. Bartolomé, C. Magén, J. Bartolomé, S.N. Varnakov, et al., Morphology of the asymmetric iron-silicon interfaces, J. Alloy. Compd. 627 (2015) 136–145. <https://doi.org/10.1016/j.jallcom.2014.12.019>.*

The XRR curve fit was performed using a model that included the thickness of each layer, the roughness at each interface, and the estimated density of each layer. In addition to the layers observed by STEM, an additional layer is required to achieve acceptable fits: an iron silicide phase between the Si and Fe layers (see Fig. 16.20 Right). The fit results also confirm the existence of a pure Si and oxidized Si as the STEM-EELS (Electron energy loss spectroscopy) observation. This oxidized Si overlayer has a thickness of 2.9 ± 0.1 nm, a roughness of 1.3 ± 0.1 nm, and a density of approximately 2.60 ± 0.10 g/cm³, which is close to that of crystalline SiO₂ ($\rho = 2.65$ g/cm³). The XRR results show that the top deposited Si layer, nominally 4.3 nm thick, is naturally oxidized, but a 2.8 (1) nm thick pure Si layer remains. The iron silicide layer at the Si to Fe interface has a thickness of 1.4(1) nm and $\rho = 5.05(10)$ g/cm³ that is quite close to that of the stoichiometrically stable ϵ -FeSi phase ($\rho = 5.19$ g/cm³), but also lies between the value of 4.73 g/cm³ of the highly defective and epitaxially stabilized c -Fe_{0.5}Si phase and close to the stoichiometric c -Fe_{0.88}Si phase, both with CsCl structure. The thickness of the Fe layer is 19.4(1) nm in good agreement with that obtained in STEM measurements. The results of the fit are shown schematically on the right side of Fig. 16.20 and summarized in Table 16.3.

Fig. 16.21 shows the corresponding HAXPES spectra of the Fe-1s and Si-1s core levels as a function of photon energy, the photon energy was varied between 9 and 15 KeV, which led to an increase in the

Table 16.3 Fitted thickness, roughness and density values of each layer forming the Si/Fe bilayer, according to the stack model used in the XRR fit.

Stack model	Thickness (nm)	Roughness (nm)	Density (g/cm ³)
SiO ₂	2.9 (1)	1.3 (1)	2.60 (10)
Si	2.98 (1)	0.8 (1)	2.33
FeSi	1.4 (1)	0.6 (1)	5.05 (10)
Fe	19.4 (1)	0.8 (1)	7.87
SiO ₂	18.7 (1)	0.7 (1)	2.51 (10)
Si substrate	—	—	2.33

The density values of the pure Si and Fe layers are both fixed parameters.

Source: Reprinted from L. Badía-Romano, J. Rubín, F. Bartolomé, C. Magén, J. Bartolomé, S.N. Varnakov, et al., Morphology of the asymmetric iron-silicon interfaces, J. Alloy. Compd. 627 (2015) 136–145. <https://doi.org/10.1016/j.jallcom.2014.12.019>.

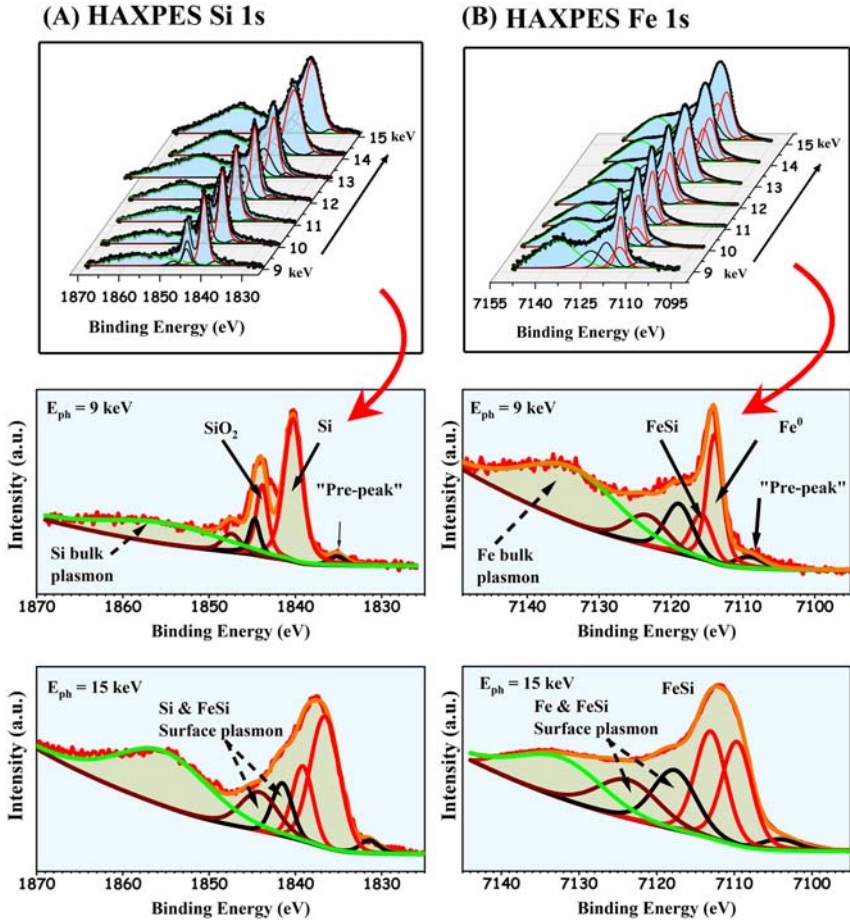


Figure 16.21 Si-1s (A) and Fe-1s (B) core level HAXPES spectra: top panel the complete series, middle and bottom panels the spectra corresponding to 9 and 15 keV photon energies, respectively. Reprinted from L. Badía-Romano, J. Rubín, F. Bartolomé, C. Magén, J. Bartolomé, S.N. Varnakov, et al., *Morphology of the asymmetric iron-silicon interfaces*, *J. Alloy. Compd.* 627 (2015) 136–145. <https://doi.org/10.1016/j.jallcom.2014.12.019>.

photoelectron kinetic energies and, consequently, to an increase of the information depth. The spectra were normalized with the photon flux, detector efficiency, analyzer transmission function, and subshell photoionization cross-sections.

The corresponding photoelectron kinetic energies range from approx. 1.9–8 keV and 7.2–13.2 keV for the Fe-1s and Si-1s, respectively,

resulting in an information depth large enough to pass through the Si overlayer and buried Fe layer. The Si-1s core level HAXPES spectra were fitted with three components: a peak at $E_{BE} = 1838.9$ eV corresponding to metallic Si⁰, and two peaks with binding energies of 1842.2 and 1843.4 eV assigned to different oxidation states of SiO₂. A proper fit is obtained by adding a “pre-peak” shifted ~ 3.5 eV towards low binding energies, which suggests that it is produced by a Fe silicide compound. The Fe-1s HAXPES spectrum is quite complex, but three main features can be discerned. A main peak at $E_{BE} = 7113$ eV related to bulk metallic Fe (Fe⁰), while the peak shifted ~ 1.2 eV towards higher energies is related to Fe silicide phases. Finally, the peak shifted +5 eV higher than the main peak is assigned to plasmon losses from Fe and Fe silicides.

The formation of iron silicide in multilayers (Fe/Si) has been studied by a combination of STEM, XRR, ARXPS, HAXPES, and CEMS. The presence of a Si/Fe interface with a thickness of about 1.4 nm and a roughness of 0.6 nm has been demonstrated. The reflectivity and HAXPES results allow us to identify that the Si/Fe interface is mainly formed by Fe_{1-x}Si, and furthermore, the existence of a SiO₂ top layer. The main phase is the paramagnetic and strained Fe_{1-x}Si with a CsCl structure. Furthermore, the possible presence of a Fe-rich ferromagnetic silicide (Fe₃Si type phase) on the Fe side of the interface is inferred.

16.4.3 Complex oxide heterostructures

The greatest current challenge in materials science is the inclusion of complex systems in the field of nanotechnologies. A fundamental aspect is the production of materials with specific and controlled properties. The required properties of the systems are often only achieved through the inclusion of complex systems. Complex oxides exhibit exotic behaviors such as superconductivity, colossal magnetoresistance, charge ordering, ferroelectricity, and multiferroicity [20,30,36,44,113,115,131–145]. In most cases, such phenomena are due to a complicated interplay of charge, spin, orbital, and lattice degrees of freedom. Understanding the fundamental mechanisms that give rise to the fascinating specific properties of matter, as well as the production of materials with exotic properties, is part of the tasks of materials science. In general, two approaches are followed: on the one hand, the search for new bulk homogeneous materials in terms of composition or by changing the nature of doping and/or their doping level and, on the other hand, the production of heterostructures

of complex materials, where it has been shown that interfaces and surfaces can play a key role in defining their properties. Dimensionality reduction combined with compositional heterogeneity, for example, at buried interfaces or at the surface of the complex heterostructure [146], offers the possibility to obtain exotic properties with a wide range of potential applications [147]. In both bi-dimensional, system interfaces and surfaces, due to the existence of steep changes in the structure and the electronic coordination, there appear a great variety of new, and even unexpected, physical phenomena [148–151]. The growth of these materials in the form of thin-film heterostructures often alters their intrinsic properties that hinder their potential application in industrial devices. This is especially important for many heterostructure systems, such as complex oxides or topological insulators, that is, strongly correlated electron systems whose macroscopic properties are closely related to an intricate interplay between charge, spin, and lattice degrees of freedom.

16.4.3.1 $\text{LaAlO}_3/\text{SrTiO}_3$ interface

After the publication of the article by A. Ohtomo and H.Y. Hwang in 2004 [152] reporting the existence of a two-dimensional electron gas (2DEG) with high mobility at the interface between LaAlO_3 (LAO) and SrTiO_3 (STO) oxide heterostructures, two insulating and diamagnetic oxides, a large number of publications have appeared. The LAO/STO heterostructure [114,138,153–156] is probably the most studied since the first reports that new metallic interface phases can be formed and induced in these systems, even when the starting materials are insulators. However, even after more than a decade of intensive research on this heterostructure, the origin of interfacial conductivity remains controversial or not fully understood. In LAO and STO, both compounds are wide-gap semiconductors with a perovskite structure. The conductivity of the interface depends critically on the SrTiO_3 termination: with TiO_2 termination the interface is metallic, whereas with SrO termination the interface is insulating. The interface becomes metallic when the LAO layer reaches/exceeds the critical thickness of 4 unit cells (uc) [137]. Different mechanisms have been proposed to explain the origin existence of the metal 2DEG interlayer in the LAO/STO interface, the most widely advanced being the polar catastrophe model [157], but also interdiffusion at the interface [158], or the presence of oxygen vacancies [150] or the possible role of adsorbates [159], but also other models have been considered. It should be noted that these models or mechanisms can occur simultaneously or be

part of the same mechanism. Numerous HAXPES experiments [111,114,137–139] have been carried out in an attempt to a better understanding of these mechanisms and also to map the electron density at the LAO/STO interface to determine the extensiveness of its confinement.

S. Mukherjee et al. [114] have recently reported on a HAXPES experiment dealing with the origin and distribution of charge carriers in $\text{LaAlO}_3\text{-SrTiO}_3$ oxide heterostructures in the limit of high charge carrier density. The measurements were carried out at the HAXPES end stations HIKE [160] at the Helmholtz-Zentrum, Berlin, and Beamline P09 [161] at Petra III, DESY, both in Germany. Their work demonstrates very well the suitability of HAXPES for depth profiling at the scale of a few tens of nanometers. Four samples, two with a thickness of 4 uc and two with a thickness of 6 uc, were grown by pulsed laser deposition in an oxygen atmosphere at two different pressures (4×10^{-7} mbar and 1×10^{-4} mbar). 4 L and 4 H and 6 L and 6 H correspond to samples of 4 and 6 uc grown at low (L) and high (H) oxygen pressure, respectively. The X-ray photon energy was varied between 2 and 8 keV, which corresponds to an information depth of about 25 nm, much larger than the thickness of the LAO layer.

In order to check for possible mixing at the LAO/STO interface, spectra of the La-3d and Sr-3d core levels were recorded at different incident photon energies. Two representative spectra of La-3d and Sr-3d core levels acquired at photon energies of 3500-eV are shown in Fig. 16.22A and B, respectively. Fig. 16.22C shows the intensity ratio (lines for calculated and triangles and diamonds for experimental data, respectively) as a function of the photon energy of the La-3d and Sr-3d core levels that are normalized with respect to their corresponding cross-section and analyzer response. After normalization, the intensity ratio depends only on the effective attenuation length and the depth dependence of the atomic density of La and Sr.

Calculated photon energy dependence of the intensity ratio of the normalized La-3d and Sr-3d photoemission spectra for LAO layer thicknesses between 2.6 and 2.9 nm are reproduced as continuous lines in Fig. 16.22C. A constant LAO thickness and an abrupt interface between LAO and STO are assumed. Experimental intensity ratios obtained for 6 H (red diamonds) and 6 L (black triangles) samples are also shown, best agreement is obtained for a LAO layer thickness of 2.75 ± 0.05 nm with a sharp interface.

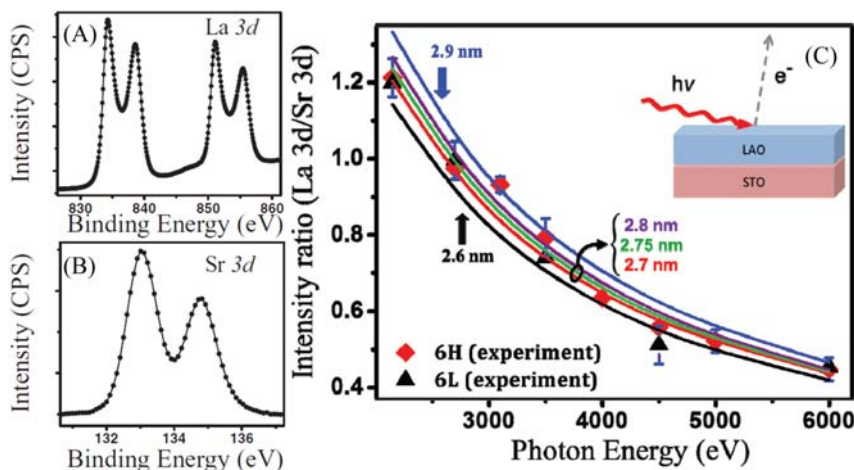


Figure 16.22 (A), (B) La-3d and Sr-3d core-level spectra recorded with an incident photon energy of 3500 eV. (C) Cross-section and transmission function corrected experimental intensity ratios between La-3d and Sr-3d core-level spectra as a function of photon energy for 6 H and 6 L samples along with the calculated variations in this intensity ratio obtained for different LAO thicknesses as shown. Reprint with permission from S. Mukherjee, B. Pal, D. Choudhury, I. Sarkar, W. Drube, M. Gorgoi, et al., *Origin and distribution of charge carriers in LaAlO₃-SrTiO₃ oxide heterostructures in the high carrier density limit*, *Phys. Rev. B.* 93 (2016). <https://doi.org/10.1103/PHYSREVB.93.245124>. Copyright (2022) American Physical Society.

Considering various models of La and Sr interdiffusion across the LAO/STO interface, it should be concluded that if such a mixture exists, it must be limited to a single atomic layer. Therefore, the authors conclude that interdiffusion must be ruled out as the origin of the existence of the 2DEG layer.

The corresponding Ti-2p spectra of the four samples acquired at a photon energy of 3.5 keV are shown in Fig. 16.23A. The main features are the peaks at 459.2 (2p_{3/2}) and 465 eV (2p_{1/2}) binding energies corresponding to the spin-orbit splitting of the Ti⁴⁺-2p from SrTiO₃. An additional signal at 457 eV is observed in the Ti-2p spectra of the 4 and 6 L samples, which is attributed to Ti³⁺-2p originating from the electronic doping of the Ti-3d orbitals. It should be emphasized that the additional signal is not observed in either the 4 H sample or the 6 H sample, that is, the samples prepared with high oxygen pressure. By performing a spectral decomposition into Ti³⁺ and Ti⁴⁺ contributions in the total Ti-2p spectrum, as shown in Fig. 16.23B, it is possible to obtain from the intensity ratio of the two components, Ti³⁺ and Ti⁴⁺, a measurement of the

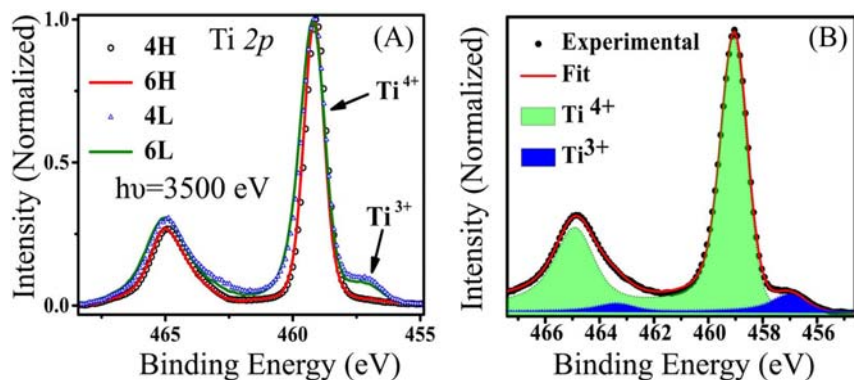


Figure 16.23 (A) Ti 2p X-ray photoelectron spectra of 4 H, 4 L, 6 H, and 6 L samples recorded with photon energy of $h\nu = 3500$ eV. (B) Illustration of a typical spectral decomposition of Ti 2p spectra in terms of Ti^{4+} and Ti^{3+} components. Reprint with permission from S. Mukherjee, B. Pal, D. Choudhury, I. Sarkar, W. Drube, M. Gorgoi, et al., *Origin and distribution of charge carriers in $LaAlO_3$ - $SrTiO_3$ oxide heterostructures in the high carrier density limit*, *Phys. Rev. B.* 93 (2016). <https://doi.org/10.1103/PHYSREVB.93.245124>. Copyright (2022) American Physical Society.

doping fraction. Hence, the photon energy dependence of the Ti^{3+}/Ti^{4+} intensity ratio is determined by the depth distribution of the doped electrons, which allows extracting the charge carrier distribution from the experimental data presented in Fig. 16.24A and B by performing an analysis analogous to that for the La-3d/Sr-3d energy dependence. The best possible result assuming a single Ti^{3+} distribution at the LAO/STO interface for the 4 and 6 L samples are displayed as dotted lines in Fig. 16.24A and B, respectively. In neither case does fitting the data with a single charge distribution at the LAO/STO interface provide an adequate description of the energy dependence of the Ti^{3+}/Ti^{4+} intensity ratio. However, the experimental data can be fitted very well if two different charge carrier density contributions are used. The fitting results obtained assuming a Gaussian distribution at the interface with a width of ~ 1 nm on the STO side and a second constant distribution inside the STO is shown as a solid line in Fig. 16.24A and B, and the corresponding distributions of charge carriers in Fig. 16.24C and D for samples 4 and 6 L, respectively. The necessary charge carrier density distribution in the STO substrate is explained by the presence of oxygen vacancies, and it has been deduced from the analyses/simulation of the energy dependence of the O-1s photoemission signal. Comparison of the O-1s photoemission signals of the sample grown at high (4 H/6 H) and low (4 L/6 L) oxygen

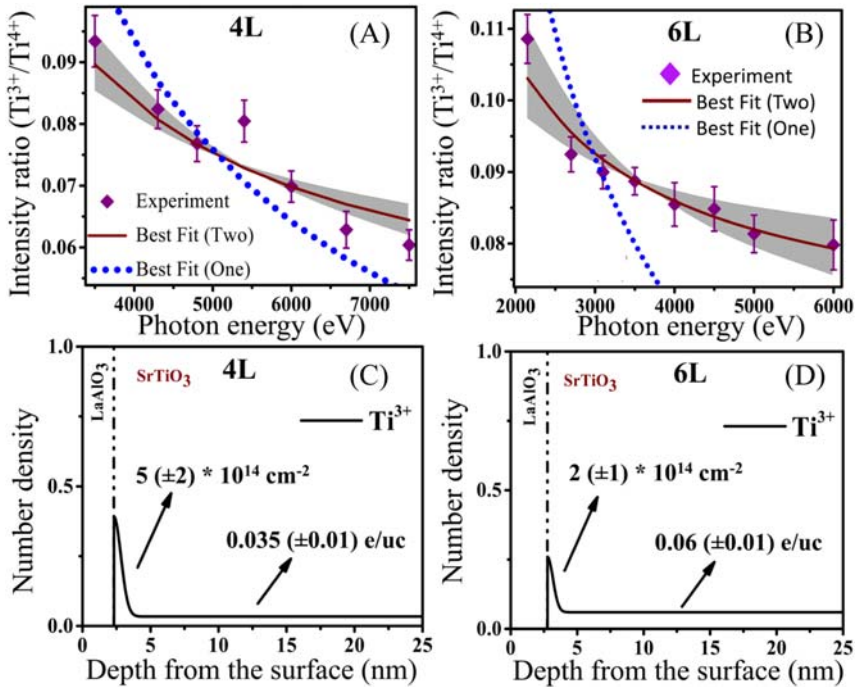


Figure 16.24 (A) and (B) $\text{Ti}^{3+}/\text{Ti}^{4+}$ intensity ratio as a function of the photon energy for 4 L and 6 L samples. Dotted and solid lines represent different fits to these intensity ratios with different models having single and bimodal charge distribution, respectively. (C) and (D) Charge carrier distributions that provide the best fit to the $\text{Ti}^{3+}/\text{Ti}^{4+}$ intensity ratios, shown for 4 and 6 L samples, respectively. The vertical dash-dotted line represents the interface, as obtained from the simulation of the La-3d/Sr-3d intensity ratio. Values of uncertainties on different numbers in (C) and (D) are obtained from extremal fits to the experimental data in Figs. (A) and (B), as shown by the shaded regions. Reprint with permission from S. Mukherjee, B. Pal, D. Choudhury, I. Sarkar, W. Drube, M. Gorgoi, et al., *Origin and distribution of charge carriers in $\text{LaAlO}_3\text{-SrTiO}_3$ oxide heterostructures in the high carrier density limit*, *Phys. Rev. B.* 93 (2016). <https://doi.org/10.1103/PHYSREVB.93.245124>. Copyright (2022) American Physical Society.

pressure reveals the presence of an additional contribution (shoulders/enhancement) at high binding energies for samples grown at low oxygen pressure. This signal is associated with oxygen atoms in the vicinity of the oxygen vacancies and is a measure of the number of vacancies. Decomposing the O-1s photoemission spectrum into two contributions, respectively associated with oxygen atoms and oxygen vacancies, it is, therefore, possible, analogously to the case of La-3d/Sr-3d and $\text{Ti}^{3+}/\text{Ti}^{4+}$, to obtain, from the fit of the photon energy dependence on the

intensity ratio of both signals, a measure of the distribution of vacancies and consequently of the number of carriers (see the original article [114] for more details). It was concluded that at least two different distributions of the oxygen vacancies are required to describe the experimental O-1s intensity ratio. The best model obtained to explain the photon energy dependence corresponds to a homogeneous distribution of vacancies within the STO layer, at least within the HAXPES information depth, corresponding to an average composition of $\text{SrTiO}_{2.97}$ and $\text{SrTiO}_{2.96}$ for 6 and 4 L, respectively, and an additional oxygen vacancy distribution confined within the topmost unit cells of LaAlO_3 . Finally, the authors conclude from these results, together with those obtained from the photon energy dependence analysis of La-3d/Sr-3d and $\text{Ti}^{3+}/\text{Ti}^{4+}$ intensity ratios, that the origin of the metallic layer at the LAO/STO interface is caused by the existence of two distinct charge carrier distributions caused mainly by oxygen vacancies. One is tied at the LAO/STO interface with a width of ~ 1 nm, while the other appears almost homogeneously distributed through the STO substrate.

16.4.3.2 $\text{Fe}_3\text{O}_4/\text{SrTiO}_3$ interface

Many important high-technology devices depend on the chemistry and physics of surfaces and interfaces. In fact, many interfaces in integrated circuits determine the performance and reliability of the device. For instance, interfaces, where either the substrate or the adsorbate has magnetic properties, are of potential interest since they find wide applications as devices for magnetic recording. Highly correlated electron systems are potential technological candidates for the magnetoelectronic industry due to the intricate interplay between lattice, charge, and spin degrees of freedom. The chemical, mechanical, electric, and magnetic properties of such devices are often intimately related to the structure, composition profile, and morphology of their surface and internal interfaces. Transition-metal oxides exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge, and lattice degrees of freedom.

Iron forms a variety of oxides that exhibit completely different physical and chemical properties [162,163]. Thus, for example, FeO (wustite) with formally divalent iron cations Fe^{2+} is paramagnetic at room temperature and becomes antiferromagnetic below the Néel temperature $T_N = 198\text{K}$ [164]. It crystallizes in the rocksalt structure. In contrast, Fe_2O_3 has only trivalent iron cations, and four polymorphs are known: $\alpha\text{-Fe}_2\text{O}_3$, $\beta\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, and $\epsilon\text{-Fe}_2\text{O}_3$, [165] being $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$

highly crystalline and found naturally; while both $\beta\text{-Fe}_2\text{O}_3$ and $\varepsilon\text{-Fe}_2\text{O}_3$ polymorphs generally exist as nanoparticles and are synthesized in the laboratory with a body-centered cubic “bixbyite” crystalline structure and an orthorhombic crystal structure, respectively. $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) is, at room temperature, a ferrimagnetic insulator with a high ferrimagnetic ordering temperature of $TC = 950\text{K}$. It crystallizes in the inverse spinel structure. While the $\alpha\text{-Fe}_2\text{O}_3$ (hematite) is an antiferromagnetic insulator that undergoes the Morin transition from a rhombohedral to a trigonal structure at 260K and the Fe^{3+} cations are located on octahedral sites. It crystallizes in the corundum structure and the Fe^{3+} cations are in octahedral sites. Finally, Fe_3O_4 (magnetite) is a ferrimagnetic half-metal with a Curie temperature of 860K , characterized by a mixed oxidation state of Fe^{2+} and Fe^{3+} [166]. It crystallizes in an inverse spinel structure with Fe^{3+} in tetrahedral sites and a 50:50 mixture of Fe^{2+} and Fe^{3+} in octahedral sites. Fe_3O_4 presents the well-known Verwey metal-insulating [167] transition at 120K and is actually the first magnet known to mankind [162]. Due to these properties, and in particular its semi-metal character and/or its metal-insulator transition, magnetite (Fe_3O_4) is an ideal material for many technological applications, in the form of thin films, heterostructures, or nanostructures. Thus, for example, it can be used as an electrode in magneto-resistive tunneling memories (TMR) [168] based on high spin-polarized currents or in photovoltaic devices. However, the quality and properties of these devices depend mainly on the structural characteristics and quality of the magnetite layer, which are closely linked to the nature/properties of the interface [169] between the magnetite and the substrate or support. To preserve the inherent properties of magnetite it is necessary to control its composition and crystalline structure, to keep the interfaces sharp to control the role of structural stresses at the interface and if possible to reduce the number of dislocations. The production of magnetite (Fe_3O_4) in thin film form is a relatively complex process that requires precise control of the growth parameters, as the other iron oxides, wustite (FeO) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), are closely related in that both are also based on regularly cubic close-packed oxygen anions. High resolution X-ray diffraction makes it possible to distinguish the different oxides [140], especially between maghemite and hematite thin films due to their crystalline similarity. The Fe-1s and Fe-2p photoemission spectra also allow for distinguishing between the different iron oxide phases [140,170] due to the characteristics of the line shape and the presence of specific satellites. There is extensive literature [115,140,169,171–180] devoted to the

growth of Fe_3O_4 on various substrates and, in particular, on SrTiO_3 using pulsed laser deposition and molecular beam epitaxy techniques.

In 2015, Rubio-Zuazo et al. [174] published a paper dealing with the incommensurate growth of Thin and Ultrathin Films of single-phase $\text{Fe}_3\text{O}_4(001)$ on $\text{SrTiO}_3(001)$. Using oxygen assisted pulsed laser deposition (PLD) and MBE growth techniques, thin (7.5 nm) and ultrathin (1.7 nm) Fe_3O_4 films were grown on $\text{SrTiO}_3(001)$ substrates. The crystal, atomic and electronic structure of the films were simultaneously followed by XRR, GIXRD, XPS, and HAXPES. Morphological characterization was performed ex-situ by scanning electron microscopy.

Fig. 16.25 shows experimental low-angle synchrotron XRR results (dots) and the corresponding fits (red solid lines) for the four grown films. Although SrTiO_3 and Fe_3O_4 have very similar electron densities, the XRR curves show clearly intense oscillations (Kiessig fringes),

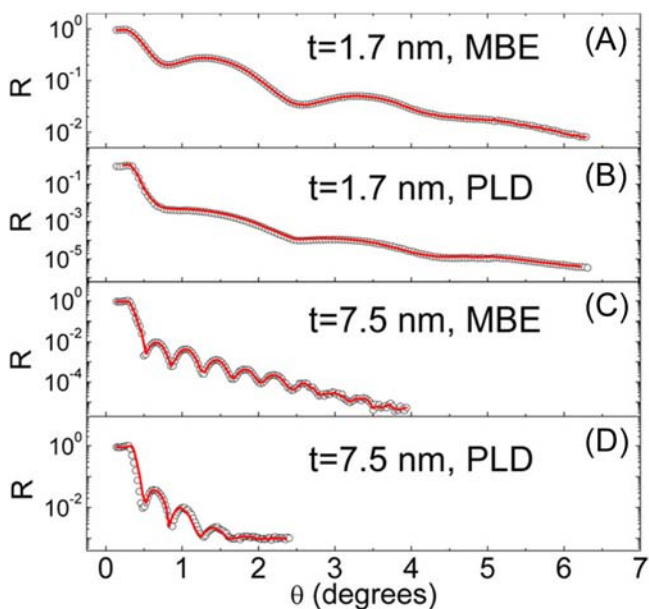


Figure 16.25 Low-angle reflectivity for a 2-unit-cell thick layer grown by (A) MBE and (B) PLD, and for a 9-unit-cell thick layer grown by (C) MBE and (D) PLD. Dots represent the experimental data while the corresponding fit is represented by a solid line. The photon energy used was 12 keV. Reprint with permission from J. Rubio-Zuazo, L. Onandia, E. Salas-Colera, A. Muñoz-Noval, G.R. Castro, *Incommensurate growth of thin and ultrathin films of single-phase $\text{Fe}_3\text{O}_4(001)$ on $\text{SrTiO}_3(001)$* , *J. Phys. Chem. C* 119 (2015) 1108–1112. <https://doi.org/10.1021/jp510615j>. Copyright (2015) American Chemical Society.

demonstrating the presence of a sharp buried interface and a smooth surface. Best fitting of the XRRs curves layer is obtained for thicknesses of 1.7 nm (2-unit cells) and 7.5 nm (9-unit cells) with interface roughness of 0.4 and 0.6 and surface roughness of 0.4 and 0.8 for the MBE- and PLD-grown films, respectively. The mismatch between Fe_3O_4 and SrTiO_3 is expected to be $\sim 7.5\%$, since both having cubic structure, the lattice parameter of Fe_3O_4 ($a = 0.8397$ nm) is about twice that of SrTiO_3 ($a = 0.390$ nm). Magnetite (Fe_3O_4) is expected to grow with its crystallographic axes along the [100] and [010] directions of the SrTiO_3 substrate; that is, both lattices are parallel, thus minimizing the stress/strain caused by lattice mismatch between the two materials.

Therefore, if the reciprocal spatial vectors (h, k, l) of the SrTiO_3 are used to describe the diffraction lattice, and since the real spatial parameter of the Fe_3O_4 lattice is approximately twice that of the SrTiO_3 , the magnetite films are expected to show additional peaks at approximate half-integer values of h , k , and l . The reciprocal spatial maps for the integer reflections (111) are shown in Fig. 16.26A and C for thicknesses of 1.7 and 7.5 nm, respectively, and those for the half-integer reflections ($1/2$ $1/2$ $1/2$) in Fig. 16.26B and D, respectively.

The RSM corresponding to the (111) reflections for both thicknesses clearly shows two different reflections, one corresponding to the substrate, with H , K values of 1, and the other corresponding to magnetite, with values close to 0.93, clearly less than 1. The corresponding half-integer RSMs show only one reflection at about 0.47, 0.47. These results clearly show that magnetite grows incommensurate; that is the magnetite does not adopt the lattice parameters of the substrate, regardless of its thickness or growth method. The magnetite grows on SrTiO_3 maintaining its bulk lattice parameter (completely stress-free), as concluded from the analysis of high-resolution scans. The structural domain size in the plane obtained is 11 ± 1 nm, regardless of the thickness of the layer and the evaporation technique. However, the results can be interpreted if a coincidence network of order 13 is assumed (13 times Fe_3O_4 lattice = 28 times SrTiO_3 lattice). Although, coincidence diffraction reflections are not observed, most probably because the in-plane structural domain is not large enough to provide constructive interference. In fact, the size of the structural domain in the plane is of the order of the size of the incommensurate lattice.

In order to check the iron-oxide phase formed, the authors employed standard XPS and HAXPES where the used X-ray photon energies were 1253.6 eV (Mg $K\alpha$) and 12.0 keV (synchrotron source). The Fe-2p

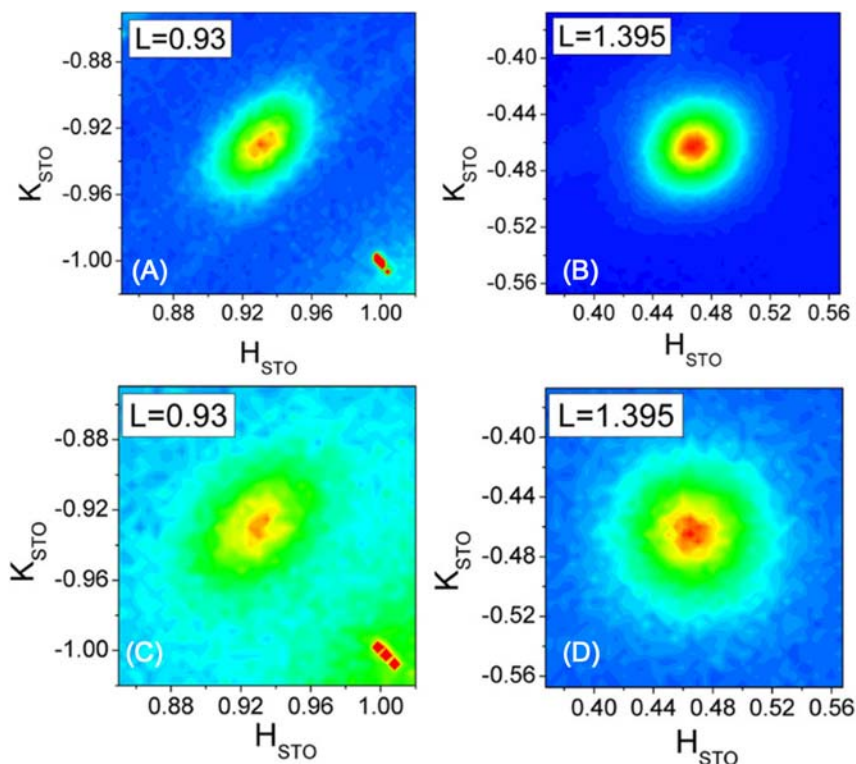


Figure 16.26 HK reciprocal space maps for 7.5 nm (A, B) and 1.7 nm (C, D) thick films. The magnetite diffraction peak does not coincide with the STO diffraction peak, evidencing an incommensurate growth. Reprint with permission from J. Rubio-Zuazo, L. Onandia, E. Salas-Colera, A. Muñoz-Noval, G.R. Castro, *Incommensurate growth of thin and ultrathin films of single-phase Fe₃O₄(001) on SrTiO₃(001)*, *J. Phys. Chem. C* 119 (2015) 1108–1112. <https://doi.org/10.1021/jp510615j>. Copyright (2015) American Chemical Society.

photoelectron kinetic energies reach values of about 500 eV and 11,300 eV for X-ray photon energies of 1253.6 eV and 12.0 keV, respectively, and for the Fe-1s photoelectron using 13.5 keV of 6400 eV. These values correspond to information depths of about 3 nm (Fe-2p@1253.6 eV), 50 nm (Fe-2p@12.0 keV), and 30 nm (Fe-2p@13.5 keV), respectively. Therefore, the photoemission results are representative of the whole iron-oxide layers, since choosing the appropriate photon energy is assured that the information depth is always greater than the layer thickness. The Fe-2p spectra of the four samples (two thicknesses and two growth modes) are shown in the left-panel of Fig. 16.27, while the right-panel shows the HAXPES

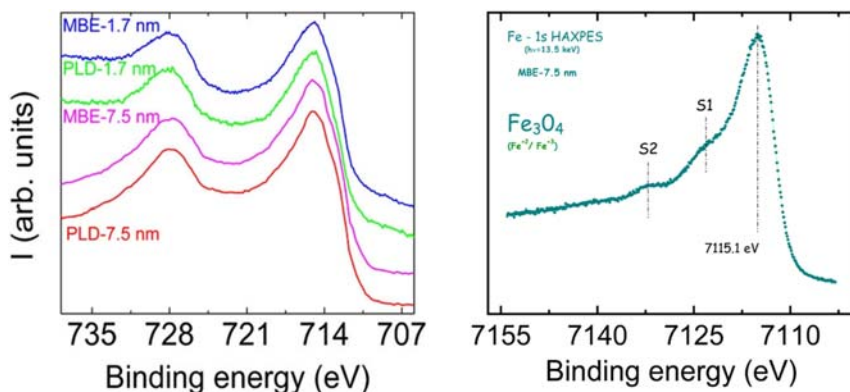


Figure 16.27 Left panel: (from top to bottom) Fe 2p XPS—Mg K α ($h\nu = 1253.6$ eV) for a 1.7 nm layer grown by MBE and 1.7 nm layer grown by PLD; Fe2p HAXPES (synchrotron beam— $h\nu = 12$ keV) for a 7.5 nm layer grown by MBE and 7.5 nm layer grown by PLD. Right panel: HAXPES Fe-1s spectrum for the 7.5 nm MBE-grown layer obtained with synchrotron radiation ($h\nu = 13.5$ keV). Adapted with permission from J. Rubio-Zuazo, L. Onandia, E. Salas-Colera, A. Muñoz-Noval, G.R. Castro, Incommensurate growth of thin and ultrathin films of single-phase Fe₃O₄(001) on SrTiO₃(001), *J. Phys. Chem. C*, 119 (2015) 1108–1112. <https://doi.org/10.1021/jp510615j>. Copyright (2015) American Chemical Society.

spectrum of Fe-1s for the 7.5 nm sample grown by MBE. Note that the Fe-2p spectra of the 1.7 nm thick samples were acquired with an Mg K α source and that of the 7.5 nm samples with a photon energy of 12 keV. The presence of satellite structures in the Fe-2p and Fe-1s spectra of iron oxides due to charge transfer screening effects [140,181] is well known and allows the identification of the +2 and +3 oxidation states of iron. The Fe-2p from Fe₃O₄ is characterized by the absence (not observed) of such a satellite structure, which is due to the presence of intercalated Fe²⁺ and Fe³⁺ ions in the lattice; while the Fe-1s spectra show two characteristic satellites. The Fe-1s photoelectron spectrum of iron-oxide films, shown in Fig. 16.27 (right-panel), consists of a main peak at a binding energy of about 7115.1 eV and two satellite features at about 7123.5 and 7131.5 eV binding energies; their positions correspond well to the Fe-1s spectra of Fe₃O₄ reported in the literature. The photoemission spectra of Fe-2p and Fe-1s (XPS and HAXPES) show that the four iron-oxide films grown are stoichiometric Fe₃O₄ (magnetite), in agreement with the diffraction results. It is important to note that the photoemission results are not only representative of the crystalline part of the sample but also of possible non-crystalline (amorphous) parts.

Therefore, from the combination of GIXRD and XPS/HAXPES, the authors conclude that $\text{Fe}_3\text{O}_4(001)$ films grow incommensurate, independent of thickness and growth technique, in a single-crystalline form with a single crystallographic orientation with respect to the substrate lattice and that no amorphous phases are present. The coupling and/or adaptation of magnetite with the SrTiO_3 lattice is achieved by the formation of a coincidence lattice of order 13, giving rise to domains of 11 ± 0.1 nm comparable to the dimension of the coincidence lattice. Antiphase boundary defects at the border of the domain play an important role in the magnetic and transport properties of $\text{Fe}_3\text{O}_4/\text{SrTiO}_3$ heterostructures.

16.5 Conclusion

In this contribution, after a general introduction, the first sections have been devoted to the description of the physical principles of photoemission with emphasis on HAXPES, as well as the basics of X-ray scattering, particularly with regard to XRR and GI-XRD. The EAL concept and its importance in photoemission were also discussed. Afterward, the possible sources of X-rays useful or applicable in hard X-ray photoemission were described, considering the possibility of being able to perform X-ray diffraction as well. Finally, [Section 16.4](#) is dedicated to the description of the methodology to obtain non-destructive compositional profiles by means of X-ray scattering and HAXPES. In addition, four examples are presented in the following sub-sections.

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CHAPTER 17

X-ray fluorescence spectroscopy

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17.1 Introduction

X-ray fluorescence (XRF) spectroscopy is a noninvasive and non-destructive analytical technique that allows for the identification and quantification of the elements present on the surface of various objects [1]. Using XRF spectroscopy, it is possible to detect most elements on the periodic table, starting with carbon and ending with uranium. This makes XRF an ideal tool to characterize the materials used or produced in various fields of industry and science [2].

The ability to directly analyze samples, speed, and ease of measurement make this method a tool for routine quality control in many industries. XRF has found wide application in material science, geochemistry, and archeology. Additionally, XRF is established as one of the most powerful noninvasive methods for the characterization of artworks.

This method is based on the interaction of X-ray radiation with atoms. XRF spectrometers analyze the elemental composition of the sample by measuring the secondary X-rays that are emitted from the sample after excitation with the primary X-ray source. In the last two decades, there has been rapid development and miniaturization of XRF spectrometers [3]. Commercially available portable or handheld units have been manufactured to enable non-destructive in situ analysis and outdoor measurements without the need for sampling. XRF spectrometer types can vary from light handheld devices to benchtop machines. This chapter highlights this state-of-the-art technique with regards to currently available XRF instrumentation on the market as well as recent applications in environmental, archeology, and especially in cultural heritage fields.

17.2 Basic principle

The X-rays can be considered electromagnetic waves with their assigned wavelength or as beams of photons with associated energies. The source of this radiation is most often an X-ray tube (for example made of W, Au, Cr, Rh, and Mo), but it may also be a synchrotron or radioactive material.

When an X-ray beam passes through a sample, some of the photons might get scattered or absorbed inside the material. There are three main interactions when X-rays contact matter: Fluorescence, Compton scattering, and Rayleigh scattering. The interaction between radiation and matter can cause X-rays to change their direction. It is known as elastic or Rayleigh scattering if the energy of the photon remains the same. That is, all the energy of the incident wave is re-emitted. If the photons lose some energy, it is known as inelastic or Compton scattering [4].

Every element has a characteristic electron structure. Another process that can occur as a result of the interaction of X-rays with an atom is the photoelectric effect. Diagrams illustrating the XRF process are presented in Fig. 17.1.

It occurs when the absorption of radiation completely absorbs and transfers energy to the interior of the atom. XRF spectroscopy is based on the use of X-rays to create ionization in the inner shells of atoms present in the sample. This phenomenon occurs if the energy of a photon is equal to or higher than the binding energy of the electron. High-energy photons induce the ionization of inner-shell electrons which are ejected, creating vacancies. These vacancies lead to an instability of the atom, thus

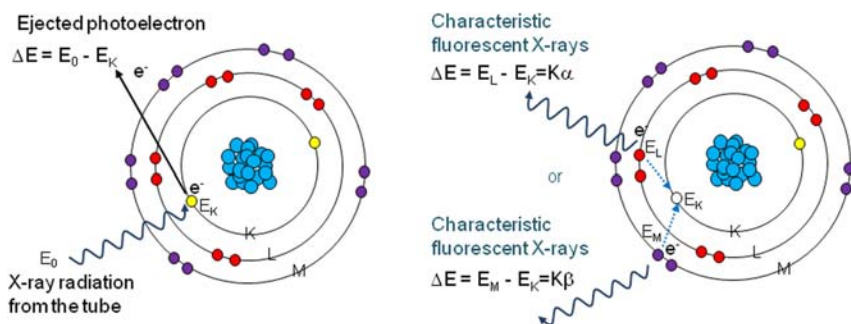


Figure 17.1 X-ray fluorescence process. X-ray radiation emitted from the X-ray tube ejects an electron from the inner K- shell, and a vacancy is created. Next, the electrons from the outer L- or M- shells fill the vacancy, emitting characteristic X-rays.

the electrons from the outer shells are transferred to the inner shells. The transition of electrons from the outer shell to vacancies created the emission of characteristic fluorescent radiation [3]. Characteristic X-ray photons are produced following the ejection of an inner orbital electron from an excited atom, and the subsequent transition of atomic orbital electrons from states of high to low energy. Each element produces secondary X-rays with its specific energies. The resulting lines are called K lines when the transition ends in the innermost, first shell. Successively, L lines are called the transition to the second shell, and so forth. The Siegbahn and IUPAC names of observed X-ray lines are widely described in the literature [3]. The fluorescent X-ray radiation emitted by the analyzed sample is the sum of the radiation emitted by all the elements included in the tested sample.

17.3 Detection systems

The fluorescent X-rays are generally measured by two varieties of detection systems: wavelength dispersive detection (WDXRF) and energy dispersive detection (EDXRF) [2].

17.3.1 Wavelength dispersive detection

WDXRF uses the phenomenon of diffraction by the dispersing system to physically separate the wavelengths of characteristic radiation emitted from the matter. Characteristic fluorescent radiation emitted from the sample passes through the collimator, and next fall on the diffraction device. In the WDXRF technology, the splitting of the radiation, and thus obtaining the spectrum of this radiation, takes place on a single crystal (e.g., LiF, NaCl, or quartz), which acts as a diffraction grating for X-rays. The qualitative analysis concerns the identification of the wavelength of the appropriate lines in the obtained spectrum using the Bragg equation. Thus, individual wavelengths are diffracted into the detector. This makes it possible to analyze the intensity of the radiation emitted by the sample depending on the wavelength measured on a single crystal. The basic design for the WDXRF spectrometer is shown in Fig. 17.2.

Multichannel spectrometers measure the spectral lines of all elements at the same time, which allows for the simultaneous analysis of up to 30 elements. Each spectral line has its crystal and its detector. This provides high elemental specificity and, often high sensitivity as a result of the high

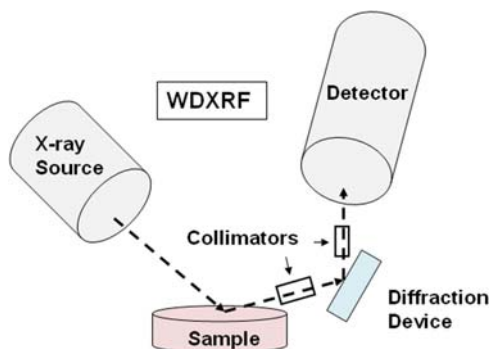


Figure 17.2 The basic design for the wavelength-dispersive XRF (WDXRF) spectrometer.

signal-to-background ratio. In the case of WDXRF, a much better spectral resolution is observed, which allows for the detection of very light elements. Also, the detection limits of WDXRF are lower.

17.3.1.1 Energy dispersive detection

The EDXRF technology enables the separation of the spectrum depending on the energy value corresponding to a specific wavelength [5]. The function of the splitting element is performed by an electronic circuit with a Si (Li) semiconductor detector allowing for the analysis of the pulse amplitude. EDXRF allows for the detection of many different elements from a wide range, simultaneously. Characteristic fluorescent radiation from the specimen is detected by a detector with a multichannel analyzer of the intensity (amplitude) of the emitted radiation. This enables sorting these signals depending on their energy because the intensity of the pulse (signal) of the detector is proportional to the energy of the photon.

Fig. 17.3 shows the basic design of the EDXRF spectrometer. In the fluorescence EDXRF spectrometers used, the so-called 45 degrees /45 degrees geometry is usually used—the angle between the excitation radiation and the sample was 45 degrees, the same as the angle between the sample and the detector. In this type of measurement geometry, not only the characteristic radiation of the sample elements but also the scattered radiation reach the detector. This results in a significant increase in the intensity of the background radiation, on which they impose the characteristic radiation in the line. Measurement resolution, that is the ability to detect individual elements, depends on the resolution of the X-ray energy of the detector and the efficiency of the counting rate. The result is an X-ray energy versus intensity spectrum.

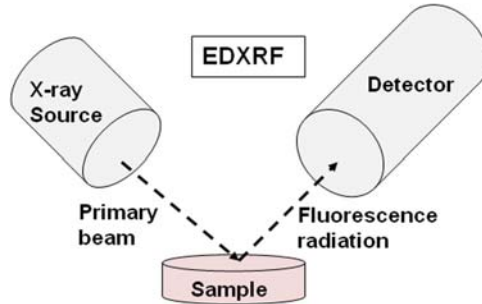


Figure 17.3 The basic design for the energy dispersive detection (EDXRF) spectrometer.

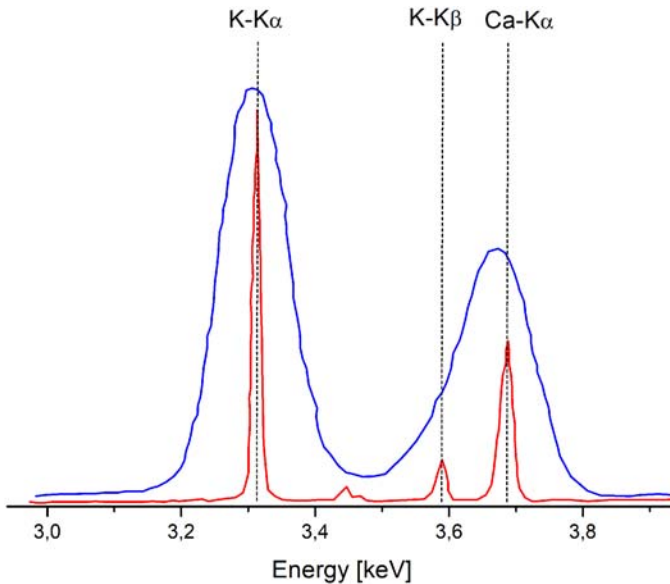


Figure 17.4 The comparison of spectra obtained for EDXRF and WDXRF.

The comparison of two exemplary spectra obtained for EDXRF and WDXRF is presented in Fig. 17.4. In the case of the EDXRF spectrum, it is clearly visible that the bands are broadened and the signals overlap. In the WDXRF spectrum, it can be seen that the higher resolution comes down to better-separated spectral lines, and the background intensity is lower. In the case of the EDXRF spectrum, mathematical elaboration and spectral deconvolution are required.

17.3.1.1.1 Total reflection X-ray fluorescence

The total reflection XRF (TXRF) method was proposed in 1971 by Japanese scientists Yoneda and Horiuchi [6]. Although the phenomenon of total reflection of this radiation was discovered in 1923 by Compton, nearly 50 years of practical application in analytics has not been found for it. Yoneda and Horiuchi proposed to analyze a small amount of material deposited on an optically smooth surface. Although both EDXRF and TXRF use the X-ray tube as the source of the excitation radiation, the techniques used in both of them differ significantly in the measurement geometry [7].

TXRF requires a different position of the sample in relation to the excitation radiation beam. In the TXRF method, the radiation exciting the sample material slides along it at a gloss angle of less than about 0.1 degrees. The primary radiation is modified by the optical systems before it reaches the sample. As a result, the radiation reaching the detector mostly consists of characteristic radiation. The reason for the low background is connected with the measurement geometry. X-rays falling at an angle less than the critical angle result in low penetration, and high reflectivity. In this system, by illuminating the sample with a fully reflected beam, absorption and scattering in the sample matrix are reduced. This reduces background noise and increases the fluorescence efficiency, resulting in a higher sensitivity to trace elements present in the sample. The basic design for the TXRF spectrometer is shown in Fig. 17.5. The minimized background significantly lowers the detection limit. TXRF allows the detection of elements whose concentration in

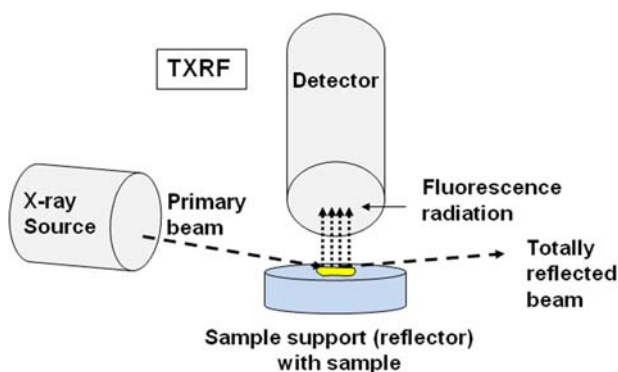


Figure 17.5 The basic design for total reflection X-ray fluorescence (TXRF) spectrometer.

the sample is at the ppb level. The remaining elements of the measuring apparatus and such as radiation sources or detectors are the same as in the EDXRF method.

17.3.1.1.2 Micro-XRF

In classic XRF analyzers, the diameter of the measuring area is up to a few millimeters. In the case of the micro-XRF technique, the area of data collection is much smaller. It is possible thanks to the use of polycapillary optics, which allows obtaining a spot of X-rays with a diameter of the order of micrometers. This allows for selecting the area of interest very precisely. The micro XRF technique enables the testing of micro-samples. Combined with the fast scanning of a larger area, it allows for the precise creation of maps of the distribution of elements for large objects. When creating a map, the area under study is scanned by the X-ray beam. The signal is collected by the detector and reads from each pixel regularly. Correlating the measurement position on the sample with the spectrum obtained allows displaying of an image reflecting the low and high intensities of the element at each of the examined points, and creates a map of the distribution of the element in the entire studied area. This method has been used in geology, electronics, and forensics. It is also especially popular in the analysis of art objects.

17.4 Samples preparation

For several decades, XRF has been used to analyze the elemental composition of various types of environmental, geological, and biological samples, such as soils, sediments, plants, air dust, food, and various types of archeological and historical objects.

Until the 1980s, samples were analyzed mainly in the form of powders or pellets. It required careful grinding of the samples and laborious preparation of the pellets. During in situ XRF analysis, the factors influencing accuracy are uniformity, homogeneity, moisture content, particle size, and surface conditions. The dependence of the characteristic X-ray intensity on the shape and size of the particles was noted [2,8,9]. When testing samples containing the same amount of the analyzed substance and differing grain size, a higher concentration of the analyte in the sample contained fine particles than a sample containing larger grains were observed. All these inconveniences can be avoided by using the micro-XRF technique. As the measurement is made from a micrometer diameter area, no sample preparation prior to measurement is required.

With a wide spectrum of analytical applications, a serious limitation of the so-called classical XRF was the direct analysis of liquid samples. It is difficult due to the high background caused by the scattering of the excitation radiation on water molecules and the low penetration depth of X-rays in the sample. The trace elements from the solutions were chemically released in the form of sediments forming thin samples on the filters. Various selective and nonselective enrichment and isolation methods were used. However, it was necessary to develop many different methods of chemical sample preparation [10]. Nowadays, procedures of preconcentration are anchored in solid-liquid extraction on sorbents such as silica gel, synthetic resins, or activated carbon [11].

17.5 Advantages and limitations

The most important thing is that XRF is a noninvasive and non-destructive method of analysis. In the case of this technique, practically no sampling is required. There is no need to take samples from larger facilities or to prepare them for special, destructive ways, such as crushing or grinding. If necessary, after XRF analysis, the same sample can later be analyzed using other techniques for further investigation.

The XRF method allows for the qualitative recognition of the elements present in the sample, as well as for their quantitative analysis. Metals and nonmetals as well as solid or liquid materials can be analyzed. The concentration of the elements tested is in the range of 1 ppm to 100%. Only in the case of TXRF is the detection of the ppb level possible. The detection limit is generally better for elements with a higher atomic number than for light elements. The precision and repeatability of the XRF method are very high.

The analysis process is very fast. The measurement time depends on the number of the examined elements and the required accuracy of the measurements and is usually in the range of a few seconds to 30 minutes. The analysis time after the measurements is only a few seconds.

These factors make it possible to significantly reduce the cost of sample analysis compared to other techniques of element analysis. Thus, it can be readily automated for use in high-throughput industrial environments.

The software used in spectrometers allows for calibration, thanks to which a wide range of elements can be measured. It can be specially designed for various branches of industry, which allows for more accurate

measurements. Other benefits are short-term delays in obtaining results and relatively low investment and operational costs.

In addition, it is possible to choose the type of spectrometer dedicated to specific research tasks. For example, outdoor measurements will require light and handy equipment, while the macro-XRF scanner is used in the study of works of art to create maps of the distribution of elements in paintings [12].

However, there are disadvantages and limitations to the XRF method. Measurements of lighter elements with EDXRF spectrometers may pose a problem. The penetration depth during the measurement depends on the analyzed material. In the case of metals, depending on the atomic weight, this depth may vary from several to several dozen micrometers, while in the case of materials that poorly absorb X-rays, for example, paint layers containing light elements, it can reach several hundred micrometers. The average intensity of the characteristic lines of the elements in the XRF spectrum depends mainly on the atomic mass of the element.

The value of the count for a given element is generally proportional to its amount in the tested sample. However, the relationship is not linear. The intensity of the recorded signal is also influenced by: reabsorption—absorption of the radiation characteristic of the elements by the matrix atoms; shielding—covering the bottom layers with the top layers; the condition of the surface of the sample and its shape (in the case of examining the paintings, for example, its texture, surface layers of dirt and varnish); measurement geometry—the relative position of the radiation source, detector and tested object/sample to each other.

17.6 XRF instrumentation

XRF spectrometers typically include an X-ray source, a detector, a digital signal processor, and a central processing unit. The most common instruments are handheld analyzers, mobile instruments with open architecture, and benchtop analyzers. Choosing the most appropriate equipment configuration requires an answer to the question of what types of samples will be analyzed and what feedback we want to receive. WDXRF is usually selected if a fast, accurate analysis of only a few elements is needed. EDXRF systems are preferred if a multielement determination is required. The solution enabling the extension of the use of XRF also for the analysis of liquid samples is TXRF. Table 17.1 summarizes the main features of various types of XRF spectrometers.

Table 17.1 Summary of the main features and applications of XRF systems.

Type of XRF system	Characteristic	Sample type	Application
WDXRF	Favorable for light elements	Solids	Routine analysis for industry (metallurgy, pharmaceuticals production, cement production etc.)
EDXRF	Good for intermediate and heavy element	Liquids after preconcentration	Quality control
	Less appropriate for light elements	Solids	Analysis of geological and environmental solid samples
TXRF	Good for intermediate and heavy element	Liquids after preconcentration	Due to determination of multielements suitable for: - Material science and geochemistry, - Environmental sciences and pollution analysis, - Agriculture and food industries, - Forensic sciences - Archeology and cultural heritage
	Surface analysis	Thin layers	Analysis for industry (semiconductors, solar materials, nanomaterials, chemicals, oils, cosmetics)
μ -XRF	Analysis of micro-samples	Micro-samples of solids or liquids	Pollution analysis (water, aerosols, solids)
			Medicine and biological samples (fluids, biofilms, proteins, blood, tissues)
	Analysis of nonhomogenous samples	Irregularly shaped samples	Analysis for industry (semiconductors, solar materials, nanomaterials), geology
	Creating maps of the distribution of elements	Micro-samples	Forensic sciences, archeology and cultural heritage

Portable spectrometers (the size of a hair dryer) and devices with mechanized sample feeders for routine analysis (metal, mining) are produced. The measuring range of most of the handheld devices available on the market allows the detection of up to 45 elements, from c (Mg) to uranium (U), but the latest spectrometers allow for analysis from carbon (C) to uranium (U). Fig. 17.6 presents the use of handheld EDXRF during the analysis of wall paintings.

Higher-class stationary instruments can perform measurements in a helium atmosphere or under a vacuum. The analysis in helium purge allows us to detect elements from sodium (Na). Recent advancements in X-ray optics have made it possible to focus an X-ray beam using polycapillary optics on spot sizes less than 20 μm . Fig. 17.7 shows the open architecture EDXRF during the analysis of oil paintings.



Figure 17.6 Wall paintings analysis by handheld EDXRF instrumentation.



Figure 17.7 Painting's examination with the use of ArtTAX μ XRF spectrometer.

The recent development of macro XRF scanners (MA-XRF) for art object investigations enables the elementary mapping of large areas of paintings. Table 17.2 summarizes the handheld and benchtop XRF spectrometers currently available on the market.

17.7 Application of x-ray fluorescence spectroscopy

The ability to directly analyze samples and the speed and ease of measurement make XRF spectroscopy a tool for routine quality control in many industries. XRF has found wide application in material science and geochemistry, environmental sciences and pollution analysis, agriculture and food industries, pharmaceuticals, and biochemical research, as well as forensic sciences. Additionally, XRF is established as one of the most powerful noninvasive methods for the characterization of artworks.

17.7.1 X-ray fluorescence technique in industrial production

In industrial production, controlling the correctness of the technological process requires tracking changes in the chemical composition, often atypical, at its subsequent stages. XRF makes it possible to obtain results quickly, which allows for the correct interpretation of changes in the material during the process and may enable the process to be corrected. In the metallurgical industry, XRF analysis is primarily used to study the chemical composition of metallic materials, including various grades of steel, nickel alloys, cobalt alloys, titanium and titanium alloys, copper alloys, aluminum alloys

Table 17.2 List of the benchtop and handheld XRF spectrometers available on the market.

Manufacturer	Type of XRF system	Instruments
Bruker AXS (http://www.bruker-axs.com)	S2 PUMA	Benchtop EDXRF
	S2 POLAR	Benchtop EDXRF
	S6 JAGUAR	Benchtop WDXRF
	S8 TIGER Series 2	Benchtop WDXRF
	S8 LION	Benchtop WDXRF
	S2 PICOFOX	Portable benchtop TXRF
	S4 T-STAR	Benchtop TXRF
	S1 TITAN	Handheld EDXRF
	TRACER 5	Handheld EDXRF
	ELIO	Portable benchtop EDXRF scanner
	M4 TORNADO	Benchtop EDXRF scanner
	M6 JETSTREAM	Portable benchtop EDXRF macro-scanner
	FISCHERSCOPE X-RAY XUL	Benchtop EDXRF
	FISCHERSCOPE X-RAY XAN Series	Benchtop EDXRF
Fischer, Ltd (http://www.helmutfischer.com)	FISCHERSCOPE X-RAY XDAL Series	Benchtop EDXRF
	FISCHERSCOPE X-RAY XDV Series	Benchtop EDXRF
GNR Italy (http://www.gnr.it)	TX 2000	Benchtop TXRF
	Horizon	Benchtop TXRF
	ProSpector	Handheld EDXRF
Malvern Pananalytical (http://www.marvelnpanalytical.com)	Epsilon 4	Benchtop EDXRF
	Epsilon XFlow	Benchtop EDXRF
	Zetium	Benchtop EDXRF and WDXRF
	2830 ZT	Benchtop WDXRF
	Axios FAST	Benchtop WDXRF

(Continued)

Table 17.2 (Continued)

Manufacturer	Type of XRF system	Instruments
Rigaku Corporation (http://www.rigaku.com)	ZSX Primus	Benchtop WDXRF
	Supermini 200	Benchtop WDXRF
	NEX Series	Benchtop EDXRF
	Nanohunter II	Benchtop TXRF
	TXRF 3760	Benchtop TXRF
	TXRF-V310	Benchtop TXRF
Shimadzu Corporation (http://www.shimadzu.com)	EDX-7200	Portable benchtop EDXRF
Spectro Analytical Instruments (http://www.spectro.com)	EDX-LE	Portable benchtop EDXRF
	Spectro Xepos	Benchtop EDXRF
	SpectroCube	Benchtop EDXRF
	Spectro Midex	Benchtop EDXRF
	Spectroscout	Benchtop EDXRF
	SPECTRO xSORT	Handheld EDXRF
Thermo Scientific Corporation (http://www.thermoscientific.com)	Niton XLSeries	Handheld EDXRF
	ARL SMS-Omega	Benchtop EDXRF
	ARL QUANT'X	Benchtop EDXRF
	ARL PERFORM'X	Benchtop EDXRF
	ARL OPTIM'X	Benchtop WDXRF
Xenometrix (http://www.xenometrix.com)	P-Metrix	Portable benchtop EDXRF
	S-Mobile	Portable benchtop EDXRF
	X-Calibur	Benchtop EDXRF
	Genius IF	Benchtop EDXRF

(except Al-Si alloys), zinc and zinc alloys, magnesium alloys, zirconium, and zirconium alloys, and lead and its alloys [13,14].

Heavy metal control is also important for manufacturers of electronic equipment. Increasingly regulating the use of hazardous substances in electrical and electronic equipment makes manufacturers, retailers, and suppliers responsible for demonstrating product compliance. All new products must be monitored for the concentration of restricted substances such as lead, mercury, cadmium, and chromium. XRF screening allows one to quickly identify the presence of hazardous substances and their distribution in the product. This test method is especially useful if a quick

overview of the end product is required [15,16]. One routine application of the XRF method is also the study of impurities in silicon wafers used in the electronics industry [17].

17.7.2 X-ray fluorescence for analysis of crude and petroleum products

XRF spectroscopy is one of the methods used to analyze solid and liquid fuels. Crude oil from which liquid fuels are produced is a mixture of many hydrocarbons containing numerous elements such as sulfur, vanadium, chromium, iron, cobalt, nickel, zinc, and lead. Testing the chemical properties of liquid petroleum products used in the automotive industry is difficult due to the variety of these products (gasoline, diesel oil, biofuels, engine oils, etc.), the variability of matrices, and the presence of various additives. One of the parameters for assessing the quality of petroleum products is the content of elements 18–20. Quality control of products burned in car engines is essential in order to protect the environment and maintain the appropriate operational properties of fuels.

Sulfur is determined in all liquid fuels used in motor vehicles and in biocomponents of fuels [21,22]. In the case of liquid fuels, sulfur has a negative effect on the mechanical components of the engine. The combustion of liquids causes the emission of sulfur oxides into the environment.

The multielement analysis, performed with the wave dispersion XRF technique, is also the basic source of information on the dosage level of additives to fresh lubricating oils [23]. Thanks to the XRF technique, it is possible to analyze the sample directly, after homogenization, but without the need for prior preparation (dilution, mineralization), which is a significant advantage of this method.

In the field of petroleum product analytics, the following standardized methods are used that enable analysis using the XRF technique:

- ISO 15597 Petroleum and related products—Determination of chlorine and bromine content—Wavelength dispersive XRF spectrometry.
Method for determining the content of chlorine and bromine in petroleum products using bismuth as an internal standard.
- ASTM D 7212 Standard Test Method for Low Sulfur in Automotive Fuels by Energy-Dispersive XRF Spectrometry Using a Low-Background Proportional Counter.

Determination of sulfur content in concentrations from 7 to 50 mg/kg.

- ASTM D 2622 Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive XRF Spectrometry.

Determination of sulfur content at concentrations from 3 mg/kg to 5.3% (m/m).

- ASTM D 4927 Standard Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength- Dispersive XRF.

The standard presents two methods of determining the above-mentioned elements. Method A is based on calibration with the use of standards of the substances (analytes) mentioned, method B introduces mathematical corrections of interelemental influences.

- ASTM D 6481 Standard Test Method for Determination of Phosphorus, Sulfur, Calcium, and Zinc in Lubrication Oils by Energy Dispersive XRF Spectroscopy.
- ASTM D 2332 Standard Practice for Analysis of Water—Formed Deposits by Wavelength-Dispersive XRF.

The method described in this standard is used for the determination of elements with an atomic number ≥ 11 , with a content of approximately 0.1%.

- ASTM D 6443 Test Method for Determination of Calcium, Chlorine, Copper, Magnesium, Phosphorus, Sulfur, and Zinc in Unused Lubricating Oils and Additives by Wavelength Dispersive XRF Spectrometry (Mathematical Correction Procedure).

Describes the analysis of 7 elements using the XRF wavelength dispersion method. Using the methodology described in this standard, it is possible to determine the content of Ca, Cl, P, Zn, and S in concentrations above 0.02% (> 200 mg/kg), Mg above 0.05% (> 500 mg/kg) and Cu above 0.01% (> 100 mg/kg).

17.7.3 X-ray fluorescence for the characterization of nuclear materials

The XRF technique as a non-destructive testing method has found application in the testing of nuclear materials [24–28]. These materials can be used for the development of standard materials applied as a reference for nuclear fuel. In addition, chemical analyses using XRF are carried out as part of nuclear protection in order to contain the proliferation of nuclear weapons. Another area where the XRF technique is used is nuclear forensics, which is used to identify the source of nuclear materials. The XRF method is used to test uranium and plutonium mixtures or their fission

products. The spent fuel or waste is also analyzed. XRF analyzers were also used to measure the level of radioactive contamination during the research of the contaminated areas [29].

17.7.4 X-ray fluorescence in the investigation of environment and earth material

The portable XRF spectrometers are used in many branches of science, such as geology, Earth science, and environmental protection. Soil is one of the most important elements of the biosphere and environmental architecture. The chemical elements contained in the soil include oxygen, silicon, iron, calcium, sodium, potassium, carbon, and chlorine. Portable XRF spectrometers are successfully used in geology, for example, for studies of igneous rocks for the content of rare earth elements [30], screening analysis of rocks from drill cores [31], determining the chemical composition of sedimentary rocks [32], as well as analyzing of regolith over mineral deposits to detect anomalies in the content of selected elements [33]. Micro XRF technologies were successfully applied to mineral identification and characterization, such as exotic-Cu deposits in Chile, epithermal Au-Ag deposits in New Zealand, and diamond deposits in South Africa [34].

The XRF method allows for precise determination of the soil composition and it is often used in the field of environmental protection to study the contamination of soils, plants, or aquatic sediments. The chemical composition of soil indirectly influences the type of food consumed by humans in relation to the food of animal and vegetable origin and drinking water. From a sanitary point of view, the most important chemical elements contained in small amounts in soil minerals are fluorine, iodine, copper, zinc, manganese, cobalt, selenium, and molybdenum [35]. High or low levels of these elements in the soil can play a leading role in diseases such as fluorosis and Keshan disease. Very dangerous soil contaminants are those associated with heavy metals such as mercury, cadmium, lead, chromium, copper, zinc, and arsenic. Heavy metals are found in the soil as natural admixtures, and their increased concentrations are related to the industry (iron and nonferrous metals, energy, chemical industry), agriculture (irrigation with polluted water), or the burning of fossil fuels and waste. XRF spectrometers are most often used in the studies of soil percentage. An important role is played by the control of the condition of the soil and the changes that take place in it. XRF was successfully used for studies on postmining soil contamination [36]. The field-portable XRF spectrometry was used in situ analysis of parts of black and silver

wattle (*Acacia mearnsii* De Wild. and *Acacia dealbata* Link) to map the extent of contamination surrounding the former Woodlawn base metal mine [37]. The ease of sample preparation and the speed of measurement combined with the obtained precision of determinations make the portable XRF spectrometer an important research instrument, successfully replacing the classic, time-consuming and expensive methods of chemical analysis. Its small size, weight, and ease of use enable the use of the spectrometer both in the laboratory and in outdoor work.

17.7.5 X-ray fluorescence in the food analysis

Food safety and quality are among the most important human environmental factors. Minerals are consumed almost exclusively with food, as the human body cannot produce them. Therefore, they must be supplied in the right proportions and quantities. Monitoring the content of elements harmful to health in food is required by law. The presence of chemical elements in food products, both toxic and necessary for the proper functioning of the human body, requires meticulous analysis. Therefore, the XRF method is used to determine the main and trace elements in various branches of the food industry.

For many years, it has been used to test the composition of powdered milk and infant flakes. XRF analysis of milk and dairy products enables the determination of minerals as well as trace elements [38,39]. In the case of powdered milk analysis, the EDXRF technique was preferred ([40–42]), however, the WDXRF technique was also used [43–45], and recently there have been reports of the use of the TXRF technique [46].

The XRF technique was used to analyze the presence of phosphorus in soya foods [10], and in edible oils [47], lead and other heavy metals in wine [48], heavy metals in vegetables [49], trace elements such as calcium, sodium, magnesium, titanium and others in fruit juices [50]. The XRF method was used also to study trace elements in tea ([51]; Min [52]), oriental spices [53], pepper [54], coffee [55], and cocoa [56]. XRF spectroscopy was used likewise to analyze the content of mineral products in food for animals such as dogs and cats [57]. In the case of the analysis of food products, the advantage of the XRF technique is the direct possibility of analyzing solid samples. This avoids wet analytical methods that require the digestion of the sample, loss of analytes, and the generation of contaminants [58].

17.7.6 Application of the TXRF method for analysis of biological samples

Due to small samples, low detection limit, and the possibility of simultaneous analysis of many elements, the XRF method has found numerous applications in the analysis of biological samples [59]. The research was conducted for the purposes of both environmental biology and medicine. In 1997, Brown et al. applied the TXRF method to study prions (proteinaceous infectious particles) showing differences in copper content in samples of brain tissue [60]. In the next few years, TXRF was used to study the Cu/Fe concentration ratio in cytochrome oxidases [61]. The elemental composition of these enzymes was carefully analyzed [62–65]. Synchrotron TXRF in combination with gel electrophoresis was used to determine the content of metals in various types of proteins [66]. From the beginning of the method's development, attempts were made to use TXRF for testing body fluids. The first attempts on this subject concern the analysis of whole blood [67,68]. Due to the high content of iron, the preparation used included the removal of iron by extraction with HCl and methyl isobutyl ketone. The possibility of chemical enrichment of the elements of transition groups (nickel, copper, zinc) and lead in the blood by mineralization and then precipitation of water-insoluble complex compounds was also investigated. The sediments were then separated by filtration [69]. The TXRF method was also applied to test the level of metals in women and infants living in contaminated area [70]. Human or animal plasma is a fluid that is easier to analyze than whole blood, mainly due to its lower iron content. The TXRF method was used both to analyze the proportions between individual elements [71] and to determine the concentrations of the most frequently determined elements, ie iron, copper, zinc, and selenium [72]. Blood plasma analysis was performed directly [73], often after dilution with a small amount of water, or in combination with sample mineralization. Mineralization increases the precision of the marking. Sometimes, however, it is not possible to carry it out due to the small amount of available material. A similar analytical problem is the analysis of the cerebrospinal fluid, but the content of elements is lower than in the blood plasma [74].

In vitro studies use TXRF spectrometry to study tissue cultures ([75–77]). In the late 1980s, an attempt was made to use TXRF to study the composition of tissues cut with a microtome and applied directly to a sample support (reflector) in the form of a thin film. In the case of this

type of measurement, detectors with a wide viewing angle (100 mm^2) were used. This technique was used to compare the distribution of elements in healthy and neoplastic tissues [78]. In other cases, mineralization with nitric acid is usually used. TXRF was used to examine bones [79], teeth [80], hair [69], placenta [81], brain tissue [82,83], lungs [84], and liver [85]. TXRF is also used in plant biology, primarily to analyze plants that are biomonitors of environmental pollution, such as lichens [86], epiphytes (*Tillandsia capillaries*) [87] or hyperaccumulators [88]. TXRF has been used in the analysis of tree growth rings [89], and tropical plants that have been used in traditional medicine for years [90,91].

In the study of aquatic ecosystems, TXRF was used to analyze not only water but also aquatic organisms. Depending on the degree of bio-availability, the toxic elements can reach high concentrations in various organisms. The subjects of the research were fish and their parasites [92,93], and water insects [94]. Whole organisms or their selected organs were analyzed. The most frequently determined were the concentrations of lead and elements of transition groups.

17.7.7 X-ray fluorescence spectroscopy in forensic investigation

XRF spectroscopy is successfully used for the forensic, classification, and imaging of forensic traces [95,96]. It is most often used for the analysis of gun shot residues. Physicochemical examination of material evidence in cases of gunshots is useful in clarifying the circumstances of the incident. The research of evidence materials is most often carried out with the use of microanalytical methods in order to detect the presence of metal blasting particles on the tested substrate. Particularly useful in revealing the presence of trace amounts of heavy metals such as lead, tin, antimony, and mercury is XRF spectrometry. It allows to detection traces of metals from abrasion of the projectile (lead, antimony, and tin), or from primer material particles traveling on the projectile. XRF techniques proved to be useful for in situ analysis of clothing or deteriorated tissues in shooting cases and in other forensic examinations [97–101].

Attempts are also being made to use MA-XRF for the detection and imaging of forensic traces on large surfaces of objects such as wall panels or entire clothing [102].

Counterfeiting of money has been known for centuries, but the use of modern analytical methods allows one to easily distinguish counterfeits from originals. Banknotes' chemical profile has become an

efficient methodology for criminal investigations. The potential of portable XRF spectrometry supported by principal component analysis has been confirmed after the rapid and non-destructive examination of different colored regions of the US dollar, Euro, and Real banknotes [103]. The chemical composition of the ink used in the original and false Peruvian Nuevo Sol banknotes was verified with a portable XRF spectrometer [104]. Rodrigues et al. recently performed measurements of genuine and counterfeit Real (Brazilian currency) banknotes employing portable XRF and portable Raman spectroscopy equipment [105]. Not only are banknotes counterfeit, but also often works of art. XRF helps to determine the technique and technology of making a given object in relation to an authentic work.

17.7.8 Application of x-ray fluorescence for analysis of art objects

During recent years there has been an increasing interest in the use of noninvasive analytical techniques able to yield valuable information on art objects by noncontact examination of entire artwork's surfaces. Several reviews can be found in the literature that summarizes the most important applications of XRF to artwork studies, conservation, and restoration, proving the suitability of this technique for non-destructive analysis [106–109].

Characterization of the materials and painting technique, involving non-destructive analysis based on X-ray analytical methods, including XRF spectrometry, and recently, MA-XRF is now widely used in the study of art objects. XRF is a technique that is very commonly used in heritage research laboratories. XRF was applied for analysis to different types of artworks such as ceramics [110,111], coins [112,113], textile objects [114,115], wall paintings [116,117], drawings [118], historic banknotes [119,120], medieval manuscripts [121], and paintings [122–124]. XRF analysis based on element analysis allows obtaining a quick and accurate detection and identification of inorganic materials, especially pigments. XRF has long been an established technique for the study of painting materials owing to its noninvasiveness and speed of analysis. XRF analyses typically consist of point measurements, but to obtain more comprehensive information about the art object is often necessary to perform analysis at various points throughout the object. Due to the limited number of spots that can be analyzed in a feasible amount of time, only local point information is obtained, which is not necessarily representative

of the whole painting. Furthermore, the interpretation of results may be complicated because the information from both the surface and underlayers are obtained in one measurement, and pigments in different layers all produce secondary X-rays.

However, most of the devices available on the market do not allow for the preparation of maps of the distribution of elements. Some offer the possibility of mapping very small areas, of the order of a few cm^2 . Additionally, the time of such measurement is long—it amounts to several hours per cm^2 with a spatial resolution of 0.5 mm. The threats resulting from the very close proximity of the sharp parts of the measuring system to the object are also significant. Fig. 17.8 shows the typical distance of the beam focusing and detector from the object.

In the case of tests carried out in a laboratory on prepared samples, the parameters such as texture, and surface layers of dirt and varnish can be controlled. Thus, approximate quantitative measurements are possible. In the case of research on real objects, and in particular the research on painting layers discussed here, the interpretation of the results is difficult and should be treated mainly as qualitative, extended, if possible, by an approximate quasiquantitative assessment. The sources of error in the quantitative assessment of the pigment in the paint layer are primarily: ignorance of the thickness of the pigment layer and the structure of the paint coating, unknown pigment concentration in the binder, the presence of highly radiation-absorbing pigments containing for example, lead, uneven surface of the paint coating, often covered with a layer of varnish and dirt of variable thickness.



Figure 17.8 Measuring head during analysis of a porcelain figurine by X-ray fluorescence spectroscopy with the use of a micro beam.

The main problem when interpreting multilayer paint coating structures with the XRF technique is the inability to distinguish between the elements/pigments visible in the fluorescent spectrum. The proportions of the counting values of the elements to each other are disturbed by the shielding of the bottom layers (the more numerous, the more difficult the interpretation) by the top layers and the reabsorption of the elements in the mixture of several pigments within one layer. The limitation of the quantitative analysis of elements, apart from screening, is also the fact that a certain part of the peak at the base does not always come from a given element only and may slightly overestimate the count value. This value also increases when the peaks of two elements overlap or coincide directly, as in the case of the La line of lead and arsenic, when they occur simultaneously in the sample.

The recent introduction of MA-XRF deals effectively with some of these drawbacks [125–128]. The MA-XRF method is a variation of the known method for determining the elemental composition of an object (pigment, material) by measuring the energy of the emitted characteristic X-rays. Recent instrumental changes enable MA-XRF analysis directly in the museum using mobile XRF scanners and enable elementary mapping of large areas. The main difference is that the measuring head is placed on rails that allow it to be moved in the X and Y directions, in a plane parallel to the tested surface, and the data on the elemental composition are obtained separately at each point of this surface. In MA-XRF, the X-ray beam scans areas and the results can be plotted as elemental distribution maps. These data are usually presented in the form of maps where the color intensity at a given point corresponds to the concentration of a given element. These images can make interpretation more straightforward and, since the points analyzed cover a wide surface area, they are more representative of the whole painting. In the case of MA-XRF imaging, the contrast is the result of the number of chemical elements and the change in their signal strength. With this method, it is possible to reconstruct the various pigments, including those containing elements with low atomic numbers used in the image composition, in opposition to the radiographic method where only the pigments which strongly absorb X-rays and prevent the X-rays from passing through the painting appear white on the developed radiograph.

The development of detectors collecting fluorescence radiation from a large solid angle allowed for a significant reduction in the time of signal measurement from one measurement point. For example, an area of

$65 \times 45 \text{ cm}^2$ can be scanned within 3.5 hours with a resolution of 0.5 mm. It carries the risk of mechanical damage, especially in cases where the object is not perfectly flat.

Since X-rays penetrate the surface to some extent, depth profiling is often possible. Hidden layers beneath the surface can be visualized and analyzed. This enables art historians, conservators, and scientists to obtain information about the technology of studied painting and the working methods of artists. This new analytical method is very useful for detecting the changes introduced by the artist, and the images hidden underneath the surface painting layer, as well as for art authentication and conservation.

In the field of researching historical objects, the method is primarily used to test:

- decomposition of the elements included in the pigments and metallic layers (e.g., gilding) making up the painting layer of the easel and wall paintings,
- revealing repaints and other conservation interventions,
- elemental composition of inks containing inorganic components (especially iron-gall), components of initials, and other manuscript decorations,
- components of historical glass (especially stained glass) and glazed paintings,
- components, especially glazes, ceramic objects,
- elements included in the archeological objects.

XRF spectroscopy is a valuable and noninvasive method for the identification of pigments. This technique was the starting point for the investigation of the pigments and paint layers in Nero's Torches by Henryk Siemiradzki [129]. This oil painting is one of the largest in size paintings in the collection of the National Museum in Kraków. ($3.76 \text{ m} \times 7.11 \text{ m}$). In situ measurements performed directly in the gallery, were necessary to analyze such a huge oil painting. To identify pigments used by the painter, the noninvasive XRF spectroscopy technique was applied using two spectrometers of Bruker AXS Microanalysis manufacture: ArtTAX μ XRF spectrometer dedicated for art objects analysis and handheld spectrometer Tracer III. Using the ArtTAX, only the lower part of the picture was measured. Other upper parts of the painting were examined using a handheld spectrometer Tracer III and working on the scaffolding.

ArtTAX μ XRF spectrometer is equipped with a Rhodium X-ray tube (50 kV), a Peltier-cooled silicon drift detector, and a set of pinhole collimators ranging from 2 mm down to 200 μm or polycapillary optical

system. The Tracer III-SD incorporates the proprietary XFlash Silicon Drift Detector (10 mm^2 , typical resolution 190 eV at 10,000 cps) and Rh target. The device is battery operated, it is relatively small ($30 \text{ cm} \times 10 \text{ cm} \times 28 \text{ cm}$), and weighs 2 kg (with battery). All these features enabled the use of the spectrometer on the scaffold.

ArtTAX is moveable, which is an advantage, but at the same time, quite big and cumbersome to use outside the laboratory. The dismantling and then reassembling are time-consuming. Moreover, the time of accumulating spectra is also relatively long (approximately 300 seconds/40 seconds each), so taking measurements takes quite a bit of time as well. The acquisition time of 300 seconds and spot size of 0.62 mm were used during the examination of Nero's Torches. However, later ArtTAX 400 was updated to ArtTAX 800. The collimators were replaced by a polycapillary optical system, thus the acquisition time and spot size were reduced to 40 seconds and 0.1 mm, respectively. However, the ArtTAX is very precise — the range of the measured spot is 0.62 mm/0.1 mm, while for Tracer III it is 3.5 mm. Another advantage of ArtTAX is a CCD camera, which allows the operator to see the analyzed point and its color precisely, and record the image.

In comparison to the ArtTAX, the Tracer III is small and can be handheld, though not very light at 2 kg. The Tracer III is operated by a battery, so the measurements can be performed in various places, without access to electricity. This device is also equipped with an XFlash Silicon Drift Detector (SDD), which provides high-speed data acquisition (e.g., 6–8 seconds). This feature saves time, allowing for more measurements to be taken within a limited duration. On the other hand, Tracer III is lower precision compared to ArtTAX. Furthermore, Tracer III has no CCD camera, which could additionally affect the accuracy of the analysis. Therefore, combining both devices optimized the effects of the investigation.

Another example is the study of pigments in the earliest painting, "Landscape from Malacoff" by Polish painter Jan Cybis. The painting has two signatures of the artist. The investigated oil painting as well as the XRF spectra from the measured point is shown in Fig. 17.9.

Spot XRF analysis showed the presence of chromium indicating chromium yellow, and iron, suggesting the use of yellow ochre. However, due to the penetration of X-rays through all paint layers, it cannot be determined whether the signature was made with a mixture of both yellow paints or just chrome yellow, and the detected yellow ochre comes

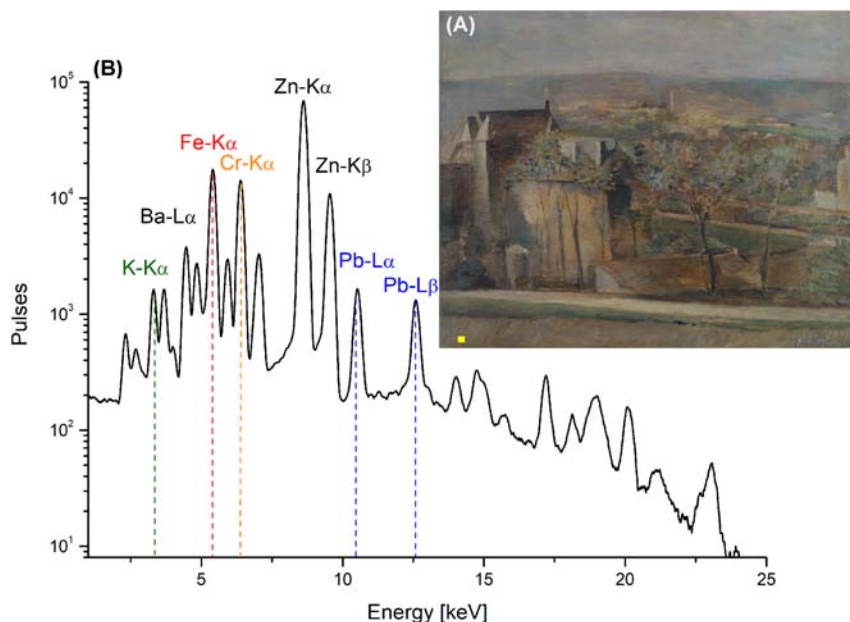


Figure 17.9 (A) The oil painting by Jan Cybis “Landscape from Malacoff” (the National Museum in Krakow collection). (B) X-ray fluorescence spectrum of the yellow paint on the artist’s signature written in the left, right corner. The point of analysis was marked as yellow square. Detected elements may suggest the presence of: Fe—yellow ochre, Cr, Zn, K, Pb—chrome yellow or zinc yellow, Zn—zinc white, Pb—lead white, Ba—barium white.

from the substrate layer. On the right, a blue signature is hardly legible because it was later covered with white paint. The distribution of the elements in the painting was visualized using the macro-XRF map as shown in Fig. 17.10.

The elemental distribution maps of chromium, iron, and cobalt facilitate the interpretation and understanding of the point analysis. The chromium distribution map shows where chromium-rich pigments are present but does not allow differentiation between chromium green and chromium yellow. However, thanks to the imaging, it was found that the left signature was written in chrome yellow. The date 27 was also made visible. The cobalt distribution map showed the use of cobalt blue in the right artist’s signature. In addition to the artist’s name and surname, the inscription “Paris,” the place where the painting was created, was also revealed.

In the case of pigment analysis, XRF is limited to the characterization of inorganic materials and is not suitable for detecting organic colorants,



Figure 17.10 Element distribution maps of Cr, Fe, and Co in the painting “Landscape from Malacoff” by Jan Cybis (the National Museum in Krakow collection).

because the elements in these pigments (like carbon) do not have enough energy to be detected. The absence of elements associated with inorganic pigments of a certain color, however, can help indicate that an artist may have used an organic colorant.

17.8 Summary

XRF spectroscopy is a noninvasive and non-destructive analytical technique that allows determining of the elemental composition of a substance. This technique is very often chosen as a method of element content analysis among other available analytical techniques. Chemical analytical techniques destroy the sample and require time-consuming preparation.

XRF spectrometry allows us to easily and quickly identify and determine the concentration of elements over a wide measurement range from PPM levels to virtually 100% by weight. XRF spectrometer testing is noninvasive, non-destructive, and requires little (or no) sample preparation. The analysis process is very fast. These factors make it possible to significantly reduce the cost of sample analysis compared to other techniques of element analysis.

An XRF spectrometer system typically consists of three main components: an excitation source, a spectrometer/detector, and a data acquisition

and processing unit. The elements are detected based on the characteristic wavelength (X) or energy (E) of the X-ray emission. The concentration of a given element is determined by measuring the intensity of its characteristic lines.

The ability to directly analyze samples, speed, and ease of measurement make this method a tool for routine quality control in many industries. XRF has found wide application in material science and geochemistry, the oil industry, environmental sciences and pollution analysis, agriculture and food industries, pharmaceuticals and biochemical research, as well as forensic sciences and art.

A clear development trend in element content analysis is a short field study using fast, inexpensive, reliable, and economical spectrometers over the long term. Increasingly, there is a need to make quick decisions on the receipt of materials, and processing in industrial installations and the field to positively identify materials or assess content from an environmental perspective and to take appropriate measures.

The variety of analytical methods using XRF analysis makes it an extremely versatile research tool that can be successfully used for the research of various materials and technologies; materials produced in industrial processes, soil, pharmaceuticals, or works of art. However, the most important advantage of XRF analysis is the ability to carry out measurements in a non-destructive manner, often also in the field.

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CHAPTER 18

Mass spectrometry

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18.1 Introduction

The intricacy of the biological, geological, chemical, and environmental processes is usually assessed using a wide range of relatively invasive methods (physical-chemical analysis, microbiological parameters, pharmacological analysis, molecular methods. . ., etc). But these procedures, as well as the invasive sampling, have limits [1]. In fact, these techniques are time-consuming and expensive. Equally, owing to the diversity of molecules to be confronted requires to development of less invasive sampling techniques and explore new reliable fast, and efficient methodologies to improve the capability to identify these molecular which could represent an adverse health outcome [2–5]. Recently, spectroscopic technologies (mass spectroscopy, X-ray diffraction, UV-Visible spectroscopy, infrared spectroscopy, scanning electron microscopy, etc.), are widely used by several scientists in several fields, as an alternative reliable, and promising for molecular characterization, thus providing complete information on functional and behavioral properties of samples [6,7].

Since the invention of mass spectroscopy, it is possible to characterize a wide variety of intact molecules in various fields. This has been extremely beneficial to scientists, thus allowing them to characterize organic matter; proteins, peptides, oligosaccharides, DNA fragments, other large biomolecules, and mineral matter [8]. Such characterization has been made possible mostly owing to the advent of mass spectrometry (Ms) [9,10].

Ms is a destructive method, thus allowing the determination of the molecular masses of the compounds analyzed as well as their identification and quantification. It is based on the separation and detection of ions formed in an ionization source or in a collision chamber [11]. The analysis

of fragments resulting from ionization provides information on the structure of the molecule. Each of the ions formed is characterized by its mass//charge ratio (m/z), which makes it possible to detect/characterize (qualitatively and quantitatively) the molecules [12].

In the current chapter, a definition of several terms conventionally used in Ms and the basic principle of this technique have been discussed. A description of the mass spectrometer will then be discussed in detail, both in terms of sources, analyzers and detectors. Then some applications will be developed in order to show the possibilities offered by Ms in the qualitative and quantitative analysis of molecules in several fields.

18.2 Basic principle

Ms is based on the fragmentation and ionization of molecules in the gas phase. More precisely, is the gas-phase separation of charged molecules (ions). The ionized molecule is in an excited state, thus inducing it to disintegrate [13]. Each of the ions formed is characterized by its m/z . The device is therefore able to separate and characterize these ions. Since molecule ionization has a unique molecule, the result of molecule ionization might be employed to acquire structural information about the composition of a given sample [10].

In several areas, Ms is becoming a useful tool for the analysis and identification of a wide range of molecules. It can be equally used in forensic science to control substances and fire debris [14]. In this respect, Ms is generally coupled with other separation methods such as liquid (LC) or gas phase chromatography (GC), which makes it more efficient. In this case, the separation of the sample is carried out by chromatography, and the area of the chromatographic peak is proportional to the quantity of product injected. Then, the separated molecules enter sequentially into the mass spectrometer which works like a conventional detector, ionization, and separation of the generated ions [15]. Using this coupling system (Ms and chromatography), two major pieces of information for each sample analyzed could be extracted: the retention time and the mass spectrum information for each separated compound, which could be employed for comparison with appropriate reference standards [10–12]. However, during quantitative studies, it is essential to use an internal standard, preferably the heavy analog (labeled with C13 or D2) of the product to be analyzed and which has the same retention time in chromatography [15].

18.3 Instrumentation

Ms is an instrument that includes different parts; a vacuum system, an ion source, a mass analyzer, an ion detector, and a data recording system, as depicted in (Fig. 18.1), placed in series and which successively allows, after the introduction of the sample, the evaporation and ionization of sample molecules (source), the acceleration of the ions formed, the separation of these ions according to their m/z (analyzer), the separated ions reach the detector, then the ion signal is amplified in the data system, thereby generating the mass spectrum which [3,16]. The first steps (ion source, mass analyzer, ion detector) are maintained in the vacuum system. The vacuum operation allows us to avoid unwanted collisions with neutral molecules in the system. Such collisions could decrease the sensitivity and/or increase the complexity of the resulting mass spectrum, making subsequent spectral interpretation more difficult [10].

- ✓ An ionization source producing ions in the gas phase from the solid, liquid, or gaseous states of the molecules of interest;
- ✓ A dispersive system (or analyzer) will fragment the ions and then separate them according to their mass and their charge;
- ✓ A detector that counts ions and amplifies their signals.

According to [1], samples can be introduced in two ways:

- Directly in the ionization source: in gaseous, liquid (infusion), or solid state;
- Coupled with a separation method: GC or LC, inductively coupled plasma (ICP).

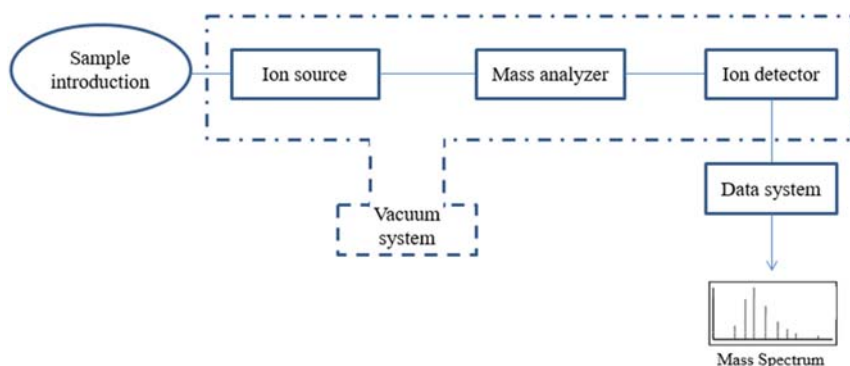


Figure 18.1 Schematic representation of the different parts of the mass spectrometer.

18.3.1 Principles and equipment of mass spectrometry

18.3.1.1 Source

The source is the first compartment of the Ms, which allows the evaporation and ionization of samples. Since there are various ionization methods, the choice of the suitable method depends on the physical-chemical properties of the molecules to be studied and the information desired [15].

The oldest methods are “Electron impact ionization” and “reduced pressure chemical ionization”. These techniques are employed for easily volatilized and low molecular weight compounds. Other methods called “soft” ionization sources have been developed over the past twenty years. They allow the ionization of molecules without fragmentation [10]. Desorption and ionization by the laser pulse and assisted by a matrix (source MALDI for “matrix-assisted laser desorption ionization”) is frequently coupled to a time-of-flight mass spectrometer (TOF) for the analysis of molecules with a high molecular mass (at least greater than 500 Da) [16].

18.3.1.2 Electron ionization source

The source comprises a heated filament that emits electrons which are accelerated towards an anode, called a trap (Fig. 18.2). The electron beam

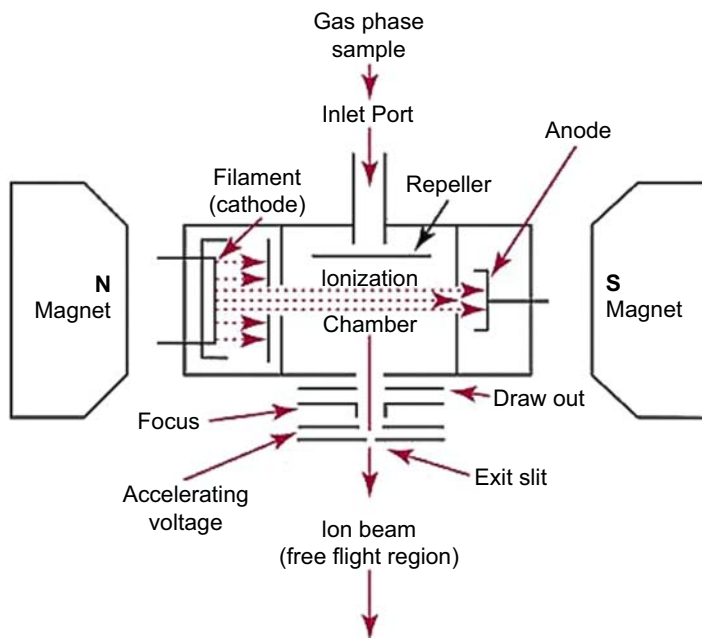


Figure 18.2 Electron ionization source.

then collides with the molecules in the gaseous form present in the source and snatches an electron from them to form the molecular ion M^+ , itself expelled towards the analyzer to a plate brought to a positive potential and called repeller [16].

This method is particularly suitable for compounds of low molecular mass (less than 1000 Da), easily volatilized, and stable at high temperatures. The mass spectra show many peaks, with a molecular ion with a higher m/z ratio and fragmented ions with a weaker m/z ratio [15,17]. This highly reproducible mode of ionization and fragmentation is widely used to obtain structural information or to formally identify a molecule by comparing the spectrum obtained to those contained in a library such as that of NIST (National Institute of Standards and Technology).

18.3.1.3 Chemical ionization

The source of this method is often identical to that used in electronic impact, except that the ionization mechanism is indirect. Reactant gas R (ammonia, methane, isobutane) is introduced into the source at a pressure of 1 mbar, collides with an electron beam generated by a filament and accelerated owing to a difference in potentials (Fig. 18.3). A kinetic energy of 10 eV allows the ionization of the gas and the formation in the ionization chamber of a plasma (mixture of positive ions R^+ and electrons) [13,15]. This ionization mode is much smoother than electronic impact. The fragmentation process is practically nonexistent (except when methane is used as a reactant). The ionization of the molecule, therefore, leads above all to the formation of pseudo-molecular ions, thus allowing it to determine the molecular mass of the compound analyzed [13]. As for

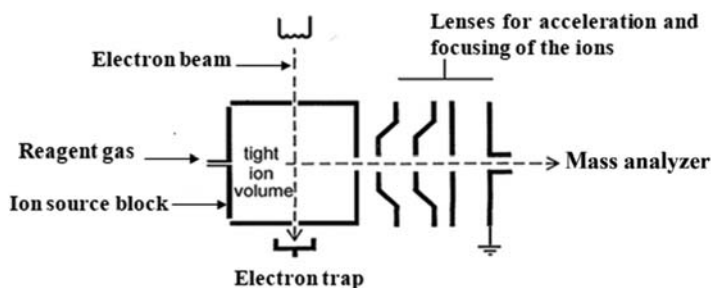


Figure 18.3 Chemical ionization source ace7ff.

the electronic impact, this ionization method is particularly suitable for compounds of low molecular mass (less than 1000 Da), easily volatilized and stable at high temperatures.

18.3.1.4 Electrospray ionization

Electrospray ionization (ESI) might be employed downstream of a liquid chromatograph. It consists in spraying a solution (a mobile phase, for example), ionizing the species which are present there, and in ensuring their evaporation [18]. This by applying at atmospheric pressure an electric field on a liquid passing through a capillary (nebulizer) (Fig. 18.4) [19]. Unlike the electronic impact, this ionization mode is poorly reproducible from one mass spectrometer to another. It forces you to build your own library of spectra for identification purposes.

18.3.1.5 Atmospheric pressure chemical ionization

This method can equally be used downstream of LC. It consists, first of all, of nebulizing, using a gas (nitrogen), a solution containing the analytes of interest. This aerosol is evaporated after its introduction into a heated sleeve. The mixture of nebulization gases and those resulting from the evaporation is entrained towards a corona discharge electrode (or “corona”) [13]. This, a constant source of electrons, creates a plasma by ionizing the ambient gas to form reactive ions (called “reactants”) (Fig. 18.5).

The ESI and Atmospheric Pressure Chemical Ionization (APCI) sources are complementary. However, the APCI source is not very

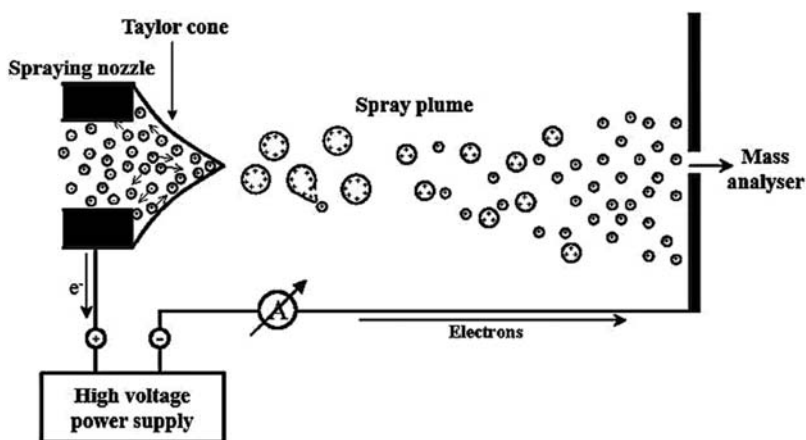


Figure 18.4 Source d'ions ESI (électronébuliseur).

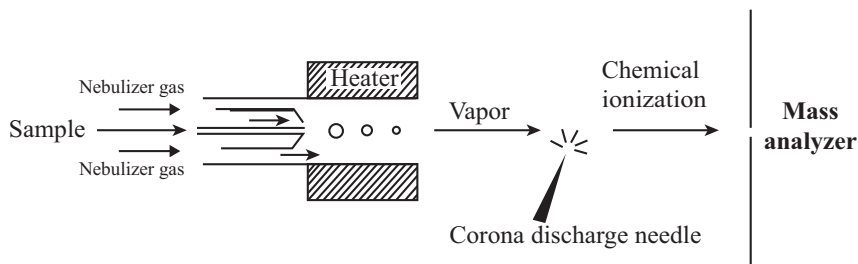


Figure 18.5 Source d'ions "Atmospheric Pressure Chemical Ionization APCI".

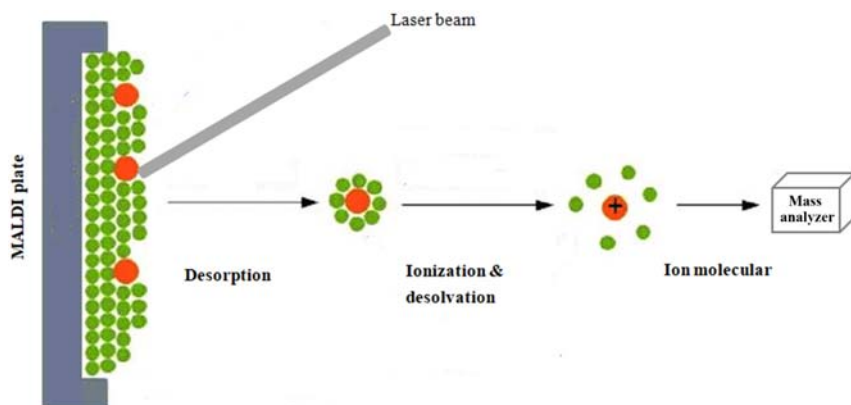


Figure 18.6 Source d'ions "matrix-assisted laser desorption ionization" (MALDI).

compatible with the nano-flow rates used in liquid-phase nano-chromatography, in contrast to the ESI source [10]. The APCI source, however, allows the mono-charged ionization of low molecular weight compounds with medium polarity.

18.3.1.6 Matrix-assisted laser desorption ionization

MALDI allows the production of intact gas-phase ions from a wide range of nonvolatile molecules such as proteins, oligonucleotides, synthetic polymers, and large inorganic compounds [16], thus using principally an aromatic solid organic matrix with strong absorption at the wavelength of the laser, in which the sample is dispersed [1,20]. Laser irradiation occurs under a vacuum inside a mass spectrometer source, resulting in an electronic and thermal excitation of matrix molecules, thus leading to its ionization (Fig. 18.6). This technique is distinguished by easy sample preparation and has a large tolerance to contamination by salts, buffers,

and detergents. Moreover, by using MALDI, it can be feasible for the desorption and ionization of molecules even with very high molecular mass in excess of 100,000 Da.

18.3.1.7 Mass analyzers

The mass analyzer is part of the mass spectrometer that separates the ions formed in the source according to their m/z ratio. Several types of analyzers are available, equally, their mode of operation is based on the use of electric and/or magnetic fields (Table 18.1). The analyzers allow the separation of ions but not their detection, which is ensured by an electron multiplication device.

18.3.1.8 Quadrupole filter

It consists successively of a series of electronic lenses allowing the convergence and acceleration of the ions leaving the source, then of a quadrupole most commonly formed of four bars between which differences in potentials are established, the assembly leading to a detector (Fig. 18.7). The ion entering the quadrupole is subjected to the influence of a total electric field, consisting of a quadrupole alternating field superimposed on a constant field.

It is this SIM mode that is used in quantification studies by coupling GC with a quadrupole-type mass spectrometer. The molecule is formally identified by its retention time and the m/z ratio of a fragment ion. It is also quantized with a low quantization limit since the signal/noise ratio is optimized in this mode of use of the mass spectrometer. Indeed, the ion selected at the retention time of the studied molecule is the most intense fragment ion in the spectrum.

Table 18.1 Characteristics of the different analyzers.

Analyzers	Resolution	Range m/z
Quadrupole (Q)	2000	8000
Ion trap	5000	6000
Analyzers using a magnetic field	20,000	20,000
Time-of-flight	20,000	500,000
Orbitrap mass analyzer	> 30,000	400

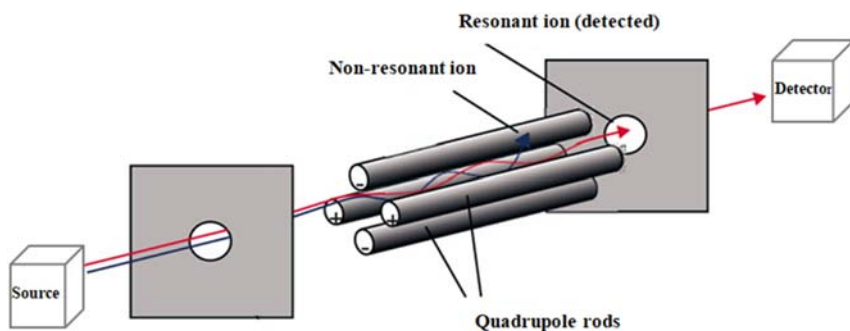


Figure 18.7 Quadrupole instrument composed of the source, quadrupole cylindrical rods and the detector.

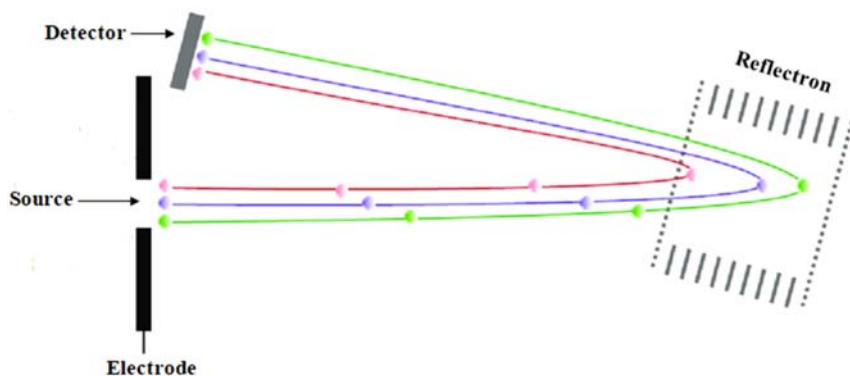


Figure 18.8 Time-of-flight analyzers.

18.3.1.9 Time-of-flight analyzers

Usually, a TOF is associated with a MALDI source. This technique consists of measuring the time it takes for an ion to cross a given distance in an area without a field, called a flight tube, after being accelerated by an electric field (Fig. 18.8).

The separation of the ions, therefore, depends only on the speed acquired during the acceleration phase. Therefore, ions with a very small m/z ratio arrive first at the detector. The reflector mode makes it possible to overcome the lack of resolution of this analyzer [21]: an electrostatic mirror imposes an electric field of direction opposite to that of the initial accelerating field, and therefore to the movement of the ions. The most energetic arrive first at the reflector and will penetrate there more deeply. They will therefore be reflected in a longer time. Thus, all the ions having

an identical m/z ratio are found focused on the same plane, the reflectron detector being placed on the focusing plane of these ions. The improvements of TOF have paved the way for new applications on biomolecules and synthetic polymers [16].

18.3.1.10 Ion trap

The ion trap consists of three electrodes, an annular electrode, and two “hat” electrodes, the latter being almost identical and of hyperbolic geometry. The upper “cap” electrode has an opening in its center that allows the introduction of ions from the source (Fig. 18.9). The lower “hat” electrode has a series of holes allowing ions to be ejected from the detector [22]. The ions entering the trap are trapped on an oscillating trajectory, of a specific frequency for each ion, forming a sort of eight in three dimensions [16].

The principle of the operation of this mass spectrometer is based on an accumulation of the ions of interest in the trap. It is therefore capable of detecting several ions, including those weakly present, since they will be “accumulated” in the analyzer. This analyzer, therefore, produces more intense mass spectra in full scan mode than a quadrupole type analyzer [22]. In addition, ion traps are generally equipped with an MSⁿ option; That is to say, they are capable of successfully fragmenting a precursor ion, then a fragment ion resulting from this first precursor ion, and so on at times. Ion trap mass spectrometers are therefore more dedicated to structural studies. However, they can be used during quantitative studies in SIM mode or in MRM mode [23].

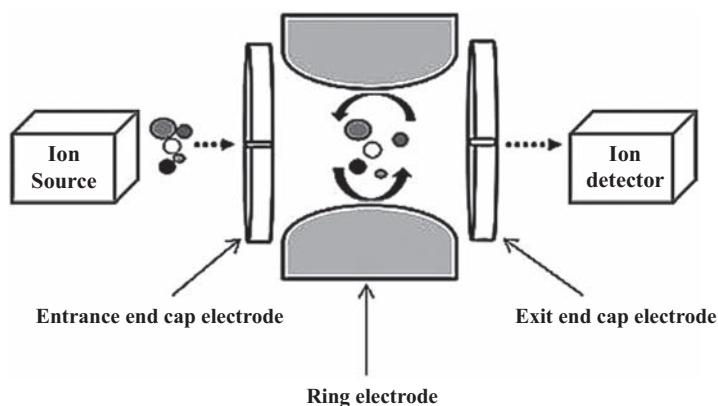


Figure 18.9 Ion trap mass spectrometer.

18.3.1.11 Hybrid analyzers; ESI source coupling—quadrupole and time-of-flight analyzers

This analyzer is made up of an ESI source connected to a series of quadrupoles and then to a TOF placed perpendicularly to obtain good resolution and good precision in the measurement of flight times [24]. This mass spectrometer combines the ESI source which is easily coupled with a liquid chromatograph and the highly resolving TOF-type analyzer [25]. This last criterion makes it possible to obtain a highly specific signal for each ion. This feature is exploited during structural studies (spectrum of fragmented ions from a precursor ion) but also during quantification studies in SIM and MRM modes. The high resolution obtained with the electrospray ionization source coupling—quadrupole and time-of-flight analyzers mass spectrometer makes it possible to reduce the background noise and thus optimize the ratio of signal/noise [15].

18.3.1.12 Hybrid analyzers; ESI source coupling—linear quadrupole and orbitrap

Recently, the linear quadrupole (LTQ)-Orbitrap has been developed, combining a linear ion trap (“linear ion trap quadrupole,” LTQ) whose role is to store the ions produced by the source, then to eject them laterally so that they are detected, or coaxially so that they enter the in-line coupled analyzer, the Orbitrap [9]. The ions are then subjected to a special electric field and follow a circular path around and along a cylindrical electrode [26,27]. The frequency of movement is inversely proportional to the square root of their m/z ratio. The performances obtained with this system, in terms of detection limit, resolution (up to 100,000), and accuracy in mass (<5 ppm in external calibration), are superior to those observed when using the hybrid system, quadrupole-TOF, the operation of which is described above [13,16]. As part of the analysis of small molecules, this mass spectrometer is mainly dedicated to structural studies.

18.3.1.13 Magnetic and electromagnetic analyzers

The property of magnetic fields to deflect the trajectory of ions has been exploited since the beginning of the twentieth century to determine the mass of ions. Bainbridge's spectrometer combined electric and magnetic fields [15]. The electric fields accelerate the ions and homogenize their kinetic energy; the magnetic field deflects them on circular paths whose radius depends on their m/z ratio. Currently, the action of these fields is exploited in the ionic cyclotron resonance mass spectrometer (Fig. 18.10).

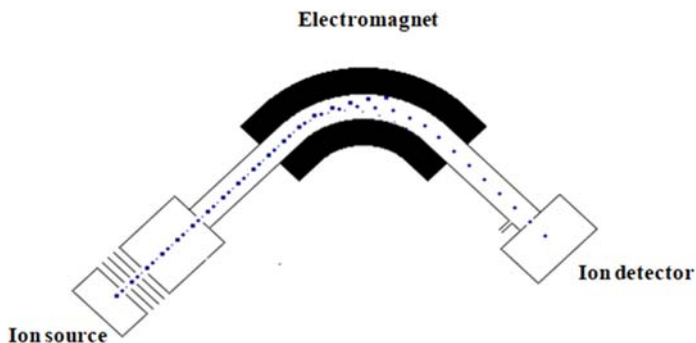


Figure 18.10 Magnetic and electromagnetic analyzers.

This analyzer is little used, but the very high resolution values that it presents (of the order of 80,000) allow the visualization of isotopic massifs and extreme precision in mass (of the order of 1 ppm) useful in determining the elemental composition of compounds ($C_x H_y O_n N_z$) [9].

18.3.1.14 Ion detector

As analyzers and sources ion, there are different types of detectors. They are all based on different physical principles, but their role remains the same, counting ions. There are several ion detectors, such as Photographic plates, Faraday cylinders, Electron multipliers and Photon multiplier.

18.3.1.15 Photographic plate

It's photographic support that consists of a glass plate with a determined size, one surface of which is coated with a photographic emulsion. The scent resulting is quantified using an optical densiometer to measure the absorbance of each mass line [10]. Among the advantages of using photographic plate detection is the simple and simultaneous multielement interpretation of mass spectra, thus providing a permanent visual record of analysis. There are also significant drawbacks. The most important thing is that the photographic plate has a rather limited dynamic range. In addition, mass spectrometers must be designed with special cartridges to allow the loading of the glass plates under a vacuum [13].

18.3.1.16 Electron multiplier detector

It's considered as the most widely used type of ion detector in Ms instruments is the electron multiplier, owing to its compact nature, signal amplification capability, and relatively low cost [16]. The energetic ions

collide with the metal surface of the conversion cathode and cause the emission of secondary electrons. The latter are accelerated and directed onto a 2nd electrode (dynode). The electron-dynode impact causes a new electronic emission [28]. The electrons from this dynode are directed to the next dynode, and so on. The amplification process thus continues until the last dynamite (on the order of 105–106). The currents reached are digitized in an analog-to-digital converter and sent to a computer system where the mass spectrum is generated [10].

18.3.1.17 Electron channel multiplier

It's a continuous form of the electron multiplier detector. The electronic channel multiplier is formed of a glass tube; the inner surface is covered with a thin film of semiconductor material [13]. The emission of secondary electrons is due to the ions coming from the analyzer hitting the open end of the multiplier. The acceleration of these ions is carried out by the applied potential further down the detector, which induces the emission of other secondary electrons owing to the collision of these electrons with walls coated with semiconductor [16]. This process continues until the electron avalanche reaches the collector at the end of the detector tube.

18.3.1.18 Faraday cage

This type of detector is the simplest and the least sensitive of the others, consisting of an elongated cylindrical box. The ions penetrate inside the cylinder through a small opening, strike the bottom and communicate their charge to it. This discharge current is then amplified and measured by an electrometer [29]. The definition plate makes it possible to focus on the ion beam coming from the analyzer. The repeller brought to a high potential, prevents the entry of metastable ions into the collector. The covering of the internal surface of the collector with carbon avoids the problems of secondary electrons [10].

18.3.1.19 Coupling of chromatography with mass spectrometry

In order to analyze a complex mixture such as natural products, a separation technique, GC, and LC, are coupled with the mass spectrometer [30]. High-performance liquid chromatography/mass spectrometry (HPLC/Ms) has become a routine tool in the analysis of drugs and their metabolites; proteolytic digests, natural extracts from plants and grains, and many other types of compounds. Whether in the gaseous state for the GC/Ms, or in solution for the LC/Ms, the products must be introduced

one after the other into the spectrometer. This could be done in two ways: offline and/or online (the chromatograph is connected directly to the mass spectrometer) [9,16]. The advantage of coupling a separation technique with Ms consists in obtaining:

- Separation of a mixture in order to obtain an identification of all the constituents;
- Provide the highest possible sensitivity;
- To be universal, that is to say to detect all the substances eluted;
- Provide as much structural information as possible;
- Be selective (identification of a targeted constituent);
- Allow quantitative analysis.

18.4 Sampling preparation

The whole diagnostic procedure can be wasted if an unsuitable sample preparation process is performed before the sample reaches the analysis step. Sample preparation is an extremely important step in SM analysis since it could affect either the reliability or exactitude of the results 31. Several studies depict that an epitome sample-preparation method, should be; nonselective as possible, faster to prevent the loss and/or the decaying of the sample during their preparation, simple, enable high-throughput and reproducible [31,32]. Despite its leverage, sample preparation is often disregarded.

For many years, several sample preparation procedures have been performed, such as liquid–liquid extraction techniques (LLE) and solid-phase extraction and/or microextraction techniques.

Liquid-liquid extraction methods are widely used in pharmacology/toxicology, thus allowing the purification and concentration of samples intended for analysis by the spectrometry method. These methods are costly and time-consuming, labor-intensive, and multistage operations. Each step can lead to losses and/or decaying of molecules, especially in the case of volatile compounds 31. Over the past years, using solid-phase extraction (SPE) has decreased many limitations of classical LLE methods. SPE methods consume a huge quantity of sorbent, typically housed in cartridge format, to thoroughly extract an analyte from a sample, which is subsequently removed from the sorbent by solvent elution [33]. Despite their leverage, this method depicts many disadvantages such as the ability of the sorbent material to increase the selectivity of the preparation procedure, thus leading to reduced metabolite coverage, it is a time-consuming

multistep process and often requires a concentration step, which may result in a loss of volatile components [34]. While **solid-phase microextraction (SPME)** is a very simple and efficient, solventless sample preparation process. SPME was commonly performed in diverse fields of analytical chemistry and is perfectly matched for coupling with Ms [31]. Additionally, the whole steps used throughout LLE such as extraction, concentration, and analysis, are incorporated into one step and one device using fused-silica fiber that is coated on the outside with an appropriate stationary phase, the analytes compounds are directly extracted to the fiber coating. SPME reduces the time necessary for sample preparation, decreases the costs of solvents, and can improve detection limits.

18.5 Data analysis

The mass spectrum generated by a mass spectrometer, depicting the relative abundance on the y-axis and m/z on the x-axis, which presents the ion current measured as a function of the mass (dalton) to charge (m/z) ratio, a unit generally omitted [35]. Through this spectrum, it is possible to identify the ion of the highest mass which exhibits a form of the molecular ion, including the particular m/z ratio, and which depends on the ionization technique used [15]. The base peak is considered to be the most abundant ion in the spectrum, which is called the peak molecular, with an abundance of 100%. Moreover, the abundance of all fragmented ions is expressed relative to that of the base peak (Fig. 18.11) [10].

Through the mass spectrum, it is possible to detect:

- Molecular mass of compound;
- Mass of certain “pieces” of this compound called fragments;

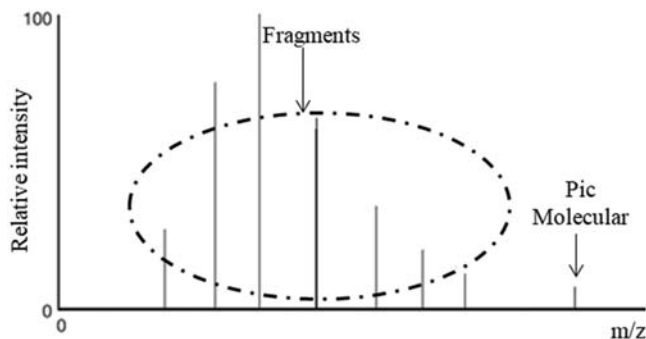


Figure 18.11 Schematic representation of a typical mass spectrum.

- Measure of quantity.

- ✓ The usual mass units:

Atomic mass unit (amu) (1/12 of the mass of the 12 isotope of carbon):

$$1 \text{ amu} = 10^{-3} \text{ kg/mol/N} = 1661 \times 10^{-27} \text{ kg}$$

(N being the number of Avogadro).

- ✓ *Dalton* (Da) (mass of isotope 1 of hydrogen):

$$\text{Da} = 1.673 \times 10^{-27} \text{ kg} = 1.007 \text{ amu}$$

Three types of mass are defined: nominal, isotopic and average masses:

- ✓ **Nominal mass:** calculated from the elemental composition using the nominal atomic masses (in whole number) of the most abundant isotopes;
- ✓ **Isotopic mass:** determined from the elemental composition using for each atom contained in the molecule, the exact atomic mass of the most abundant isotopes;
- ✓ **Average mass or chemical mass:** calculated from the elemental composition using the average atomic masses (which takes into account the relative abundance of isotopes) [15].

The purpose of quantitative analysis in Ms is to correlate the intensity of the signals and the amount of the compound present in the sample [27]. The identification of unknown things such as compounded environmental contaminants, drugs and metabolites, pharmaceutical products, and so on, is carried out on electronic libraries of ionization spectra [16]. Three main mass spectra databases now exist:

- ✓ The NIST/Environmental Protection Agency (EPA)/National Institutes of Health (NIH) mass spectrum database is a fully evaluated collection of mass spectra, through which, it could be feasible to identify your own unknown spectra, which contains 190,000 spectra of 163,000 compounds, this database is produced by the NIST in collaboration with the assistance of expert advisers from the EPA and the NIH.
- ✓ McLafferty and Stauffer published in The Wiley Registry of Mass Spectral Data a collection of about 380,000 spectra of over 200,000 compounds. It is the largest and most comprehensive library of reference spectra that contains over 180,000 searchable structures and over 2 million chemical names [36].
- ✓ The Eight-Peak Index of Mass Spectra published by the Mass Spectrometry Data Center of the Royal Society of Chemistry is a popular printed index of mass spectral data for identifying unknown

compounds by unaffectedly comparing between mass spectral data of the unknown compounds with the equivalent data of known compounds contained in the Eight Peak Index. This database contains about 81,000 spectra of over 65,000 different compounds [16].

The ionization technique employed could determine the complexity of the interpretation of the data, as well as the information which can be provided [10]. In this regard, there are techniques that could produce dozens of singly-charged ions, such as electron ionization, as there are techniques that can provide multicharged ions, which is the case with ESI [19].

To have much more reproducible results, it is strictly recommended to couple the mass spectrometer with another ion source such as an ICP and GC or LC (HPLC), which makes it versatile and allows us to generate elementary and complementary information for each sample analyzed [28,37]. ICP, on its side, could act to atomize and ionize the sample. The results obtained will then be in the mass spectrometer for subsequent separation and detection [10]. From the generated mass spectrum, the elemental composition of the sample can be determined based on the masses of the ions present.

Before starting any interpretation of the spectra, it is strictly recommended to carry out research in the database to verify if this spectrum belongs to an existing collection.

18.6 Major application

In recent years, Ms has been widely used as a physical technique for detecting and identifying molecules of interest by measuring their mass over charge (m/z) and characterizing their chemical structure by fragmentation [16]. Since, (Ms) technologies have continued to improve intensely, and advanced strategies that were impossible a decade ago are progressively available now. The basic characteristics behind these advancements are Ms resolution, quantitative accuracy, and information science for appropriate data processing. Its fields of application are very numerous: metabolomics, proteomics, drugs (assessment of impurities during drug development), hormones, doping (analysis of illegal drugs in urine, blood...etc) as well as numerous DNA applications (determination of hereditary disorders of amino acid, fatty acid, and organic biosynthesis) and/or in studies of environmental pollution (drinking water, groundwater, surface water, and wastewater), pesticides, pigments and dyes [10,38]. Spectroscopy methods allow the development of fully automated

methods. These methods are known to be more sensitive and reproducible than analytical methods, which is owing to the fact that the whole sample is transferred into the system and sample handling is reduced.

18.6.1 Bioanalysis

Since the field of forensic science is constantly evolving, it is conceivable that these advances should be accompanied by a development of the analytical techniques used. Recent advances in separation techniques, Ms, and computer data processing for the biological sciences is very useful for biomarker research. Ms has therefore clearly improved the capacities for detection, quantification, and identification of biomarkers and metabolizing enzymes with faster and more sensitive analysis [10].

Since the invention of mass spectroscopy, the analysis of biological macromolecules has become possible. Due to the sensitivity, selectivity, and speed of analysis higher than most biochemical techniques, Ms has become essential for the study of proteins and their modifications, and genetic mutations and for discovering new pathological markers [39]. Thus, any increment or fault in mass-generated following a modification can in principle be detected by Ms.

18.6.2 Functional analysis of proteomic data

In this regard, biological fluids are characterized by great complexity. Indeed, thousands of proteins are present, which can carry various posttranslational modifications, but also undergo proteolytic degradations due to proteases present in the medium [1,39]. The proteome of these biological fluids is characterized by a wide dynamic range, with molecular masses of 1 to 1000 kDa and concentrations varying from femtomole/L to millimolar/L [11]. Due to this great heterogeneity, the entire proteome of a complex protein mixture cannot be analyzed at one time (and probably not even analyzed in full in the current state of knowledge and techniques). It is therefore necessary to simplify it. To reduce the complexity of the mixture, and thus obtain a better identification of the proteins present. The qualitative and/or quantitative analysis of proteins or fractionated peptides is carried out mainly by Ms [40]. Indeed, the use of ionization techniques coupled with increasingly resolved, sensitive, and rapid mass analyzers makes it possible to analyze very small quantities (down to a few femtomoles) of proteins and/or peptides [1]. Ms might also be employed to determine the protein amount of clinically relevant metabolizing enzymes in human liver microsomes and human intestinal microsomes [41].

18.6.3 Forensic toxicology

Another application of Ms which is considered to be very important is the case of toxicological analysis. Pharmaceutical researchers argue the time to change bioanalytical techniques in drug discovery. Analytical toxicology deals with hundreds of toxicologically relevant substances that must be rapidly and reliably detected and identified [42]. In emergency clinical toxicology, time is paramount. To transport samples, the laboratory analyzes and communicates results. The staff has only 2 hours. This time restriction imposes a strict demand for rapid and reliable analytical methods. Owing to their rapidity and ease of execution, immunoassay techniques are the most prevailing in many hospital laboratories. Fabbri et al. [37,43], have compared immunoassay and Ms and concluded that Ms depicts in some patients the presence of some substances which were not detectable by the immunoassay used, and equally some results of the immunoassay are not consistent with the results provided by Ms. These authors recommended if it is available to use both of techniques (Ms and toxicological screening) to compare the results, especially in the critical cases. Ultimately, the use of this technique allows you, with a single injected sample, to analyze several major compounds, thus saving time and resources [14].

18.6.4 Human sport doping control

In the case of doping control for athletics, hundreds of compounds and their metabolites have to be identified in a limited volume of samples in a short period of time (24 hours) with absolute certainty [12,42]. Traditionally, doping control laboratories have adopted control tests for urine samples. Recently, the detection of these components has been carried out by spectroscopic methods (LC-Ms), thus allowing a complete analysis with considerably shortened analysis times and lower sample consumption [44]. Using spectroscopic methods, several researchers have been able to create a database. This database is formed by parental components of pharmaceutical and illicit drugs including numerous metabolites, with approximately 6000 phase I metabolites and 180 glucuronides. Through this database, it is also possible to differentiate isomers by the use of mass shifts corresponding to predefined biotransformations [12].

18.6.5 Environmental analysis

Regarding the environment, with the growing water demand from farmers, governments are tending to seek alternative water resources. This was

achieved through the treatment and reuse of wastewater to cover the water demand [45]. Although the safety of sewage distinguished from agricultural irrigation has already been brought about, it can also be a source of chemicals and organic compounds which are not completely degraded during the treatment process, such as pharmaceutically active compounds (carbamazepine, diclofenac, and ibuprofen, and various pesticides). In this regard, there are few analytical methods for the detection of these organic contaminants in the environment, such as water, soils, and plants [46]. In this respect, [38], developed an analytical method based on LC-*Ms* (*Ms*/*MS*) to simultaneously detect 13 widely used drugs commonly present in treated wastewater in lettuce leaves, and this was another major application of mass spectroscopy.

18.6.6 Geographic and geochemical analysis

Geographic researchers were equally served by the *Ms* to examine a geographical distribution of major and trace elements in many environments and/or locate a deposit by analyzing the hydrocarbons in the rocks or even analyzing and dating archeological pieces [7,47]. Additionally, *Ms* is the only technique capable of deducing the geochemical history of samples up to the accretion age of the Earth, thus allowing not only the interpretation of isochronous data as a function of the age of a sample but equally very precise isotopic measurements such as the inert gases presented in meteoritic samples and therefore produce data on the nuclear-synthesis process relating to the origin of the universe [16].

18.7 Relevant standards

Ms is a method based on the generation of fingerprints that allows us to identify and quantify a desired molecule. To fulfill this purpose, several standardization methods have been employed [4]. The role of a standard is to detect the relationship between the selected signal intensities and the mixture composition.

18.7.1 External standard method

This method consists of preparing a series of samples with a known increasing quantity of the molecule to be identified, then introducing it into the spectrometer with a precise volume of this solution and recording the intensity of the response signal [4,16]. A calibration curve is then

required, thus allowing the calculation of the quantity of a compound to be measured in the unknown samples, and therefore the determination relationship between the selected signal intensity (I_x) and the quantity of the molecule to be measured (M_x) that is present in the mixture.

18.7.2 Internal standard method

This method consists of a comparison between the intensities of the signal corresponding to the product to be quantified with that of a reference called an internal standard, thus allowing to eliminate and minimizing intrinsic error [16]. For this reason, it is necessary to carry out measurements on samples with the same known quantity of internal standard and increasing quantities of the compound to be measured, then and depending on the results obtained, a calibration curve has been constructed, thus allowing you to determine the relationship between the intensities of the signals corresponding to the compound to be analyzed and the internal standard and the quantity of compound present in the sample, then the quantity of has been measured using the calibration curve [15].

Internal standards can be classified into three categories:

- Structural analogs labeled with stable isotopes;
- Structural homologs;
- Compounds of the same chemical family.

The internal standard should be pure, absent from the sample, and inert to the compounds in the sample. The use of an internal standard is strongly recommended [15]. It should be noted that the internal standard compensates for the lack of reproducibility of the method of analysis from one sample to another.

18.8 Conclusion

For many years, Ms provided a promising and sensitive technique, thus improving the capabilities of detection, quantification, and identification of a wide range of organic and inorganic molecules in different fields. This chapter on Ms will serve as a reference for scientists and researchers working in biology, chemistry, geology, and environmental-related fields, to better understand their principle, its instrumentation, its applications in different fields as well as relevant standards. Ultimately, the use of Ms will certainly serve to reduce many analytical and time-consuming problems in different fields, especially in clinical and forensic toxicology.

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CHAPTER 19

Atomic absorption spectrophotometry

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19.1 The atomic spectra and their use in chemical analysis

Scientists have long found that when an element is placed in a flame, it emits light of a specific wavelength, resulting in specific colors. This phenomenon formed the basis of the Flame Test in Qualitative Analysis.

These colors can often be used to qualitatively identify the elements present in a substance, however, if there are mixtures of elements in a substance, multiple colors may be emitted simultaneously, resulting in mixed colors. Also, if the element of interest is not the main element in the substance, for example, copper in seawater, the bright yellow flame produced by sodium from sodium chloride will prevent any other color from being visually identified.

The fact that specific colors are present when an element is excited implies that unique wavelengths are emitted by excited atoms. This becomes clear when the atomic spectrum of the elements is observed. If we look at sodium shown in Fig. 19.1, we will see that light is emitted in the yellow region, with two dominant lines present. This gives sodium a distinctive yellow color when put under a flame. On the other hand, lithium emits lines at the red, blue, and yellow wavelengths, however, the color of the flame is red. This is due to the relative intensities of these lines with the red lines (670.8 and 610.4 nm) being much more intense than the others. Flame color, therefore, depends on both the wavelength of light being emitted and the relative intensities of each emission line.

The emission lines observed for each element stem from the movement of electrons back to a state of rest after being excited by a heat source.

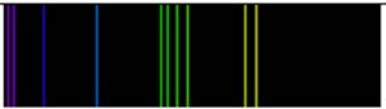
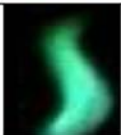
Element	Flame Color	Atomic Spectrum	Flame
Na	Yellow/Orange		
K	Lilac		
Li	Red		
Cu	Green		

Figure 19.1 The atomic spectra of several elements with their corresponding flame test.

Consider the Bohr Model for Hydrogen [Fig. 19.2](#):

The transition of elements from the $n = 2$, $n = 3$, and $n = 4$ orbitals down to the $n = 1$ orbital produce the Lyman series of lines, occurring in the UV spectrum. Electrons transitioning from the $n = 3$, $n = 4$, $n = 5$, and $n = 6$ down to the $n = 2$ orbital result in the Balmer Series, and these lines appear in the visible spectrum. Electrons transitioning from the $n = 6$, $n = 5$, $n = 4$ to the $n = 3$ orbital result in the Paschen Series occurring in the very wide IR spectrum.

The location of each line in the emission spectrum of an element, in this case, hydrogen is related to the energy level of the transition.

Consider Einstein’s equation:

$$E = \frac{hc}{\lambda} \tag{19.1}$$

where:

E = Energy of a photon

h = Plank’s constant = 6.62607×10^{-34} Js

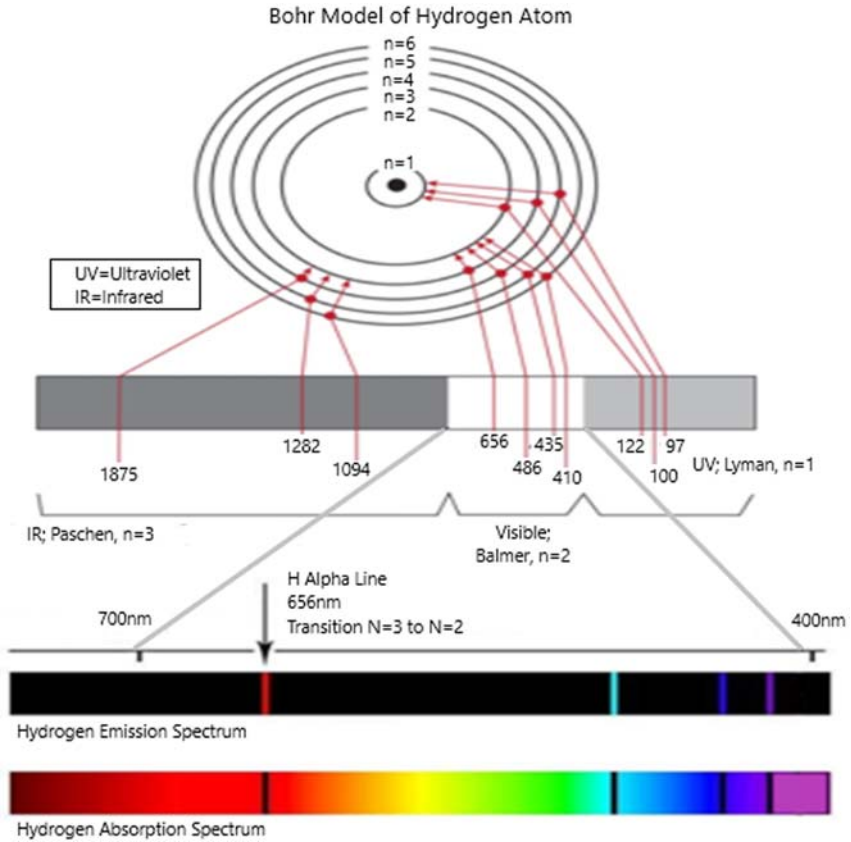


Figure 19.2 The Bohr model of Hydrogen and the resulting absorption and emission spectra.

c = Speed of light in a vacuum = 2.998×10^8 m/s

λ = Wavelength of photon.

This equation tells us that the relationship between energy and wavelength is inverse. That is, the smaller the wavelength the greater the energy of the photon.

Using this explanation it can be deduced that as shown in Fig. 19.2, the Lyman series transitions are of higher energy than the Balmer series, with the Paschen series being the lowest in energy.

Each element emits a unique spectrum and no two elements are identical. The emission spectra are the result of electrons transitioning down to a ground state after being excited in a heat source and influencing the color of the flame.

19.1.1 Atomic absorption

Consider Fig. 19.2, when the spectrum of hydrogen is observed as the gas is placed in a heat source, several dark lines are observed at the exact wavelengths corresponding to the emission lines previously discussed. These dark lines represent the wavelengths of light being *absorbed* by the element as the electrons transition to higher orbitals. The wavelengths being absorbed by the electrons as they transition to a higher orbital are the same wavelengths that are emitted when the electrons return to rest. The analytical technique of Atomic Absorption Spectrophotometry (AAS) is based on the absorption of radiant energy at specific wavelengths by gaseous atoms. If a photon of energy E of exactly the right magnitude is applied to an atom in a gas phase, the electrons in that atom will absorb that energy and move from the stable ground state to the less stable excited state. The wavelength and frequency of radiant energy being absorbed by electrons in an atom can be predicted by Einstein's equation $E = hc/\lambda$. The energy absorbed is the difference in energy between the higher (excited) energy state and the ground state. Electrons can absorb energy to move from the ground state to an excited state by absorbing a specific wavelength of light, resulting in a specific absorption line at that wavelength. This is called the “resonance lines” for the element. Electrons may also absorb more energy to move from the excited state to an even more excited state, resulting in “secondary lines.” Electrons can however move into “allowed” orbitals. Each movement into an “allowed” orbital results in a specific absorbance line.

Consider the element sodium (Na), which has 11 electrons in the configuration $1s^2 2s^2 2p^6 3s^1$ in the ground state. Only the outermost valence electron can be excited by the absorption of a photon of UV or visible light. The inner shells are filled and there is insufficient energy for inner electrons to transition to higher states. Therefore it is the 3s electron that can transition to the unoccupied p and d orbitals. In AAS, the transition of the outermost electron for all elements by the absorption of a specific wavelength of light is measured.

The absorption lines can be predicted using “Grotrian” charts as well as the Maxwell–Boltzmann equation, but are most commonly identified using the AAS “Cook Book” feature typically available from each instrument manufacturer and defines the more prominent absorption lines for up to 70 elements, mostly metals, and metalloids. Each element typically has two to five lines that can be used for the analysis of the element, but

the primary line or wavelength is used as this one will be the wavelength with the largest level of absorbed energy.

The fraction of light absorbed by an atom at a specified wavelength is directly proportional to the number of atoms. The relationship between absorbance and analyte concentration (the number of analyte atoms in the light path) may be defined by the Beer–Lambert Law:

$$A = \epsilon cl \quad (19.2)$$

Where

A = Absorbance

ϵ = Molar absorbance coefficient in $\text{M}^{-1}\text{cm}^{-1}$

c = Concentration in M

l = Path length of light in cm.

The molar absorption coefficient is a sample-dependent property and is a measure of how strongly the sample absorbs at a particular wavelength of light. The concentration is simply the moles L^{-1} (M) of the sample dissolved in the solution, and the length is the path length of the light passing through a sample. In AAS, this path length is either 100 or 50 mm.

The Beer–Lambert law states that there is a linear relationship between the concentration and the absorbance of the solution, which enables the concentration of a solution to be calculated by measuring the absorbance of ground-state atoms in the light path. In AAS, samples are atomized by the use of flames or electrothermally.

Unlike atomic emission, the amount of radiant absorption is not dependent on temperature. In AAS, temperature influences the efficiency of free atoms formation in a sample, but not the process of absorption by these atoms. Therefore, the temperature only indirectly affects the amount of energy absorbed.

Some metals possess low ionization energies and are easily ionized. Ions do not absorb atomic absorption wavelengths, therefore atoms that become ionized due to low ionization energies of the atom or high temperatures are removed from the absorbing population, resulting in a weaker signal.

19.2 The atomic absorption spectrophotometer

The atomic absorption spectrophotometer is designed like most conventional spectrophotometers. Fig. 19.3 shows a simple layout of an AAS.

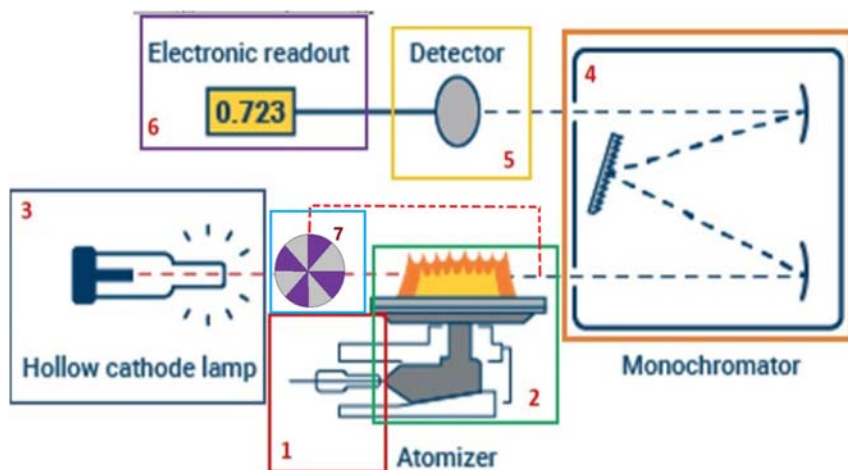


Figure 19.3 Basic layout of a flame atomic absorption spectrophotometer (FAAS). From Agilent. How does AAS work? <<https://www.agilent.com/en/support/atomic-spectroscopy/atomic-absorption/flame-atomic-absorption-instruments/how-does-aas-work-aas-faqs>>, n.d. (accessed 1.12.21).

The sample must first be in a liquid form to be analyzed on the AAS. The liquid sample is aspirated into a flame or electro thermal atomizer (2) through a pneumatic nebulizer and spray chamber (1&2). The sample enters the flame where it is converted into gaseous atoms. A hollow cathode lamp (HCL) (3) produces light of a specific wavelength, and this light passes through the gaseous atoms. The atoms absorb light at specific wavelengths as the electrons move to a higher electronic orbital. The light passing through the sample is separated into its respective wavelengths by the monochromator (4), and is detected by a detector, typically a photomultiplier tube (PMT) (5), and displayed as an electronic readout (6). An optical chopper rotates at a specific rate such that in one instant, light from the HCL will be reflected around the flame and directly into the monochromator, and in another instant, the light will pass through the atomized gases in the flame. The light passing through the gaseous atoms will be absorbed by the electrons whereas the light deflected around the flame will not. The difference between the two spectra will give the amount of light absorbed at the wavelength of interest.

19.2.1 Radiation sources—hollow cathode lamps

Atomic absorption lines are very narrow, typically 0.002 nm or less, as such, if we were to use a continuous source of radiation such as hydrogen,

deuterium, or tungsten lamp as is used in other forms of spectrophotometry, we will not be able to detect the very thin absorption line of AAS. Such narrow lines are only detectable using very high-resolution optics and extremely narrow band pass [1]. Such systems are not used in commercial AAS as the cost and complexity become prohibitive, and versatility is greatly reduced.

The most suitable source for AAS is one that produces very narrow emission lines at the exact wavelength capable of being absorbed by the gaseous atoms. Since the absorption line spectrum for any element is the inverse of the emission spectrum, and the narrow absorption lines are identical to the emission lines for a particular element, then the perfect radiation source is the emission spectra of the element being measured. This is achieved by the use of a HCL, which is shown in Fig. 19.4.

The cathode of the HCL is typically formed by hollowing out a cylinder of pure metal or making a cylinder of the foil of pure element. The metal used to make the core of the HCL is the same metal to be analyzed, therefore if we were to analyze copper, we will use an HCL with a pure copper cathode. If we were to analyze Iron, we will use an HCL with a pure Iron cathode.

The metal cathode and an anode are sealed in a glass cylinder filled with either neon or argon gas at low pressure (fill gas). A quartz or glass window is used to seal the forward end of the HCL (Fig. 19.4). Where the wavelength of light to be transmitted by the HCL falls in the UV range (10–400 nm), a Quartz window is used, as opposed to a glass window, which is used when the wavelength emitted falls in the visible light range. Glass is known to absorb UV light at wavelengths 300 nm and shorter whereas quartz does not absorb wavelengths in the UV range.

When a high voltage is applied across the cathode and anode, an emission spectrum of the cathode metal is formed, composed of intense narrow lines. These intense lines are emitted at the precise wavelengths that are absorbed by the analyte atom when it becomes excited. The amount



Figure 19.4 The hollow cathode lamp used in FAAS. From Agilent. *How does AAS work?* <<https://www.agilent.com/en/support/atomic-spectroscopy/atomic-absorption/flame-atomic-absorption-instruments/how-does-aas-work-aas-faqs>>, n.d. (accessed 1.12.21).

of light absorbed is directly proportional to the concentration of the analyte as defined by the Beer–Lambert Law (Eq. 19.2).

The emission lines of the HCL are produced when a high voltage is applied across the anode and cathode. These emissions are produced in three steps:

- *Sputtering*—The filler gas, which is an inert gas, either Ar or He at low pressure, ionizes at the anode, emitting electrons and forming positive (+) ions, which accelerate towards the cathode. As they strike the metal, they dislodge metal atoms from the surface of the cathode.
- *Excitation*—The metal atoms discharged from the cathode are excited by bombardment with the free electrons emitted when the inert filler gas became ionized at the cathode.
- *Emission*—The excited gaseous atoms return to rest, emitting the characteristic emission spectrum of the atoms of the cathode. The ground state atoms now deposit along the inner walls of the HCL, resulting in the reflective metallic coating seen in most HCLs.

The lines emitted by the HCL are very narrow and are absorbed almost entirely by the gaseous unexcited analyte atoms. These narrow lines not only provide high sensitivity, but also high selectivity. As the lines produced by a Zn HCL are absorbed by only Zn atoms and no other elements, interferences are very rare. Other resonance absorption lines may be produced by the HCL, but since these are not absorbed by the element, they don't produce spectral interferences.

One of the main inconveniences of AAS is the fact that the instruments are almost exclusively sequential. Because analysis of a particular element requires the use of its specific HCL (Cu analysis requires Cu HCL and Zn analysis requires Zn HCL etc.), only one element can be determined at a time. That is if you wanted to measure Cd, Cu, and Zn in multiple samples, you would have to analyze all the samples for one element, then repeat for the second element and then repeat again for the third element. So if you had to determine 5 elements in 10 samples, then you would have to perform five different calibrations followed by 5×10 analyses. This inconvenience is a tradeoff for the sensitivity, selectivity, and interference-free analyses.

Modern AAS manufacturers have been able to improve the uni-elemental disadvantage of AAS by developing multielement lamps which allow for up to three elements to be analyzed on the same lamp, and in the case of one manufacturer, a Fast Sequential System has been developed that allows for up to 10 elements to be analyzed simultaneously on a single sample.

19.2.1.1 Multi-element lamps

Multi-element HCL are constructed with electrodes that contain multiple elements. When these elements are excited, they emit their typical spectra, resulting in a much more complex lamp output with multiple lines. Elements used in multielement lamps must be very carefully chosen to reduce spectral interference between the elements. Some element combinations used in multielement HCLs include:

- Co/Cr/Cu/Fe/Mn/Ni,
- Na/K,
- Al/Ca/Mg,
- Ag/Cd/Pb/Zn

Multi-element lamps have the advantage of providing multiple elemental analyses from the same lamp. However, the analysis remains sequential [2].

It is also generally considered that multielement lamps use secondary wavelengths for atomic analysis due to interferences from the other combined elements. This can result in multielement lamps performing marginally poorer than single element lamps [3].

HCL do not function indefinitely and deteriorate over time. As the excited cathode atoms in their gaseous form emit radiant energy as they return to rest, they deposit on the inner surfaces of the HCL (see Fig. 19.5). As the metals deposit, they absorb filler gas onto their porous surface. This reduction in filler gas results in successively weaker “sputtering” and reduced cation atom concentration in the vapor. The net result is lower emissions and diminished sensitivity.

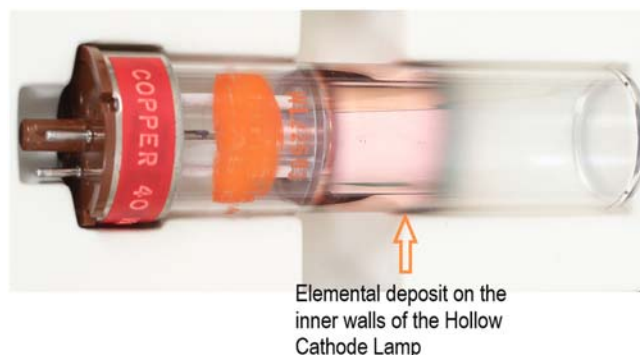


Figure 19.5 Hollow cathode lamp with metallic deposits on its inner surface.

19.2.1.2 *Fast sequential*

In conventional Flame Atomic Absorption Spectrophotometry (FAAS), a single element is determined each time a sample is aspirated into the instrument. If we require multiple elements to be determined on several samples, all samples must be analyzed separately for each element. This can be a very time-consuming process. One manufacturer has developed the very successful “Fast Sequential” instrument that is capable of analyzing multiple elements in a sample very rapidly. The HCL are all turned on during analysis, and a high speed mirror drive quickly switches between the lamps. A high speed monochromator drive is also used to rapidly change between wavelengths for each element, and a programmable gas control system quickly changes gas flows so each element can be analyzed under the optimal conditions [4]. An AAS of this nature is shown in Fig. 19.6.

The “Fast Sequential” AAS allows multiple elements to be analyzed one sample at a time, and this can have certain advantages depending on the number of elements to be determined, the number of samples, etc.

19.2.2 Atomizers

In AAS, the atomizer is considered the sample cell and its purpose is to produce the gaseous atoms of the analyte to be determined. Elements are typically present in samples as salts, complexes, and compounds both inorganic and organic. The analyte is introduced into the atomizer as a fine mist mixed with combustion gases in the case of FAAS, or directly as a liquid drop as in the case of Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). The atomizer must be able to convert these complex molecules into unexcited gaseous atoms. This is typically achieved using thermal energy in the form of a flame or electro thermal heat sources. Both forms of atomization processes are commercially available, however, greater thermal control is achieved using electro thermal heat sources than flame heat sources, resulting in electro thermal systems achieving lower detection limits [5]. Conversely, flame atomizers are cheaper and simpler to use, therefore, the decision to use either FAAS or GFAAS is totally up to the user.

19.2.2.1 *Flame atomizers*

In all AAS systems, the sample to be analyzed is converted to a liquid and aspirated into a flame via the spray chamber. The purpose of the spray



Figure 19.6 The Agilent 280FS flame atomic absorption spectrophotometer. Agilent Technologies Inc. All rights reserved. Printed with permission. <<http://www.agilent.com>>.

chamber is to convert the liquid sample into a fine aerosol that mixes with the fuel and oxidant and enters the flame where the sample is converted into gaseous atoms. Some of the critical components of the spray chamber can be seen in Fig. 19.7 and include:

- *Nebulizer*—a device that aspirates the liquid sample into the spray chamber.
- *Glass or impact bead*—typically made from glass or another inert material. The stream of liquid exiting the nebulizer collides with the glass bead, shattering into a fine mist and mixing with the nebulizer gases.
- *Mixer paddles*—impart a rotational motion to the aerosol, allowing the liquid droplets to break into smaller more evenly distributed droplets before entering the flame [6]. The centrifugal forces arising from the

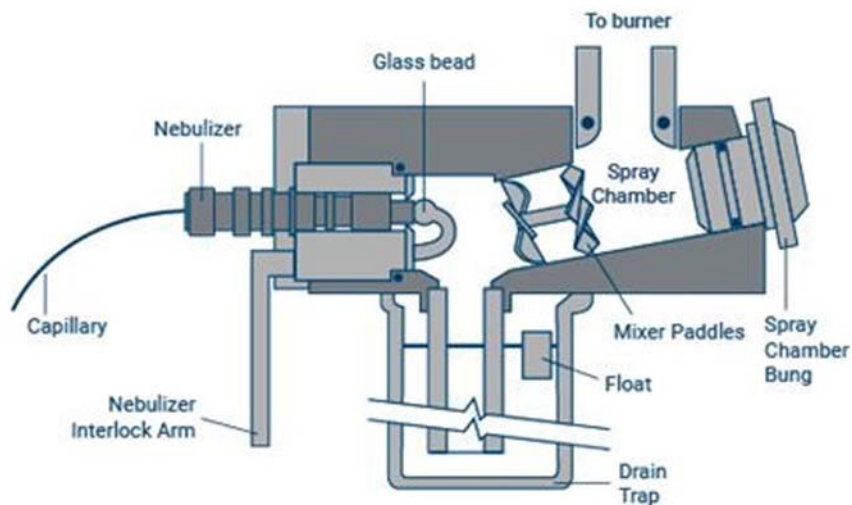


Figure 19.7 Diagram of a typical faas spray chamber. From Agilent. *How does AAS work?* <<https://www.agilent.com/en/support/atomic-spectroscopy/atomic-absorption/flame-atomic-absorption-instruments/how-does-aas-work-aas-faqs>>, n.d. (accessed 1.12.21).

rotational motion of the gases also force larger heavier droplets in the aerosol to move outward and collide with the walls of the spray chamber, leaving only the finer particles to enter the flame. This significantly reduces the sputtering of the flame and enhances flame stability.

The Nebulizer is designed to make use of the Venturi effect. It places a flow restriction at the exit of the nebulizer, resulting in reduced flow of the nebulizer gas, but the increased velocity of the exiting gases. The increase in velocity induces a pressure drop at the nebulizer tip as defined by.

$$\Delta p = \rho/2(v_2^2 - v_1^2) \quad (19.3)$$

where

Δp , is the pressure differential before and after restriction; ρ , is the density of the fluid traveling in pipe; v_2 , is the velocity of the fluid after restriction; v_1 , is the velocity of the fluid before restriction.

The pressure at the nebulizer tip becomes lower after the restriction, resulting in a net drop in pressure and aspiration of the liquid sample into the spray chamber (Fig. 19.8). The greater the exit velocity of the gases from the nebulizer, the larger the pressure differential (Δp). Some AAS Instruments include an adjustable nebulizer that allows the user to optimize the flow rate of the nebulizer.

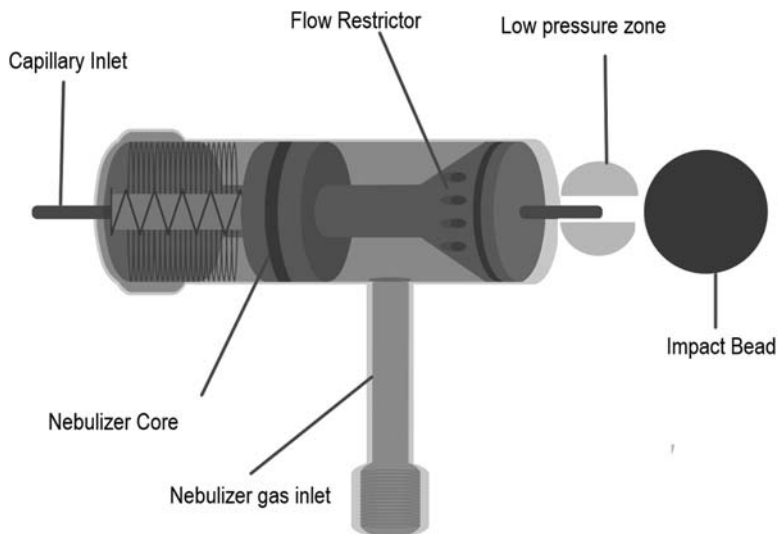


Figure 19.8 Typical AAS Nebulizer with adjustable impact bead *Illustration by Mr. Derreck Sealey (<http://www.instagram.com/littletokyoproductions>).*

Many AAS manufacturers also include in their spray chamber design an adjustable Impact bead, whose distance from the nebulizer exit can be adjusted for maximum aerosol dispersion (Fig. 19.8).

Nebulizer flow optimization and impact bead optimization constitute part of the AAS's optimization process. The sample exiting the nebulizer collides with the impact bead, producing a fine mist while it mixes with the nebulizer gases. The gases then flow through the mixer paddles or “spoiler” where larger droplets are further broken by collisions with the spoiler. The design of the spoiler also imparts a spiraling of the gases, forcing the larger droplets to collide with the walls of the chamber and flow into the drain. The impact bead and mixer paddles together prevent large droplets from entering the flame where they can cause sputtering. The fuel aerosol mixture entering the flame is therefore homogenous with aerosol droplets rarely ever exceeding $4\text{ }\mu\text{m}$. The drain of the spray chamber always remains partially filled to produce a liquid barrier between the waste container and the gases/aerosol inside the spray chamber, preventing a “flash back.” This can be achieved by either having a float system designed and integrated as part of the spray chamber, or a liquid loop along the drain line.

As the sample is converted to a fine aerosol, it mixes with the fuel and oxidant gases and enters the burner, where the sample atomizes to

produce gaseous atoms. The AAS burner provides a steady state of ground state atoms. In flame AAS, the burner converts the aerosol/gas mixture created by the spray chamber and nebulizer, into free, ground state atoms. The burner design generates a laminar gas flow, which produces a very steady flame. The steady flame reduces “flame flicker” and improves precision. Spray chambers are highly inefficient with only about 5% of the sample reaching the flame. The other 95% of the sample goes to waste.

As the aerosol enters the flame AAS burner, it undergoes four processes:

- The aerosol undergoes *De-solvation or drying*. The solvent evaporates under high temperatures leaving dry nanoparticles of the sample. At this point, the sample may exist as compounds, complexes, ions, etc.
- The high temperature of the flame converts the nanoparticles into gaseous particles. The sample at this stage may still be in the form of molecules and complexes. This is called *Vaporization*.
- The most critical stage *Atomization* is defined as when the gaseous species are converted to gaseous atoms and exist in the flame as freely dissociated ground state atoms. It is these ground state atoms that undergo atomic absorption, which is used to quantify the analyte.
- Some, but not all, free atoms will undergo *Ionization*. This will depend on the flame conditions (gas mix) and the ionization potential of the analyte in the solution. Ionization reduces the number of atoms available for atomic absorption thus reducing signal strength.

The gas mixture passes through the spray chamber and migrates upwards into the burner. The gas mixture is ignited above the burner head and the flame, and a reaction between the fuel gas and oxidant propagates rapidly. Ignition is achieved by the use of either a pilot flame or an electric spark and is controlled by the AAS, igniting after a programmed ignition sequence, which involves purging, and gas flow regulation. The fuel and oxidant gas flow rate is maintained above the “burning velocity” of the flame before ignition and this velocity must be maintained throughout the use of the instrument. Each flame type has a pre-programmed burning velocity which the AAS is programmed to maintain. Should gas velocities fall below burning velocity, the flame can propagate into the spray chamber, igniting the fuel oxidant mixture in an event called “flashback.” Flashback is a very dangerous event that can permanently damage the spray chamber and burner and injure the analyst.

Some specific causes of flashbacks include:

- Air being drawn back into the mixing chamber of the premix burner through the drain.

- Drop in air pressure to the burner before the fuel has been shut off.
- Incorrect proportioning of air and fuel while adjusting the fuel or air flow rates.

Many modern AAS possess several mechanisms that prevent the occurrence of a flashback [7]. These include the integration of a liquid trap in the spray chamber design, rupture disks or pressure release bungs in the spray chamber, building limits for each gas into the software and automatically switching off the flame when gas limits are exceeded or a gas pressure drop is detected. In addition to this, flash arrestors are installed in the “gas box” of the instrument preventing the flash back flame from reaching the gas cylinders. Proper training as well as the safety redundancies available in most commercial AASs make flash back events very rare occurrences.

Ground state atoms residing in a flame absorb light at specific narrow wavelengths. This light is produced by an associated HCL, which emits the exact wavelength of light the analyte will absorb. The amount of light absorbed is directly proportional to the concentration of free atoms of the analyte in the flame or path length. This relation is defined by the Beer–Lambert Law (Eq. 19.2) and discussed in section 1.1.

One of the factors that affect the Beer–Lambert law is path length, which can vary according to the burner being used. Unlike UV/vis spectroscopy where the sample cell has a path length of 1 cm, in AAS, due to the design of the burner, the path length is typically the length of the burner slit as this is aligned parallel to the light path to maximize cell length (Fig. 19.9). The burner slit may be either 50 or 100 mm (Fig. 19.10). As suggested by the Beer–Lambert law, the 100 mm laminar flow AAS burner will give double the absorption of a 50 mm laminar flow burner. The 100 mm burner, therefore, has the advantage of producing superior sensitivity and lower detection limits than the 50 mm burner. Therefore if we wish to determine an analyte at very low levels, we may wish to utilize the 100 mm burner.

Burners used in AAS may be made from either Stainless Steel or Titanium and may contain multiple fins to allow for air-cooling.

Two popular types of flame are utilized in commercial AAS, these are the “air/acetylene flame” and the “nitrous oxide/acetylene flame.” The air/acetylene flame can be used on both the 100 and 50 mm burners and can reach temperatures of 2100°C to 2400°C and a maximum burning velocity of 158–266 cm/s. The nitrous oxide/acetylene flame is used only with the 50 mm burners and can reach temperatures from 2600°C to 2800°C and a maximum burning velocity of 285 cm/s [8].

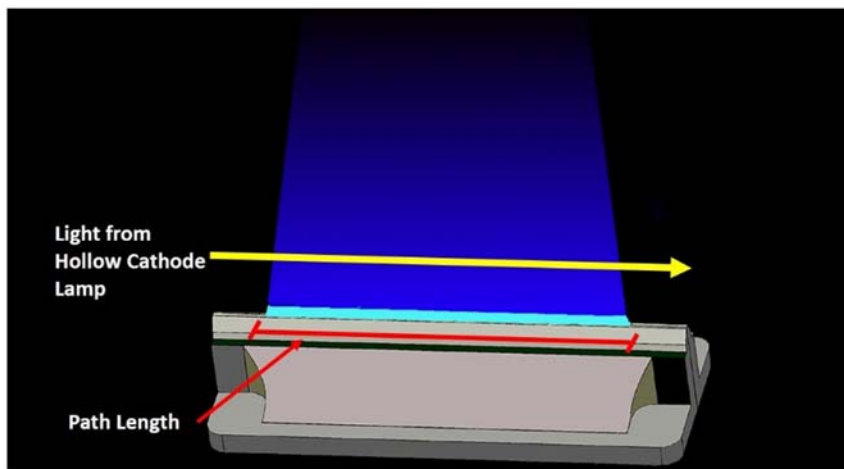


Figure 19.9 Path length of an AAS burner. From Agilent. How does AAS work? <<https://www.agilent.com/en/support/atomic-spectroscopy/atomic-absorption/flame-atomic-absorption-instruments/how-does-aas-work-aas-faqs>>, n.d. (accessed 1.12.21).



Figure 19.10 AAS burners 50 mm (left) and 100 mm (right). From AAS Burners, <https://www.agilent.com/store/en_US/Prod-210164000/210164000>, 2021.

The air/acetylene flame is suitable for the determination of most elements and is by far the most common flame type used in AAS. However, for elements such as aluminum, silicon, alkaline earth metals, and vanadium, the formation of poorly absorbing refractory oxides in the air/acetylene flame is undesirable. For these elements, the nitrous oxide/acetylene flame is preferred [9].

19.2.2.2 *Electrothermal atomization*

FAAS is among the most common form of AAS available. This is due to its reliability, accuracy, low cost can be used to analyze a wide range of metals, and safety. However, this was not always so, and flame instability, poor precision, and dangers of flash back led researchers to explore alternative forms of atomization. B.V. L'vov built the first electrically heated graphite tube atomizer and this improved element sensitivity by several fold [10]. Commercial units began appearing on the market around 1970.

The most common atomizer of this type used a hollow tube of graphite coated with pyrolytic graphite and heated by electrical resistance. This form of Electrothermal Atomizer is commonly referred to as a Graphite Furnace Atomizer and the technique is called Graphite Furnace Atomic Absorption Spectrophotometry or GFAAS.

Electrothermal atomization provides enhanced sensitivity because the entire sample is atomized in a short period and the average residence time of the atoms in the optical path is a second or more. Recall that the flame atomization is very inefficient as <5% of the sample enters the flame and the optical path. In GFAAS, only a few microliters of the sample are injected into the graphite tube which is heated firstly to about 150°C to evaporate the sample, then 600°C to ash the sample. The temperature is increased to between 2000°C and 3000°C where the sample is atomized in a light path for up to several seconds. The absorbed light is measured and the sample is quantified. GFAAS does not use spray chambers but instead uses a Graphite Furnace into which the sample is directly injected.

The graphite furnace consists of a graphite tube as shown in Fig. 19.11C, which is about 5 cm long and 1 cm in diameter with a small hole at the top for the introduction of the sample with a micropipette or auto sampler. Since graphite is porous and this can cause poor precision, the tubes are always coated with a layer of pyrolytic carbon which is more densely packed than graphite and forms an inert layer on the tube. As seen in Fig. 19.11B, the graphite tube (*red*) is nestled inside a water-cooled furnace housing, heated by two graphite terminals (*blue*). The

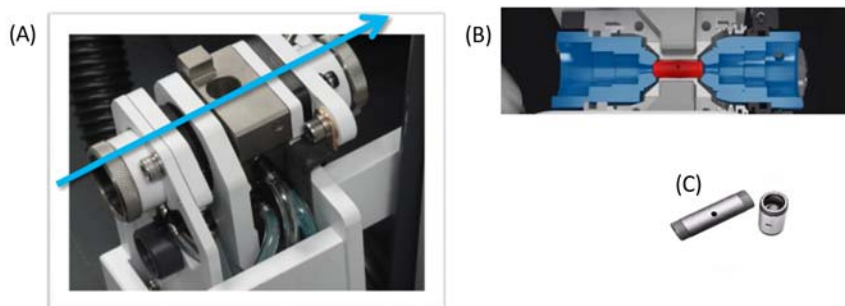


Figure 19.11 (A) A Graphite Furnace assembly with the light path shown as the blue arrow. (B) Cut away view of a Graphite Furnace showing placement of the Graphite Tube. (C) Graphite tubes used in GFAAS. From <<https://www.agilent.com/cs/library/eseminars/Public/AA%20Troubleshooting%20and%20Maintenance.pdf>>, n.d. (accessed 1.12.21).

graphite tube is always configured such that the sample introduction hole is aligned with the sample introduction port located at the top of the furnace as shown in Fig. 19.11A. Two streams of inert Argon gas passes through the furnace. The first form an external protective jacket around the graphite tube, preventing oxygen from the air to enter the tube. At these high temperatures, oxygen will react with the carbon tube to form carbon dioxide and totally corrode the tube reducing its longevity. The second stream of inert argon passes through the graphite tube purging the residue of the sample before another sample is analyzed. This helps prevent cross contamination. The furnace is aligned parallel to the light source and adjusted so that the beam of light from the HCL passes directly through the hollow graphite tube.

The furnace is heated in a series of programmed steps, with each step serving a specific function in the analysis (Table 19.1).

Drying usually takes place around 150°C which dries solvents, solutions, digests, and liquid biological samples. This process concentrates the sample into an even smaller mass. The temperature is ramped for a period of 10 s and then held at 150°C for a further 15 s. Argon flow removes the evaporated moisture and solvents.

- The *Ashing* step is where the sample matrix is destroyed leaving only the elemental atoms. The temperature is ramped up from 150°C to 1200°C for a period of 20 s and held at 1200°C for a further 30 s. This is usually the longest step as sufficient time is needed to ash the matrix. More resilient matrices may require more ashing time. Argon removes the volatile material from the sample.

Table 19.1 Simple graphite furnace temperature program.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon Flow (mL/min)
Drying	150	10	15	300
Ashing	1200	20	30	300
Atomizing	2100	0	3	0 (read)
Purge	2300	1	3	300

- The atomization step is performed at 2100°C with no ramping and a 3 s hold time. Argon flow is also halted during this step so as to not purge any of the gaseous atoms. At this temperature, elements form gaseous atoms, which absorb lines of light from the HCL. The hold time of 3 s is also the read time.
- The sample is then *Purged* at 2300°C to remove all the residue sample. Argon gas flow assists in evacuating the sample residue from the graphite tube.
- The Graphite Furnace is then *cooled* back to room temperature by the circulating water-jacket. The whole process takes about 2 min and uses only a few microliters of sample.

Because of the temperature program, the sample matrix is completely eliminated from the sample, removing virtually all chemical and most spectroscopic interferences from the analysis. This results in the detection limit of GFAAS being several-fold lower than FAAS [11]. The process is typically automated to improve precision as sample injection is a difficult process to reproduce in GFAAS.

19.2.2.3 Other atomization techniques

19.2.2.3.1 CVAAS

The technique of Cold Vapor Atomic Absorption Spectrophotometry or CVAAS is a technique applicable only to the analysis of mercury. The element mercury is the only element that exists as gas phase-free atoms at room temperature since the liquid metal possesses a very high vapor pressure [12]. As such, mercury does not require a heat source to achieve atomization as it already exists in an atomic gas phase.

The analysis of mercury is very important to environmental studies due to its very high toxicity and to industrial samples as this element poisons catalysts used in many industrial reactions. The method of choice for this analysis is CVAAS and the metal can be detected at ppb levels.

The sample must be digested using strong oxidizing acids to produce the Hg^{2+} ion; this can be achieved by digestion with nitric, sulfuric, or hydrochloric acids, or a mixture. The Hg^{2+} ion is stable at high temperatures as well as soluble in most aqueous solvents. The solution is then pumped into the vapor generation apparatus or VGA coupled with an AAS (Fig. 19.12) via a peristaltic pump where it mixes with concentrated HCl and a reducing agent such as 23% SnCl_2 . The reducing agent reduces the Hg^{2+} to the Hg^0 state, which forms a very stable vapor at room temperature. The mercury vapors are stripped from the solution using a liquid/gas separator with argon being the stripping gas. The mercury/argon gas mixture then flows into a 100 mm quartz sample cell located at the top of the burner with the light path passing directly through the center of the cell (see Fig. 19.12). Absorption is measured at 233.7 nm. The sensitivity of this technique is typically 0.02 ppb but can be as low as 0.01 ppb when all parameters are optimized [13], which is superior to FAAS and GFAAS.

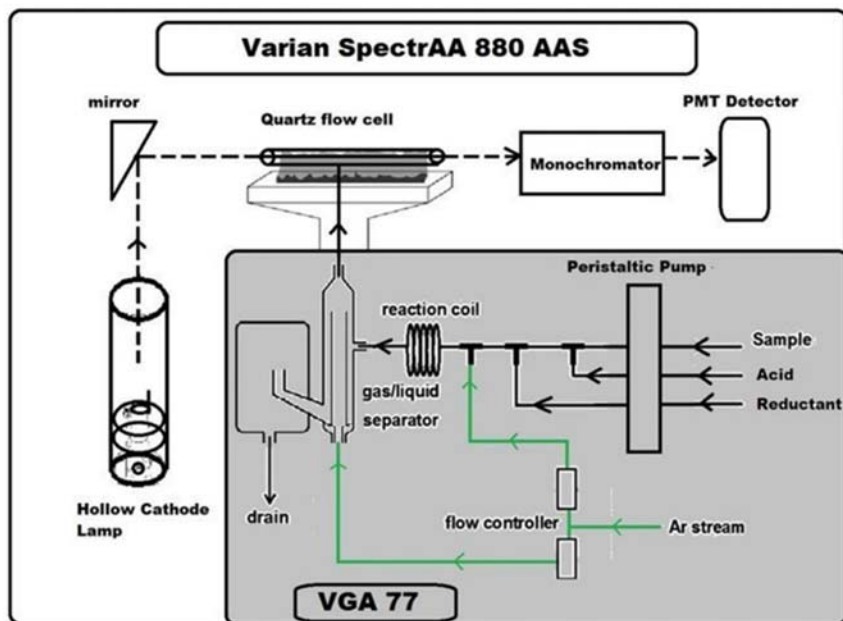
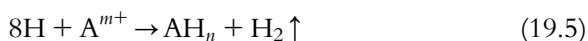


Figure 19.12 Schematic lay-out of the Agilent VGA77 Vapor Generation Apparatus coupled with a Varian SpectrAA 800 Atomic Absorption Spectrophotometer. *Mercury can be analyzed using this configuration with flame off. Arsenic, Selenium and Antimony are analyzed in this configuration with the flame on.*

The CVAAS technique is 100% efficient as all samples are used to generate the signal instead of the 5% used in FAAS. Larger sample sizes are used and interferences are virtually eliminated.

19.2.2.3.2 HGAAS

The technique of hydride generation atomic absorption spectrophotometry (HGAAS) is very similar to CVAAS as described previously. The equipment and the configuration used are identical except that the elements are not free gaseous atoms at room temperature as with mercury, and heat is needed to achieve atomization. Just as with CVAAS, the sample is pumped through the VGA via a peristaltic pump. The sample is mixed with 0.6% NaBH₄ in 0.5% NaOH as the reductant and 5 M HCl in the acid stream [14]. Elements such as As, Bi, Ge, Pb, Sb, Sn, and Te form stable hydrides under these conditions.



The hydride and hydrogen formed are stripped from the solution by argon gas and carried to the quartz cell. Unlike CVAAS, the cell in HGAAS sits on an ignited flame where the hydrides are atomized forming the gaseous atomic metals. These metals absorb atomic radiation at specific wavelengths and this absorption is measured.

HGAAS is a very sensitive technique for the same reasons as CVAAS. About 100% of the sample is used to produce the hydride, with large sample sizes used, and interferences are eliminated.

19.2.3 Monochromator and detector

In modern atomic absorption spectrophotometers, the monochromator and detector are integrated into one unit and work in conjunction with each other to detect the wavelengths of light absorbed by the gaseous atoms present in the atomizer. This unit is located after the atomizer and is the final destination for the light emitted by the radiation source.

19.2.3.1 Monochromator

The monochromator is that part of the AAS that collects the light passing through the atomizer from the radiation source and separates it into its

various wavelengths to be detected by the detector. The monochromator and detector module is outlined in Fig. 19.13.

Radiant emissions in the form of discrete wavelength lines exit the HCL and pass through the atomizer where gaseous atoms absorb specific wavelengths and become excited, thus moving to a higher energy level. The unabsorbed light moves into the monochromator. The light passes through an entrance aperture or entrance slit that creates a very narrow beam of light entering the monochromator. The light beam is reflected by a parabolic mirror onto a diffraction grating mounted on a rotating stepping motor which can change the angle of incidence of the light beam on the grating. The diffraction grating separates the beam of light into its various wavelengths, which are reflected onto a second parabolic mirror. This mirror focuses the spectrum on the exit slit, and only a very narrow band of wavelength exits the monochromator on its way to the detector.

The wavelengths exiting the monochromator can be altered by adjusting the angle of the diffraction grating. This is achieved by incremental movements of the stepping motor on which the diffraction grating is mounted. The inner walls of the monochromator are typically coated in a matt black layer to prevent internal reflection and absorb wavelengths of light not passing through the exit slit. The width of the exit slit is measured in mm and can be adjusted. A narrower slit width allows for a narrower bandwidth of light reaching the detector, which improves resolution and reduces the signal-to-noise ratio [15]. A wider slit width allows a wide bandwidth of light to reach the detector, allowing for improved sensitivity at the expense of increased noise.

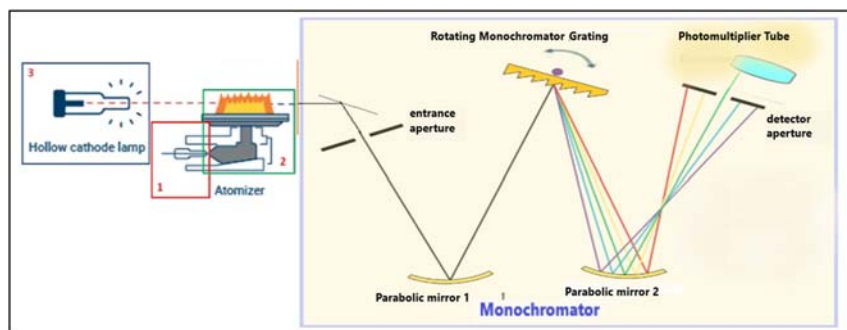


Figure 19.13 The monochromator and detector component of the atomic absorption spectrophotometer.

19.2.3.1.1 The detector

In AAS, the detector most commonly used is the PMT. The PMT is unique in that it is the only detector that can offer the same degree of sensitivity throughout the full wavelength range used by AAS. This detector converts incident light into an electrical signal that can be used to measure the light's intensity. The PMT also amplifies this signal by several magnitudes allowing even weak signals to be detected by AAS. The PMT therefore:

- Converts any photon of light exiting the monochromator into a current pulse of secondary electrons and
- Amplifies the current pulse to several magnitudes that can be easily detected.

The PMT is constructed of an outer glass surface encapsulating an inner vacuum. A photon of light exiting the monochromator strikes the inner photocathode (see Fig. 19.14). The photocathode consists of a photosensitive material such as an alkali-metal film that produces photoelectrons when bombarded with photons of light [16]. The photoelectrons produced at the initial photocathode are accelerated toward a positively charged dynode. The dynode is made of a metal plate coated with a bi-alkali material which emits secondary electrons upon impact. These electrons are further accelerated towards another dynode where even more electrons are emitted. The PMT contains multiple dynodes in sequence, significantly increasing the number of electrons produced with each impact on a dynode. This final avalanche of secondary electrons is collected as a significantly enhanced current pulse, which can be as much as 10^9 orders of magnitude larger than the initial signal.

The PMT tube was one of the early detectors used in AAS and is still the most popular detector used in AAS today.

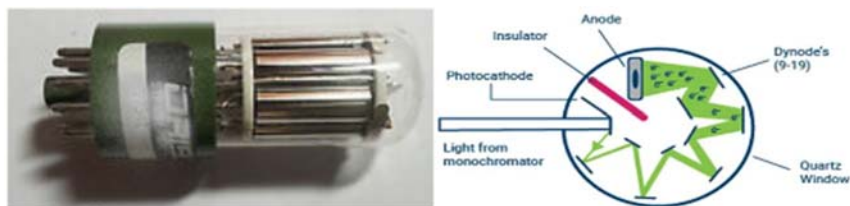


Figure 19.14 Photograph (left) and cross sectional outline (right) of a typical Photo Multiplier Tube. From Agilent. How does AAS work? <<https://www.agilent.com/en/support/atomic-spectroscopy/atomic-absorption/flame-atomic-absorption-instruments/how-does-aas-work-aas-faqs>>, n.d. (accessed 1.12.21).

19.3 Interferences in atomic absorption spectrophotometry

Interferences are physical or chemical processes that may cause positive or negative errors in an analytical signal. In AAS, two categories of interferences are generally encountered, each having different origins; these are spectral interferences and nonspectral interferences. Spectral interferences may cause the absorption of light to be higher than expected due to the absorption by species other than the analyte. Nonspectral interferences can have a positive or negative effect on the signal and may be caused by chemical interferences, ionization, and matrix.

19.3.1 Spectral interferences

AAS is a technique based on the absorption of specific spectral lines. These lines are typically unique to the element and it is unlikely that many elements will absorb at identical wavelengths. However, several elements do absorb at wavelengths very close to each other such as aluminum (308.211 nm) and vanadium (308.215 nm). Unless the instrument being used is equipped with a very high-resolution monochromator, it would be difficult to resolve these lines, and the absorption values for both vanadium and aluminum at these wavelengths will be higher than the true value. Also, there exist some elements, such as Nb, that produce over a thousand spectral lines, ensuring that there is going to be spectral overlap with several other elements.

Spectral interferences can also occur when alkali hydroxides such as CaOH are present in the matrix. CaOH is only decomposed at high temperatures, but at the relatively low temperatures present in an air/acetylene flame, CaOH exists as a molecule and due to molecular absorptions, it absorbs in bands instead of discrete lines. One such band occurs between 550 and 556 nm and significantly interferes with the absorption line for elements such as barium (553.6 nm) resulting in higher absorption.

Another down side of the air/acetylene flame is the formation of metal-oxides, which can be produced at lower flame temperatures and result in light scattering. A scattering of radiant energy in the flame can appear as an increased absorption as the net result is a lower intensity of the radiant energy after the flame.

In many cases, variations in the analytical parameters can avoid some of these interferences. The first avenue would be to use alternate wavelengths that may not be subject to interference from other species. Another technique would be to use a narrower slit width, which would improve resolution and

hopefully separate the analyte signal from interference. An alternative procedure that can be used to avoid spectral interferences would be to use a higher temperature flame such as nitrous oxide/acetylene. This flame would atomize interfering molecular species such as alkali hydroxides and metal-oxides, which absorb in bands and cause scattering.

Several techniques have been developed to correct these spectral interferences, they are known as “Background Correction.”

19.3.1.1 Continuum source background correction

Many modern AAS instruments use fully automated continuum source background correction as the primary background correction. In fact, the most common background correction used in AAS by far is continuum source as this method is accurate, reliable, and lower priced than the alternatives. As per Fig. 19.15, a deuterium lamp is used to provide the continuum source for background correction through the ultra violet range. The system is configured such that radiation from the HCL and the deuterium lamp passes through the atomizer alternatively. A rotating chopper is used that has mirrored and transparent segments allowing at one time for only radiation from the HCL to pass through the atomized sample, and at another time, only radiation from the deuterium lamp will pass through the sample. The rate of rotation of the chopper is controlled by the detector electronics. The absorbance of the deuterium radiation is then subtracted from the analyte signal.

Absorption of light from the continuum source by the analyte is considered to be negligible and only multiatomic species and molecules will absorb this radiation. Therefore, when the deuterium light passes through the sample, scattering, and broadband absorption from the sample matrix reduce its intensity. By removing this from the analyte signal, background correction is achieved.

Continuum background correction is common for all techniques in AAS, but it has its limitations. The addition of a lamp and a chopper introduces additional noise to the system, degrading the signal-to-noise ratio and negatively affecting analytical sensitivity. Hot gases in a flame or graphite furnace are very inhomogeneous and therefore different degrees of absorption may occur at different points in the flame or furnace or even at different times for the same sample at an identical position in the flame. Such events can lead to over correction or under correction. The deuterium lamp is only effective at wavelengths below 350 nm. For wavelength above this, deuterium lamp correction cannot be used.

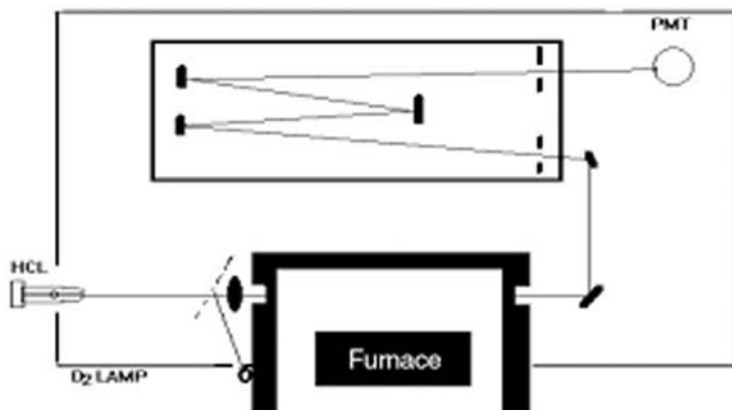


Figure 19.15 D2 Background correction applied to a GFAAS. From C. Flajnik, F. Delles, *Evaluation of deuterium and zeeman background correction with the presence of spectral interferences determinations of arsenic in an aluminium matrix and selenium in an iron matrix by GFAAS*. Agilent Application Note, AA119, 2010, 8. <<https://www.agilent.com/cs/library/applications/aa119.pdf>>.

19.3.1.2 Zeeman background correction

Because each atomic transition occurs between two discrete levels, atomic spectra are composed of discrete lines, each line representing energy absorbed or emitted during the transition of an electron to a higher or lower energy level. However, when the gaseous atoms are placed within a strong magnetic field, the electronic energy level split and this gives rise to several absorption lines for each discrete transition as shown in Fig. 19.16. This phenomenon is known as the “Zeeman Effect” or “Zeeman Splitting.”

The split lines are formed when a strong magnetic field between 10 and 15 kG is used, and the split lines are typically less than 0.01 nm apart.

The π and σ lines respond differently to polarized light. The π line absorbs light that has been polarized in a direction parallel to the induced magnetic field. The σ line absorbs light that has been polarized in a direction 90° to the induced magnetic field. By placing a rotating polarizer in the light path exiting the source, one can induce at one instant parallel polarized light, and at another instant perpendicular polarized light. The π absorption represents the analyte signal plus the background. The σ absorption represents the background only. The difference between the two is the net atomic absorption, free of spectral background interference. The use of a rotating polarizer within the light path and subtracting the σ from the π is descriptive of a DC Zeeman correction system.

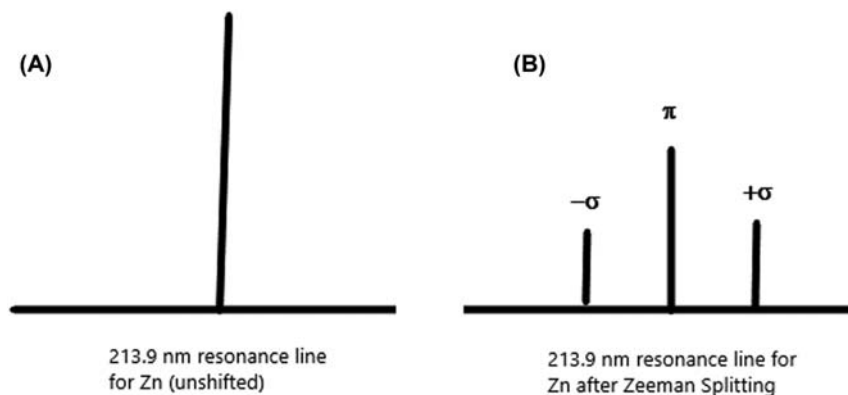


Figure 19.16 Zeeman splitting of the Zn 213.9 nm resonance line.

Some AAS systems use Traverse AC Zeeman correction. In this case, instead of a rotating polarizer, these use a fixed polarizer with light being polarized 90 degrees to the direction of the magnetic field. The signal is measured with the magnetic field switched off (atomic + background) and then with the field switched on (background only) the difference between the two signals is the net atomic absorption.

Zeeman background correction provides a much more accurate means of removing background than the Deuterium continuum source. Zeeman background correction is particularly useful when complex matrices such as biological samples are being analyzed and are more commonly found in GFAAS where samples are analyzed with immensely complex background interference. The use of polarizers reduces the light intensity significantly, resulting in weaker signals for instruments using Zeeman background correction, however, the instrument's ability to remove background is superior to other methods and this compensates for the lower signals. Instruments using Zeeman background correction are significantly more expensive and use more power than their continuum source counterparts, however where complex sample matrices are to be analyzed and particularly for GFAAS, Zeeman background is preferred.

19.3.2 Nonspectral interferences

Interferences in AAS may be either spectral or nonspectral in nature. Spectral interferences are less common in AAS but can be corrected by the use of background correction, which was discussed in the previous section. Nonspectral interferences on the other hand are much more

common in AAS and very often require procedural changes to correct. Nonspectral interferences may take the form of chemical interferences, physical interferences, and ionization interferences.

19.3.2.1 Chemical interferences

The chemical species of the analyte may influence the absorption of the atoms in the gaseous phase and result in suppressed signals. Consider calcium analysis in an air/acetylene flame; calcium in the form of calcium chloride atomizes very easily at the temperature of the flame and produces a very strong signal. Calcium sulfate or calcium phosphate on the other hand are much more stable at flame temperatures and do not degrade easily to form calcium atoms. This form of chemical interference is known as “anion interference” and is strongly dependent on the anion species present in the solution [9]. Matrix composition and digestion acid can contribute to these interferences and require specific procedural alterations to prevent them. For example, if one were to analyze a sample for calcium, using sulfuric acid or phosphoric acid to digest the sample, this will introduce severe anionic interference and reduce signal intensity. As such, sulfuric and phosphoric acids are avoided when digesting samples that require calcium analysis. Cationic interferences can also occur in AAS, one example being the analysis of magnesium in samples high in aluminum. At flame temperatures, aluminum and magnesium form a very stable oxide complex that does not readily decompose into the gaseous atoms needed for AAS. This form of interference is more common in the analysis of alkali and alkali-earth metals.

Several techniques can be employed to reduce or eliminate these effects and they constitute procedural modifications.

Higher temperature flames such as nitrous oxide/acetylene flames can be used to atomize stable molecules that are difficult to atomize in an air/acetylene flame. The analysis of calcium in particular recommends the use of nitrous oxide/acetylene flames at 2600°C–2800°C, which in most cases are sufficient to atomize the calcium sulfate and calcium phosphate molecules to gaseous atoms.

Releasing agents are also commonly used to correct chemical interferences. The concept is to introduce ions that form very stable molecules with the interfering anions, thus reducing the likelihood of these anions bonding with the analyte atoms. Strontium and lanthanum are two common cations that form very thermally stable compounds with phosphorous, preventing the formation of calcium phosphate [17]. For the analysis of calcium by AAS, it is generally recommended to add up to 2000 ppm

of lanthanum or strontium to the sample matrix to reduce calcium phosphate formation and the subsequent signal suppression.

Protective agents are another species that are commonly used to reduce chemical interferences. Protective agents act differently from releasing agents by bonding with the analyte atoms to form stable yet volatile compounds that are easily atomized in a lower temperature flame. Ethylenediaminetetraacetic acid (EDTA) is among the most commonly used protective agents in use [18].

In some cases, it may be difficult or even impossible to totally eliminate the interfering species. In these cases, it may be more appropriate to include the interference as part of the instrument calibration to ensure that it is accounted for as part of the analysis. In order to achieve this, *Matrix Matching* and *Standard Addition* may be used. Matrix matching involves matching the matrix of the calibration standard with the sample. The working standards should contain the same anions and cations in the same concentrations as the sample solution. In this way, the chemical interferences are compensated for in the instrument calibration. Standard addition is similar to matrix matching, but instead of trying to match the working standard matrix with the sample matrix, the sample itself becomes the matrix for the working standard as several spiked samples are now used as the working standard.

19.3.2.2 Nonchemical matrix interference

The sample matrix can induce a physical interference on an analytical technique that in many cases may go undetected. Among the more common physical interference are sample viscosity and sample flow dynamics. Samples such as biological samples including blood and plasma possess a different fluid dynamic than water or diluted acids. The presence of proteins and salts makes biological fluids more viscous, which can alter the amount of sample entering the atomizer in a given time. For the analysis of biological samples, Triton-X is added to the working standard which makes its viscosity similar to that of blood [19]. This produces similar fluid dynamics and reduces the matrix effect. Similarly, for the analysis of metals in heavy oils and fats, by solvent dilution, mineral oils are added to the working standard to make the viscosities of the standard and sample similar [20]. An alternative to this would be to excessively dilute the sample with solvent, bringing the matrices of both standards and samples similar. The down side of this is a reduction of sensitivity due to dilution.

Samples containing large amounts of dissolved solids can present a special challenge, especially for FAAS. As samples are aspirated into the spray

chamber, salts can deposit on to the tip of the nebulizer reducing the flow rate of the sample. As more samples are aspirated through the nebulizer, salt deposits build up gradually reducing the flow rate with every subsequent sample analyzed. This can lead to a severe diminishing of the analytical signal and inaccurate results. This interference can be reduced by diluting samples, however, the down side of this is reduced sensitivity. Alternatively, one may choose to use high-solids nebulizers or v-groove nebulizers which are specifically designed for high solids samples [21].

19.3.2.3 Ionization interferences

The technique of AAS requires that the analyte is in the form of gaseous ground state atoms such that the outermost electrons are capable of absorbing radiant energy from a HCL at specific absorption lines. The degree of absorption is proportional to the quantity of the analyte in the atomizer and is defined by the Beer–Lambert Law. If the elements to be determined possess low ionization energies, then they may ionize even in low-temperature flames. Ions do not absorb light to move to a higher energy state as atoms do, therefore as more atoms ionize, the lower the absorbance will be. This phenomenon is known as “Ionization Interference,” and is most commonly observed with alkali and alkali-earth metals in cooler air/acetylene flames. Other elements tend to ionize in hotter nitrous oxide/acetylene flames as well as in GFAAS.

Ionization interference can be controlled by introducing an element that ionizes at a lower temperature than the analyte, which leads to a flooding of free electrons in the flame. The free electrons bombard the analyte ions forcing them to return to the atomic state and in so doing eliminate the effects of ionization interference. Elements that are used in this manner are called “ionization suppressants” and commonly used elements include cesium, potassium, and rubidium. An example of ionization suppressants in use is the addition of 1000 ppm of potassium to samples requiring the analysis of barium. Potassium is added to all the standards, blanks, and samples to ensure a consistent matrix. As potassium ionizes, the electrons produced prevent the ionization of barium [22].

19.4 Analysis using atomic absorption spectrophotometry

19.4.1 Sample preparation

FAAS has the disadvantage of only being capable of analyzing liquid samples. Therefore, for FAAS analysis, all samples must be solubilized before

the analysis can proceed. Liquid samples can be analyzed with minimal sample preparation. Samples such as tap water can be analyzed directly by FAAS, and samples that may contain solids such as juices, oils, wines, or wastewater can simply be filtered before analysis. Concentrated or viscous samples need to be diluted before the samples are aspirated into the AAS, samples such as sirups, honey, or fruit concentrates need to be diluted with water or diluted acids, whereas heavy oils and soluble fats can be diluted with an appropriate solvent such as xylene or petroleum spirits and calibrated using organo-metallic standards. In order to avoid the ill effects of matrix interference, heavy mineral oil is added to calibration standards to match the viscosity of the diluted samples [20].

Samples that are soluble in water such as salts and sugars or in solvents such as fats and waxes should be dissolved in their appropriate solvent before analysis. High solids liquid samples such as seawater, urine or milk should be diluted to prevent matrix interferences. Alternatively, complexation of the analyte using a complexing agent such as ammonium pyrrolidine dithiocarbamate or a similar chelating agent can be performed followed by filtration of the complex and redissolving in an appropriate solvent can be used to eliminate the high solid matrix.

Solid and semisolid samples that are not 100% soluble in a solvent must be decomposed and solubilized before analysis by FAAS. One of the methods that are commonly used to solubilize solid samples is referred to as “wet ashing” or “digesting.” In this process, the sample is treated with a mineral acid such as nitric acid, hydrochloric acid, sulfuric acid or perchloric acid, or a combination at high heat. Usually, the temperature of digestion is the same as the boiling point of the acid since this is the highest temperature the solution can achieve at atmospheric pressure. High temperature digestion is an energy intensive process that could lead to the loss of volatile elements such as mercury, however, digestion at lower temperatures can prevent this loss [23]. Closed vessel *microwave digestion* is becoming the preferred mode of wet ashing since the temperature can be closely controlled and the sealed vessels allow for high pressure digestion, facilitating higher than boiling point temperatures to be achieved with no loss of volatile species. Wet digestion techniques can also be efficiently used to solubilize fatty samples such as cosmetics. In this case, a surfactant such as Triton X-100 can be added to the digestion mixture allowing grater contact between the aqueous acid and the hydrophobic sample [24]. The addition of hydrogen peroxide can further assist in sample digestion by breaking down the organic matrix of the sample.

Wet ashing techniques are simple and applicable to a wide and diverse array of samples. Samples can easily be digested with concentrated nitric acid or any other mineral acid at a temperature at or near the boiling point of the acid until the sample is completely solubilized. The digest can then be filtered through a hardened ashless filter paper into a volumetric flask and diluted to the mark with deionized water. This prepared sample can now be analyzed using FAAS and aqueous acidic calibration standards.

Dry ashing techniques are also commonly used in trace metal analysis by FAAS. This technique is used to completely destroy the matrix of inert samples not easily digested by acids but may be combustible, such as rubber and plastics [25]. The sample is first placed in a ceramic crucible and burnt in an open flame to combust the solid matrix, converting it to solid carbon and inorganic ash. The crucible is then placed in a muffle furnace at 500°C to convert the solid carbon deposits formed from burning into carbon dioxide, leaving only inorganic ash in the crucible. The inorganic ash is then digested with a concentrated mineral acid to totally solubilize it, like wet ashing. In fact, the process of dry ashing is a combination of combustion followed by wet ashing.

Geological and mineral samples are particularly difficult to solubilize since the covalently bonded silicon matrix is resistant to both mineral acids and heat. The technique of *chemical fusion* is commonly used to solubilize these samples [26]. This process involves mixing a small portion of the solid sample with an inorganic flux in a platinum, zirconium, or fused silica crucible. Fluxes such as lithium tetraborate, sodium peroxide, lithium carbonate, and potassium hydroxide are commonly used in chemical fusion [27]. About 1 g of a sample is mixed with 5 g of flux in a platinum crucible and heated on a bunsen burner until the mixture melts. The high heat is sufficient to break the strong covalent bonds holding the crystal structure of the sample together. The atoms that are now free from the confines of the crystal lattice form weaker ionic bonds with the flux producing a fusion mixture. The fusion mixture is cooled and is solubilized by dilute mineral acids since the weak ionic bonds holding the fusion together are easily broken by the diluted acids, resulting in a clear aqueous solution. Analysis by FAAS can now be performed using aqueous acidic calibration standards.

GFAAS unlike FAAS does have the ability to analyze high solid solutions, semisolids, and solids. This is due to the insertion of the sample directly into the graphite furnace instead of using a nebulizer. As spectral

and chemical interferences will still occur in GFAAS, the effects of viscosity and surface tension are completely eliminated. The advent of the solid sample GFAAS or SS-GFAAS adds a new dimension to the technique of AAS. The analysis of solids by traditional AAS is very time consuming and is prone to numerous sources of error. Multiple steps and numerous chemicals make this type of analysis both costly and risky. The SS-GFAAS allows for the direct measurement of solid samples by introducing the sample into the graphite furnace as a slurry. This development reduces analytical cost and analysis time significantly while simultaneously reducing sources of error [28].

19.4.2 Calibration and analysis

AAS follows the relationship between concentration and absorption as defined by the Beer–Lambert Law (Eq. 19.2). However, the conditions of a flame or furnace are impossible to reproduce every time. Gas flows, fluid dynamics, atomization rates, and even source output are not reproducible, requiring that calibrations be performed on a daily basis. Therefore, every batch of samples analyzed will need to have a unique calibration.

Another deviation from the Beer–Lambert law is the loss of linearity at high absorbance. Typically, calibration curves are linear up to the established linear range and flatten out as the absorbance exceeds this range. The linear range for each calibration curve must be established and analytical absorbance exceeding the linear range must be discarded, the sample diluted, and reanalyzed. The linear range for an element varies depending on several factors such as instrumental conditions, sample type, matrix, and even the element itself. The establishment of a working linear range involves the analysis of multiple analytical standards in increasing order of concentration up to the maximum detectable concentration to establish the *Dynamic Range*. The range up to where the instrument response to increasing concentrations ceases to be linear is defined as the *Linear Range*. Generally, it is observed that absorbance exceeding 0.8 results in a loss of linearity and this can be even lower if Zeeman background correction is used.

When analytical results are reported, two terms are encountered frequently and should be defined when generating a suitable calibration curve. These are Limit of Detection (*LOD*) and Limit of Quantification (*LOQ*). The *LOD* is defined as the lowest detectable concentration obtainable by the instrument and is defined by many regulatory bodies as

the concentration that gives a signal three times the standard deviation of a blank solution [29]. However, when reporting data, the LOQ is the preferred mechanism to define the lowest valid concentration and is defined as the concentration that gives 10 times the standard deviation of a blank [29]. When analytical concentrations fall below the LOD, they should be reported as “Not Detected.” When analytical concentrations exceed the LOD but fall below the LOQ, they should be reported as “Not Quantifiable.”

Calibration of the AAS is commonly performed using single element working standards or multiple standard additions (Fig. 19.17). Mixed standards can also be utilized but the AAS can analyze only one element at a time. Internal standards are not utilized in AAS. Calibration standards or working standards are usually single use, are prepared from a stock standard typically sold in 1000 or 10,000 ppm concentrations, and are usually traceable to NIST. The stock standard may be sold as single standards or mixed standards with multiple elements and are produced from ultrapure reagents. Working standards are produced by serial dilution of the stock standard with diluted nitric acid or a similar matrix matching the samples to be analyzed. Usually, five working standards are used to calibrate the

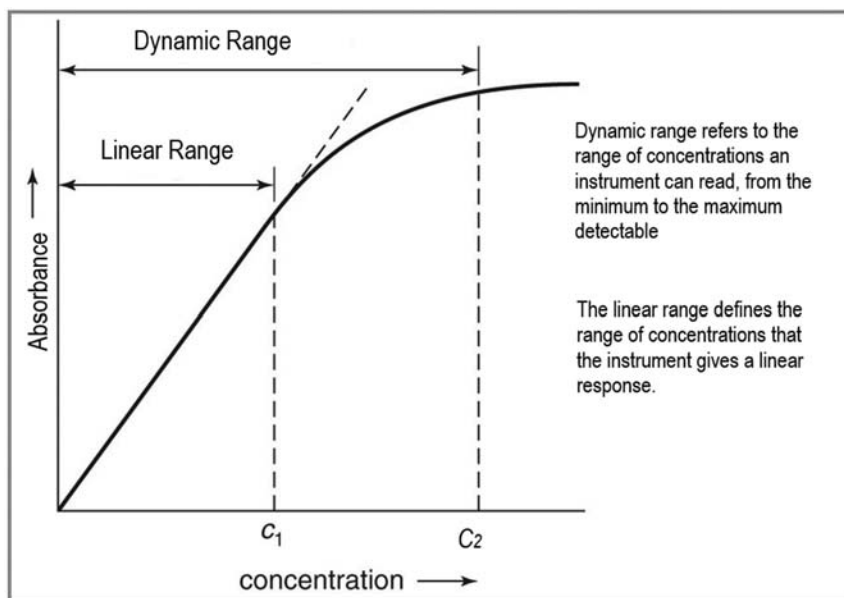


Figure 19.17 Typical calibration curve used in AAS identifying the linear range and dynamic range of the instrument.

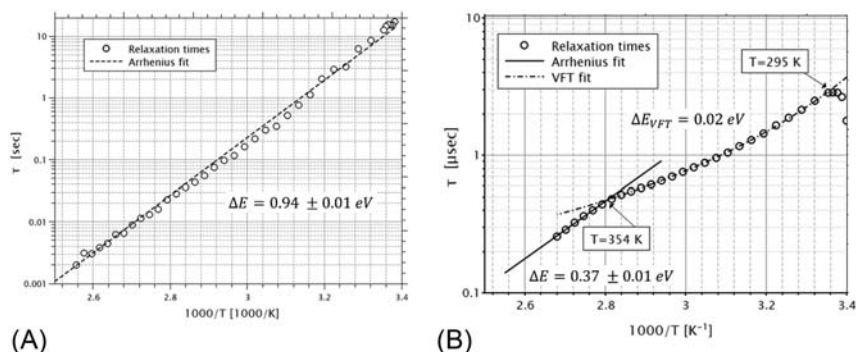


Figure 19.18 Linear Regression used to determine the equation of a calibration curve.

AAS and are made up of concentrations ranging from just above the LOD to the Linear Limit; however, more standards may be used as needed. For example, if Zn is to be analyzed, and the LOD for Zn is 0.01ppm with the range of linearity extending to 2.0 ppm, working standards can be made to the concentrations of 0.1, 0.5, 1.0, 1.5, and 2 ppm. A plot of concentration vs absorption results in the usable calibration curve, which should possess an $r^2 > 0.95$. Extrapolation of the unknown sample's absorbance along the calibration curve yields the concentration of the analyte in the unknown sample. Alternatively, the equation of the linear line derived from the calibration curve may be used to calculate the concentration of the unknown sample (Fig. 19.18).

19.5 The future of atomic absorption spectrophotometry

Since the first commercial AAS was introduced in the 1950s, the application has developed steadily with improvements in light sources, nebulization, flame technologies, background correction, optics, and detectors creating what is now a staple in every research and production laboratory globally.

The AAS is considered the gold standard for trace metal analysis throughout the world and is synonymous with accuracy, reliability, and cost-effectiveness. When one mentions trace metal analysis, they almost always refer to AAS.

Several innovations have been developed and are currently in development to improve the technique of AAS even more. Some manufacturers

have focused on improved detector technologies including High-Resolution 3D CCD detectors to produce a three-dimensional spectrum that contain much more data than conventional AAS and allows for easier removal of background noise. Other manufacturers have even replaced the HCL so common in traditional AAS with a high-resolution single xenon short-arc lamp that covers the entire relevant wavelength spectrum.

Improvements in monochromator technology, more stable burners, and improved software are keeping the technique of AAS the most relevant method for metals analysis. As scientists continue to improve critical areas of the technique, the AAS will remain the most important and most used method of metal analysis for a long time to come.

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CHAPTER 20

Dielectric spectroscopy and techniques

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20.1 Introduction

Between 1745 and 1746, the empirical basis of a capacitor was independently and almost simultaneously discovered by Ewald Georg von Kleist and Pieter van Musschenbroek [1]. Decades later, in 1837, Michael Faraday initiated the study of insulation materials, which he called *dielectrics* [2]. During the following years, Faraday studied the difference between the measured capacity of an empty capacitor and its capacity when filled with a dielectric material. This quantity was later denominated *dielectric constant* and *permittivity* [2,3]. The method used by Faraday is, even today, one of the most widespread for experimentally determining the value of static permittivity, that is, the permittivity measured at a very low frequency. In his publication “Experimental Researches in Electricity” [3], Faraday reported on the first methodical studies on multicomponent dielectric systems. His discoveries reached great diffusion and acceptance in the scientific community of the time.

In the middle 1860s, James Clerk Maxwell unified the theory of electromagnetic phenomena with his publication of “A Dynamical Theory of the Electromagnetic Field” [4], giving birth to Maxwell’s equations. Particularly, he defined *permittivity* as the ratio between the electric displacement field and the electric-field intensity. This macroscopic interpretation was widely accepted [5,6].

Based on the work of Cavendish [7] and Faraday [3], Mossotti and Clausius independently found a relation between the polarization of a virtual sphere of a continuous isotropic dielectric medium and the permittivity of such dielectric when a constant electric field is applied to it [8,9]. Considering the polarized sphere as molecules, they related the permittivity with the molecular polarization. The analytical expression of these

concepts constitutes the well-known Mossotti–Clausius relation [10]. This was the first successful attempt to relate the macroscopic permittivity to the molecular property of polarization. The Mossotti–Clausius formula applies without modification only to nonpolar gases but over a wide range of pressures [11]. During the first few decades, these equations were applied to studying any dielectric, either pure substances or mixtures of solids, liquids, or gases. The experimental results soon showed limitations. Dependence on pressure, temperature, and state of aggregation was evident. Soon, systems of two or more components were constituted in specific study subjects. Nevertheless, complexity was of such magnitude that although the objective was the study of mixtures in general, efforts were concentrated only on binary mixtures for many years [10,11].

It was soon suggested that the discrepancy between the theory and the experimental results resided in the existence of a dipolar moment in the molecules [5,12]. When applying an external electric field through a sample, a nonzero macroscopic dipole moment arises, that is, the material is polarized. Several authors during the 19th century dedicated their efforts to discussing this polarization's physical description [5]. In 1912 Debye published a quantitative theory that gave a solid basis to this phenomenon [13]. The average macroscopic dipole moment density defines the polarization of the sample. When the electric field ceases, the induced macroscopic dipole moment returns to zero, in a phenomenon called “dielectric relaxation” [5,6].

Dielectric spectroscopy (DS) studies the dynamics of dielectric relaxation. DS is sensitive to relaxation processes in an extensive range of characteristic times, that is, 10^{-11} up to 10^5 seconds. As a result, a complex system comprising different molecular moieties and their interactions will give rise to intricate and rich dielectric spectra. Complex systems render the appearance of a new *mesoscopic* length scale, intermediate between molecular and macroscopic. We find emulsions, porous materials (like glasses and silicon), glass-forming liquids and polymers (including composites), and the vast types of biological systems and tissues among these complex systems [14].

The versatility of DS of complex systems is an asset in understanding the underlying mechanisms of the physics of complex systems and soft matter.

20.1.1 Phenomena of dielectric polarization and models

Upon applying an external electric field E through a dielectric sample, a nonzero macroscopic dipole moment arises, that is, the dielectric is

polarized. The polarization $\mathbf{P}$ of the sample is the average macroscopic dipole moment density, or dipole density, as in Eq. (20.1) [5,6,15].

$$P = \frac{\langle M \rangle}{V} \quad (20.1)$$

where $\langle M \rangle$ is the ensemble average macroscopic dipole moment of the sample in the volume V . In a linear approximation, the macroscopic polarization of the dielectric sample is proportional to the strength of the applied external electric field $\mathbf{E}$, that is

$$P_i = \varepsilon_0 \chi_{ik} E_k \quad (20.2)$$

where χ_{ik} is given by the relative dielectric susceptibility tensor of the material, E_k is the k th component of the electric field, and $\varepsilon_0 = 8.854 \times 10^{-12}$ [F/m] is the dielectric permittivity of a vacuum. When the material is isotropic and homogeneous, then χ is a scalar, and Eq. (20.2) becomes:

$$P = \varepsilon_0 \chi E \quad (20.3)$$

Within the macroscopic classic Maxwell approach, matter is a continuous distribution of charges, and the electrical displacement (or electrical induction) vector $\mathbf{D}$ is defined as the electric field corrected by the polarization, as given by Eq. (20.4).

$$D = \varepsilon_0 E + P \quad (20.4)$$

For a uniform isotropic dielectric medium, the vectors $\mathbf{D}$, $\mathbf{E}$, and $\mathbf{P}$ have the same direction, rendering Eq. (20.5).

$$D = \varepsilon_0(1 + \chi)E = \varepsilon_0 \varepsilon E \quad (20.5)$$

where $\varepsilon = 1 + \chi$ is the relative dielectric permittivity [5,14].

Naturally, polarization of the material reaches its equilibrium value not instantaneously but within a characteristic time. By analogy, when the field is suddenly removed, the polarization decay (caused by thermal motion) follows the same law, rendering a relaxation process characterized by the so-called dielectric relaxation function $\phi(t)$ [6,14,15].

Under the linear regime, the polarization fluctuations caused by thermal motion are the same as for the macroscopic rearrangements induced by the electric field [16]. The rate and laws governing the relaxation process are directly related to the structural and kinetic properties of the sample and characterize the macroscopic properties of the system under study.

Thus, the relaxation function can be used to obtain information about the dynamic properties of the material under test.

The relationship for the dielectric displacement vector $D(t)$ and time-dependent fields follow Eq. (20.6) [6]:

$$D(t) = \varepsilon_0 E(t) + P(t) = \varepsilon_0 \left[\varepsilon_\infty E(t) + \int_0^t E(t - \tau) \cdot \phi(\tau) d\tau \right] \cdot u(t) \quad (20.6)$$

where ε_∞ is the extrapolated high-frequency permittivity limit, and $u(t)$ is the Heaviside function.

The complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ is defined by the frequency-domain equation for the displacement field vector:

$$D(\omega) = \varepsilon_0 \varepsilon^*(\omega) \cdot E(\omega) \quad (20.7)$$

In turn, the complex dielectric permittivity is related to the relaxation function by Eq. (20.8), where the operator F represents the continuous-time Fourier Transform [17].

$$\varepsilon^*(\omega) - \varepsilon_\infty = F\{\phi(t)\} \quad (20.8)$$

Since the data for the dielectric relaxation properties of the sample being tested is equivalent in frequency and time domain, the dielectric response might be measured experimentally as a function of frequency or time, providing data in the form of a dielectric spectrum $\varepsilon^*(\omega)$, or the macroscopic relaxation function $\phi(t)$.

The difference between the low-frequency (static) permittivity ε_s and the high-frequency permittivity ε_∞ of a relaxation process is called dielectric strength and is represented by $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$. Fig. 20.1 depicts a typical dielectric spectrum with two relaxation processes; the real and imaginary parts of the complex permittivity are plotted against frequency. The characteristic time of the relaxation process is given by the critical frequency in which the imaginary part of the complex permittivity is maximum. The real and imaginary parts of the complex permittivity are related by the Kramers–Kronig relationship [18].

Additionally, most dielectrics (like biological systems) have a specific DC conductivity (σ_{DC}) [19]. Hence, the definition of the complex dielectric permittivity expands to the form in Eq. (20.9):

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i \left(\varepsilon''(\omega) + \frac{\sigma}{\omega \cdot \varepsilon_0} \right) \quad (20.9)$$

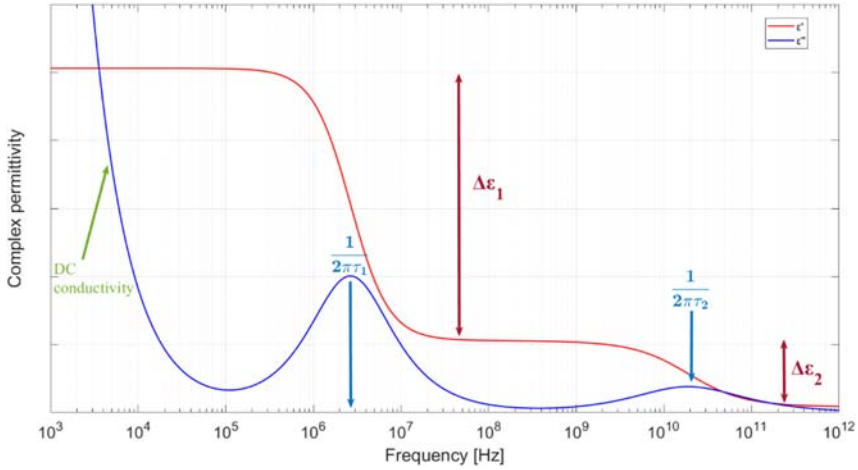


Figure 20.1 Typical dielectric spectrum: two processes and DC conductivity are shown. In red is the real part and in blue is the imaginary part of the complex permittivity plotted against frequency. The dielectric strength and the characteristic time of each relaxation process are marked.

In Fig. 20.1 the DC conductivity appears as the hyperbolic descent from 0 Hz of the imaginary part of the complex permittivity.

A simple first-order exponential model of one relaxation process function renders the well-known *Debye* formula, introduced in 1913 by Peter Debye [6,13]:

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau} \quad (20.10)$$

This models the dielectric response of a collection of rigid noninteracting dipoles. Debye's relaxation model succeeds in describing a large family of polarization processes. Some materials present polarization processes that follow a finite superposition of Debye's models. However, a wide variety of them needs a more general model described in terms of a continuous distribution of relaxation times $G(\tau)$ [6,20]. This implies that the complex dielectric permittivity can be presented as:

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \int_0^\infty \frac{G(\tau)}{1 + i\omega\tau} d\tau \quad (20.11)$$

where the distribution function $G(\tau)$ should satisfy the normalization condition:

$$\int_0^\infty G(\tau) d\tau = 1 \quad (20.12)$$

However, the physical interpretation of the distribution function is not a straightforward task. Therefore, other models in both the frequency and time domains that can bypass the $G(\tau)$, have gained acceptance. Even though applying the *Laplace* transform operator on the corresponding decay function would be fraught with mathematical difficulties [17], most *nonDebye* phenomena have been empirically described by the so-called *Havriliak–Negami* dispersion function [21]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^\alpha]^\beta}, 0 \leq \alpha, \beta \leq 1 \quad (20.13)$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric strength of the relaxation process, and α and β are empirical-phenomenological exponents.

This approach can be split into three cases, originally empirically introduced to allow a practical and analytical representation of experimental spectra:

- The case of $\alpha = 1, \beta = 1$ describes the *Debye* relaxation Eq. (20.10).
- The case of $\alpha < 1, \beta = 1$ corresponds to the *Cole–Cole* equation [22].
- The case of $\alpha = 1, \beta < 1$ corresponds to the *Cole–Davidson* equation [23].

The abovementioned models are certainly suitable for modeling the relaxation processes at a given fixed temperature, pressure, and other extrinsic thermodynamic variables. Temperature-dependent DS has proven to provide a more profound and better understanding of the underlying physics of the material under test [14,15]. This dependence, given by the balance between thermal and electrical interaction energy, follows the Boltzmann statistics [5,6,14]. The contribution of the temperature to the dielectric strength of the material is described as

$$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty \propto \frac{\mu^2}{k_B T} \quad (20.14)$$

where μ is the dipole moment of the material under test, k_B is Boltzmann's constant, and T is the system's temperature.

Not only is the dielectric strength influenced by the temperature, but the relaxation time also strongly depends on the system's temperature. In the case of a single relaxation process over the whole temperature's range of interest, the relaxation time is expressed as

$$\tau \propto e^{\frac{E_a}{RT}} \quad (20.15)$$

where E_a is a constant called *activation energy* [6,14]. This quantity can be interpreted as the energy required to make polarization possible. Its most

straightforward interpretation is the energy required for molecular reorientation in solids, which equals the energy required to overcome the energy barrier for reorientation [14,17].

20.1.2 Dielectric spectra on mesoscale

As stated above, Complex systems are defined by multiple lengths and time scales. For example, among the fastest relaxation processes, we find water clusters; escalating in the relaxation times, we can find glass-forming liquids, single droplets, macromolecules, ice, and porous materials [14,15]. Fig. 20.2 presents those examples placed among the spectrum in Hz.

Dielectrics are often divided into two basic categories: polar dielectrics and nonpolar dielectrics [15]. Polar dielectrics are formed by molecules with a permanent electric dipole (i.e., an intrinsic nonzero net electric field). Nonpolar dielectrics are formed by molecules that do not exhibit a net electric dipole, roughly due to a symmetrical distribution of charges.

Biological materials have gained particular interest in the DS community [14]. In his earliest publications, Schwan et al. [24,25] introduced the term “dispersion” to refer to the different relaxation processes observed in biological tissues. Those dispersions span overgenerally accepted different frequency ranges, although their origin resides in the nature of the relaxation processes.

Fig. 20.3 presents examples of biological tissues and materials that exhibit strong relaxation processes in each dispersion. The α -dispersion appears primarily due to charge (ion) movement overrelatively large tissues and can be observed with relaxation times of several milliseconds and above [26]. The mechanisms found to generate the α -dispersion include counter-ion effects on and close to the membrane surfaces, gated channel

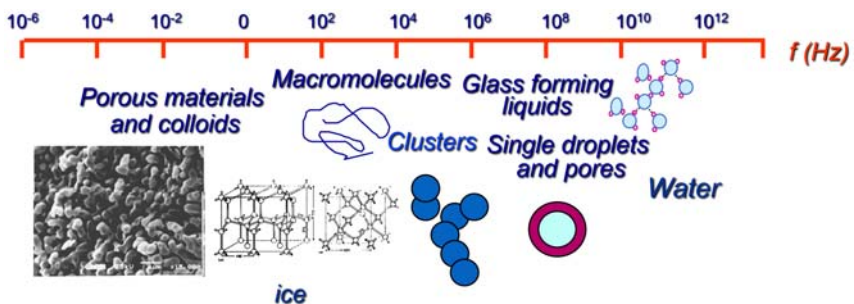


Figure 20.2 Example of materials presenting relaxation processes along the broad-band spectrum of DS.

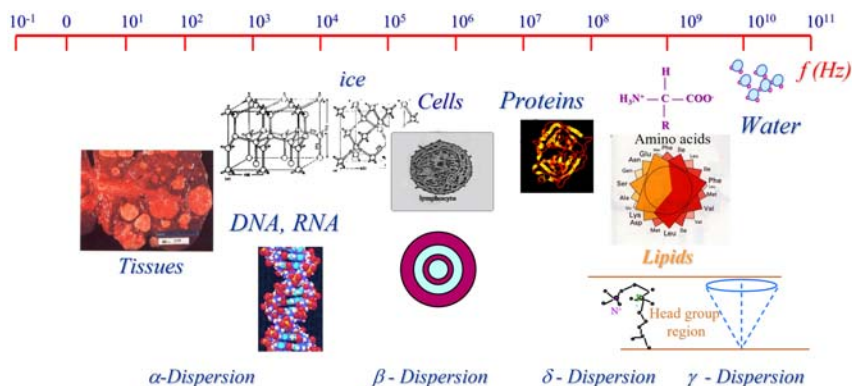


Figure 20.3 Example of biological materials and dispersions along the broadband spectrum of DS.

ion and active movements (pumps), and ionic diffusion through the cell membrane [27].

The β -dispersion arises when interfacial polarization occurs; the polarization of cell membranes in a suspension is the classic example of β -dispersion, also called Maxwell–Wagner polarization [28]. The relaxation time of the process is a function of the size of the interface; it is generally present in the range of tens of nanoseconds upto microseconds. This dispersion can also be sensitive to intracellular organelle membranes [29].

Schwan et al. observed a third fundamental dispersion present in biological tissues; the name γ -dispersion was given to those relaxation processes, present within the frequency range of about 10–40 GHz. This dispersion is mainly a consequence of the relaxation processes of dipolar clusters, for example, water [30]. Water is an essential substance present in every living tissue and, given the presence of charged ions and particles in the tissue's water, its dielectric signature has lately become a novel marker for biosensing [31].

A while after defining the three main dispersions, a fourth one was added in the frequency range of hundreds of MHz upto a few GHz: the δ -dispersion [14,15]. The origin and description of this dispersion have not yet reached a consensus [32,33]. Among the different explanations, we find dielectrophoresis, the effects of hydration shells (causing a relaxation process similar to γ -dispersion but at lower frequencies because of binding the dipole to a protein surface), and macro-molecule tumbling or reorientation seen in proteins, lipids, and amino acids [33–35]. In other words, there is still a long road to pass before there is an explanation for this phenomenon.

20.2 Measurement techniques

The broadband dielectric characterization of materials has been widely developed since the origins of DS. The nature of its metrology requires, in most cases, fast and high-precision equipment. In addition, intrinsic differences in the measurement techniques exist between low frequencies and high frequencies due to the nature of electromagnetic wave propagation in the material [36]. This phenomenon gives rise to two main groups of modeling: lumped elements and distributed elements.

20.2.1 The difference between lumped elements and distributed elements

The definition of lumped and distributed elements depends on whether one can consider the probing signal to be approximated as a quasistatic field or not. This depends on the relative dimensions of the sample compared to the probing wavelength; practically, whether the electric field along the sample can be considered uniform or not, as shown in Fig. 20.4. If yes, we are dealing with lumped elements, and the electrostatic approach can be applied [36].

As a rule of thumb, we consider the sample small if it is smaller than one-tenth of half a wavelength. In such a case, the sample fills a capacitor, and the system measures the effective load capacitance. The complex permittivity of the sample, $\varepsilon^*(\omega)$, is then calculated as the quotient between the complex effective capacitance, $C^*(\omega)$, and the empty capacitance, C_0 , of the capacitor:

$$\varepsilon^*(\omega) = \frac{C^*(\omega)}{C_0} \quad (20.16)$$

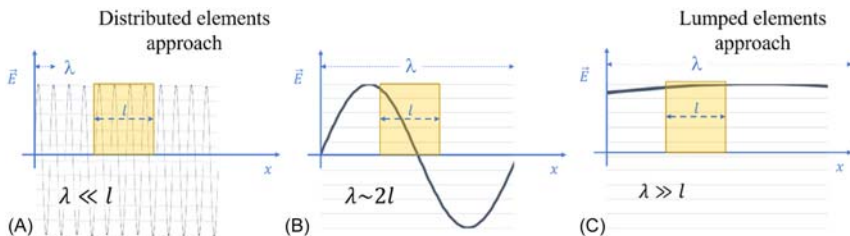


Figure 20.4 Schematic representation of the difference between lumped and distributed elements models based on the electric field distribution through the sample under test. (A) for a wavelength, λ , much smaller than the sample dimension, l , (distributed elements), (B) for a wavelength on par with the sample dimension (distributed elements), and (C) for a wavelength much greater than the sample dimension (lumped elements).

When the condition for using the lumped elements approach is not met, it is necessary to employ the distributed elements approach; in other words, to solve the wave equations at the interface of the sample and the measuring device or transmission line. Reflectometry and transmission measurements allow the extraction of the complex permittivity of the medium. The following subsections discuss the challenges and solutions that these approaches present.

20.2.2 Broadband dielectric spectroscopy in the frequency domain for lumped elements

When working under the lumped elements paradigm, the sample holder is generally a condenser for which the material under test becomes the *dielectric between the plates*. Since the dielectric can be conductive and lossy, the condenser's capacitance is a nonconstant complex value in the frequency domain, and related to the dielectric permittivity by

$$\varepsilon^*(\omega) = \frac{1}{i\omega Z^* C_0} \quad (20.17)$$

where ω is the cyclic frequency, Z^* is the measured complex impedance and C_0 is the geometric capacitance of the empty sample cell. From the point of view of impedance measurements, such capacitance can be represented as simply as a capacitor (of real capacitance) in parallel to a resistor, sometimes connected in series to a second capacitor (Debye impedance model) or a second resistor (Lapicque impedance model) [37]. However, those simplistic models cannot represent the impedance observed on the sample holder when the material under test presents more complex dielectric models such as Cole—Cole, Cole—Davidson, and Havriliak—Negami [14,15].

The main goal of DS is to obtain a measurement of the complex capacitance of the sample holder; upon dividing it by its empty capacitance, one obtains the complex permittivity of the material. A frequency sweep allows broadband spectroscopy of the load, ultimately allowing the calculation of the complex dielectric permittivity. In general, the study includes fitting its spectrum to the analytical models discussed in Section 20.1. The measurements are generally based on two main architectures: bridges and resonators.

20.2.2.1 Bridges

A bridge is an electrical assembly comprising four loads connected between four nodes: N_1 — N_4 (see Fig. 20.5). An input voltage is applied

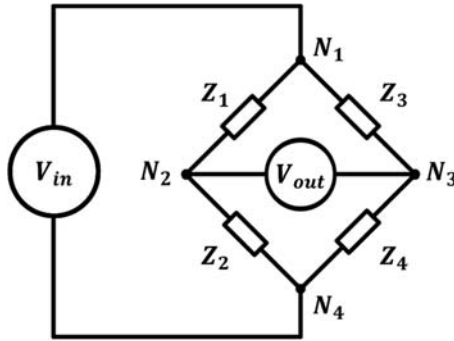


Figure 20.5 Schematic circuit of a bridge.

between nodes N1 and N4, and the output voltage is measured between nodes N2 and N3.

It follows that the output voltage will be zero when the bridge's branches are balanced, that is, the impedance ratios are equal: $Z_1/Z_2 = Z_3/Z_4$. Deviations from this balance will render changes in V_{out} that reflect the value of the impedances. Thus, by knowing the exact value of the three impedances of the bridge, an impedance-undertest (e.g., Z_4) can be evaluated by solving the bridge, as given in Eq. (20.18).

$$Z_4 = \frac{Z_2 \cdot V_{in} - (Z_1 + Z_2) \cdot V_{out}}{Z_1 \cdot V_{in} + (Z_1 + Z_2) \cdot V_{out}} \cdot Z_3 \quad (20.18)$$

where V_{in} and V_{out} are expressed as phasorial complex numbers to obtain the complex impedance value of Z_4 . As previously discussed, a frequency sweep allows broadband spectroscopy of the load, ultimately allowing the calculation of the complex dielectric permittivity.

20.2.2.2 Resonant circuits

Resonant circuits are essential components in general electronic circuits. They can generate, filter, and select frequencies as a function of their intrinsic capacitance and inductance. The quality (Q) factor is a figure which relates a resonant circuit's ability for energy storage with its energy dissipation. Thus, it has found a great application in the material analysis [38]. The material under test is used as the dielectric material in the capacitance; therefore, its dielectric properties set the resonant frequency of the circuit and its Q-factor, allowing the extraction of the complex permittivity of the material at the working frequency.

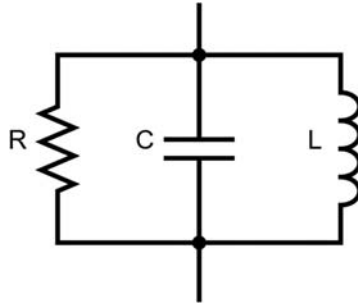


Figure 20.6 Discrete resonant impedance. The capacitor is filled with the material under test.

A typical discrete resonant impedance is shown in Fig. 20.6, where C and R are modeled for a simple approximation of the dielectric under test in the vicinity of the working frequency. The input admittance Y for the system is

$$Y = \frac{1}{R} + i \cdot \sqrt{\frac{C}{L}} \cdot \left(\frac{\omega}{\omega_0} - \frac{\omega_0}{\omega} \right) \quad (20.19)$$

where $\omega_0 = 1/\sqrt{LC_0}$ is the resonant frequency when the capacitor is empty. It follows that deviations from the resonant frequency and Q-factor of the system with an empty capacitance allow a direct measurement of the material's real and imaginary part of the dielectric permittivity under test when the sample cell is filled.

20.2.3 Distributed elements: microwave frequency domain

As stated previously, once wavelengths approach the sample dimensions, one must consider distributed elements. This leads to slightly different techniques and mathematical models. The analysis of a system in terms of distributed elements involves the solution of Maxwell equations in terms of electromagnetic waves [36,38]. In this regard, transmission lines are responsible for confining electromagnetic energy to a region of space limited by the physical medium that constitutes the line itself. The transmission line consists of electrical conductors with a particular geometric arrangement that conditions the electromagnetic waves' properties [39].

Microwave sensors in general (and DS sensors in particular) usually constitute a load connected to one end of a transmission line [38]. The reflection coefficient at the interface or connection varies as a function of

the load, which in turn is a function of the dielectric permittivity of the material under test. The following subsections present a description of classical sensors used in DS.

20.2.3.1 Resonators

Expanding on the description presented in Section 20.2.2.2 for an approach of distributed elements, it is observed that the input impedance of a resonator at the resonance frequency is purely real since its reactance is proportional to the difference between the electric and magnetic energy storage [40].

The *quality factor* or Q-factor of a resonator is well defined as the ratio between the electromagnetic energy stored in the fields of the resonator and the energy lost per cycle [38,40], as given by Eq. (20.20).

$$Q = 2\pi \times \frac{\text{Energy stored}}{\text{Energy lost per cycle}} \quad (20.20)$$

The Q-factor quantifies the relative rate of energy loss in the resonator. It follows that a lossy dielectric placed in the resonator cell will render a decrease in the Q-factor. This principle forms the basis of many techniques for measuring dielectric loss.

On the other hand, the resonator's resonance frequency is such that an entire half-wavelength can exist within the resonator walls. This means that the resonance frequency is determined by the geometry of the resonator and the permittivity (real part) of the dielectric filling the resonator. For instance, a cylindrical resonator working in the TM_{010} mode has an electric-field distribution, as shown in Fig. 20.7, and its resonance frequency is determined by its diameter [41].

The complete analytical solution of the resonator system is a nonlinear multivariable system for which an exact solution rarely can be obtained. Perturbation methods are semianalytical techniques for calculating approximate solutions to such nonlinear systems [42]. Typically, they refer to linearization methods; this linearization limits the validity of the results to a relatively narrow range of perturbation values [38].

In the particular case of a resonator for dielectric measurements, a small specimen is placed in the resonator to affect the effective wavelength in it and the ratio of energy storage and energy loss per cycle. Thus, the *perturbation* generated by the specimen under test renders a shift in the resonance frequency and a change in the Q-factor [38,41].

Since the wavelength is affected by the real part of the permittivity, the frequency shift is proportional to the difference between the specimen's ϵ'

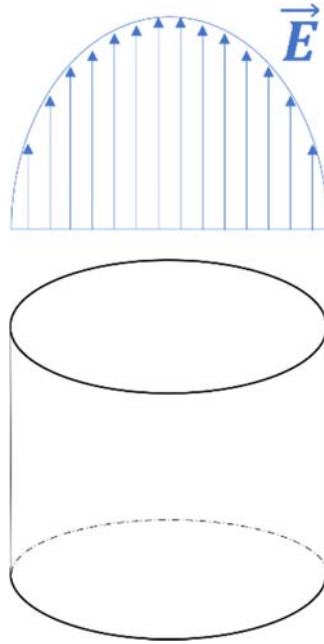


Figure 20.7 Electric field distribution of a TM_{010} cylindrical resonator.

and that of the material filling the resonator (e.g., air). In addition, if the volume of the specimen under test is much smaller than the resonator's volume, the energy storage of the system is almost unchanged; thus, the change in the Q-factor is a consequence of the change in the energy loss per cycle, that is, a function of the specimen's ϵ'' .

The general formulae for calculating the real and imaginary parts of the complex permittivity can be expressed by Eq. (20.21):

$$\begin{aligned}\epsilon' &= 1 - a \cdot \frac{f_s - f_r}{f_r} \cdot \frac{V_o}{V_s} \\ \epsilon'' &= b \cdot \frac{V_o}{V_s} \cdot \left(\frac{1}{Q_s} - \frac{1}{Q_o} \right)\end{aligned}\quad (20.21)$$

where f_r is the resonance frequency without the specimen in the resonator, f_s is the resonance frequency with the specimen in the resonator (note that it should be smaller than f_r due to the change in the effective wavelength), V_o is the volume of the resonator, V_s is the volume of the specimen, and Q_s and Q_o are the quality factors of the system with and without the specimen, respectively [38].

Each type of resonator needs a different specimen geometry undertest for maximizing the sensitivity, precision, and accuracy of the measurements. In many cases, especially at microwave frequencies, in addition to the initial linearization of the system, a calibration using well-known materials is needed, preferably with materials with similar dielectric properties to that of the specimen undertest.

20.2.3.2 Coaxial lines as broadband probes

Coaxial transmission lines allow TEM waves to propagate along them. As long as the line's characteristic impedance is conserved, the wave continues its trajectory. When the incident wave finds a discontinuity in the characteristic impedance, the part is reflected, and the part is transmitted forward. In the plane of interface between the two characteristic impedances, the reflection coefficient is defined as the phasorial ratio between the reflected electric field and the incident electric field [38,43,44].

Broadband frequency-domain measuring devices (such as Vector Network Analyzers or VNA) typically use an output impedance of $50\ \Omega$ (some use $75\ \Omega$), and that is why it is recommended to connect them to transmission lines of $50\ \Omega$ (or $75\ \Omega$) practical applications [36,39]. A coaxial line serves as a probe for DS by exploiting the measurement of the reflection coefficient [36,39]. As shown in Fig. 20.8, part of the coaxial line is filled with a lossless dielectric (e.g., Teflon) to create a characteristic impedance of $50\ \Omega$ (or $75\ \Omega$); a second section of the coaxial line is filled

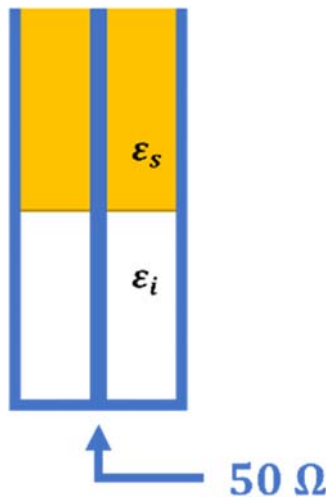


Figure 20.8 Coaxial line probe. The yellow material is the specimen undertest.

with the substance undertest. In general, the characteristic impedance of the second section will be different. In this geometry, the reflection coefficient at the interface has the expression in Eq. (20.22) [36]. A full sweep over the frequency range will render a broadband DS of the specimen undertest.

$$\Gamma(\omega) = \frac{\sqrt{\varepsilon_t(\omega)} - \sqrt{\varepsilon_s(\omega)}}{\sqrt{\varepsilon_t(\omega)} + \sqrt{\varepsilon_s(\omega)}} \quad (20.22)$$

Eq. (20.22) is valid only in case the geometry of both sections is similar, that is, the same outer and inner radii. If the material undertest is lossy, the length of its section should be long enough, so the wave decays within that length. If the material is lossless (or near-lossless), multiple reflections due to the end of the coaxial line probe must be considered when extracting the reflection coefficient at the interface from the measurements obtained with the VNA [38,39]. The system presents maximum sensitivity when the material undertest has a permittivity similar to that of the material in the first section.

If we wish to measure materials with much higher permittivity, a lumped elements approach should be used: The second section should be filled with a low amount of the material undertest so the load can be considered a cylindrical capacitance. In that case, Eq. (20.23) holds true for extracting the reflection coefficient in the interface, where Z_L is the capacitance load.

$$\Gamma(\omega) = \frac{Z_L(\omega) - 50}{Z_L(\omega) + 50} \quad (20.23)$$

From the geometric characteristics of the second section, its empty capacitance is easily calculated to extract the material's complex permittivity using Eq. (20.23). Due to the relatively small length of the second section (lumped-element approach), multiple reflections must be considered, as explained above [45].

Using the lumped elements approach on the load, we can also note that the 50 Ω transmission line can be terminated with any capacitance geometry. It is necessary to ensure the continuity of a 50- Ω characteristic impedance through the line until its termination on the lumped capacity load. In such a case, Eq. (20.23) is still valid. This technique is widely used when using radio frequencies above several MHz.

The geometric characteristics of the transmission line also influence its cutoff frequency, which is the maximum frequency for which only the

fundamental mode is present, that is, TEM mode. As a rule of thumb, Eq. (20.24) allows the calculation of the cutoff frequency.

$$f_{\text{cutoff}}[\text{GHz}] \approx \frac{190.85}{(D[\text{mm}] + d[\text{mm}]) \cdot \sqrt{\epsilon_r}} \quad (20.24)$$

where D and d are the outer and inner radii of the transmission line, respectively (expressed in mm), and ϵ_r is the relative permittivity of the material filling the transmission line; the cutoff frequency is then expressed in GHz [36,39].

20.2.3.3 Open-ended coaxial probes

The open-ended coaxial probe is a coaxial transmission line abruptly ended, which is in contact with the material under test (see Fig. 20.9) [38,43,44]. The electromagnetic wave propagates through the transmission line; upon reaching the line's end, the wave is partly reflected and partly transmitted due to the impedance mismatch. The wave impedance seen at the reflection plane is given mainly by the fringing fields penetrating the material under test (as shown in Fig. 20.9B), although a fully analytical solution includes a radiating element into the dielectric [43].

Several numerical and analytical approximations have been proposed to extract the dielectric properties of the material from the measured reflection coefficient [45–48]. However, nowadays, measuring systems use calibration to well-known materials for extracting the dielectric permittivity of the substance under test [49]. Once again, practical experience teaches us that the calibration needs to be performed with well-known materials that present similar dielectric behavior that the substance to be measured.

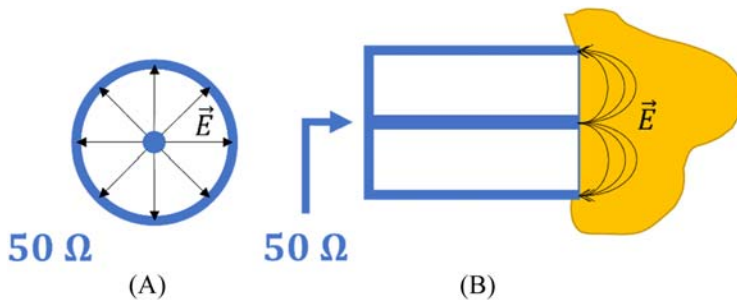


Figure 20.9 (A) Open-ended coaxial probe frontal cross-section (B) Open-ended coaxial probe in contact with the material-under test (side cross-section). The fringing electrical fields are represented.

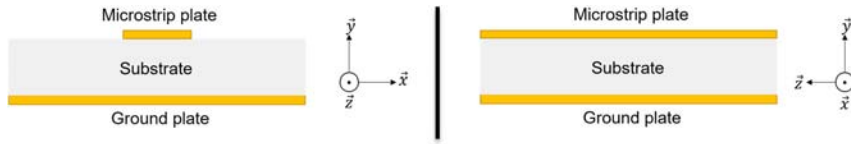


Figure 20.10 Microstrip schematic: (A) front view (B) side view.

This method has the great advantage that requiring minimal sample handling, allowing even (at least in some cases) in situ measurements. On the other hand, in situ measurements are bound to be susceptible to systematic errors such as contact pressure, angle, etc. To overcome those drawbacks, mechanical systems that guide the coaxial probe towards its contact with the material-under-test are advisable in most practical settings, as they can ensure consistency during a series of measurements [48].

20.2.3.4 Microstrip sensors

Building on the previous subsections, most of the wave power gets reflected in the interface with the material-under-test in all those configurations. Such a reflection renders an almost insignificant response for monitoring the substance's dielectric spectrum in several cases. As opposed to that, the microstrip transmission line configuration “forces” the electric and magnetic fields to penetrate the material under-test, providing a more sensitive response [50,51]. The microstrip is a flat transmission line consisting of a strip of conductive material separated from a ground plane by a dielectric material, as shown in Fig. 20.10.

The propagation is essentially TEM mode (along the z -axis in Fig. 20.10) since the relative permittivity of the substrate between the strip and the ground plane differs significantly from that of the air above the strip.

During the last decades, there has been an explosion of research in modeling microstrip transmission lines on semiconductors, which led to the development of models describing the propagation modes and energy losses within lossy substrates [50–55]. The most common approach is using microstrip patch antennae to characterize the dielectric permittivity of a solid lossy substrate. The real and imaginary parts of its complex permittivity will specify the working frequency and Q-factor of the antenna in the function of the geometry of the strip and the patch.

20.2.4 Dielectric spectroscopy in time domain

The Time-Domain Dielectric Spectroscopy (TDDS) technique is based on Time Domain Reflectometry (TDR), which is widely employed to

pinpoint cabling problems by analyzing reflected waveforms [56–59]. A voltage step propagates from the signal generator along the transmission line, and structural discontinuities along the line generate reflected pulses. As the reflected pulse's shape contains information about the discontinuity, this method can be used to extract dielectric properties of any material placed at any section of the transmission line; Hugo Fellner-Feldegg, from the Hewlett-Packard Laboratories, first demonstrated this in 1969 [58].

The basic concept of TDDS is illustrated in Fig. 20.11: A step voltage is applied from the generator and propagates along the transmission line; the signal is then reflected from the sample section filled with the sample material. The reflected signal, superimposed on the incident pulse, contains information about the dielectric properties of the sample. The resulting signal (sum of the step voltage and the reflected signal) is recorded and processed. The frequency range limits are determined by the voltage pulse duration and rise time, the sample cell's geometry, and the transmission line's characteristics [58,59].

In most practical systems of the lumped elements approach, the sample cell that terminates the transmission line is a capacitor with geometric capacitance C_0 and filled with the material under test. Fig. 20.12 shows the characteristic signal shape recorded during a TDDS session.

The total voltage across the sample $V_s(t)$ is given by Eq. (20.25), while the total current through the sample is given by Eq. (20.26).

$$V_s(t) = V_{in}(t) + V_R(t) \quad (20.25)$$

$$I(t) = \frac{1}{Z_0} \cdot [V_{in}(t) - V_R(t)] \quad (20.26)$$

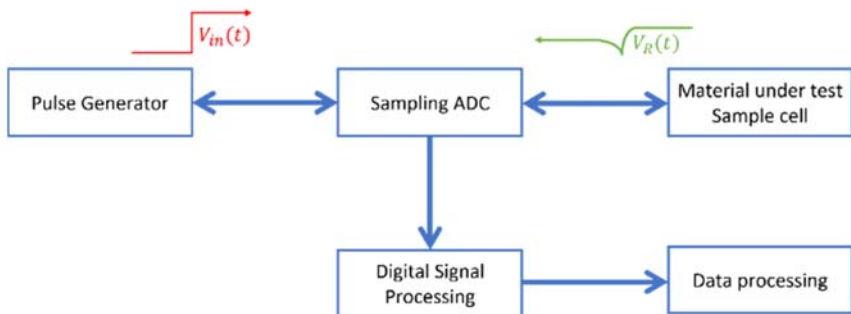


Figure 20.11 Schematic set-up of a TDDS system.

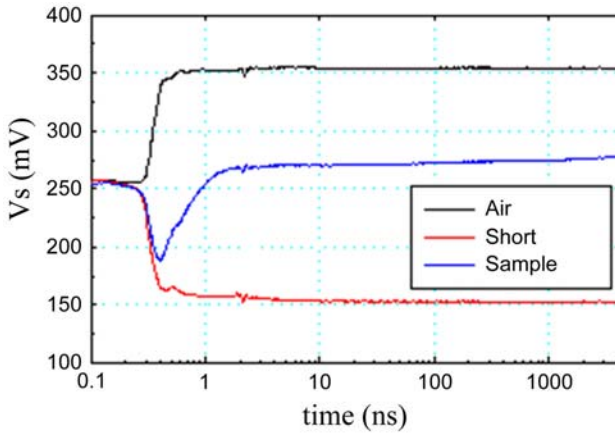


Figure 20.12 Characteristic shapes of TDDS signals during measurements.

where $V_{in}(t)$ is the incident voltage (step function), $V_R(t)$ is the reflected signal, and Z_0 is the characteristic line impedance [39]. Since $V_{in}(t)$ is known, by measuring $V_s(t)$, $V_R(t)$ can be calculated and, thus, also $I(t)$. The dielectric permittivity is then given by

$$\varepsilon^*(\omega) = \frac{1}{i\omega Z_0 C_0} \frac{\mathcal{F}\{I(t)\}}{\mathcal{F}\{V_s(t)\}} \quad (20.27)$$

where the operator $\mathcal{F}\{\cdot\}$ is the Fourier transform. The dielectric parameters can also be expressed in terms of a response function to the impinging step voltage at the point of reflection from the sample/transmission line interface. In this case, the charge build-up, $Q(t)$, across the electrode interfaces is given by:

$$Q(t) = C_0 \cdot \left[\varepsilon_\infty \cdot V_s(t) + (\varepsilon_s - \varepsilon_\infty) \cdot \int_0^t \frac{d\phi(t-t')}{dt} \cdot V_s(t') dt' \right] \quad (20.28)$$

where $\phi(t)$ is the response function, and it is related to the permittivity by

$$\varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \cdot \mathcal{F}\left\{\frac{d\phi(t)}{dt}\right\} \quad (20.29)$$

Several approaches to calibrate the measurement parameters have been proposed in the last decades [44,59–63]. To enhance the calibration of the system and increase the SNR, well-known reference materials are used to override the effect of the transmission line transfer functions. When filled with a well-known material (i.e., with a well-known dielectric permittivity

spectrum), reflection from the sample cell is used along with the open-load and short-load to better model the sample-cell capacitance. A significant advantage of the reference method is its higher sensitivity when the well-known material has a dielectric spectrum similar to that of the material under study. It is worth noticing that the approaches presented here hold true only for situations where hardware instabilities (including jitter, time drift, sweep speed errors, etc.) can be neglected.

20.3 Data-treatment

Upon obtaining from the measurements the raw data of the dielectric spectrum (complex permittivity), one needs to perform some data-treatment procedures to subtract common artifacts and noise and obtain an analytical model that fits the numerical results.

20.3.1 Electrode polarization

Typically, when performing DS of conducting systems that contain dissolved free ions (for example, colloids and cell suspensions), a phenomenon called Electrode Polarization (EP) occurs: When applying an electric field, dissolved free ions tend to move towards and accumulate on the electrode-suspension interfaces, leading to the development of ionic double layers in such regions (Fig. 20.13A). Simply put, the electric potential drops significantly in the polarization layers, leading to a strong polarization of those

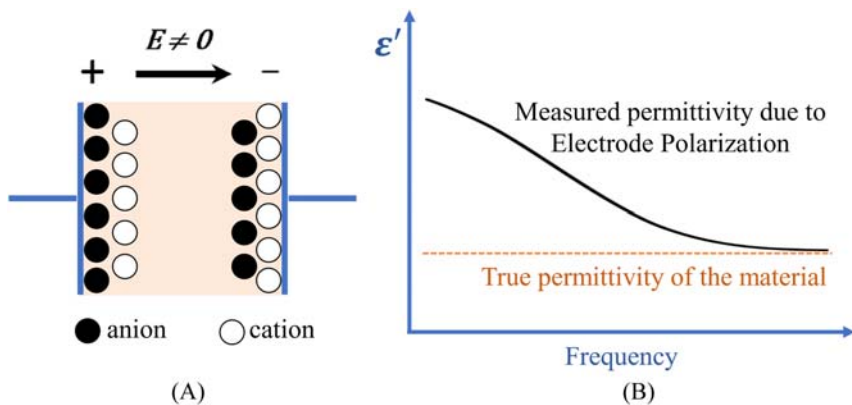


Figure 20.13 A schematic explanation of the Electrode Polarization (EP) effect: (A) The ionic double-layer development nearby the electrodes; (B) The masking of the measured signal due to the EP phenomena.

layers and, in the worst case, an almost absence of the electric field in the actual suspension [64,65]. EP represents one of the most significant challenges when characterizing the complex permittivity at low frequencies. The resultant capacitance of these layers can dominate the signal at the lower frequencies, masking the relaxation of the bulk sample (see Fig. 20.13B). This phenomenon depends on the electrical conductivity and temperature of the sample, the structure, composition, and roughness of the electrode surface, and it can present a significant impediment to the analysis of dielectric spectra. The resultant spectra can overlay the relaxation process of interest, leading to difficulties in interpreting the data. Electrochemical reactions on the electrode can further complicate the interpretation of the data by adding long-term instability to the measurements, thereby affecting reproducibility. This depends on the material of the electrode and the amplitude of the signal.

Consequently, EP's understanding, treatment, and correction lie at the heart of any successful DS or impedance spectroscopy application to biological systems [64–67]. Correction of EP is based on two approaches (generally both are used): apparatus-based compensation (e.g., using different sample holder designs and electronic circuits) and analytical postprocessing methods. Among the apparatus-based approaches, one can find electrode separation variation, four-electrode sample cell, high surface area electrodes, and high current density methods [14,25]. Postprocessing methods rely on a description of the electric double layer by a detailed many-body theory, incorporating long-range interactions of the motion of charges in a solid or liquid. These models yield analytical functions, either in the frequency domain or in the time domain of the EP process [68].

One particularly successful analytical approach is to consider the equivalent circuit of series impedances shown in Fig. 20.14, where Z_s represents the impedance of the bulk sample and $C_v(i\omega)$ is the complex impedance of a fractal ionic double layer at the electrode/solution interface, giving rise to EP (see Eq. 20.30) [69].

$$C_v(i\omega) = R_p(R_p C_p)^{-\nu}(i\omega)^{-\nu} \quad (20.30)$$

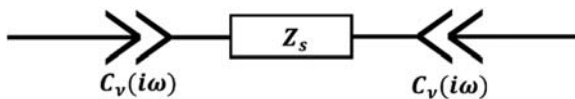


Figure 20.14 The equivalent circuit for a conductive dielectric sample with recaps representing the electrode polarization contribution to the signal.

The exponent, $0 < \nu \leq 1$, results from the fractal double layer at the electrode surface. If the electrodes are identical, they can be summed to a single element, as it depends on the electrode material, surface, and geometry. Consequently, for cylindrical cells, the contribution to EP from each electrode will be different. For $\nu = 1$, one obtains $C_\nu(i\omega) = (i\omega C_p)^{-1}$, where C_p is the pure capacitance of a perfect double layer. For $\nu = 0$, one has $C_\nu(i\omega) = R_p$, that is, the electrode surface resistance. Reality falls somewhere between. The values of C_p , R_p and ν greatly depends on the quality and preparation of the electrode surface [69].

In practice, special care must be taken for an apparatus-based reduction of the EP process, for example, ultrapolishing the electrodes using rotatory electrochemical mechanical polishing [70]. In Fig. 20.15 a mirror effect on the electrode surface can be appreciated. This picture was taken during the experiments of David et al. [71] for measuring the β -dispersion of a suspension of red blood cells. Minor mesoscopic scratches on the electrode surface will distort the EP process models (see Fig. 20.15) and directly affect the β -dispersion frequency range of the suspension.

Analytical descriptions of the EP phenomenon were first offered by Helmholtz [72]. The model considered the formation of a layer of absorbed ions along the electrode surface due to the migration of free ions in solution under the influence of an external field. This layer will attach to a further layer of an oppositely charged ion, held by electrostatic attraction. According to the difference in adsorption and solubility between different ions, the formed layer might be charged with the same polarity as the electrode. This arrangement is called the electrical double layer or the *Helmholtz* double-layer model [73].

Other models have considered diffusion of ion transport [73,74], a model in which the potential drop over the diffuse layer is modeled as an

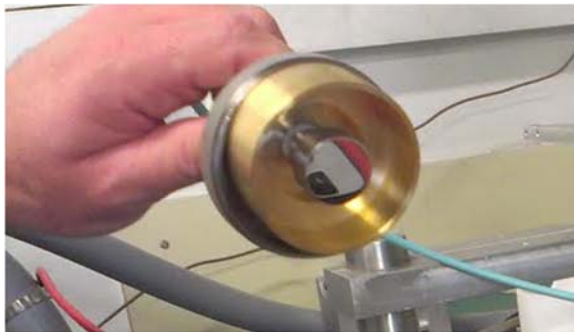


Figure 20.15 Electrode surface after electrochemically aid mechanical polishing.

exponentially decreasing function of distance. More robust models include a fractal approximation of the double-layer formation [68,75].

It is important to note that EP governs the response signal at low frequencies. For instance, in the time domain, the parasitic signal is time delayed from the sample's step response function, making it relatively easy to extract and correct the acquired signal [71,75].

20.3.2 Analysis of experimental data and fitting

The practical challenges, possibilities, and limitations of fitting the data obtained from the measurements to accepted theoretical models deserve an honest discussion. Dismissing its importance to just the ability to find “good-enough” numerical values to the parameters can be misleading, especially when working with complex systems (such as biological samples). Systematic work during data fitting is the critical element for extracting accurate models able to describe the physics of the system.

A simplified workflow for the researcher looks as follows:

1. Carefully reduce electrode polarization effects according to the specific sample cell used.
2. Identify relaxation processes in the spectrum and assign them an appropriate model function.
3. Fit the models' parameters to the spectrum.
4. Are the values obtained logical?
 - a. If so, you have fitted the model successfully.
 - b. If not, some perturbation at the initial values of the fitting may render some different results while escaping undesired local minima. Then, return to step 3.

Answering the question of step 4 requires experience and a solid understanding of the underlying physics of the process under study. In some cases, a researcher can use the reverse approach: fit the spectrum to some model and then compare the physical model to the system's behavior observed with other methodologies. As discussed earlier, the dielectric permittivity is an intrinsic property of the system, which is a function of its thermodynamic state, that is, in addition to being a function of frequency, it also depends on external variables like temperature, pressure, and others. This dependence is especially useful for obtaining the proper fitting to the spectrum. For instance, having measured the system at different temperatures, do the fitting parameters behave through the temperature sweep as expected from the theoretical models? Do they change

accordingly? If so, we have successfully fitted the data to the model. An illustrative discussion of the pitfalls and problems of fitting complex dielectric data can be found in [14].

In addition to the physics problem, fitting a model to numerical data presents the eternal problem of solving nonlinear equations. Systems of nonlinear equations are heavy and complex and require a significant volume of computation, and their success depends as much on the method chosen as on the numerical problems involved and the researcher's skills. Generally, this system does not allow the so-called exact methods that a solution is obtained after a certain number of iterations, except for some lucky (educated) inspiration. Only approximate iterative methods are available; they approximate the solution until certain conditions are satisfied.

In 2004 Axelrod et al. [75] developed software that reduces the problem of dielectric data analysis to choosing the appropriate model functions and an initial estimation of their parameters' values. The use of the maximum likelihood method, based on a temperature sweep of the sample, has provided consistent and accurate results of the numerical fitting to the spectrum. This methodology also allows a phenomenological approach to obtain the dependence of dielectric parameters on temperature without assuming a particular physical model. Nevertheless, if such a routine is incautiously overused, the final result will most likely be erroneous.

20.3.3 Literature example

The data in Fig. 20.16, taken from [76], present the dielectric losses of a Potassium Tantalate Niobate (KTN) crystal measured in the temperature range -120°C to 460°C and frequency range from 101 to 1 MHz. The figure shows only the paraelectric phase of the crystal (above $T_c = 295\text{K}$). The dielectric landscape is rich, showing in the paraelectric phase two activated processes and dc conductivity component. The measurement was made using a Novocontrol GmbH alpha dielectric spectrometer, with the sample temperature controlled by a Quattro temperature controller [76]. The measured complex dielectric permittivity for each temperature was modeled using a sum of two Cole–Cole functions: Eq. (20.13) with $0 < \alpha \leq 1$, $\beta = 1$, and a DC conductivity component.

The workflow described in Section 20.3.2 was followed to make the fitting. An important point to note here is the $\chi\{x_i\}$ function used to

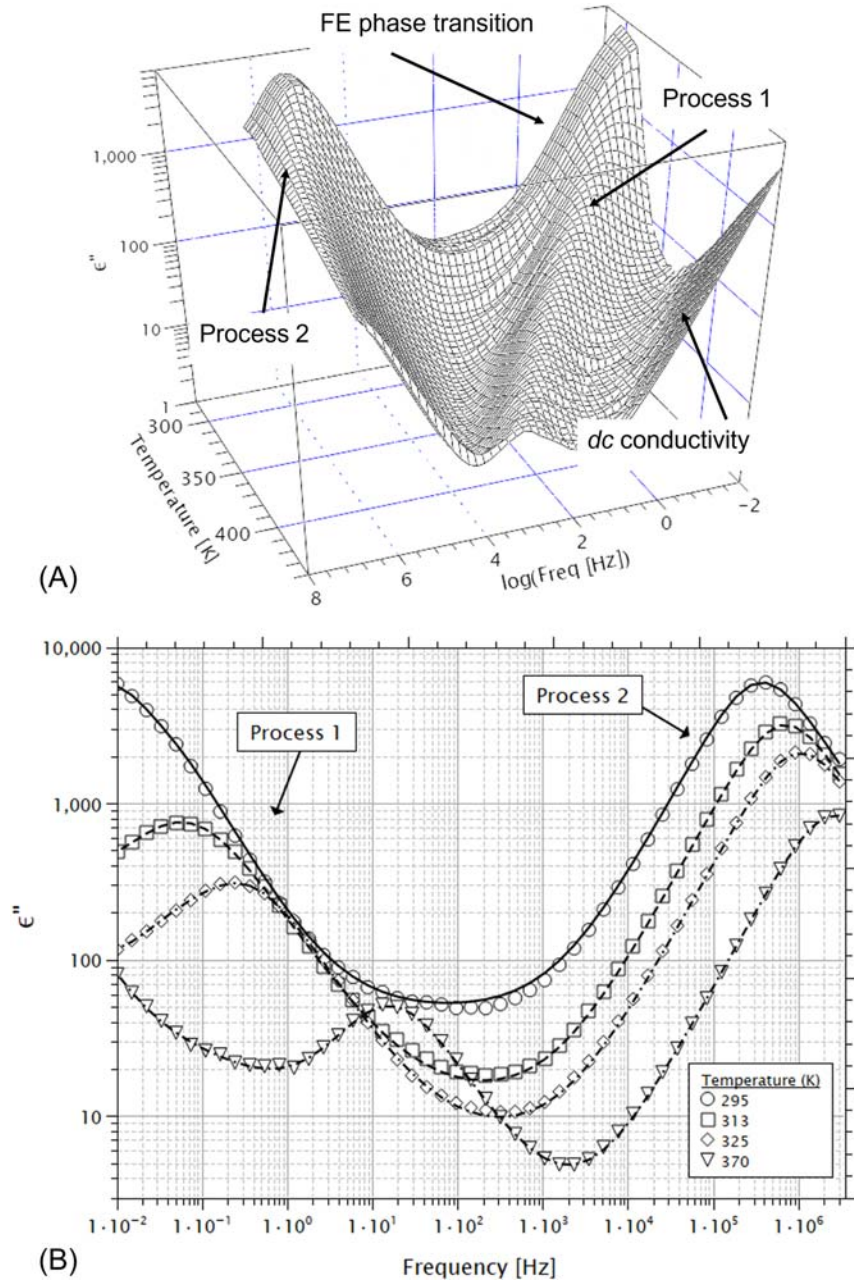


Figure 20.16 The dielectric losses of a ferroelectric crystal as a function of frequency and temperature (A) 3D representation and (B) frequency dependences at different temperatures. The symbols are the experimental data, and the lines are the relevant fitting function data. *Reproduced from P. Ben Ishai, C.E.M. De Oliveira, Y. Ryabov, Y. Feldman, A.J. Agranat, Glass-forming liquid kinetics manifested in a KTN: Cu crystal, Phys. Rev. B. 70 (13) (2004).*

assess the fit. In common iterative optimization algorithms, such as Levenberg–Marquardt algorithm [77], the $\chi\{x_i\}$ function is defined as:

$$\chi(\varepsilon, \hat{\varepsilon}) = |\varepsilon - \hat{\varepsilon}\{x_i\}|^2 \quad (20.31)$$

where ε represents the experimental dielectric permittivity, $\hat{\varepsilon}$ is the model function dependent on the parameter set $\{x_i\}$; the summation over the parameter set and frequencies is implied. The variation of the parameter set leads to the minimization of $\chi(\varepsilon, \hat{\varepsilon})$.

The definition above is quadratic and in the case of a large variation in dielectric values between low and high frequencies (see the values of the dielectric losses in Fig. 20.16B), it is almost impossible to converge to a suitable fit. In such a case one can employ a logarithmic measure:

$$\chi(\varepsilon, \hat{\varepsilon}) = |\log(\varepsilon') - \log(\hat{\varepsilon}')|^2 + |\log(\varepsilon'') - \log(\hat{\varepsilon}'')|^2 \quad (20.32)$$

where the summation is once again implied. This measure allows the $\chi(\varepsilon, \hat{\varepsilon})$ function to converge, despite orders of magnitude differences in values of the dielectric permittivity between high and low frequencies. This routine is implemented in the software described by [75].

Representative fits are shown in Fig. 20.16B. The derived fitting parameters reveal much of the nature of these activated processes. However, we will discuss only the relaxation times of each process [τ in Eq. (20.13)] presented in Fig. 20.17.

Process 1 exhibits Arrhenius temperature behavior [Eq. (20.33)]:

$$\tau(T) = \tau_0 \cdot e^{\Delta E/k_B T} \quad (20.33)$$

where k_B is Boltzmann's coefficient. The activation energy $\Delta E = 0.94 \text{ eV}$ coincides with the activation of DC conductivity in the crystal (Fig. 20.17A). This implies an electron hopping process that manifests as a DC conductivity in higher temperatures. Process 2 (Fig. 20.17B) is more complicated, exhibiting Vogel Fulcher Tammann (VFT) behavior [Eq. (20.34)] [78]:

$$\tau(T) = \tau_0 \cdot e^{\Delta E_{VFT}/k_B(T-T_0)} \quad (20.34)$$

with $\Delta E_{VFT} = 0.02 \text{ eV}$ and $T_0 = 228 \text{ K}$. This process originates from the hopping of Cu dopants, stochastically distributed in the crystal, around the A site of the perovskite structure of the crystal lattice. At low temperatures, this behavior is cooperative, akin to a glass-like system. Differential Scanning Calorimetry confirms that the presence of these dopants leads to an excess of entropy at the ferroelectric phase transition

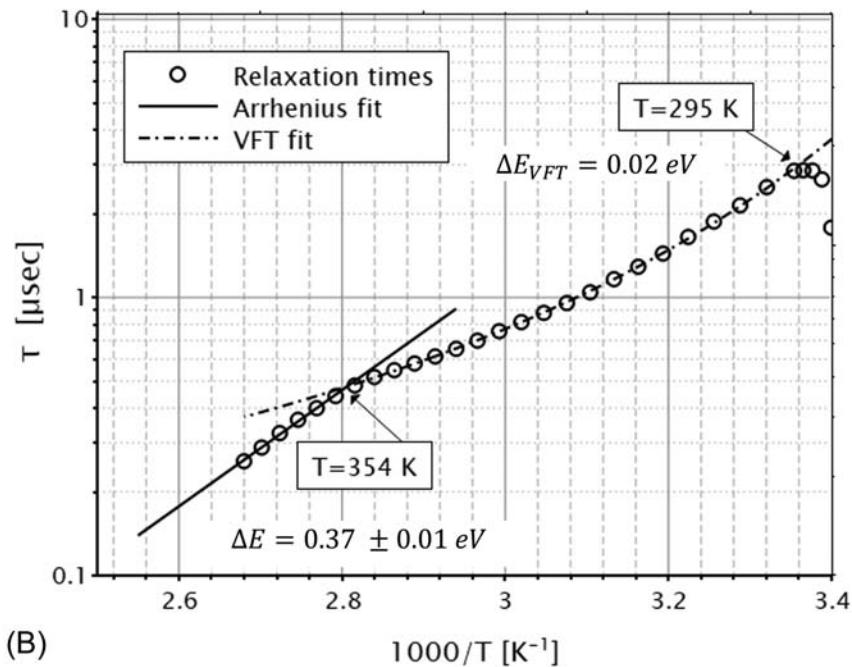
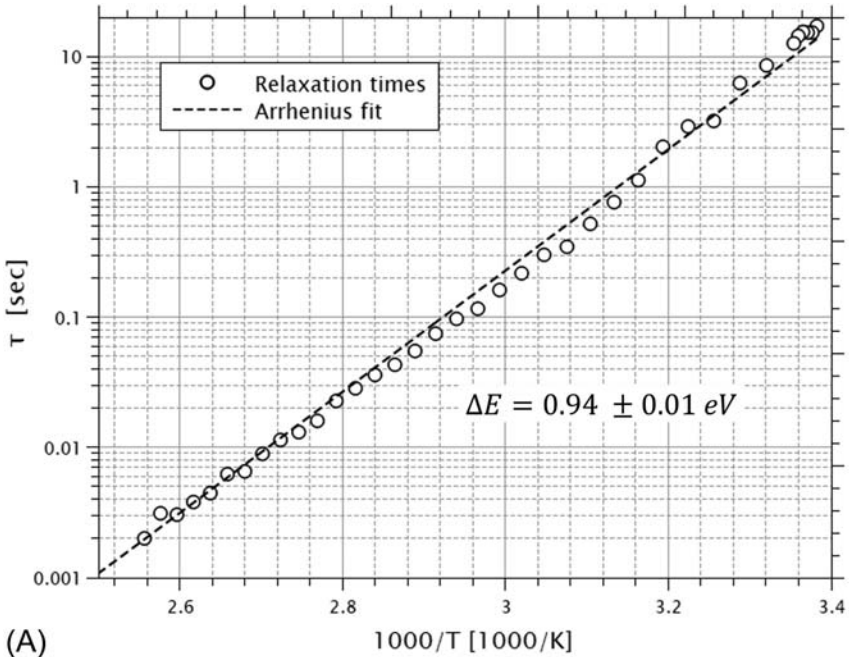


Figure 20.17 The derived relaxation times of (A) Process 1 and (B) Process 2 of the measured data in Fig. 20.17. Reproduced from P. Ben Ishai, C.E.M. De Oliveira, Y. Ryabov, Y. Feldman, A. J. Agranat, *Glass-forming liquid kinetics manifested in a KTN: Cu crystal*, *Phys. Rev. B* 70 (13) (2004).

equivalent to the characteristic energy derived from the VFT fitting [76]. At temperatures T above 354K this process degrades to an Arrhenius law with $\Delta E = 0.37\text{eV}$, where thermal agitation is such that these dopants behave independently.

20.4 Summary

Broadband Dielectric Spectroscopy (BDS) has now been a mainstay materials science tool for 60 years. Yet, it is still an evolving field, as new theoretical input sheds light on microscopic reorientations in complex systems that influence the measured signal. At its core, it is sensitive to cooperative relaxations of the molecular moieties of the sample. This leads to the emergence of the mesoscopic as a critical length scale, and BDS is preeminent in its ability to probe the entire time scale involved.

Advances in instrumentation and technique have made the method accessible to a wide range of researchers who are not necessarily experts in dielectric science. However, as we have pointed out earlier, there are several pitfalls of which to be wary. The description above of the methodology pertains to what one would describe as traditional DS. In recent years, however, the basic principles of the method have been expanded to nanoscale length scales by applying dielectric theory to the I/V curves read from Atomic Force Microscopy, accessing directly atomic polarizability [79–81]. Other notable emerging fields are in nonlinear DS techniques [82].

In short, the versatility of DS can be harnessed in a wide scope of scientific disciplines, including communications, biomedical sciences, materials monitoring, and remote sensing. A bright future awaits.

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CHAPTER 21

Chemical analysis with neutrons

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21.1 Introduction

Neutron activation analysis (NAA) methods belong to nuclear analytical techniques. This is a branch of analytical science, where natural or induced radioactivity or nuclear reactions are used to obtain information on the composition of the sample. Two basic types of NAA exist from a practical point of view—NAA and Prompt Gamma Activation Analysis (PGAA, or PGNAA). They are common in the roots, that is, the identification and quantification of neutron-induced reaction product nuclei in a sample are carried out via the detection of emitted gamma radiation. Still, the experimental procedure, instrumentation, and energy range of gamma rays differ, which makes them two distinct but complementary techniques. If the irradiation and the detection of neutron-induced radioactivity are separated in time and space, this is the “traditional” NAA. In Instrumental NAA (INAA) no chemical sample treatment is applied, but we rely on gamma spectroscopy to achieve selectivity, in contrast to Radiochemical NAA (RNAA) where the separation and/or concentration of single elements is done before and/or after the irradiation by wet chemical methods. We focus only on the more non-destructive approach of INAA and call this simply NAA throughout the following chapter. In PGAA, the neutrons are transferred to the sample in form of a beam, and the irradiation and the detection take place simultaneously.

The history of NAA is a fundamental pillar for its present and future. In its early days, the method was very closely intertwined with the progress in the fields of radioactivity research with well-known pioneers such as Antoine-Henri Becquerel, Marie Skłodowska Curie, Pierre Curie, and Ernest Rutherford. The discovery of the neutron [1] (see Chapter 8) was soon followed by works on so-called “artificial radioactivity” induced by α particles or neutrons, which were of crucial importance. Initially,

nuclear reactions with α particles were investigated [2], and later, also neutron-induced reactions [3,4] were utilized. The real cornerstone of NAA as a method of analysis was finally laid by György Hevesy and Hilde Levi in 1936. Their publication “The Action of Neutrons on the Rare Earth Elements” [5] was the first paper on the analysis of the elemental composition in samples by neutron activation. Hevesy and Levi compared the activation of an unknown mixture with that of well-defined mixtures of rare earth elements. The neutrons were produced with a radium-beryllium source by an (α, n) reaction and additionally moderated by paraffin wax. Because they simply used Geiger–Müller counting tubes at that time, which do not provide energy resolution, the elements could not be identified by specific gamma peaks. Instead, the different half-lives were used to quantify the mixing ratios. During the bombardment of paraffin with neutrons, the phenomenon of radiative neutron capture has also been recognized [6]. The first useful prompt gamma experiments were only realized in the 60s [7]. In the following decades, the NAA developed into a highly effective method for trace element analysis. Reactors play a key role in its success because high neutron flux is necessary to achieve high analytical sensitivities.

Other significant milestones were the development of detectors with energy resolution—at first scintillators and later semiconductors (especially HPGe), the introduction of advanced electronics and computers for fast signal processing, and the use of anticoincidence setups for active background reduction, also known as Compton-suppression. Nowadays, several related methods are available, which evolved from the classical NAA, such as the aforementioned PGAA with the first reactor-based application in the 1960s [7,8]. The continued success of these methods is based on a unique combination of advantages such as low matrix dependence, a high degree of non-destructiveness, comparatively simple sample preparation, low detection limits for many elements, as well as high reliability, traceability, precision, and accuracy of the results.

21.2 Physical principles and theory

21.2.1 Neutron characteristics

The neutron is not an elementary particle, as it is composed of three quarks. A neutron is only stable if it is bound to the atomic nucleus; free neutrons disintegrate into a proton, an electron, and an antineutrino (See Chapter 8). Therefore, neutrons have to be produced whenever they

are needed. Free neutrons are classified based on their kinetic energies (Fig. 21.1). Neutrons that are liberated from nuclear reactions have high kinetic energies, in the order of MeV ($100 \text{ eV} < E < 20 \text{ MeV}$), therefore they are called fast neutrons. The distribution of the fission neutrons that are produced in research reactors for scientific applications follows the Watt formula [9]. The neutrons interact with the atoms of the surrounding medium and gradually lose kinetic energy. These partially slowed-down neutrons ($0.5 < E < 100 \text{ eV}$) are called epithermal. In the epithermal energy range, the energy distribution can be approximated with a $1/E^{1+\alpha}$ function [10]. In the end, most of the kinetic energy is transferred to the medium by subsequent collisions, and the neutron gets into thermal equilibrium with its environment; these are called thermal neutrons and follow the Maxwell-Boltzmann distribution [11]. Thermal energy is equivalent to $k_B T = 25.26 \text{ meV}$ as characteristic energy at room temperature. The corresponding wavelength is $1.8 \text{ \AA}$, while 2198 ms^{-1} is the most likely velocity [12]. Neutrons having even lower kinetic energies (about 5 meV) are called cold neutrons, while thermal and cold neutrons are collectively called slow neutrons.

21.2.2 Nuclear reactions

Nuclear reactions are abbreviated with a shorthand notation: $A(b, c)D = A + b \rightarrow c + D (+ Q)$, where A is the target nucleus, D is the

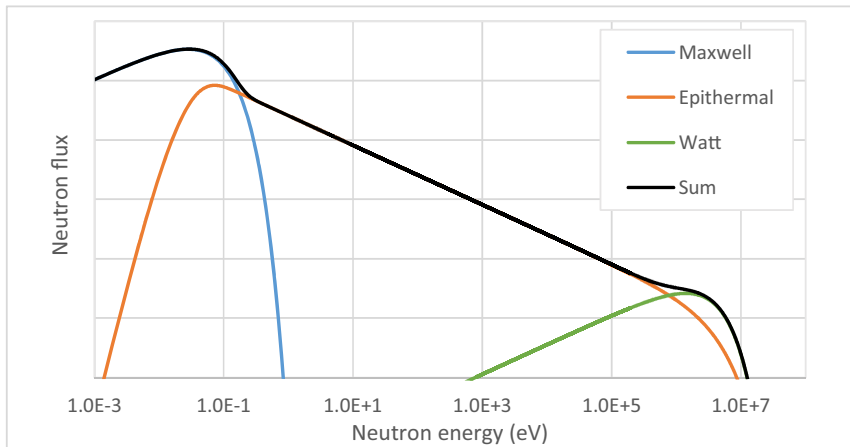


Figure 21.1 Energy distribution of neutrons in a research reactor (drawing by L. Szentmiklósi).

product nucleus, b is the projectile particle, c is the emitted particle, while the Q is the energy balance of the reaction. The reactions that take place only over a certain minimum kinetic energy of the projectile are called threshold reactions.

When a slow neutron is captured, the kinetic energy of these neutrons ($\sim \text{meV}$) is negligible, so the excitation energy of the compound nucleus originates from the binding energy of the neutron (7–9 MeV). The excited compound nucleus can release energy via various de-excitation channels, for example, by the emission of γ photons or a charged particle (Fig. 21.2). During the (n,γ) -reaction, which is the basis of the neutron activation techniques, the compound nucleus emits prompt- γ photons, starting from the capture state, and directly or via emission of a gamma cascade, it reaches the ground state ($\gamma_1 \dots \gamma_5$). The energies and intensities of the γ photons characterize the de-excitation process of the daughter nucleus with $(A+1)$ mass number and thus can be related to the parent nucleus. This nuclear reaction occurs mostly within 10^{-12} seconds, that's why these photons are called “prompt.” When the $({}^A_{Z+1}\text{X})$ product nucleus is stable, the reaction ends with the emission of prompt- γ photons, while if a radioactive daughter nucleus is formed, that transforms further to a stable one—mostly by emitting β^- particles with a $T_{1/2}$ half-life (or λ decay constant: $\lambda = \frac{\ln 2}{T_{1/2}}$). In a few cases, β^+ decay or electron capture may occur. These result in the emission of decay γ -photons (γ_6) that are the basis of the instrumental NAA.

21.2.3 Fundamental equations

For a nuclear reaction of interest, for example, (n,γ) reaction, our goal is to quantify the reaction rate, which is the linkage between the unknown

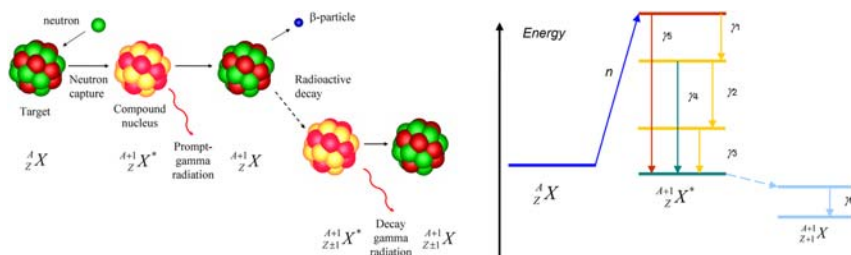


Figure 21.2 The (n,γ) reaction, which is the basis of the neutron activation techniques. The excited compound nucleus can release energy via the emission of gamma rays or charged particles (drawing by L. Szentmiklósi).

amounts of atoms to be analyzed and the experimental observables. To make the chemical analysis, in general, we need to know neutron field properties, that is the intensity and the energy distribution of the neutrons, $\Phi(E_n)$. This can be measured by irradiating a set of flux monitor foils, whose physical and activation parameters are precisely known [10].

The probability of a nuclear reaction between neutrons and the atomic nucleus is described by the quantity called cross-section (σ); its unit is the barn ($1 \text{ barn} = 10^{-28} \text{ m}^2$). For different reactions, we use specific cross sections, such as capture cross-section, scattering cross-section, neutron-induced fission cross-section, etc. In the activation analysis, we are interested in the capture cross-section: this is strongly dependent on the neutron energy, $\sigma(E_n)$, and it may differ by orders of magnitude between elements and even between isotopes of the same element. These values are tabulated in compilations [13]. In the case of slow neutron capture, every nucleus follows the $1/\nu$ law [14]. This means that the neutron capture cross-section (σ) is inversely proportional to the velocity of neutrons, that is with the square root of the neutron kinetic energy. A plausible explanation for this is that lower-energy neutrons spend more time near a given nucleus, therefore there is an increased chance of being absorbed. The σ is easy to calculate for slow neutrons from a reference σ_0 value, a cross-section corresponding to $\nu_0 = 2198 \text{ m s}^{-1}$ neutron velocity:

$$\sigma = \sigma_0 \frac{\nu_0}{\nu} \quad (21.1)$$

where $\sigma_0 = \sigma(\nu_0)$ is the thermal neutron capture cross-section.

As long as the $1/\nu$ law is valid, the exact knowledge of the neutron energy distribution can be eliminated from the calculations. The reaction rate, that is the number of capture reactions per second and per number of atoms in a polychromatic neutron field, can be expressed as follows:

$$\begin{aligned} R &\equiv \int_{E_n=0}^{\infty} \Phi(E_n) \cdot \sigma(E_n) dE_n = \int_{E_n=0}^{\infty} \nu \cdot n(E_n) \cdot \frac{\sigma_0 \nu_0}{\nu} dE_n \\ &= \sigma_0 \int_{E_n=0}^{\infty} \nu_0 \cdot n(E_n) dE_n = \sigma_0 \cdot \Phi_0 \end{aligned} \quad (21.2)$$

With this expression, we introduce the quantity of thermal equivalent flux, Φ_0 , in a way that the product ($\sigma_0 \cdot \Phi_0$) accounts for the observed capture rate. The thermal equivalent flux is a comparable measure between facilities to describe the elemental sensitivities or minimum detectable quantities in PGAA.

In NAA, however, the neutron energies cover a very broad range, from meVs to MeVs, where this simple concept is not valid. It is practical

to obtain the $R \equiv \int_{E_n=0}^{\infty} \Phi(E_n) \cdot \sigma(E_n) dE_n$ quantity as a sum of three terms, each dealing with the reaction rate related to a specific neutron energy domain: thermal, epithermal, and fast neutrons. The fast neutrons usually lead to a different product nucleus, so they have importance only when correcting for interference reactions. There are two commonly used conventions, the Høgdahl [15] and the Wescott [16] formalisms, to account for the other two, that is the thermal (Φ_{th}) and epithermal (Φ_e) activation. The Høgdahl convention splits the two domains at 0.55 eV, corresponding to the effective cut-off energy of a Cd cover (E_{Cd} or $\nu_{Cd} = \sqrt{2E_{Cd}/m_n}$), and by defining the so-called sub-cadmium and epicadmium fluxes. This comes from a practical point of view, as when irradiating a sample with or without a 1-mm thick Cd cover, the (n, γ) reaction rate is impacted by the strong neutron absorption of thermal neutrons by the ^{113}Cd .

$$R = \int_0^{\nu_{Cd}} \sigma(\nu) \varphi'(\nu) d\nu + \int_{E_{Cd}}^{\infty} \sigma(E) \varphi'(E) dE = G_{th} \Phi_{th} \sigma_0 + G_e \Phi_e I_0(\alpha) \quad (21.3)$$

Here, $I_0(\alpha)$ is the resonance integral, the integral of the cross-section over the epithermal energy range, modified with the epithermal shape parameter α .

$$I_0(\alpha) = \int_{E_{Cd}}^{\infty} \frac{\sigma(E) dE}{E^{1+\alpha}} (1\text{eV})^\alpha \quad (21.4)$$

G is the self-shielding factor, accounting for neutron depression which depends on the nucleus density. G_{th} is the same for all (n, γ) reactions, but the epithermal neutron self-shielding factor G_e differs between nuclides. With adequate sample preparation practices, both can be kept close to unity or can be corrected numerically [17,18].

When exposing the sample to a steady neutron field, the activity of a radionuclide of interest does increase linearly over time but approaches a maximum that is called saturation activity. At this point, the production and the decay of the radioisotope get into a dynamic equilibrium. This is quantitatively and generally described by the Bateman-Rubinson equations [19,20]. For each k radionuclide, one can define $\Lambda = \lambda + \Phi\sigma$, the total disappearance constant, considering both the production and decay, and $\Lambda^* = \lambda^* + \Phi\sigma^*$, the specific disappearance constant for the given decay branch, where λ is the decay constant. Using these notations, one

can solve the set of differential equations for various activation-branching-decay scenarios [21]:

$$\frac{dN_k(t)}{dt} = \Lambda_{k-1}^* N_{k-1}(t) - \Lambda_k N_k(t) \quad (21.5)$$

In the simplest case, the activity achieved during the t_{act} irradiation time relative to the maximum attainable is expressed by the saturation constant $S = 1 - e^{-\lambda t_{\text{act}}}$. After the end of the irradiation, the production is terminated but the decay of the radionuclide continues and the amount of radionuclide decreases exponentially until we start the counting, and even during its measurement time. This is considered via the decay-correction factor, $D = e^{-\lambda t_d}$, and the counting factor, $C = \frac{1 - e^{-\lambda t_c}}{\lambda t_c}$, respectively (Fig. 21.3).

The quantification of the radionuclides is usually done by means of gamma spectrometry.

21.2.4 Basics of gamma-ray spectrometry

21.2.4.1 Interaction of gamma rays with matter

Gamma radiation is electromagnetic radiation of high energy, that is short wavelength. Its interaction with matter is highly energy-dependent and three types of interaction mechanisms are relevant to our considerations. These are the photoelectric effect, the Compton scattering, and the pair production (Fig. 21.4). Photoelectric interactions are dominant at low energy, the pair production is at high energy, with Compton scattering is the most important in between.

The photoelectric effect is the most abundant interaction of low-energy gamma rays, where the total energy of the photon is transferred to a bound electron of the material (usually in the inner shells). That atom gets ionized, and an energetic electron is ejected that loses its kinetic

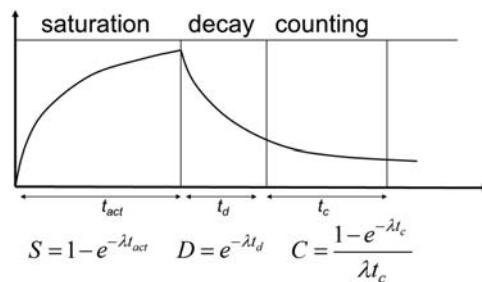


Figure 21.3 The saturation-, decay-, and counting-correction factors in NAA (drawing by Zs. Révay & L. Szentmiklósi).

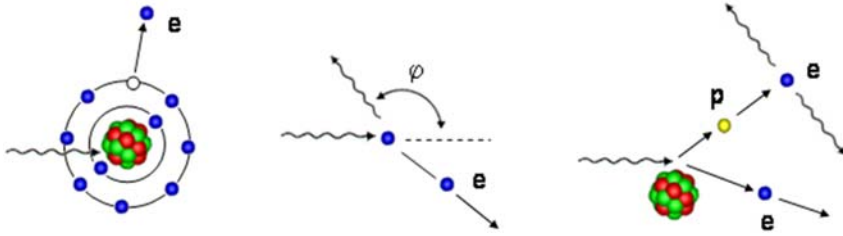


Figure 21.4 Three major types of interactions between gamma radiation and matter: the photoelectric effect (*left*), the Compton-scattering (*middle*), and pair production (*right*) (drawing by L. Szentmiklósi).

energy quickly and creates secondary electrons. The generated charge is proportional to the energy of the gamma photon.

During the Compton effect, the gamma photon is scattered on an electron in a loosely bound outer shell, which, like the photoelectric effect, is released from the electronic shell. Here, the energy transfer of the photon is only partial, and the energy is split between the photon and the recoil electron. Later, the photon may escape from the detector or take part in subsequent other interaction(s). The amount of energy transfer during Compton scattering is dependent on the angle of deflection and is given by the formula $E' = \frac{E_\gamma}{1 + \frac{(1 - \cos\varphi)E}{m_e c^2}} = \frac{E_\gamma^2}{255.5 \text{ keV} + E_\gamma}$. The maximum amount of energy is transferred when φ reaches 180 degrees, while no energy transfer takes place at 0 degree.

During the pair production, the photon creates an electron and a positron pair within the Coulomb field of a nucleus. For this, the energy of the photon must be greater than the combined rest mass of the electron and the positron, that is, 1022 keV. The resulting electron and positron also slow down in the material. After deceleration, the positron annihilates with an electron of the matter, and two photons, each with an energy of 511 keV are generated that, due to the conservation of energy and momentum, propagate in opposite directions. These photons can afterward take part in a Compton scattering and/or a photoelectric effect. If one or both photons escape from the detector's active volume without interaction, the detector will measure 511 or 1022 keV less than the original photon energy, respectively. This makes the single and double escape (DE) peaks in the gamma spectrum.

A fourth interaction type is called Rayleigh (elastic) scattering, when the energy of the gamma photon does not change, only the direction of the propagation.

One gamma ray can go through a chain of interactions before complete absorption or leaving the volume of interest. As its energy decreases step by step, the final step before absorption is often a photoelectric effect. During this chain of interactions, the entire energy of the original photon may or may not be transferred to the solid medium. In gamma spectrometry, we are interested in the full-energy transfer, which gives rise to the analytically useful peak.

21.2.4.2 General characteristics of gamma spectra

The complexity of interaction mechanisms is reflected in the features of the gamma spectrum (Fig. 21.5). For each gamma-ray energy, we make use of the full-energy peak (FEP), which is the result of a photoelectric effect, or a sequence of interactions resulting in a complete energy deposition. During Compton scattering, the energy is shared between the electron and the scattered photon as a function of the scattering angle [22]. If the photon escapes from the detector, a continuum is formed in the spectrum from the Compton-edge (CE, a sharp cut-off at the maximum possible energy transfer) towards lower energies, called Compton plateau (CP).

The low-energy part of the spectrum extends until the lower threshold energy, which is set by the discriminator level of the spectrometer to

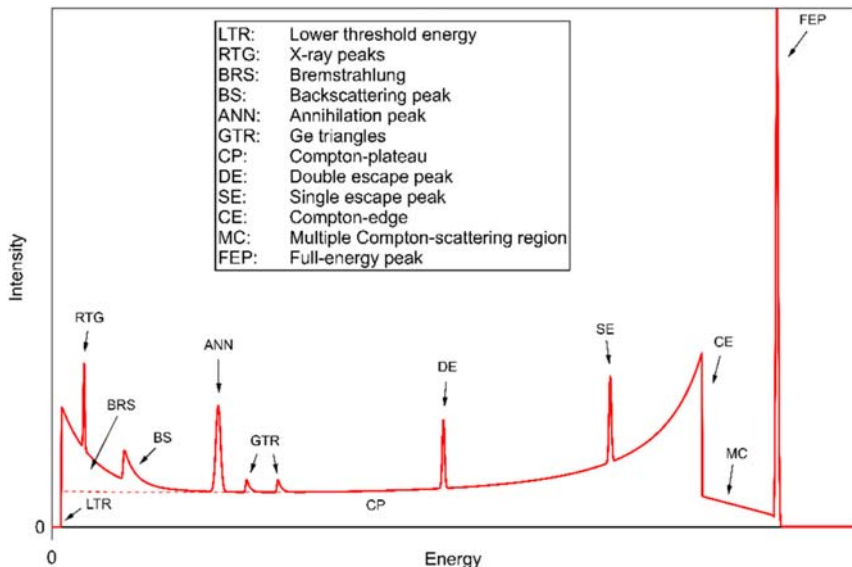


Figure 21.5 Characteristic features of gamma spectra (drawing by L. Szentmiklósi).

exclude the electronic noise. X-ray fluorescence peaks, bremsstrahlung (BRS), and backscattering (BS) components, as well as the annihilation peak at 511 keV (ANN), originate from the materials surrounding the detector [23]. Germanium triangles are the results of fast neutron interaction with the detector's material and therefore they are present only in PGAA. Single (SE) or DE peaks appear if one or both annihilation photons leave the detector, and the energy of the original gamma ray exceeded 1022 keV.

The response function of the detector for a given gamma photon energy is composed of the energy-dependent combination of the FEP, the Compton plateau, and the escape peaks. If the gamma radiation has more than one characteristic energy, these individual response functions stack up to form the spectrum. A lower-energy analytical peak, therefore, sits on the Compton background(s) of the higher energy gamma-ray(s) (Fig. 21.6). As the gamma spectra obey the Poisson distribution, the detectability of the peak is influenced by its amplitude relative to the standard deviation of the baseline. A higher level of baseline implies a larger amplitude of the peak to detect. This fact limits the dynamic range of gamma spectrometry, that is, the peak area ratio of two peaks in practice to 10^3 – 10^4 , and makes it necessary to assess the detectability conditions case by case, for each analyte-matrix combination separately.

The NAA spectra are simpler than those of PGAA (Fig. 21.7). They are recorded in the gamma energy range of 15 keV to about 3 MeV and typically consist of a few (dozen) well-separated, Gauss-like peaks, on a baseline increasing towards low energies. Peak positions identify the radionuclides, while peak areas, corrected with the half-lives, determine the quantities. If the spectrum contains radionuclides with highly different half-lives and is taken at a changing count rate, the Poisson statistics may be violated. This fact is addressed during the acquisition and evaluation

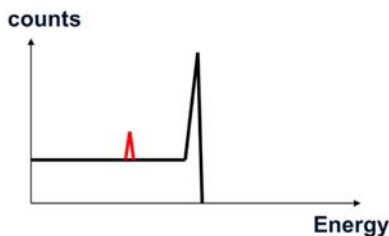


Figure 21.6 A lower-energy analytical peak, detected on the Compton plateau of a higher energy gamma-ray (drawing by Zs. Révay & L. Szentmiklósi).

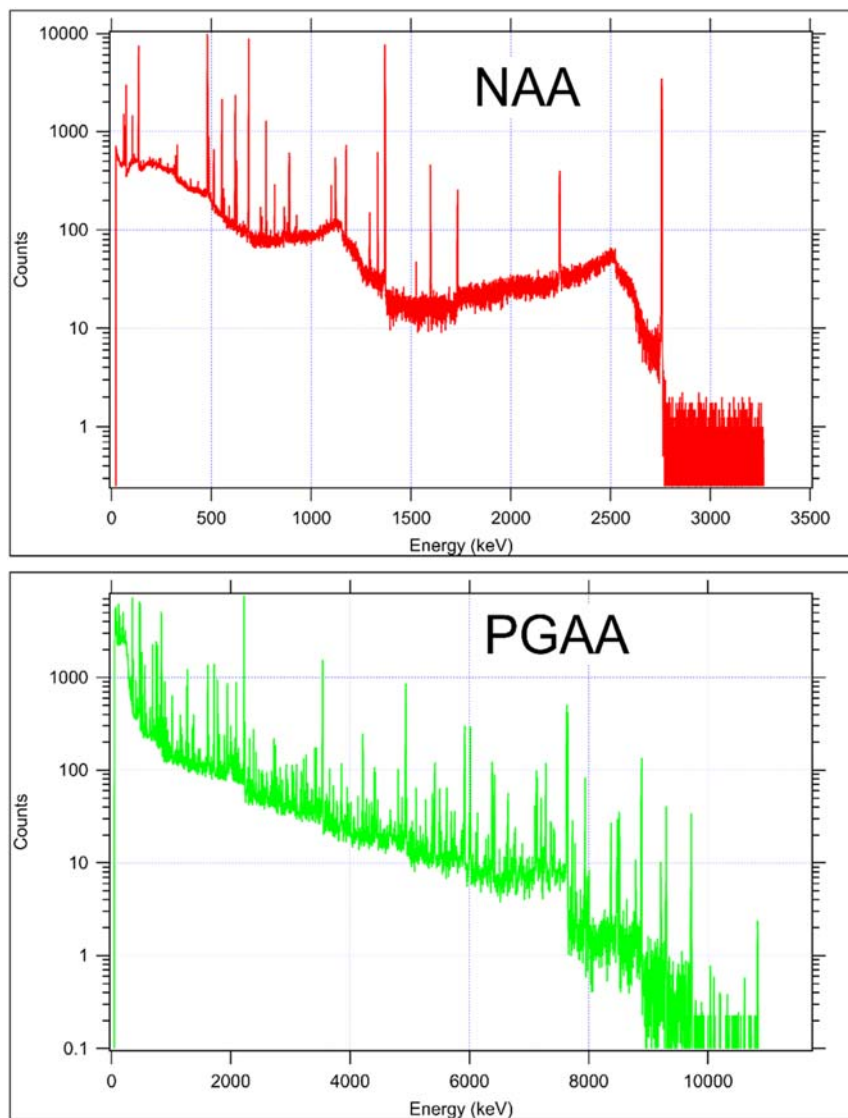


Figure 21.7 Comparison of NAA and PGAA spectra. In the NAA spectra (upper panel), the gamma energy range is from 15 keV to 3 MeV, and the spectrum consists of a few well-separated peaks. PGAA spectrum (lower) is more complicated, the energy range is between 45 keV and 12 MeV and consists of 100–1000 of analytical peaks (drawing by L. Szentmiklósi).

stages. In PGAA, the typical energy range is much broader, from 45 keV to 12 MeV. A complicated spectrum with hundreds-thousands of Gauss-like peaks is experienced, where it is critical to keep the baseline level as low as possible.

The dynamic range in the PGAA is determined by the nuclear parameters of the components, the beam background and the detector's peak-to-background ratio. In NAA, the time of the counting is an additional parameter to tune the detection conditions. Therefore, we record multiple spectra at different times following the irradiation, so that long-lived components can be better detected when the short-lived radionuclides had already decayed away.

21.2.4.3 Detector types

During the detection process, we aim to transfer the gamma photon's energy to the detector material and extract an electronic signal proportional to the gamma energy. Suitable detectors shall have high efficiency, energy resolution, count rate tolerance, good stability as well as affordable price.

In activation analysis, a scintillator and semiconductor detectors are applied. The scintillation detector transfers the energy to atoms that de-excite by emitting visible (or UV) light which is then collected and amplified by a photomultiplier. In semiconductor detectors, energetic primary electrons are created at first that lose their energies by ionizing and exciting the atoms of the detector medium, resulting in large amounts of electron-hole pairs. One electron-hole pair is formed in Ge by only 2.96 eV energy; this is the key factor behind its excellent energy resolution. The number of electron-hole pairs is strictly proportional to the gamma photon's energy deposited in the detector crystal. Finally, this charge will be converted to a pulse, whose amplitude (or time integral) is related to the photon energy. High-purity Germanium (HPGe) detectors can be classified based on their doping materials (p-type or n-type) and geometries of the crystal: planar detectors are suitable to detect low-energy gamma radiation with the best possible energy resolution, while the coaxial arrangement is the most appropriate choice in routine analytical practice.

21.2.4.4 Electronics

The raw signal of the detector is typically an exponential pulse with a time constant of about 45 μ s (RC feedback preamplifier) or a voltage-level step

(transistor reset preamplifier). Traditionally, the goal of the first stage of signal processing, realized by the spectroscopy amplifier, is to form the pulses to shorter Gaussian-like signals (about 4–6 μs time constant) that are still strictly proportional to the amplitude (area) of the original pulse but is smoothed and noise-filtered. This signal shaping improves the signal-to-noise ratio and the count rate tolerance of the spectrometer. This shaped signal is then fed into an analog-digital converter (ADC) that reads its peak amplitude. Finally, a multichannel analyzer stores the event in a bin of the energy histogram, according to the corresponding voltage value. To operate the detector, a low-voltage power supply, and a high-voltage unit are needed as well. All these electronic units were manufactured in a modular NIM format since the seventies, which standardized the interfaces and geometrical specifications, so models of different suppliers are interchangeable and compatible.

After the year 2000, a new technology started to be commercialized based on digital signal processing (Fig. 21.8). The signal of the detector preamplifier is immediately digitized by a flash ADC at the speed of tens or hundreds of MHz and the rest of the signal forming is carried out

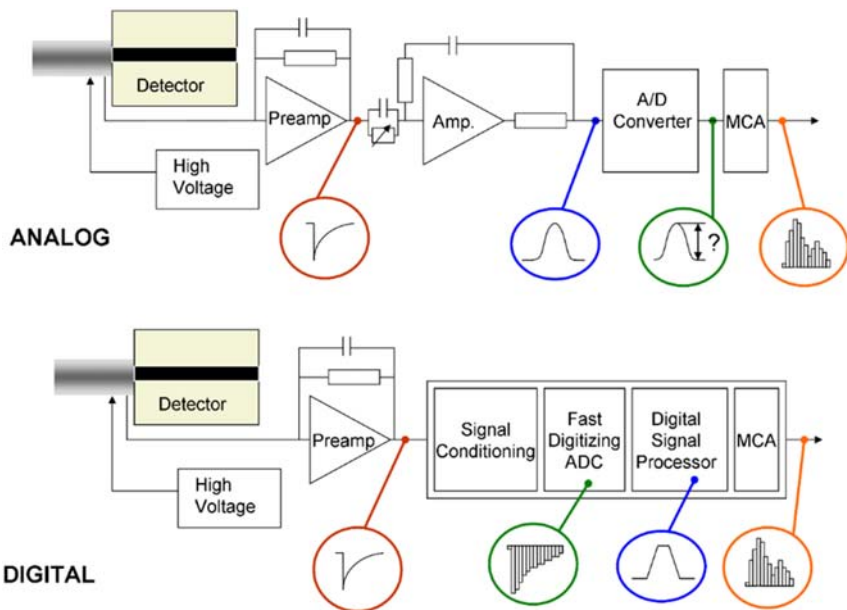


Figure 21.8 Block diagram of the analog and the digital signal processing (drawing by L. Szentmiklósi).

numerically, using mathematical algorithms applied to the digitalized voltage data stream. The simplest form of digital data processing is a paired moving average filter that results in a trapezoidal signal shape rather than a Gaussian. The numerical signal treatment offers greater flexibility for the on-the-fly data processing, as well as facilitated the list-mode data acquisition, where energy and timing properties of individual events are computed and stored in the computer for detailed offline postprocessing. These devices are often integrated desktop models, where most settings can be done within the control software, a great approach to improve reproducibility.

In some cases, we use more than one detector in our detection system, connected to a more complex signal processing chain. This makes it possible to apply time coincidence or anticoincidence patterns. Coincidence detection allows relating gamma rays to each other, establish the level schemes, and study the de-excitation processes of the radionuclides, while anticoincidence gating may be set up to reduce the level of the Compton continuum in the gamma spectrum relative to the analytical peak. This measurement technology is called Compton-suppression and is extensively used in PGAA. For this purpose, the main detector made of HPGe is surrounded by bismuth germanate (BGO) or sodium iodide (NaI) scintillator-based crystal(s) and heavy external shielding (e.g., lead), blocking all external radiation except for the photons arriving from the sample through a collimator. If the HPGe and the suppressor detectors detect valid signals at the same time, we can be sure that it is not an event that had full energy deposition within the HPGe crystal, so those events are selectively discarded. This technique can result in up to an order of magnitude reduction in the Compton baseline, without any loss from the FEP, as shown in Fig. 21.9.

The nuclear spectrometers, while being busy with processing an event, cannot deal with an other one properly. This time interval is called the dead time (DT). Its complement, the live time (LT) as well as the real (RT) measurement time are monitored by the spectrum acquisition software. The dead time, $DT = (RT - LT) / RT$, is dependent on the settings of the spectrometer and the count rate, so at high count rates, the DT loss is higher. Using the spectrometers at high count rates is generally not favorable, as it may lead to compromised spectrum quality. One can adjust the sample-to-detector distance (NAA) or the neutron beam intensity (PGAA) to keep the DT under control. Further, if the count rate changes during the acquisition, it cannot be characterized by a single number.

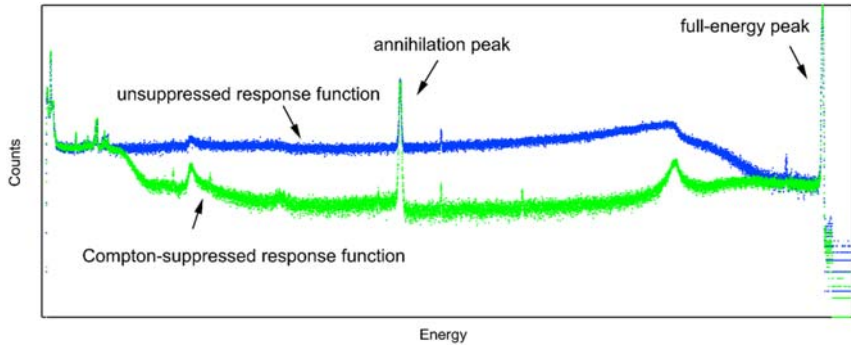


Figure 21.9 Compton-suppression mode is extensively used in PGAA, as it results in up to an order of magnitude reduction of the Compton baseline, without any loss from the full-energy peak (drawing by L. Szentmiklósi).

The proper assessment of this fact is especially important to handle cases where short-lived and long-lived radioisotopes are to be detected alongside. Special technologies exist (loss-free counting, LFC, or zero dead time, ZDT), where two spectra, a corrected and an uncorrected, are accumulated concurrently, and each event is corrected by the DT valid for the narrow time interval when it has been processed. This restores the true peak areas but results in the non-Poisson distribution in the corrected spectrum, while improper peak areas, but correct Poisson statistics are obtained in the uncorrected one [24]. Only the combined evaluation of the two spectra leads to unbiased peak areas and counting statistics. This has become routine in the modern NAA practice.

21.2.5 Monte Carlo simulations

The Monte Carlo method is a computational algorithm where computer-generated (pseudo-) random numbers are used to model the propagation of the neutrons, photons, or electrons in the matter at the event level and draw conclusions about the physical effect based on the law of large numbers. In this way, complex interaction schemes and geometries can be handled that cannot be calculated with closed formulae. To quantify the probabilities of the elementary interactions, a comprehensive nuclear reaction cross-section library is used. The measurement geometry can be defined with planes, simple geometrical bodies, and logical operations (union, intersection) on them. Thus, highly complex geometry and radiation field can be studied with success. Two prominent and widely validated Monte Carlo software are MCNP6 [25] and geant4 [26].

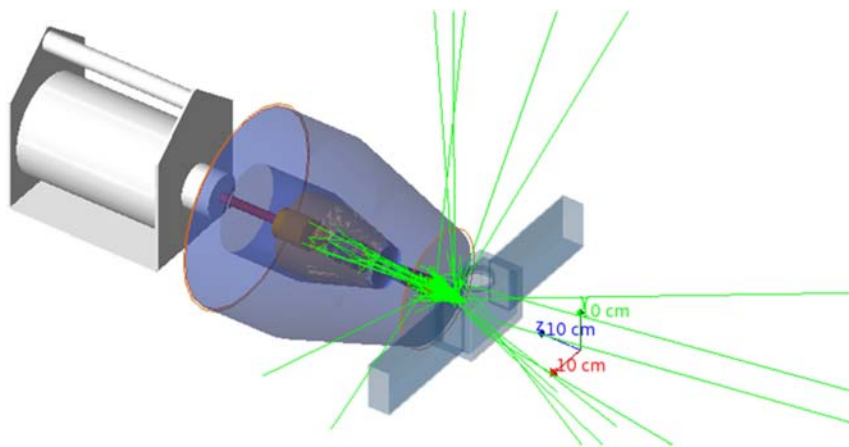


Figure 21.10 geant4 Monte Carlo simulation of a Compton-suppressed HPGe spectrometer, presenting an event shower originating from the sample position (drawing by L. Szentmiklósi).

In the activation analysis, the Monte Carlo technique can be advantageously used to design new setups, to simulate the irradiation conditions of existing facilities, that is the neutron field distribution, the capture rate, predict postirradiation specific activities, or correct for neutron self-shielding. The other major application field is gamma spectrometry, where the shape and detection conditions of the spectrum can be addressed, and the detector efficiency, shielding, and gamma-ray self-absorption can be quantitatively computed (Fig. 21.10).

21.3 Instrumental neutron activation analysis

21.3.1 Instrumentation

Instrumentation of NAA requires a neutron source with well-characterized irradiation positions; a radioactive laboratory or a hot cell, where the activated samples can be handled; a low-background counting chamber; an HPGe detector connected to a spectrometer with a ZDT or a LFC option to accurately account for the different time-dynamics of the isotopes of interest. For the spectrum evaluation, peak fitting software (e.g., Genie, GammaVision, Hypermet PC, HyperLab) and concentration calculation programs (e.g., Kayzero for Windows and k_0 -IAEA) are needed.

In general, at the in-core irradiation position of the research reactors, neutrons have a continuous energy distribution while interacting with the sample. Depending on the purpose of the irradiation, the irradiation channels can be fitted with cooling, rotation, or a pneumatic rabbit system. Rotation of the channel can compensate for the spatial inhomogeneities of the radiation field during irradiation in the reactor. For irradiations as short as a few seconds or minutes, a rabbit system ensures that the irradiated sample travels from the reactor to the counting lab in the shortest time possible and with reproducible timing.

After short- or long-term irradiations, the decay gamma measurements follow the same procedure. Low-background counting stations with accurately calibrated HPGe detectors are used to detect the gamma rays from the samples. The gamma measurement results in an energy spectrum, that is a multichannel histogram, where Gaussian-like FEPs appear at the energies of the gamma photons. Channel numbers of the gamma spectra can be converted to energy units (keV), after assigning literature energy values to the positions of two known peaks. The qualitative identification of radioactive nuclei is based on the comparison of the measured peak energies to an analytical library, while the quantification of isotopes (elements) makes use of the background-corrected net peak areas. Therefore, the goal of the spectrum evaluation is the precise determination of the FEP positions and net peak areas.

21.3.2 Detector calibration

The precise calibration of the gamma spectrometer is an essential requirement for both qualitative and quantitative analysis. Spectrometer calibration comprises the determination of three instrument parameters: the detection efficiency as a function of gamma-ray energy, the deviation from the linear energy calibration as a function of channel number, called nonlinearity, and the energy-dependent energy resolution. To determine these parameters, certified sealed radioactive sources are counted, whose gamma energies, emission probabilities, and activity data are known to high precision, and their gamma lines cover evenly the relevant energy range (50–3300 keV). The same set of spectra can be used to establish all three curves.

21.3.2.1 Detection efficiency

One of the most important parameters of gamma-spectrometers is absolute FEP efficiency $\varepsilon_p(E_\gamma)$. The efficiency is the ratio of the FEP area to

the number of gamma photons emitted by the source of E_γ energy. A 6–8-degree polynomial on a log-log scale is an appropriate fitting function. The efficiency depends on the measurement geometry, that is the source-to-detector distance, the shape, and extent of the source and its radiation energy, as well as the intrinsic efficiency, which is dependent on the detector crystal. The detection efficiency can be determined with the lines of ^{241}Am , ^{133}Ba , ^{60}Co , ^{137}Cs , ^{152}Eu , ^{226}Ra sealed (Fig. 21.11), certified radioactive point sources, and with optional additional radioisotopes created in reactors or accelerators, like ^{24}Na , ^{51}Cr , ^{56}Co , ^{65}Zn , ^{198}Au , $^{110\text{m}}\text{Ag}$, and ^{75}Se , whose data can be mathematically scaled up to the calibrated core dataset.

21.3.2.2 Nonlinearity

The detection and signal processing steps are in principle linear so that the channel number in the spectrum is expected to be proportional to the gamma energy. In reality, there is a minor deviation from the linearity that is caused by electronics. It is constant over a longer period for a given setup. The accuracy of the energy determination can be improved during the spectrum evaluation by correcting for this small but systematic deviation, the so-called nonlinearity (Fig. 21.12). The nonlinearity calibration can be experimentally determined from the same set of data as the efficiency. Peaks of well-known energies are measured, and the difference in the observed positions and literature data are fitted with a 6–8-order

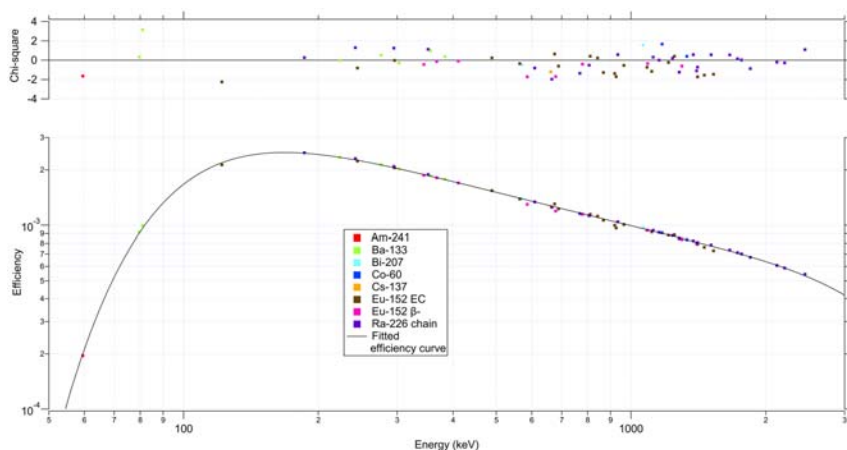


Figure 21.11 The absolute efficiency for a point source geometry at 250 mm from the HPGe crystal (drawing by L. Szentmiklósi & K. Gmélíng).

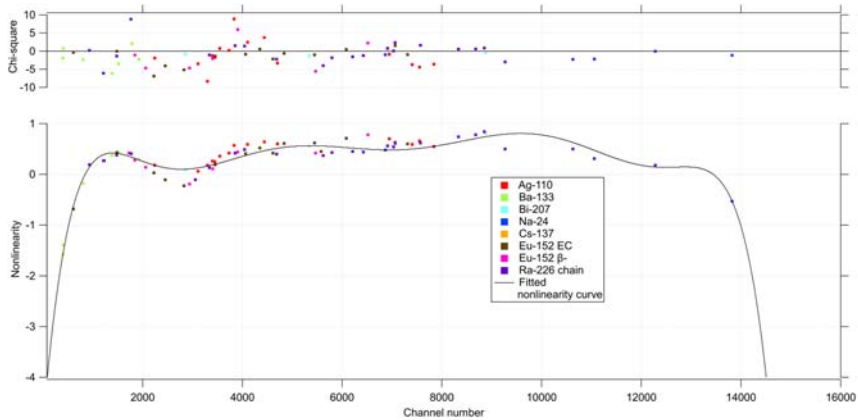


Figure 21.12 The nonlinearity of a gamma spectrometer in channel units (drawing by L. Szentmiklósi & K. Gméling).

polynomial. Peak positions in channel units evaluated during the spectrum analysis are then corrected with this function, and only thereafter translated to energy units. This practice is considered to be superior to polynomial energy calibration, as it delivers more accurate peak energies.

21.3.2.3 Energy resolution

In gamma spectrometry, the detector's energy resolution affects the selectivity. It is characterized by the *full width at half maximum (FWHM)*, which is usually specified for the ^{60}Co peak at 1332.5 keV and is about 1.8–2.2 keV. The spectrometer's energy resolution is determined by the properties of the signal processing electronics and the detector together. The curve can be given as a function of energy in form of $FWHM = \sqrt{A + BE + CE^2}$, where the first term represents the contributions of electronics (A), the second is the statistical fluctuation of charge production (B), and the third is the effect of the imperfect charge collection (C). A typical curve is presented in Fig. 21.13.

21.3.2.4 Background

The gamma spectrometer is usually placed within a low-level counting chamber (Fig. 21.14) to improve the detection limits (DLs), reduce peak interferences and avoid the cross-talk between nearby counting stations. The radiation from outside is absorbed by the shielding made of massive and high- Z material, for example, Fe or Pb. It is advantageous to design a

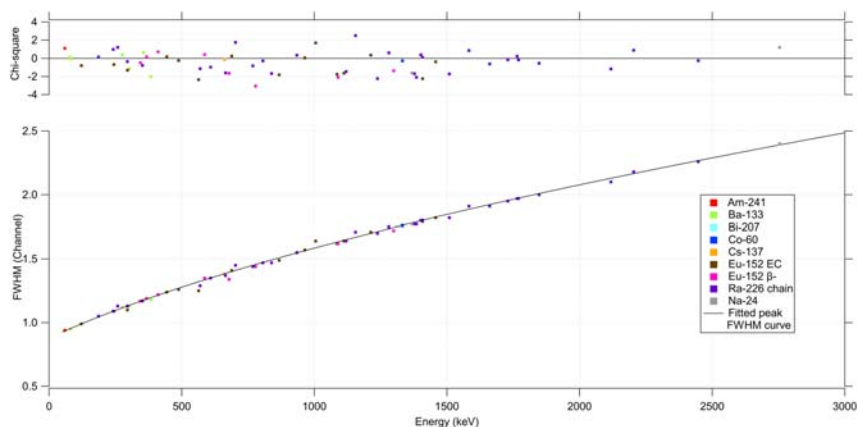


Figure 21.13 The energy resolution (FWHM, in keV unit) of an HPGe detector coupled with a digital spectrometer as a function of gamma-ray energy in keV (drawing by L. Szentmiklósi & K. Gmélíng).

“large” chamber with a graded shielding layer structure, as in this case, the secondary background effects, such as X-ray fluorescence peaks or BS are smaller in the spectrum. Once we determine the peak count rates of the background spectrum for every counting station, we subtract them during the analysis from the peak areas determined from the sample’s spectrum.

21.3.3 Sample handling

As the chemical state of the elements does not influence the analytical results, instrumental NAA measurements (unlike radiochemical NAA) require only little sample preparation (e.g., homogenization, drying, removal of the surface contamination, or preconcentration), and just a few milligrams of samples needed. Several samples may be bundled and irradiated in one batch under identical irradiation conditions. This feature is extremely relevant in comparative analysis.

Irradiation planning is a very important aspect of NAA since activated samples can be dangerous to human health. Working with samples over a certain radiation dose rate is not permitted. The weight of the sample, the duration and position of the irradiation, the decay time, and measurement conditions of the unknown sample are to be assessed to avoid overactivation. Time parameters are chosen based on calculations and earlier routines, knowing the irradiation conditions at the channel. The optimization of irradiation,



Figure 21.14 A vertical HPGe gamma spectrometer, placed in a low-level counting chamber. The sample-to-detector distance can be adjusted stepwise with a set of plastic spacers (drawing by L. Szentmiklósi).

cooling, and measuring times should be done together, considering the most important radionuclides formed that influence the selectivity as well as the sensitivity of the analysis.

Sample preparation depends on the irradiation time, and also on the standardization method. As NAA is a bulk method, homogeneity, and representativity of the sample are important, as it probes only a mass of a few tens to hundreds of milligrams. Or, if we are interested in the composition of a particular spot or particle, it must be properly prepared or separated from the rest of the sample. It is also important to weigh and pack the sample for irradiation in a clean environment and into a pure and cleaned sample holder, as NAA is a very sensitive method to detect contaminants at a $\mu\text{g/kg}$ (ppb) level.

For short (few minutes) irradiations, when the sample has to be counted immediately after returning from the reactor, only a few (5–10) mg sample are used. They are packed generally into small plastic capsules, which are further encapsulated into an inner and a carrier plastic holder (Fig. 21.15), to prevent them from breaking or leaking. Longer (> 1 hour) irradiations in a reactor environment with higher neutron flux demand sample holders with higher radiation and heat resistance. The dried samples, after weighing, are sealed into high-purity plastic (at low-power irradiation facilities) or quartz tubes (at high-flux irradiation facilities) (Fig. 21.16). These ampoules tolerate harsh irradiation conditions and can be manipulated like a sealed radioactive source.



Figure 21.15 Only a few milligrams of samples are packed in plastic capsules and irradiation containers for short irradiation through a pneumatic rabbit system. (Photos by K. Gmélíng).



Figure 21.16 Precisely weighed amounts of samples are encapsulated in high-purity quartz ampoules or heat-resistant plastic holders and wrapped in aluminum foil. A set of 6–7 samples can be packed together enabling simultaneous irradiation under identical irradiation conditions in case of long irradiation. (Photos by K. Gmélíng).

21.3.4 Irradiation and measurement protocols

In the case of short irradiation (1–10 minutes), the capsules are loaded to the irradiation channel with a pneumatic transfer (also called rabbit) system, driven by pressurized air (Fig. 21.17). During the irradiation, the sample can be cooled with the flow of an expanding inert gas (e.g., CO_2). At the end of the irradiation, compressed air brings back the capsule to the sample loading station or directly to the counting position. The samples may be repacked into an inactive holder. Counting can follow the short irradiation almost immediately, that is after cooling times of seconds or a few minutes, thus short-lived activation products can be determined (e.g.: Al, Ba, Br, Ca, Cl, Co, Cu, Dy, I, K, Mg, Mn, Se, Ti, U, V).

During the long irradiation, several quartz ampoules are wrapped together with aluminum foils, preventing damage and also to facilitate



Figure 21.17 For short irradiation, samples are loaded into the irradiation channel through a rabbit system operated with pressured air, and after irradiation, they are repacked into an inactive holder. (Photos by K. Gméling).



Figure 21.18 After long irradiation, the samples are unwrapped from aluminum foils and etched with mixtures of acids to get rid of potential external surface contamination. Thereafter they are measured at different distances from the HPGe detector at different decay times (Photos by K. Gméling).

heat dissipation. They are then irradiated in closed Al carriers. In the case of average siliceous samples, a typical decay time of 3–4 days is needed. The quartz vials are then unpacked and their surfaces are cleaned by chemical etching (Fig. 21.18). Each sample is counted two, three, or even more times. The first measurement can be as short as 10–15 minutes, when the elements As, Br, Ca, K, La, Na, Sb, and U can be determined. A second, 1–2 hour long measurement may take place 7–14 days later, when ^{24}Na and ^{42}K have decayed, thereby improving the DLs of the medium- and long-lived products (e.g., Ca, Lu, Nd, Rb, Th). After an even longer cooling period of 15–30 days (when the ^{82}Br and ^{140}La also decayed away), we may want to count the samples for a third time, for 2–6 hours, when typically Ba, Ce, Co, Cr, Cs, Eu, Fe, Rb, Sb, Sc, Ta, Tb, Yb, Zn, Zr can be determined. For quality management purposes [27], it is useful to measure from time to time certified reference material (CRM) samples, and also blanks.

21.3.5 Calculation of the mass

From a spectrometry point of view, the reaction rate is experimentally determined via the following formula:

$$R = \frac{\frac{N_p}{t_m SDC m}}{\frac{N_{Av} \theta \varepsilon P_\gamma}{M}} \quad (21.6)$$

where N_p is the number of counts observed in the FEP, t_m is the measurement time, S , D , and C are the correction factor for saturation, decay, and counting, respectively, m is the mass of the irradiated element of interest in grams, θ is the isotopic abundance of the relevant isotope, ε is the FEP detection efficiency of the spectrometer, while P_γ is the gamma emission probability. There are three approaches to quantitative data evaluation—calculating the concentration—in NAA for multielement analysis: absolute, relative, and comparator standardization.

21.3.5.1 Absolute standardization

One straightforward way to obtain the mass of the element of interest with NAA is to rearrange Eqs. (21.2) and (21.6) as follows:

$$m = \frac{M}{N_{Av} \theta \varepsilon P_\gamma (\Phi_{th} \sigma_{th} + \Phi_e I_0)} \cdot \frac{N_p / t_m}{SDC} \quad (21.7)$$

High-precision experimental determination of ε_p , the absolute detection efficiency is an important prerequisite to accurate analysis this way. The M , N_{Av} , θ , P_γ , and λ constants are precisely known (uncertainty <1%) and are tabulated in online databases. The inaccuracies of the activation cross sections (σ , I_0) and some decay constants can be, however, problematic. The uncertainty of experimental determination for neutron field parameters (Φ_{th} and Φ_e) can be up to 5%–20%, which may degrade the quality of the analysis results. A strong disadvantage is that it can only be applied to a given measurement setup.

21.3.5.2 Relative standardization

In the relative standardization approach, a chemical standard (index s) with known mass (m_s) of the element to be determined is coirradiated with the sample, and they are measured one after the other on the same spectrometer, under identical spectroscopic conditions. The unknown

mass, m_x , is obtained from the following formula:

$$m_x = \frac{\left[\frac{N_p/t_m}{D \cdot C} \right]_x}{\left[\frac{N_p/t_m}{D \cdot C} \right]_s} \cdot m_s \quad (21.8)$$

For spectrometry, the same analytical lines of the nuclei are applied. The advantage is that the characterization of the neutron field, use of any nuclear constants (Φ_{th} , Φ_e , σ , I_0 , except for the half-life that is needed for the D and C factors), or the detector (ε) efficiency is not necessary, as the method is based on a direct comparison of decay-corrected count rates and weighed masses. Although about 1% uncertainty can be achieved in this way, it is very laborious for routine multielement analyses. Metrologically, this approach is recognized as a primary method of measurement [28]. The drawback of this approach is that standards may not contain all relevant elements, or their mass fractions are not all certified, and the proportions might not be optimal to attain the best detectability conditions for the trace components.

21.3.5.3 Comparator standardization

In this case, one carefully chosen comparator is coirradiated with the sample, and all elements are analyzed relative to this. A flexible comparator standardization has been worked out by Frans de Corte and András Simonits and was named the k_0 -method [29]. The novelty of this approach has been to separate the nuclear constants, the characterization of the neutron field, and the instrumental quantities. Assuming that the sample is point-like and the sample-to-detector distance is large enough to make any coincidence effects negligible, the k_0 factor can be defined as:

$$k_0 = \frac{M_{Au} \theta P_\gamma \sigma_0}{M \theta_{Au} P_{\gamma, Au} \sigma_{0, Au}} \quad (21.9)$$

Here Au refers to the ultimate comparator, gold. It was chosen because it has only one stable isotope and one prominent gamma line, also the nuclear data for the (n, γ) reaction are well-known. The k_0 factors can also experimentally be determined. Their values are available in the literature [30], therefore it is sufficient to obtain the thermal/epithermal flux ratio of the irradiation channel, $f = \frac{\Phi_{th}}{\Phi_e}$, and the α epithermal shape factor using flux monitor foils, and the efficiency of the gamma detector

for data evaluation. The concentration of the unknown element c_x in a sample that has mass m_{sample} can be calculated as follows:

$$c_x = \frac{\left[\frac{N_p}{t_m \cdot S \cdot D \cdot C \cdot m} \right]_{\text{sample}}}{\left[\frac{N_p}{t_m \cdot S \cdot D \cdot C \cdot m} \right]_{\text{Au}}} \cdot \frac{1}{k_{0,\text{Au}}(x)} \cdot \frac{f + Q_{0,\text{Au}}(a)}{f + Q_{0,x}(a)} \cdot \frac{\varepsilon_{\text{Au}}}{\varepsilon_x} \quad (21.10)$$

where $Q_0 = \frac{I_0}{\sigma_0}$ is the resonance integral-to-thermal cross-section ratio.

21.3.6 Automation and software for neutron activation analysis

NAA is a highly labor-intensive technique. The samples are usually measured 2–3 times, and the scheduling of the measurements is critical for detecting the component of interest. On the other hand, the analyst works with radioactive samples in a radiation environment, where the dose rate, that is the impact of the radioactivity on human health has to be minimized. Recently, therefore, more and more labs deploy automated irradiation facilities and sample changers for the gamma spectrometry stations to increase productivity, minimize human errors, and reduce the workload of the staff. In the ideal case, a lab-wide LIMS (Laboratory information management system) shall be implemented that deals with all phases of the analysis workflow, from the receipt of the sample through the packaging, weighing, irradiation, gamma spectrometry, concentration calculations, to the final steps of reporting. Such an initiative was recently managed by the IAEA (Development of an Integrated Approach to Routine Automation of NAA at IAEA).

21.3.7 Databases for neutron activation analysis

NAA requires nuclear data for calculations and fitting, and evaluation of gamma spectra. Gamma-ray catalogues, tables of nuclides, activation calculators, and decay schemes can be found on the internet. [31] From these, we have compiled a useful selection below:

- NUCLEUS information resources at IAEA (<https://www.iaea.org/resources/nucleus-information-resources>) [32]

Chart of nuclides:

- Live Chart of Nuclides: <https://www-nds.iaea.org/relnsd/vcharthtml/VChartHTML.html> [33]
- Nuclear Data Center at KAERI <https://atom.kaeri.re.kr> [34]

- Nuclear Data—Laboratoire National Henri Becquerel_ <http://www.lnhb.fr/nuclear-data/> [35]
- k_0 -Neutron Activation analysis link page (<http://www.kayzero.com>) [36]
Activation Calculators:
- Activation Calculator V2 (tum.de) (<https://webapps.frm2.tum.de/activation/>) [37]
- Neutron Activation Calculator (wise-uranium.org) (<http://www.wise-uranium.org/rnac.html>) [38]
- Rad Pro Calculator: Free Online Gamma Activity, Dose Rate, and Shielding Calculator (<http://www.radprocalculator.com/Gamma.aspx>) [39]
- NUCLÉIDE-LARA on the web (2022) (nucleide.org) (<http://www.nucleide.org/Laraweb/index.php>) [40]

21.4 Prompt gamma activation analysis

21.4.1 Instrumentation

The PGAA measurement takes place outside of the neutron source, so the neutrons have to be delivered from the research reactor's core to the irradiation position. Neutron flux decreases quickly with the distance, so in the early days, one could not install a PGAA facility too far away from the reactor. Near the biological shielding of the reactor, however, the gamma background was found to be too high for achieving reasonable signal-to-background ratios. This problem was mitigated by the advent of cold neutron sources and neutron optical devices called neutron guides [41]. Cold neutron sources are small tanks installed next to the reactor core and filled with a low-temperature medium, for example, 20-K liquefied hydrogen, reducing the kinetic energy of the neutrons as they pass through it. The output of the cold source is fed into the neutron guides. They make use of the wave nature of the neutrons and the total reflection principle, similar to the fiber-optics in the case of the visible light. The neutrons are reflected from the guide wall by a special Ni-coating, or a well-engineered sequence of Ni-Ti layer pairs, known as neutron supermirror [42]. With this technology, one can deliver neutrons even to a 30–60 m distance with a moderate loss, where the gamma background is already low. Neutron guides transfer slow neutrons efficiently, while they filter out the more energetic epithermal or fast components. This shifts the neutron energy distribution towards the favorable range, where almost every nuclide follows the $1/\nu$ law (meaning fewer problems with

quantification), and the general reaction rate per atom is higher (resulting in higher analytical sensitivities).

The out-of-core irradiation of the sample needs adequate safety measures (Fig. 21.19). The guide system must be surrounded by massive shielding against neutrons (^6Li - or B_4C -loaded polymer sheets, boron-containing polyethylene blocks, Cd layers) and gamma radiation (lead bricks, concrete walls). The neutron beam needs a shutter to enable sample changes and instrument maintenance. To regulate the count rate or to selectively irradiate certain spots of the sample, a set of neutron apertures, beam-shaping slits, or attenuators are placed after the shutter. The structural materials of a PGAA facility have to be selected with great care. One shall use preferably low-activation materials that have also short half-lives (e.g., Al-alloys, Teflon, Sb-free lead, Na-free glass) to minimize the dose-related operation problems. The target chamber accommodates the sample fixed into a holder ensuring a reproducible geometry and also providing adequate radiation protection. The unused neutrons are finally absorbed by a beam dump.

21.4.2 Detector calibration

The detector looks at the sample through a cylindrical gamma collimator with a typical diameter of 20–30 mm. The spectrometer is covered with 100–200 mm thick lead shielding to keep the gamma background low.

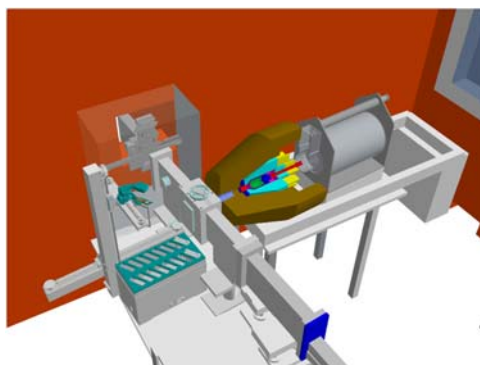


Figure 21.19 a 3D sketch of the PGAA station (Budapest). All components of a PGAA facility are visible: massive concrete (*orange*) and lead (*brown*) shielding against neutrons and gamma radiation, respectively; a beam-shaping device with a set of collimator apertures and slits, attenuators downstream of the shutter (*dark gray*) within a lead shielding block (transparent); sample chamber; automated sample changer (*light gray*); HPGe detector (*green*); BGO detector system (*light blue*); beam stop (*dark blue*) (drawing by L. Szentmiklósi).

This results in a larger sample-to-detector distance, for example, 250 mm, reducing the geometric efficiency to about 0.001. The low solid angle is also needed to limit the true and random coincidence summing effects.

The detector calibration follows the same principles and procedures that we described for NAA in section 3.2, with the exception that here we have to cover a broader energy range, from about 45 keV up to 11 MeV. At low energy, commercial radioactive sources (^{152}Eu , ^{207}Bi , ^{60}Co , ^{133}Ba , ^{226}Ra) are used, while for the 2–11 MeV region, neutron-activated radionuclides, such as ^{24}Na or ^{56}Mn , and reference prompt- γ lines of N (e.g., in form of a deuterated urea pellet) and Cl (thin PVC foil) are measured [43,44]. For the determination of the absolute efficiency curve, the activity of the most precisely calibrated radioactive source is used, and the rest of the data are normalized to this. The efficiency may be two orders of magnitude smaller around 10 MeV than at 100 keV, so the quality of the calibration curve is usually determined by the statistics of the high energy lines.

The nonlinearity of the energy calibration is even more important than in NAA due to the lower amplification of the detector signal, to still fit it in the conversion range of the ADC. This means the same nonlinearity translates to a higher energy offset, given the bin width is wider. As the PGAA library may contain thousands of entries, even a small energy shift may result in the misidentification of the analytical line. The energy resolution is also worse than in NAA, for the same reason. Still, every effort has to be made to optimize the peak shape and achieve the best possible resolution, as it is essential to handle complicated multiplets and achieve proper selectivity.

21.4.3 Sample handling, irradiation, and measurement

One of the most significant characteristics of the PGAA method is non-destructivity. In most cases the samples are analyzed as received, thus, no prior sample preparation is required. Depending on the form of the analyte (Fig. 21.20) the samples are heat-sealed in fluorinated ethylene-propylene copolymer (FEP) foils, ultrathin polyethylene films, or placed in Teflon vials. If carbon or fluorine (the major components of FEP) is an element of interest, the sample can be filled into a vial made of another material, for example, in pure quartz, or wrapped into thin Al foil. The sample is then placed in the chamber in a holder that is most often made of pure aluminum or aluminum alloy. The minimum sample requirement

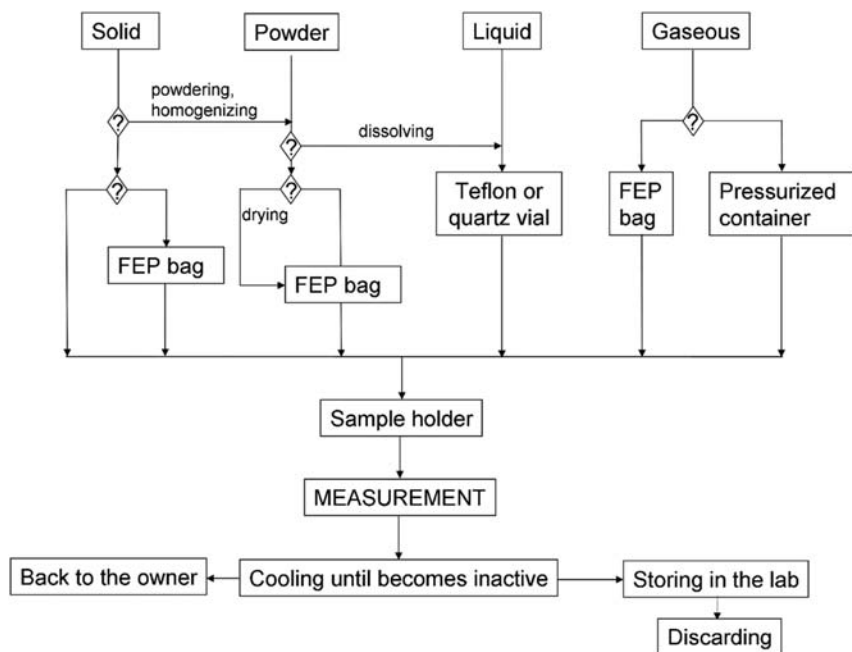


Figure 21.20 Sample handling workflow for PGAA (drawing by L. Szentmiklósi).

differs depending on the thermal equivalent neutron flux of the facilities. The higher the neutron flux, the lower amount of sample required. In the case of a low or medium-flux facility (thermal equivalent neutron flux is 10^5 – 10^8 cm^{-2}/s), the typical analyzed sample amount is 0.5–10 g, while in a high-flux facility, where the thermal equivalent neutron flux is 10^9 – 10^{10} cm^{-2}/s , the smallest required sample quantity can be around 1–10 mg. Generally, smaller samples or low cross-section materials require longer acquisition times. Elements present in the beam background are also more difficult to quantify in a small sample. The typical beam background components originate from the structural components, such as Pb, Li, and B from the shielding, Al from the sample holder, N and H from the air; Fe and Ni from the steel structural parts of the setup; C and F from the Teflon bag; Ge due to the activation of the germanium detector [45]. The beam background can be further reduced by evacuating the sample chamber or flushing it with an inert gas.

Depending on the facility arrangement, a few mm^2 – cm^2 spots of oversized samples can be also analyzed, even by partial dismounting of the

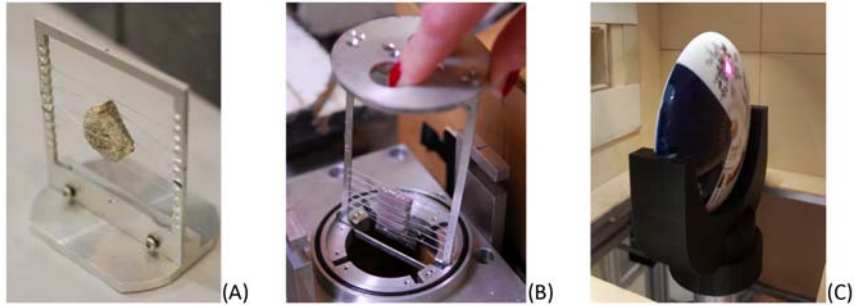


Figure 21.21 PGAA sample holders, (A) bare solid sample fixed to an Al frame with Teflon strings, (B) powdered material, heat-sealed in an FEP bag, and attached to an Al sample frame, is being placed into the sample chamber, (C) 3D-printed custom sample holder applicable to securely fixing sensitive and valuable objects (Photos by B. Maróti).

sample chamber and setting up ad-hoc shielding. At some facilities, the local chemical composition of samples can also be measured by scanning.

With the spread and increasing availability of 3D scanning and printing, custom sample holders can be designed and produced to secure valuable objects [46] (Fig. 21.21).

The irradiation and the acquisition of the prompt gamma spectrum are simultaneous. The acquisition time is a trade-off between the sample amount, the required statistical precision, and the available beam time. During the PGAA irradiation, short or medium-lived radionuclides are also produced, such as ^{56}Mn (2.5789(1) h), ^{24}Na (14.997(12) h), ^{64}Cu (12.7006(20) h), ^{66}Cu (5.120(14) min), ^{28}Al (2.245(2) min), ^{122}Sb (2.7238(2) d), and ^{124}Sb (60.20(3) d). The radioactive samples must be safely stored inside lead shielding until they reach the legal clearance levels. After that, the samples can be returned to their owners and can be used for further experiments.

21.4.4 Calculation of the mass fraction

Unlike NAA, where the half-life may limit the counts one can collect in a peak, the PGAA signal, that is, the net peak area at a gamma energy E_γ , is proportional to the measurement time, and the statistical precision of the results improves by the square root of the acquisition time.

The simplest form of the analytical equation is as follows:

$$N_P(E_\gamma) = m \cdot S \cdot t; \quad \text{where} \quad S = \frac{N_A}{M} \cdot \underbrace{\theta \cdot \sigma_0 \cdot P}_{\sigma_\gamma} \cdot \Phi_0 \cdot \varepsilon(E_\gamma) \cdot f(E_\gamma) \quad (21.11)$$

and m : mass of the element, S : sensitivity of the analytical peak (cps/mg), t : measurement time (s), N_p : net peak area at a gamma energy E_γ , N_A : Avogadro number, M : molar weight, θ : isotopic abundance, σ_0 : thermal neutron capture cross-section, P_γ : gamma emission probability per neutron capture, σ_γ : partial gamma-ray production cross-section, Φ_0 : thermal equivalent neutron flux, $\varepsilon(E_\gamma)$: detector efficiency, $f(E_\gamma)$: matrix effect correction (neutron self-shielding, gamma self-absorption).

As one element may emit more than one prompt gamma line, several of them may be used to independently calculate the mass (m_i , and the corresponding uncertainties, δm_i) of the element found within the irradiated volume. This redundancy offers an inherent way to check the self-consistency of the results. Once we remove the statistical outliers, the weighted average of all these masses is calculated for every element, based on Eq. (21.12).

$$\bar{m} = \frac{\sum_{i=1}^n \frac{m_i}{(\delta m_i)^2}}{\sum_{i=1}^n \frac{1}{(\delta m_i)^2}} \quad (21.12)$$

To obtain the concentrations, we compute the mass fraction of element k over the summed mass of all detected elements [47,48].

$$c_k = \frac{\bar{m}_k}{(\bar{m}_1 + \bar{m}_2 + \dots + \bar{m}_k + \dots + \bar{m}_n)} \quad (21.13)$$

We note here that in the case of a two-component sample, the absolute uncertainties of the concentrations are equal for the two components due to the correlations.

Another approach is to obtain the elemental sensitivities [S in Eq. (21.11)] for an analytical line by calibration or standard addition [49] for a particular beam and detection geometry and read the unknown mass from the calibration curve. This needs a constant beam intensity, a well-defined sample shape, and a very stable gamma spectrometer. This approach is more prone to unrecognized interferences in a complex matrix, as well as to sample and beam inhomogeneity issues.

21.4.5 Automation and software for prompt gamma activation analysis

When the neutron beam is on, the beamline is usually not accessible due to the elevated dose rates. This calls for an automated operation. Several mission-critical components are redundant to ensure an

adequate level of operational safety. All system components, such as beam shutter(s), pinhole exchangers, gamma spectrometer, and the operation of a sample changer must be synchronized, and remote-controlled by a computer. To comply with the ALARA principle of health physics, to minimize the dose rates of the analysts and allow 24/7 operation, the facility has to be able to take data in unattended batch mode, without the physical presence of the operator. This necessitates that many instrument parameters, for example, beam monitor intensity, statuses of the shutter(s), count rate of the spectrometer, dose rates, sample-change events, spectrum clear/start/save, and various I/O signals must be logged.

The careful evaluation of PGAA spectra by an analyst may take up to an hour, therefore, automated spectrum evaluation solutions are also highly desirable. In the future, artificial-intelligence-based real-time evaluation of the spectra is envisaged to help in tuning the setup and assist the decisions already during the data taking.

21.4.6 Databases for prompt gamma activation analysis

The catalog derived from spectral data recorded at Budapest Research Reactor can be considered the most reliable database for elemental analysis with PGAA. The *Handbook of Prompt Gamma Activation Analysis* [50] lists up to 100 gamma peaks for each element from H to Bi, Th, and U (exceptions are He and Pm) with the corresponding partial prompt gamma-ray production cross sections. Additional information is given on atomic mass, k_0 -conversion, as well as short-lived decay modes, and other neutron-induced reactions of relevance. Among others, the Budapest data are also available online in an IAEA Technical Report [51] and on the IAEA webpages under the name Evaluated Gamma-ray Activation File [52–54]. The standardization of the PGAA method and the related nuclear data are described by Révay et al. [55]. All data are under continuous review and an updated version will be released soon. For sake of completeness, previously available databases should be mentioned: Lone et al. [56] as well as Reedy and Frankle [57]. While the suitable Reedy-Frankle dataset reaches up to $Z = 30$ only, the Lone data were generated without including nuclear structure information, and the assignment of the gamma energies to the elements is not always correct. Lindstrom et al. [58] provide further discussion about modern databases.

For prompt gamma activation analysis induced by (n,n') reactions, there is only one catalogue published by Demidov in 1978 [59]. Currently, the database has been digitalized by Hurst et al. [60–62]. There is an ongoing revision for several elements [63,64].

21.5 Good laboratory practice, quality management for prompt gamma activation analysis and neutron activation analysis

Activation analytical laboratories provide elemental concentrations, whose quality should be controlled to assure the accuracy and precision of the results. Some form of formal quality management accreditation is highly recommended for labs doing regular services to industrial partners. As NAA is a complex methodology compared to mainstream techniques like XRF or ICP, accreditation is challenging and only sometimes economically profitable. In any case, it is expected to follow Good Laboratory Practice (GLP). The GLP is more than a comprehensive set of routines, it is an attitude with attention to all details to ensure accurate analytical results.

This philosophy is implemented in form of formal rules, Quality Assurance procedures (QA, minimizing the probability of an error) and Quality Control procedures (QC, measures to recognize an error) that can contribute to preventing the eventual reporting of incorrect results [65]. This covers the complete process of sample identification, preparation and handling, irradiation, decay, and measurement parameters, through evaluation and data reporting.

Scrutinizing the trend of measurement parameters over time in form of control charts is a good way to recognize unsatisfactory measurement results or instrument malfunctions. The precision is used to verify the absence of unknown sources of variability, while the trueness can be regularly tested by the analysis of CRM, or samples from interlaboratory comparisons to ascertain the absence of systematic biases or calibration errors [66].

Some recommended guidelines to consider when implementing GLP in an activation analysis laboratory:

ISO Guide to the Expression of Uncertainty in Measurement (GUM) [65]

EURACHEM CITAC Quantifying Uncertainty in Analytical Measurement, 3rd Edition [67]

EURACHEM CITAC Quality Assurance for Research and Development and Nonroutine Analysis [68]

IAEA Quality Assurance and Quality Control in NAA: A Guide to Practical Approaches [27]

IAEA Use of research reactors for NAA [69]

21.6 Further methods

21.6.1 In-beam neutron activation analysis and the combination of prompt gamma activation analysis and neutron activation analysis

In-beam NAA is a way of combining the traditional PGAA with the advantages of decay gamma measurements [70]. Thus, the sample is irradiated not in the reactor, but at the PGAA station with a guided neutron beam [71], and the decay gammas are measured after the irradiation, which may be right after the PGAA measurement [72]. This requires a longer measurement time, but it can give information on a few more components with much higher sensitivity.

A more general approach is to combine the results of PGAA and NAA measurements on the same sample set. The complementarity of NAA and PGAA allows nearly panoramic analysis. The combination of the two methods gives the amounts of a wide range of elements: from light elements to rare-earths. The good comparability of the results is due to the same nuclear physical basis of the methods [73].

21.6.2 Other neutron-based methods

In addition to the most widely used methods—NAA and PGAA—there are other more specialized techniques to quantify elemental composition using neutrons. In order not to go beyond the scope of this chapter, well-established methods are discussed here, but no recent developments in the concept phase. Activation analyses can also be performed with neutrons of higher energies than in the thermal region, which can be advantageous for the determination of certain elements such as nickel, titanium, or barium. Suitable filter materials, such as cadmium, suppress the dominant fraction of thermal neutrons to make reactions in the higher energy range more pronounced—capture reactions in resonance regions or threshold reactions such as (n,p) , (n,α) , or $(n,2n)$. Epithermal neutron activation analysis is usually referred to as using energies above 0.55 eV, linked to the threshold energy of the Cd filter. From energies 1 MeV and upwards, the threshold reactions become available. This is called fast neutron activation analysis. Cyclic neutron activation analysis [74] is another variant of

NAA, which uses periodically repeated irradiations and measurements to improve the detection of elements with short-lived activation products.

Using strong collimation of both the neutron beam and the emitted prompt gamma radiation, one can achieve spatial resolution in the mm range by scanning the sample. This PGAA-based approach is called prompt gamma-ray activation imaging (PGAI) [75,76] and is often combined with macrostructural information from neutron imaging (NT) or neutron radiography (NR) [77]. It allows an elemental mapping of an object and even internal regions of bulky objects can be analyzed non-destructively [78]. However, due to the lower statistics associated with the smaller sampling volumes, fewer elements can usually be detected than with classical bulk analysis. Another method related to PGAA is based on irradiation in a beam of fast, fission neutrons. In this case, the production of prompt gamma rays is induced by inelastic scattering reactions (n,n'). The irradiation takes place outside the reactor core and the high penetration depth of the fast neutrons enables the analysis of samples in the dimension of a few ten centimeters. A corresponding instrument (FaNGaS) can be found at the MLZ in Germany [79].

In Neutron Depth Profiling (NDP), charged reaction products are measured instead of the characteristic gamma radiation. From the information on the energy loss of these particles when passing through matter, it is possible to obtain information about the concentration distribution in near-surface layers. For lithium and boron, the DL reaches ppb_a range (parts per atom) with depth resolution down to 5 nm, while the maximum depth in solids is a few 10 μm-s. The limits are highly dependent on the material. NDP is mainly used in battery research on Li-ion batteries, for which also operando measurements are possible [80].

Neutron resonance transmission analysis and neutron resonance capture analysis [81] are time-of-flight setups based on the fine selection of neutron energy. This allows the resonance spectra of irradiated samples to be recorded and analyzed. The methods require more complex instrumentation. In addition to the elemental composition, isotope effects can also be detected with these methods.

21.7 Characteristics and applications

21.7.1 General merits and limitations

An important advantage of PGAA and NAA techniques is that the obtained results are valid for the entire irradiated volume, unlike in many

other techniques, where the source of the signal is near-surface. This deep penetration is the reason for the little-to-none sample preparation. PGAA is unique in the determination of H and B and it can analyze all the other light elements, which are difficult to quantify with other methods. NAA complements PGAA, as it finds its major application in trace element analysis, for example, in the determination of rare-earths.

In NAA, we determine the masses of the components. Precise concentration values can be obtained by relating them to an accurate sample mass. In the case of PGAA, the best way is to determine the mass ratios of the constituents, because many systematic error sources can be reduced in this way. If we can assume that all major and minor components were determined, we can derive the composition of the sample. This is the case for samples of natural origin: rocks and minerals, archeological objects, and building materials, where the major and minor components can be all observed. Oxygen, even as a major component is difficult to determine accurately because its neutron capture cross-section is orders of magnitude lower than for other elements. In many cases, we can calculate its amount from stoichiometry [47].

In many practical cases, PGAA provides the matrix composition together with a few trace elements, while NAA detects the typical trace elements. For a more complete analysis, we may want to combine the results of the two methods. In cases like this, common elements must be found in the analytical results to be used for normalization. In geological samples, these are usually Fe or K, sometimes Na, Ca, or Mn. In the case of alloys, the common elements can be Cu, Fe, and in higher amounts As and Sb. When alloys are irradiated in NAA and PGAA, the neutron self-shielding and gamma-ray self-absorption must be corrected.

Though PGAA and NAA complement each other, there are a handful of elements, which are difficult to determine with any of them. Examples are, amongst the heavier elements, Pb and Bi. The DLs of Pb and Bi with PGAA are in the m% range (see Figs. 21.22 and 21.23, and Ref [82]), and they have practically no measurable delayed gamma lines. Pb and Bi both have low neutron capture cross sections, and their contributions to the PGAA beam background is also not negligible (Bi is the major component of the commonly used BGO Compton-suppression systems, while Pb forms the biological gamma shielding around the detector, often exceeding 1 ton).

Because of their low cross sections, it is difficult to determine the light elements as minor components (e.g., P, Si, S, C). However, hydrogen can

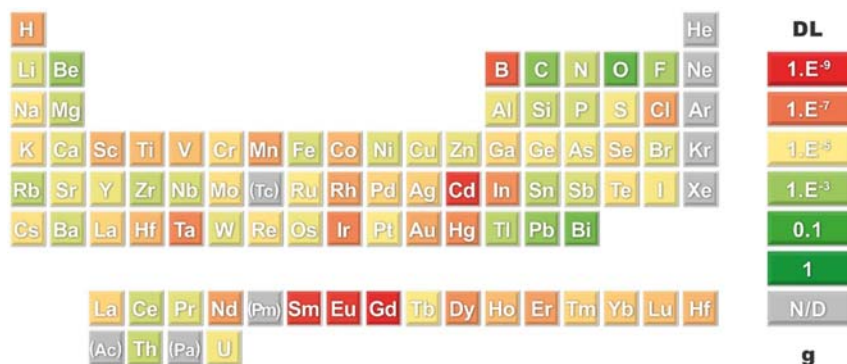


Figure 21.22 Detection limits of PGAA for the instrumentation at MLZ (cold neutron beam, thermal equivalent neutron flux $\sim 10^9 \text{ s}^{-1}/\text{cm}$). Shown for a typical mineral sample. Picture: Zs. Révay, C. Stieghorst and R. Müller, TUM.

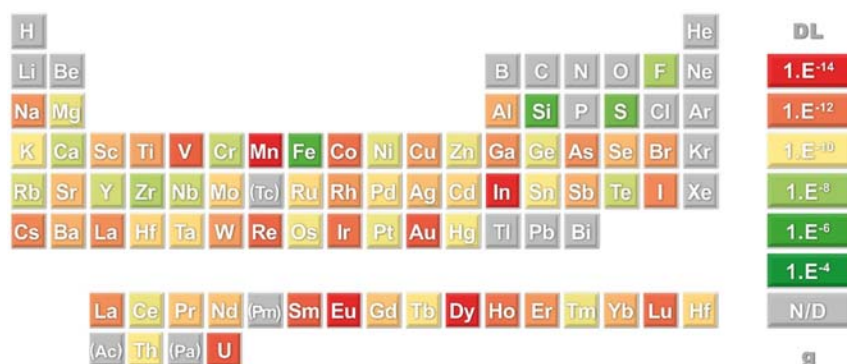


Figure 21.23 Detection limits of NAA for the instrumentation at MLZ (thermal neutron flux $\sim 10^{14} \text{ s}^{-1}/\text{cm}$). Shown for a typical mineral sample. Zs. Révay, C. Stieghorst and R. Müller, TUM.

be determined also in trace amounts. It has a DL of a few tens of ppm in typical metallic samples. In a low-cross-section matrix, such as Zr, it is 10–20 ppm [83], while in Fe and Ti, it is about 50–100 ppm [84]. The DLs can be improved only by significantly increasing the measurement times. Boron, thanks to its exceptionally high cross-section, can be determined in the ppb range in most matrices. For NAA, the best DLs are achieved when the matrix component has no long-lived activation products (e.g., C, Si, Ti, Pb) and/or the half-life of the daughter nuclides is significantly shorter than that of the components of interest.

An important merit of the PGAA technique is that due to the simultaneous irradiation and counting, it enables the real-time contactless measurement of time-dependent processes.

The mentioned advantages make the neutron activation methods competitive in comparison to other instrumental analytical techniques, like XRF or ICP-MS. It is important to emphasize that these neutron-based methods are not only element-specific but isotope-specific. PGAA and NAA are used in many fields of science and utilized by the industry as well [85].

21.7.1.1 Detection limits for typical matrices

The DL in PGAA is inversely proportional to the analytical sensitivity [86]. In addition to the maximum σ_γ values of the individual elements, and the conditions during irradiation and measurement, the DL also depends strongly on the sample matrix. A typical mineral sample composition forms a good guide here, see Fig. 21.22. The DL values can typically be an order of magnitude more or less. For the NAA, the situation is even more complex due to the individual irradiation and measurement procedure adapted to the sample, although the example in Fig. 21.23 provides also a rough estimation. Especially in very pure short-lived matrices, trace elements with single long-lived activation products can be determined with much lower DLs. A prominent example from practice is the analysis of impurities due to transition metals in high-purity silicon. Here, DLs in the ppq range can be achieved for several elements [87].

21.7.1.2 Comparison to competing methods

X-ray fluorescence spectrometry (XRF) is one of the most commonly used methods for the determination of the main components in siliceous samples. PGAA results show good agreement with XRF results on reference samples, however, the DLs differ individually for the elements. For instance, phosphorus cannot be measured with NAA and is only in the percent range with PGAA. Hydrogen also forms a major oxide in silicious samples, however, it is hard to measure its concentration with most of the common element analytical methods, while PGAA is very sensitive to H. The determination of H₂O is usually done by: (a) Karl–Fischer titration [88]; (b) the Penfield method [89,90]; or (c) IR gas absorption spectrometry; all heating the samples while losing other volatiles, or decomposing fluid inclusions, etc. The H present in hydroxyl groups of the lattice

structures of minerals should be differentiated with hydrogen in the moisture absorbed by the samples [91].

One of the most common trace element analytical methods nowadays is the solution-based Inductively-Coupled Plasma Mass Spectrometry (ICP-MS). It is capable of measuring the trace element composition of the samples relatively fast, with low DLs and with high accuracy. However, ICP-MS is a relative method requiring standards. The sample preparation is lengthy, labor-intensive, and expensive, while the incomplete dissolution or volatilization of solid samples, contamination of the sample, and the variability of the recovery efficiency [92] of digestion (or extraction) cannot be excluded. The isobaric interference in mass spectrometry detection and the matrix effect during sample nebulization/evaporation can also result in a systematic bias if not adequately dealt with [93]. In the case of Laser-Ablation ICP-MS (LA-ICP-MS), the measurement is micro-destructive, that is the samples do not need to be dissolved for measurements, but the measured concentrations correspond only to a small crater comparable to the diameter of a laser beam, making it less representative overall.

Comparing PGAA and NAA results on trace elements, except for a few elements, like B, Cl, and Gd which are reliable and can only be measured with PGAA, all the other tracers, especially REE, are more reliably determined with NAA. The greatest disadvantage of nuclear analytical methods is that they require a radiation source, for example, the neutron source is a reactor or generator. The radioactive working environment requires great caution and radiation protection measures. Most of the research-grade NAA laboratories are not equipped for handling a large series of samples for analysis. These techniques generally have a long turn-around time, whereas the results from other elemental analysis methods can be made available in a few minutes.

21.7.2 Illustrative applications

NAA and PGAA are used for elemental analyses in a wide range of applications. It includes, in particular, archeology and cultural heritage, biology & medical research, chemistry, environmental science, food & agriculture, forensics, geology, recycling research, and materials science. For PGAA, Lindstrom et al. [58] provide a comprehensive overview of recent research topics. In Munita et al. [94] exemplary projects using NAA are listed for geology, medical research, forensics, environmental, and heritage sciences.

Another overview of NAA applications can be found in [95]. In the following, we focus on the applications in materials science and related topics. Most of these case studies are unique to the activation analytical methods, as they cannot be performed by competing techniques.

21.7.2.1 High-purity silicon and solar cells

NAA is well suited for the determination of traces and ultratraces in highly pure materials such as silicon. Silicon is still the most important semiconductor material for solar cells. The presence of impurities, in particular of 3d transition metals, can lower the efficiency of the solar cells significantly. The activation of the silicon matrix is comparatively low and the residual activity decays after a short time ($T_{1/2}(\text{Si-31}) = 2.6$ hour), so elements with long-lived activation products (e.g., Co, Fe, Cr) can be analyzed with very low DLs down to the ppt/ppq level. NAA studies of multicrystalline silicon produced by directional solidification have been performed in the last few years, for instance [96–98]. The content of hydrogen and the dopant boron in mc-Si can be sensitively analyzed with PGAA [99]. Other promising materials for cost-effective printable photovoltaics are metal halide perovskites, which have also been analyzed with NAA [100]. In Gustafsson et al. [101] the recycling option of high-purity selenium from copper indium gallium diselenide (CIGS) cells is investigated with NAA. Industrial users from the field of silicon production mainly request two services from research reactors: Phosphorus doping of high-purity monocrystalline silicon via the reaction $^{30}\text{Si}(n, \gamma)^{31}\text{Si}$ and β^- decay to ^{31}P [91] as well as analysis of impurities in silicon using PGAA and NAA.

21.7.2.2 Batteries and energy storage

Recently, the most important nuclear analytical technique for the research on Li-ion batteries is NDP, and with this method even operando analyses are possible. A considerable number of publications have appeared on this subject in recent years, such as [80,102–112]. In this context, the understanding of solid electrolyte interphase (SEI) and lithium plating processes is the key to optimizing the lifetime of Li-ion batteries. PGAA has also been used for lithium-ion battery research, but much less frequently than NDP. One of the most recent works was published by Starke et al. [113] in which PGAA was used to analyze manganese in $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4/\text{Graphite}$ Cells. In context with solar energy, thermal energy storage (TES) systems are in use to store the excess thermal energy

collected during the day. To improve these systems, the change in the specific heat of nitrate salt-alumina nanoparticle-containing fluids was analyzed. NAA was used to determine the mass fraction of the alumina nanoparticles [114].

21.7.2.3 Circular economy and waste characterization

Sustainable recycling of valuable materials is playing an increasing role, which is reflected in research projects with activation analysis. PGAA and NAA are both used for the development of more efficient processes. The prompt gamma activation analysis technique is one of the few analytical methods that can quantify light elements, including Li, C, O, P, F, and H, as major constituents, as well as metallic elements (Co, Ni, Mn, and Al) and some other “exotic elements,” “critical elements” or valuable components in solid form. NAA is perfectly suited for the measurement of gold and other noble-metal constituents.

Downcycling, that is the increasing contamination of the materials with unwanted elements during the recycling processes, has a negative impact on the quality of the end products. Using element analysis, one can follow the material flow during the steps of recycling, by quantifying the relevant elements in each technological step. Some examples of using activation analysis for recycling research can be found in [115–117]. Apart from the study of recycling processes, activation analysis is also used to characterize the composition of waste to estimate its impact on the environment. Some examples here are textiles [118], hospital waste [119], as well as emitted dirt particles into the air like fly ashes [120].

21.7.2.4 Nuclear industry, safeguards, homeland security

Due to neutron-induced fission and the gamma emission of short-lived fission products, nuclear materials produce an extremely strong signal, when interrogated with neutrons. Neutrons and gammas can pierce through even several cm of lead containers, delivering visual and compositional information about packaged or masked fission materials [121].

A special application of prompt and delayed neutron-induced gamma radiation is the characterization of toxic and radioactive elements containing waste in larger drums with mobile devices. Numerous studies were published, and the technique is still under development [122–129]. For homeland security, entire cargo containers can be screened with neutron-generator-based PGAA [130]. The detection of landmines by neutron-induced gamma radiation has also been demonstrated [131].

21.7.2.5 *Materials science*

NAA and PGAA are suitable for the determination of major constituents as well as impurities in the trace concentration range in materials science samples. Exemplary applications are the analysis of carbon nanotubes [132–135], fullerenes [136], zeolites [137], (super-)alloys [138–141], materials for the operation and decommissioning of nuclear power plants [142–145], membranes [146,147], ceramics [148], thermoluminescent materials [149], as well as quantification of low-Z elements, such as hydrogen [150–154], nitrogen [155,156], sulfur [157] or boron [99,158,159] in a variety of matrices.

In catalysis research, PGAA and NAA are well-proven techniques to characterize *exsitu* the active component of supported catalysts [160]. Thanks to the non-destructive nature of PGAA, the identical item can be analyzed before and after a catalysis process, making it possible to use for wear studies [161]. Catalysts are known to be highly sensitive to the chemical environment, so the best approach is to observe them *in situ*. By installing a chemical flow reactor into the external neutron beamline of a PGAA station, one can probe real-time the adsorbed and absorbed amounts of reactants on a catalyst and correlate this with the chemical parameters, such as flow rate, yield, and conversion [162–164].

21.7.2.6 *Reference material certification, metrology, and method validation*

As a primary measurement method, NAA is fundamental in metrology. All analysis steps and corrections of nuclear methods are methodologically well described and a corresponding uncertainty budget is comprehensive and accurate, PGAA and NAA produce results of high metrological quality. These techniques are genuinely applied to reference material certification by NIST [165–167] and other metrological bodies, as well as contributing laboratories [168–170]. Further, NAA and PGAA can be used in the method validation of cheaper, more productive mainstream analytical techniques, especially where no matrix-matched reference materials are available [171]. Nuclear analytical techniques play an important role in fundamental research related to SI metrology, for example, in the attempts to redefine the Avogadro number or the unit of kilogram [172–175].

For routine analyses, dilute standard solutions of chemical elements are used in analytical laboratories to calibrate instruments. In the first step, a primary reference solution is prepared by a metrological institute from pure and well-characterized solid material. This is further diluted to

secondary solutions, which are distributed to the customers. The mass fractions of the element in these solutions can be obtained by NAA relative to the primary reference solution, establishing the unbroken chain of traceability to the SI [176].

21.7.2.7 Cultural heritage

Though archeology and cultural heritage is not an explicit topic of this book, it is one of the most frequent fields of application [75,177–179]. In addition, the analysis of materials from antiquity, such as stone building materials, metals, or glasses, definitely shows parallels with the analysis of modern materials. Ancient bronzes were investigated to benchmark and improve analytical approaches for copper alloys [70]. The analysis of the elemental composition in historical or ancient samples by means of NAA and PGAA is mostly carried out to determine the origin (provenance analysis) and the authenticity of archeological objects [180,181]. In addition, certain old manufacturing techniques can be inferred (reverse engineering) [182]. Historical catastrophes can be assessed, like cosmic impacts [183]. The analysis of the hair of Emperor Napoleon Bonaparte in the context of his possible poisoning with arsenic is an example of a historic-forensic application [184]. Another task is to find ways to prevent archeological iron objects from corrosion [185,186]. PGAA proved to be useful in the non-destructive bulk analysis of glasses and bronzes with weathered or completely corroded surfaces, where surface-confined analytical techniques alone could not provide the desired information [187,188].

21.7.2.8 Other selected applications

The field of forensics relies on materials science knowledge and advanced analysis methods. There are recent studies on car glass to identify the manufacturer with the element composition and to use this information in the framework of car accidents and crimes [189]. The element ratios between H, C, and N make the identification of explosives possible [190]. Further examples of forensic material analyses, such as gunshot residue, drugs, hair, or clothing are reviewed in Ref. [191].

Environmental pollution from industrial activities, traffic, and energy production is also investigated with NAA, for example, with fine dust filters [192–194], biomonitors [195–200], and sediment or soil analyses [201–204]. Also, food and agricultural products [205–210], fertilizers [211,212], as well as medical, pharmaceutical [213], and cosmetic products [214], and their impact on the human body [215] are frequently analyzed.

Another field is raw material extraction, transport, and processing. Examples in this context are the analysis of geological samples [216–218], the development of techniques using fast neutrons for finding blockages in oil pipelines [219], or the analysis of cement [220], using factory-installed or portable neutron generators [85].

21.8 Activation analysis facilities at research reactors

The utilization of most research reactors around the world started with the instrumental neutron activation analytical laboratories, as one of the most straightforward methods. Even though many other trace-analytical methods have been developed in the meantime, NAA still kept its rank and importance due to its advantages.

There is the website neutronsources.org, which is an initiative of neutron research facilities and neutron communities around the world. The aim is to provide up-to-date information material and news on research using neutron beams. This site gives information about NAA laboratories around the world. Also, there is information about research reactors and connected NAA facilities around the world on the IAEA website of the Research Reactor Database [221], searchable by region and power.

For PGAA, the Handbook of Prompt Gamma Activation Analysis lists nearly 40 reactor-based facilities that have been established worldwide since the 1960s [222]. Lindstrom and Révay reviewed the changes and new facilities for the period 2004–2017 [58]. For maximum sensitivity, PGAA requires a well-thermalized or a cold neutron beam. For this reason, neutron guides are used and the PGAA facility should be placed as far as possible from the reactor to reduce the gamma and neutron background. Due to these specific requirements, PGAA is a less abundant technique than NAA. A worldwide enumeration of the most significant NAA and PGAA laboratories is given in, where NAA labs are classified into three categories based on the power of their reactors. (Fig. 21.24)

21.9 Outlook

As analytical techniques have become more sophisticated and detection capabilities have improved, NAA techniques face increasing competition from mainstream analytical techniques, such as atomic spectrometry, and X-ray-based methods. They may have nowadays adequate analytical merits to cover most of the routine analytical tasks [223]. The majority of



Figure 21.24 Major PGAA and NAA laboratories around the World (drawing by K. Gméling).

these methods, however, require liquid samples, while laser-induced, X-ray, and nuclear techniques excel in the analysis of solid samples. Wherever the analyte is solid and too valuable or irreplaceable to digest or take out a subsample, it must be measured non-destructively. In this case, X-ray and neutron-based techniques are the methods of choice.

Neutron-based techniques are also matrix insensitive, or the matrix effects can be precisely corrected, while due to the high penetration depth of the radiation, the probing volume is large, and the results are highly representative. This makes them appropriate to characterize the bulk components of samples whose surface is covered with contamination, corrosion products, patina, decoration, and paint layer [224], and the limited lateral and in-depth sampling of surface-confined analytical techniques may be biased.

The fact that nuclear methods of analysis are based on principles fundamentally different from those of the other analytical techniques implies that they are less likely to be prone to the same systematic biases [225]. The long-proven accuracy of activation techniques makes them particularly useful as reference techniques in method intercomparison (round-robin) studies and reference material certification.

Activation analytical methods will continue to be indispensable for many of the above-mentioned applications. We foresee that activation analysis will develop by improving the throughput of the analytical process using advanced irradiation and measurement control, automated data analysis, and artificial intelligence, and thus it will continue to be of great method to serve the needs of science and industry.

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CHAPTER 22

X-ray stress analysis

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22.1 Introduction

Mechanical structures and components are designed with an estimate of the stresses required during their operation to prevent service failures. Formulas in textbooks of mechanics can be used to calculate stress, and finite element analysis can provide a more detailed analysis of the stress state. However, the manufacturing process of materials and products introduces stationary stress into the body, called residual stress, which adds to service-related stress [1,2]. Thus, residual stress may result in unexpected failure during product use or shorten its lifespan. Studies have reported that residual stress does not only have a negative impact but can also improve fatigue and prevent corrosion cracking by introducing compressive residual stress to the surface of the product, such as by peenings [3–6] in particular areas where failure could occur due to tensile stress in operations or areas where tensile residual stress has been introduced during production. However, because of the difficulty in predicting residual stresses with computations, actual measurements are necessary to determine the stress and confirm the validity of the prediction [7].

Although several methods to measure residual stress have been identified, including curvature measurement, hole-drilling, [8] and contour [9], X-ray stress analysis (XSA) offers an advantage (e.g. non-destructive and noncontact) over other methods. Therefore, stress measurements with X-rays are widely used in academia and industry [3,6,7]. Synchrotron X-rays [2,5,10,11] and neutrons are also useful sources for more advanced stress measurements [4,12–18].

Based on the above background, this chapter is intended for students, engineers, and researchers who are learning about XSA for the first time. Although the main focus of this chapter is the laboratory X-ray diffraction measurement using the $\sin^2\psi$ method, which is the basic measurement method, the other techniques were also proposed (e.g. the $\cos \alpha$ [19], the

2D method, [20] and whole back reflection ring methods [21]). While the $\sin^2\psi$ method is useful, it is based on some significant assumptions. To prevent misuse of the method and ensure its accuracy, it is essential to understand its basics. In this chapter, the XSA is described comprehensively, but in practice, extensive knowledge is required for measurement and analysis.

Additionally, neutrons are used for stress measurement, including internal stresses that cannot be measured by X-rays [4,14–18], because of their penetrability. Thus, stress analysis with neutrons is also introduced in this chapter.

22.2 Fundamentals of X-ray diffraction

22.2.1 X-ray source

Generally, in X-ray diffractometers, X-rays are supplied by sealed tubes or rotating anodes, and the characteristic X-rays are used for measurements. Accelerated electrons collide with a target metal after applying a high voltage between the cathode where the electrons are emitted from and the target metal. Then, the electrons in the electron shell around a nucleus are punched out (Fig. 22.1). Simultaneously, the electrons are transferred from the upper orbits to the empty orbit, and the energy difference between these orbits is emitted as characteristic X-rays. Notably, $K\alpha$ lines emit energies corresponding to the energy gap between the L and K shells. The wavelengths of characteristic X-rays and absorption edges used for XSA are listed in Table 22.1. Although the K line includes

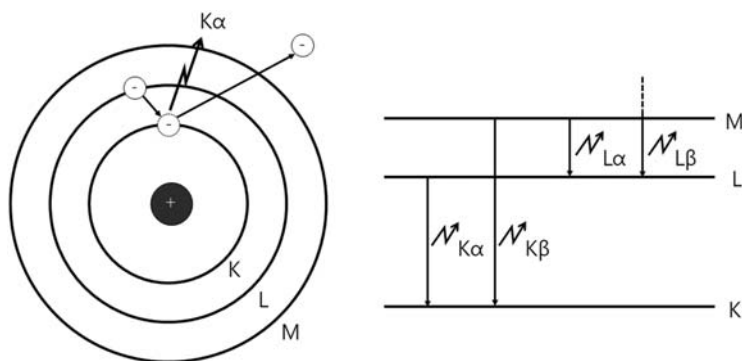


Figure 22.1 A simplified atom model of a target metal (*left*) and the energy bands on each shell (*right*).

Table 22.1 Wavelengths of characteristic X-rays and absorption edges [$\text{\AA}^*$]^a [23].

Element	$K\alpha$	$K\alpha_2$	$K\alpha_1$	$K\beta_1^b$	K absorption edge
Ti	2.74973	2.75216	2.74851	2.51391	2.49734
V	2.50483	2.50738	2.50356	2.28440	2.2691
Cr	2.29100	2.293606	2.28970	2.08487	2.07020
Mn	2.10314	2.10578	2.101820	1.91021	1.89643
Fe	1.937355	1.939980	1.936042	1.75661	1.74346
Co	1.790260	1.792850	1.788965	1.62079	1.60815
Ni	1.659189	1.661747	1.657910	1.500135	1.48807
Cu	1.541838	1.544390	1.540562	1.392218	1.38059

^aThe wavelength in $\text{\AA}^*$ is equal to $\text{\AA}$ within 5 ppm [23].

^bThe wavelength of $K\beta_1$ is generally used as the wavelength of $K\beta$.

$K\beta$, which corresponds to the emission energy of electrons falling from the M shell to the K shell, $K\alpha$ lines, which have a higher intensity than $K\beta$ lines, are commonly used for the measurement, but at that time, the $K\beta$ rays are eliminated by optics in the diffractometer. Conventionally, although metal filters have been used because of their absorption edges, the wavelength separation by energy band-pass using a semiconductor detector has also been adopted [22]. Note that each characteristic X-ray line has multiple lines. For example, $K\alpha_1$ and $K\alpha_2$ are in the category of the $K\alpha$ line. Due to their identical intensity ratios, the wavelength of the $K\alpha$ line can then be calculated using the weighted average of $K\alpha_1$ and $K\alpha_2$ by a 2:1 ratio. Diffraction lines can be separated into two if their profile is sharp, such as in annealed samples. However, since separating $K\alpha_2$ from $K\alpha_1$ is difficult due to their close wavelengths, both lines are commonly used as a combined $K\alpha$ doublet line for XSA. Thus, the doublet lines must be considered when determining the diffraction angle.

22.2.2 Crystal structure

Since crystals have the periodic structure of atoms, metals (e.g. Al, Cu, Fe, Mg, Ti, etc.) and their alloys are common crystalline materials for engineering materials, with each material having a specific crystal structure. In metallic materials, typical structures are body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp) as shown in Fig. 22.2. In bcc and fcc, atoms are placed at the corner and body or face center of the cube, respectively.

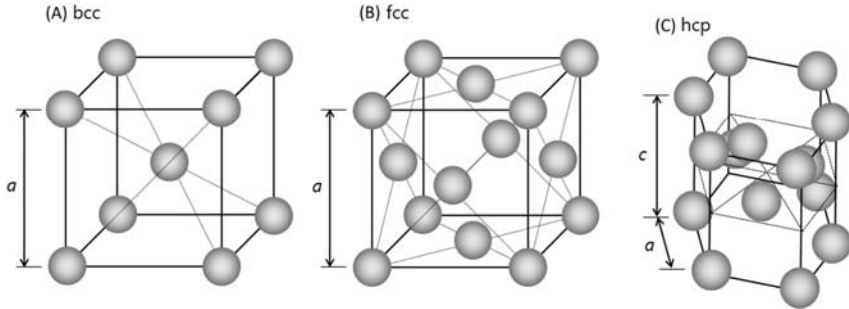


Figure 22.2 Schematic showing (A) the body-centered cubic (bcc), (B) face-centered cubic (fcc), (C) and hexagonal close-packed (hcp) lattice structures. Each sphere corresponds to an atom.

X-rays irradiated onto crystal materials produce diffraction X-rays corresponding to hkl in each lattice spacing. A Millar notation exists, in which h , k , and l are indicated with the smallest common divisor. However, a common divisor is not used in the diffraction phenomenon. The diffraction indices are expressed as hkl without brackets to distinguish them from the Miller index (e.g. 200, 220 and 222).

As shown in Fig. 22.3, lattice spacing, d^{hkl} , is subsequently obtained from the following relationships with the lattice constants a and c :

Cubic

$$d^{hkl} = \left(\frac{l^2 + k^2 + l^2}{a^2} \right)^{-1/2} \quad (22.1)$$

Hexagonal

$$d^{hkl} = \left\{ \frac{4}{3} \left(\frac{l^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right) \right\}^{-1/2} \quad (22.2)$$

The lattice constants and structures of common metals are listed in Table 22.2.

22.2.3 Diffraction from crystals

While angle dispersion measurements are taken using specific wavelengths, energy-dispersion measurements are taken using a fixed diffraction angle. In XSA, angle dispersion is generally adopted in the measurements. The diffraction line measurements based on the angle dispersion will be described.

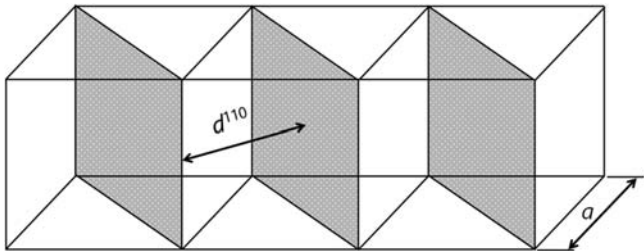


Figure 22.3 Example of a lattice with spacing, d^{110} , between $\{1\ 1\ 0\}$ planes in a cube with lattice constant a .

Table 22.2 Lattice constants and structures of common metals [23].

Metallic element	Structure	a [$\text{\AA}^*$]	c [$\text{\AA}^*$]
Al	fcc	4.0497	—
Cu	fcc	3.6148	—
Fe	bcc (α)	2.8665	—
	fcc (γ)	$3.555 + 0.0044 \times \text{wt\%C}$	—
Mg	hcp	3.2095	5.2107
Ni	fcc	3.5239	—
Ti	hcp (α)	2.9512	4.6845
	bcc (β)	3.3066	—

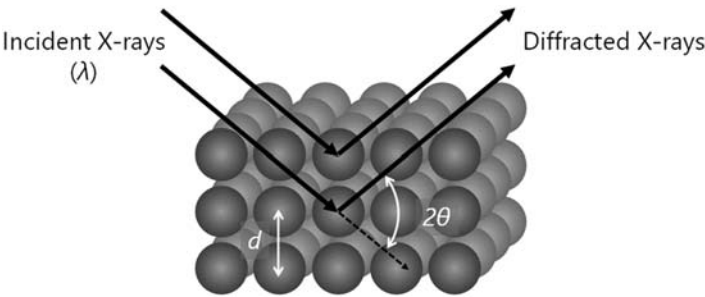


Figure 22.4 Schematic showing X-ray diffraction from a crystal.

Fig. 22.4 illustrates X-ray diffraction from a crystal with a specific wavelength, λ , diffracting at a diffraction angle, 2θ , according to Bragg's diffraction condition,

$$\lambda = 2d^{hkl} \cdot \sin\theta \tag{22.3}$$

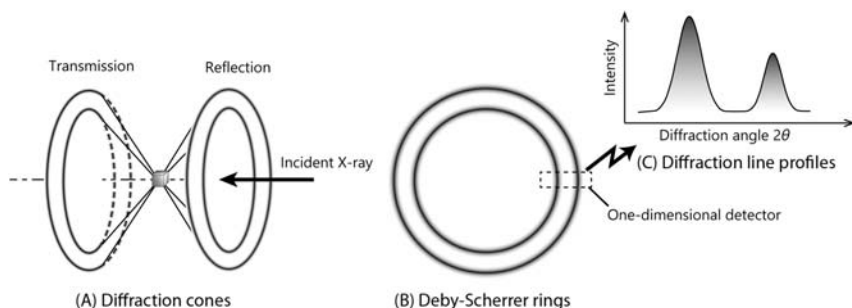


Figure 22.5 Diffraction from polycrystalline and diffraction line profiles. The figures (A–C) depict diffraction cones, Debye–Scherrer rings, and diffraction line profiles, respectively.

Although θ called the Bragg angle, is the angle between the incident X-ray and the diffraction plane, the diffraction angle (2θ), the angle between the incident and diffracted X-ray, is measured during actual measurements.

When incident X-rays are irradiated onto a piece of a polycrystalline sample, X-rays scatter and diffract in forward and backward directions, forming cone shapes (Fig. 22.5A). Subsequently, diffraction rings (called Debye–Scherrer rings) can be observed if a two-dimensional detector is placed to cross the cones. However, with a one-dimensional detector, which is more common than a two-dimensional detector, once the one-dimensional detector is placed to cross the rings as shown in Fig. 22.5B, diffraction line profiles are obtained (Fig. 22.5C). The ring radius corresponds to the diffraction angle. In the absence of enough crystal grains or when crystal grains have preferred orientations, the diffraction ring becomes discontinuous and spotty. The diffraction angle cannot be accurately determined in this case. Therefore, it is necessary to choose enough irradiation area or to increase the number of crystal grains that contribute to diffraction by oscillations.

22.2.4 Factors affecting diffraction lines

Although diffraction angles correspond to lattice spacing, as described in Section 22.2.3, the diffraction line has width and intensity in addition to the angle. The angle of diffraction depends on macroscopic stress, the intensity depends on the area¹ of the crystal contributing to diffraction

¹ Diffraction X-rays come from a specific volume, but since the penetration depth of ordinary X-rays is small, the volume is considered and expressed as an area.

and the width of the diffraction line depends on the nonuniformity of the stress fields. As metals are polycrystalline consisting of many crystal grains, although the measured sample has a macroscopically uniform stress, each grain has a different stress (Fig. 22.6). As a result, the obtained information after X-ray diffraction is the averaged information from the crystal grains, contributing to diffraction in the irradiation area (not the average of all crystal grains), since diffraction lines are generated by the oriented grains in a particular direction if they satisfy the diffraction conditions. In contrast to macroscopically uniform or averaged stress in a medium (named type I), grain-level stress, which is the average value in each grain, is named type II. Even when the macroscopic stress is small, it may have large intergranular stress [18,24–26]. Therefore, type II stress should be considered. As the integrated intensity of the diffraction line is proportional to the crystal area that contributes to diffraction, the intensity ratio corresponds to the texture or fraction of the crystal structure phases. However, suppose stress gradients exist beneath the surface within the X-ray penetration depth, for example, due to surface treatment, in such a case, the diffraction angle becomes different at each depth, so that the diffraction line profile becomes deformed due to the superposition of each diffraction line profile [27].

Inhomogeneous stresses in a grain are mainly caused by dislocations and are called type III stress. This inhomogeneous stress affects the diffraction line profile, particularly its width. Although its details are not contained in this article, one can obtain the dislocation density, crystallite size, etc. The inverse analysis of line profiles (line profile analysis) with broadening models is determined, depending on lattice defects or crystallite size

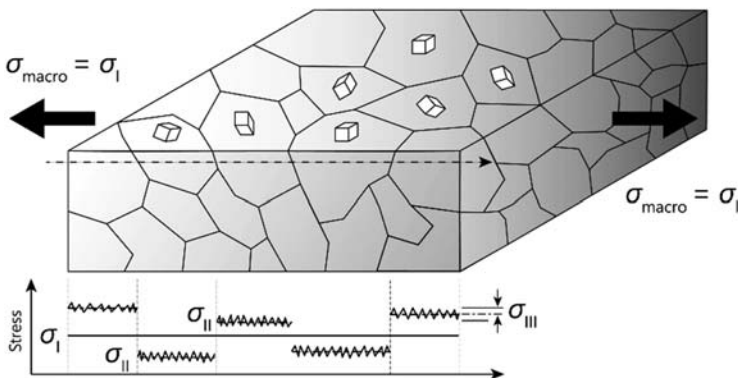


Figure 22.6 Macro- and microstresses in crystal grains and polycrystalline.

from the measured line profile. Although this basic principle has been known for a long time, as explained in detail by Warren's 'X-ray diffraction [28]', various applications have also been recently reported because analytical theories have been advanced (e.g. [29,30]) and analysis has become relatively easy with the development of computers. Some application examples include the characterization of work-hardening due to peening surface treatment [3,6,31], characterization of dislocation structures on fatigued austenitic stainless steel [32], development of metallurgical processing [33,34] and assessment of lattice defects due to irradiation [35–37].

22.3 Stress analysis

22.3.1 Stress and strain tensor

Fig. 22.7 shows the schematic of the deformation of a bar by applying tensile stress in an axial direction. Normal strain in the axial direction, ε_L , and the width direction, ε_W , are respectively defined as the deformation per unit length:

$$\varepsilon_L = \frac{\Delta l}{l_0} \quad (22.4)$$

$$\varepsilon_W = \frac{\Delta w}{w_0} = -\nu \cdot \varepsilon_L \quad (22.5)$$

where Δl and Δw are the deformation, l_0 and w_0 are the initial length of the specimen and ν is Poisson's ratio. In a three-dimensional Cartesian coordinate system, strain components towards each axis are denoted as ε_{ij} . The strain is the normal strain when $i = j$ and a shear strain when $i \neq j$.

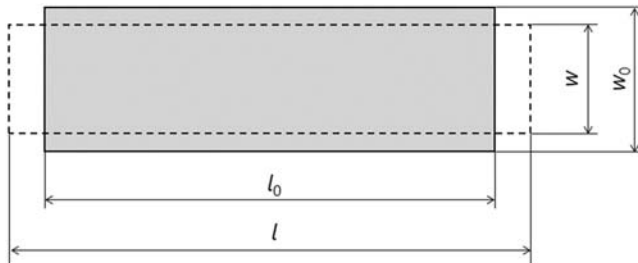


Figure 22.7 Deformed bar in the longitudinal direction with an axial load.

Work stress at a certain volume has six independent components, as shown in Fig. 22.8, and σ_{ij} denotes the tensor. σ_{ij} is expressed as τ_{ij} when $i \neq j$ in the figure to show shear stresses.

Since the principle of superposition can be applied to elastic strain, strains caused due to normal stress and the Poisson strain due to normal stress working in the vertical direction can simply be added and expressed with elastic compliance, s_{ijkl} , based on the equation below, following the Einstein summation convention.

$$\varepsilon_{kl} = s_{ijkl} \sigma_{ij} \quad (22.6)$$

In isotropic elastic materials, with Young's modulus, E , and Poisson's ratio, ν , the strain and stress tensors can be expressed as shown in Eq. (22.7), with strain and stress components denoted using x , y and z , and only the normal components ($\{\varepsilon_x, \varepsilon_y, \varepsilon_z\}^T$ and $\{\sigma_x, \sigma_y, \sigma_z\}^T$) are shown.

$$\begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \end{bmatrix} = \begin{bmatrix} 1/E & -\nu/E & -\nu/E \\ -\nu/E & 1/E & -\nu/E \\ -\nu/E & -\nu/E & 1/E \end{bmatrix} \begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{bmatrix} \quad (22.7)$$

Stress tensor can also be expressed with elastic stiffness, c_{ijkl} , as follows (22.8):

$$\sigma_{ij} = c_{ijkl} \varepsilon_{kl} \quad (22.8)$$

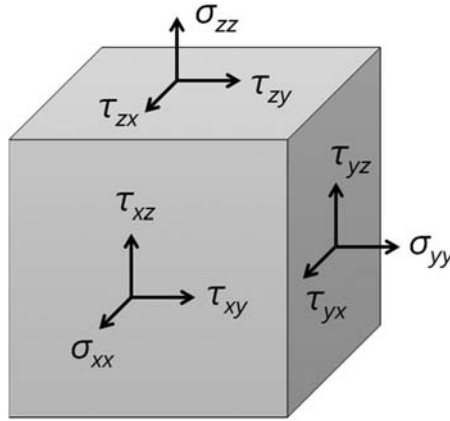


Figure 22.8 Stress tensor at a certain volume in an xyz -coordinate system. The first and second characters of the subscript indicate the work plane and direction, respectively.

22.3.2 Diffraction line shift

Deviation of Bragg's Eq. (22.3) by θ becomes

$$\Delta\theta = -\frac{\Delta d^{hkl}}{d^{hkl}} \tan\theta \quad (22.9)$$

where the symbol of deviation is indicated as Δ .

Considering the change in lattice spacing ratio the strain, ε , becomes

$$\varepsilon = -\Delta 2\theta / 2 \cdot \cot\theta \quad (22.10)$$

Based on these changes, an elastic strain can be obtained from the change in the diffraction angle (2θ) (Fig. 22.9).

Subsequently, assuming that the three vertical directions x , y , and z , the three stress components (σ_x , σ_y , σ_z) can be computed using the three strain components obtained by measuring the lattice spacing in respective directions. Their strains can then be computed using Eq. (22.11).

$$\varepsilon_{x,y,z} = \frac{d_{x,y,z} - d_0}{d_0} \quad (22.11)$$

where the subscript denotes the directions x , y , or z .

Despite omitting the indication of hkl for simplicity, all analysis protocols still rely on diffraction indices, hkl . However, a difficulty is encountered in the lattice spacing for a nonstrained sample, d_0 [38]. Although values obtained from literature on lattice constant are what is often used, the lattice constant of the actual sample is not always clear. For example, in steel materials, the lattice constant easily changes depending on carbon content during heat treatment. This issue also exists during neutron experiments. Finally, the stress components for each direction are obtained using Eq. (22.11), as shown below:

$$\begin{aligned} \sigma_x &= \frac{E^{hkl}}{(1 + \nu^{hkl})(1 - 2\nu^{hkl})} \{ (1 - \nu^{hkl})\varepsilon_x + \nu^{hkl}(\varepsilon_y + \varepsilon_z) \} \\ \sigma_y &= \frac{E^{hkl}}{(1 + \nu^{hkl})(1 - 2\nu^{hkl})} \{ (1 - \nu^{hkl})\varepsilon_y + \nu^{hkl}(\varepsilon_z + \varepsilon_x) \} \\ \sigma_z &= \frac{E^{hkl}}{(1 + \nu^{hkl})(1 - 2\nu^{hkl})} \{ (1 - \nu^{hkl})\varepsilon_z + \nu^{hkl}(\varepsilon_y + \varepsilon_x) \} \end{aligned} \quad (22.12)$$

where Young's modulus and Poisson's ratio, E^{hkl} and ν^{hkl} , depend on the diffraction indices, hkl .

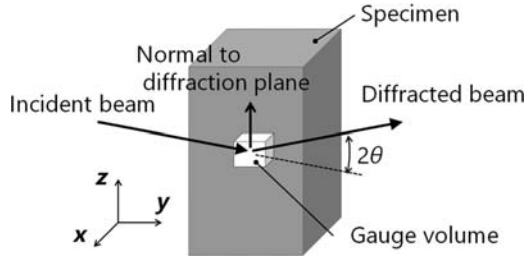


Figure 22.9 Measurement coordinate system for the three strain components.

Since high-energy X-rays are needed to perform the above-mentioned transmission measurements, the measurements are usually conducted using synchrotron X-rays. The most common XSA method, the $\sin^2\psi$ method performed using laboratory X-rays, is introduced in Section 22.3.3. Another source option for transmission measurement is neutrons. Traditionally, nuclear reactors have been used for stress measurements, but proton accelerators are increasingly being used (e.g. J-PARC in Japan, ISIS in the UK, and SNS in the USA). When measuring with synchrotron X-rays or a reactor neutron source, the angle dispersion method is often used, but in the case of an accelerator neutron source, the time of flight (TOF) method is used [13–18].

Where, the momentum (p) is expressed as $p = \lambda h$, using 'Planck's constant (h)', and the neutron flight velocity is expressed as $v = \lambda h/m$ because $p = mv$, where the mass of the neutron is m and the velocity is v . In the TOF method, the detector is located at a distance L ($=L_1 + L_2$) from a certain point (e.g. a neutron source), as shown in Fig. 22.10, thus the TOF (Δt) is expressed as $\Delta t = (\lambda h/m)L$. Therefore, due to Bragg's law with a fixed diffraction angle, lattice spacing can be determined by analyzing the diffraction intensity as a function of the TOF. This is a kind of energy dispersive method. Thus, the strain is obtained as $\varepsilon = \Delta t/\Delta t_0 - 1$, where Δt_0 denotes the TOF for a nonstrained sample with d_0 .

22.3.3 The $\sin^2\psi$ method

22.3.3.1 Fundamental equations in the $\sin^2\psi$ method

This section explains the $\sin^2\psi$ method, which is a de facto standard XSA method [39–41]. The $\sin^2\psi$ method analyses the in-plane stress of the sample surface, assuming a plane stress state in polycrystalline, after which the stress value is obtained from measuring diffraction angles at a same diffraction plane of individual crystal grains at several angles, ψ , between the normal and diffraction surfaces of the sample.

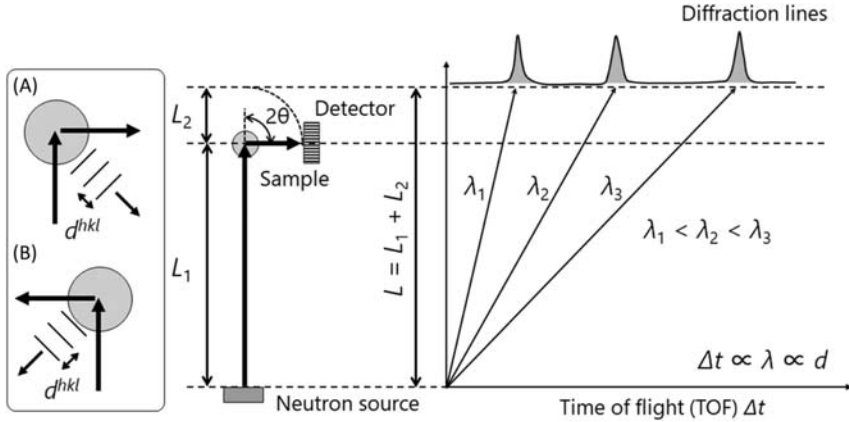


Figure 22.10 Neutron diffraction measurement by the TOF method using a pulsed neutron source. (A) and (B) show the relationship between measuring the lattice plane direction and the diffraction direction. Consequently, two orthogonal lattice spacings can simultaneously be measured when two detectors are placed in opposite directions.

During this measurement, two Cartesian coordinate systems are considered: the sample coordinate (S_i) and laboratory coordinate (L_i) systems (Fig. 22.11). The sample coordinate system is arbitrarily determined on the S_3 > the sample and the S_3 , the S_3 is normal to the sample surface. The laboratory coordinate system is determined based on this X-ray measurement system, after which the spacing of this lattice towards L_3 is measured every $\sin^2\psi$. As a result, stress (σ_φ) is obtained in the direction of which rotated φ around the S_3 from S_1 . Overall, the stress component σ_{km}^L in the laboratory coordinate system is calculated using the stress component σ_{ij}^S in the sample coordinate system and the direction cosine n_{ij} as following Eq. (22.13).

$$\sigma_{km}^L = \sigma_{ij}^S n_{ki} n_{mj} \quad (22.13)$$

As an example, σ_{33}^L is obtained, as shown in (22.14)

$$\sigma_{33}^L = \sigma_{11}^S n_{31}^2 + \sigma_{22}^S n_{32}^2 + \sigma_{33}^S n_{33}^2 + 2\sigma_{12}^S n_{31} n_{32} + 2\sigma_{23}^S n_{32} n_{33} + 2\sigma_{31}^S n_{31} n_{33} \quad (22.14)$$

The transformation matrix, n_{ij} is obtained by rotating φ first around the S_3 axis, followed by ψ around the S_2' axis ($//L_2$ axis) as (22.15)

$$n_{ij} = \begin{bmatrix} \cos\phi\cos\psi & \sin\phi\cos\psi & -\sin\psi \\ -\sin\phi & \cos\phi & 0 \\ \cos\phi\sin\psi & \sin\phi\sin\psi & \cos\psi \end{bmatrix} \quad (22.15)$$

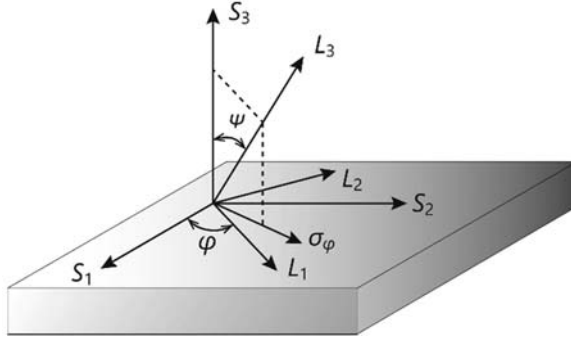


Figure 22.11 Coordinate systems (S_i and L_i) in samples and in the laboratory.

The relationship between strain, ε_{33}^L , and stress, σ_{33}^L , is shown in (22.16) from Hooke's law and invariant J_1 in the elasticity theory ($\sigma_{11}^L + \sigma_{22}^L + \sigma_{33}^L = \sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S$),

$$\varepsilon_{33}^L = \frac{S_2^{hkl}}{2} \sigma_{33}^L + S_1^{hkl} (\sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S) \quad (22.16)$$

where $S_1^{hkl} = -\nu^{hkl}/E^{hkl}$ and $S_2^{hkl} = (1 + \nu^{hkl})/E^{hkl}$ are hkl dependent, called the X-ray elastic constant or diffraction elastic constant to avoid confusion with mechanical constants. Substituting Eq. (22.16) into (22.14) gives Eq. (22.17):

$$\begin{aligned} \varepsilon_{33}^L = & \frac{S_2^{hkl}}{2} (\sigma_{11}^S \cos^2 \phi + \sigma_{12}^S \sin 2\phi + \sigma_{22}^S \sin^2 \phi - \sigma_{33}^S) \sin^2 \psi + \frac{S_2^{hkl}}{2} \sigma_{33}^S \\ & + S_1^{hkl} (\sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S) + \frac{S_2^{hkl}}{2} (\sigma_{13}^S \cos \phi + \sigma_{23}^S \sin \phi) \sin 2\psi \end{aligned} \quad (22.17)$$

$\sigma_{11}^S \cos^2 \phi + \sigma_{12}^S \sin 2\phi + \sigma_{22}^S \sin^2 \phi$ refers to in-plane stress on the specimen's surface. Eq. (22.17) can be rewritten with σ_ϕ , which denotes a stress in the ϕ direction from S_1 axis, as shown in (22.18)

$$\begin{aligned} \varepsilon_{33}^L = & \frac{S_2^{hkl}}{2} (\sigma_\phi - \sigma_{33}^S) \sin^2 \psi + \frac{S_2^{hkl}}{2} \sigma_{33}^S + S_1^{hkl} (\sigma_{11}^S + \sigma_{22}^S + \sigma_{33}^S) \\ & + \frac{S_2^{hkl}}{2} (\sigma_{13}^S \cos \phi + \sigma_{23}^S \sin \phi) \sin 2\psi \end{aligned} \quad (22.18)$$

In plane stress state, out-of-plane component stresses (σ_{33} , σ_{13} , and σ_{23}) are zero, ε_{33}^L becomes as in the following Eq. (22.19):

$$\varepsilon_{33}^L = \frac{S_2^{hkl}}{2} \sigma_\phi \sin^2 \psi + S_1^{hkl} (\sigma_{11}^S + \sigma_{22}^S) \quad (22.19)$$

Since the strain component (ε_{33}^L) is obtained to measure the diffraction angle (2θ) and Eq. (22.10), Eq. (22.19) is modified as shown below (22.20)

$$2\theta = S_2^{hkl} \tan\theta_0 \sigma_\phi \sin^2\psi - 2S_1^{hkl} \tan\theta_0 (\sigma_{11}^S + \sigma_{22}^S) + \theta_0 \quad (22.20)$$

Differentiating this equation with $\sin^2\psi$ results in another expression (22.21)

$$\frac{\partial(2\theta)}{\partial(\sin^2\psi)} = -S_2^{hkl} \tan\theta_0 \sigma_\phi \quad (22.21)$$

As a result, in-plane stress, σ_ϕ , is obtained following Eq. (22.22)

$$\sigma_\phi = \frac{\partial(2\theta)}{\partial(\sin^2\psi)} \cdot -\frac{1}{S_2^{hkl} \tan\theta_0} = M \cdot K \quad (22.22)$$

Here, $M = \partial(2\theta)/\partial(\sin^2\psi)$ is the slope of the 2θ – $\sin^2\psi$ diagram ($\sin^2\psi$ diagram) and $K = -1/S_2^{hkl} \tan\theta_0$ is the constant that is determined by the elastic constant and diffraction angle of the nonstrained sample.

It is important to remember that the plane stress condition is assumed. Suppose those shear stresses (σ_{13} and σ_{23}) are not zero, the $\sin^2\psi$ diagram will not be a straight line (Fig. 22.12). Additionally, in frequent concerns, stress gradients on X-ray penetration depths cause $\sin^2\psi$ diagrams to be nonlinear [27]. Both effects can appear at once in a $\sin^2\psi$ diagram.

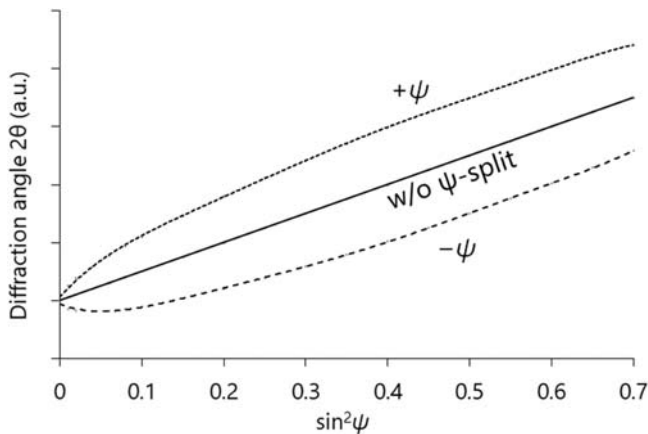


Figure 22.12 Schematic showing a $\sin^2\psi$ diagram exhibiting ψ -split, caused by shear stress in the depth direction (σ_{13} and σ_{23}).

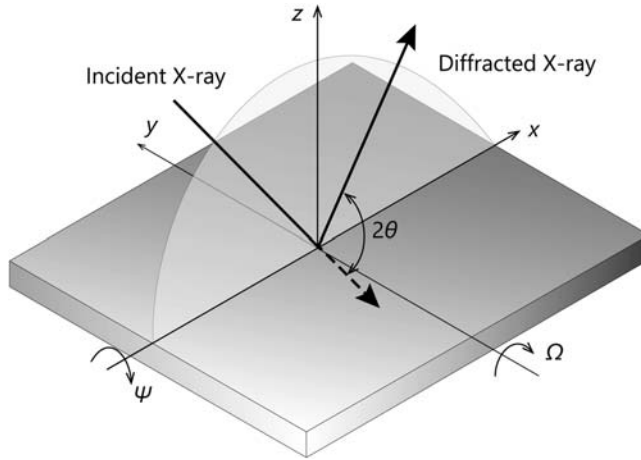


Figure 22.13 Tilting direction of the ψ -angle and measurement systems, showing the iso-inclination (Ω -diffractometer) and side-inclination (Ψ -diffractometer).

22.3.3.2 Inclination direction of the ψ -angle

To draw the $\sin^2\psi$ diagram, diffraction angles must be measured at several ψ -angles. As shown in Fig. 22.13, there are commonly two directions of tilting the ψ -angle. In the iso-inclination method (Ω -diffractometer), while the incident and diffracted X-rays are on the x - z plane, the y -axis is rotated to have the diffracted surface's normal inclining toward the x -axis (the normal to the diffraction plane shown is parallel to the z -axis in Fig. 22.13). As a result, an in-plane stress component in the x -direction can be obtained. Using this method, the X-ray detector and source are both rotated around the same y -axis, making the measurement system relatively simple to set up. On the contrary, in the side-inclination method (Ψ -diffractometer), the x -axis shown in Fig. 22.13 is rotated to measure the lattice spacing in the several ψ -directions so that a plane stress component can be obtained in the y -direction. With this method, the measurement range of ψ can be widened since the surface containing both incidents and diffracted X-rays is inclined in the direction of stress measurement.

22.3.4 Stress constant

Based on Eq. (22.22), stress can be obtained by multiplying the slope, M , in the $\sin^2\psi$ diagram by the stress constant, K . The stress constant is then derived from the elastic constant, S_2^{hkl} , wavelength of X-rays, diffraction indices, and lattice constant, which are dependent on material and X-ray

conditions. It is important to remember that although the elastic constant depends on the diffraction indices (hkl), it differs from mechanical elastic constants. Therefore, the constant is measured using X-ray diffraction measurements under known stresses or calculated theoretically using the elastic constant of a single crystal.

22.3.4.1 Experimental method

In Eq. (22.22), when known stresses, σ_a , is applied, the stress constant equals the stress divided by the slope in the $\sin^2\psi$ diagram. Subsequently, the stress constant is determined as the inverse of the slope against the applied stress by measuring the $\sin^2\psi$ diagram using different loads to reduce the measurement error (Fig. 22.14). Four-point bending is often employed to achieve this, which uses a small force to accomplish large and constant stresses in the X-ray irradiation area.

22.3.4.2 Theoretical method

The elastic constant of a polycrystalline can be calculated using the elastic constant of the single crystal since a polycrystalline is an aggregate of single crystal grains. Here, the elastic constant in XSA is a constant relating the change in diffraction plane spacing (i.e. strain) with the macroscopic stress of the sample. Consequently, two opposing polycrystalline models exist, one in which crystal grains with different crystal orientations are connected in parallel (the Voigt model) and the other in which crystal grains with different crystal orientations are connected in series (the Reuss model).

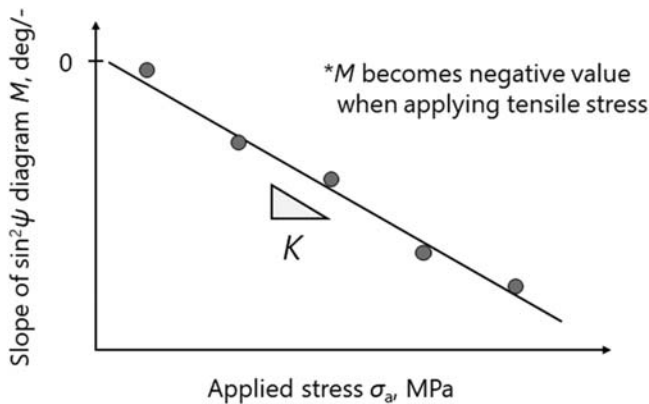


Figure 22.14 Graph showing the determination of stress constant, K , from the regression line of the slope, M , of the $\sin^2\psi$ diagram against applied stress, obtained in experiments.

In the Voigt model, since the strain generated in each crystal grain is equal, it is called a constant strain model. The diffraction elastic constant of a cubic crystal can then be expressed using Eq. (22.23) below and the compliance s_{ij} of a single crystal.

$$\begin{aligned}\frac{S_2^{hkl}}{2} &= \frac{5(s_{11} - s_{12})s_{44}}{6(s_{11} - s_{12}) + 2s_{44}} \\ S_1^{hkl} &= \frac{(2s_{11} - 2s_{12} - s_{44})(s_{11} + 2s_{12}) + 5s_{12}s_{44}}{6(s_{11} - s_{12}) + 2s_{44}}\end{aligned}\quad (22.23)$$

It is obvious from this equation that the elastic constant is not dependent on crystal orientation and that its value is constant regardless of crystal orientation.

Meanwhile, in the Reuss model, the stress generated in each grain is equal. Therefore, it is called the constant stress model and expressed by Eq. (22.24) using the function $\Gamma(h, k, l)$ of the crystal orientation.

$$\begin{aligned}\frac{S_2^{hkl}}{2} &= s_{11} - s_{12} - 3s_0\Gamma \\ S_1^{hkl} &= s_{12} + s_0\Gamma \\ (s_0 &= s_{11} - s_{12} - s_{44}/2)\end{aligned}\quad (22.24)$$

Where the orientation function for cubic crystals is expressed using the diffraction indices, hkl .

$$\Gamma = \frac{h^2k^2 + k^2l^2 + l^2h^2}{(h^2 + k^2 + l^2)^2}\quad (22.25)$$

In addition, Eq. (22.26) described the relationship between compliance and stiffness.

$$\begin{aligned}c_{11} &= \frac{s_{11} + s_{12}}{(s_{11} - s_{12})(s_{11} + s_{12})} \\ c_{12} &= -\frac{s_{12}}{(s_{11} - s_{12})(s_{11} + s_{12})} \\ c_{44} &= 1/s_{44}\end{aligned}\quad (22.26)$$

While crystal grains in actual materials are randomly oriented in all directions, these models provide upper and lower limits, which are approximately mean values. Compared to the above models, Kröner's model provides the stress constant more accurately. In this model, sphere

inclusions are assumed to be present in the matrix based on Eshelby's inclusion theory, resulting in a value close to the previous average values.

22.3.5 Practical conditions for steel

The measurement conditions for two types of steels having different lattice structures, bcc (α Fe) and fcc (γ Fe), are presented in this section. According to Eq. (22.10), the resolution of the measured strain increases with the diffraction angle. Therefore, selecting a combination of the X-ray wavelength (i.e. characteristic X-rays) and the diffraction indices is recommended to increase the diffraction angle. With α Fe, 211 reflections are measured using the Cr $K\alpha$ line. Since its lattice constant, a , is 2.8665 Å, and its wavelength is 2.2897 Å, the lattice spacing, d , and diffraction angle, 2θ , respectively, become 1.1702 and 156.49 degrees, according to Eqs. (22.1) and (22.3). Contrastively, with γ Fe, 311 reflections are measured using the Mn $K\alpha$ line. As a result, the lattice spacing and diffraction angle become 1.0996 and 146.09 Å, similar to α Fe, since its lattice constant, a , is 3.6469 Å, and its wavelength is 2.1031 Å. The lattice constant and wavelength values are based on literature [23].

Subsequently, the stress constants are calculated based on the Kröner model to be $-319 \text{ MPa}/^\circ$ for α Fe and $-375 \text{ MPa}/^\circ$ for γ Fe, including their stiffness values ($c_{11} = 228$, $c_{12} = 132$, $c_{44} = 116.5$ for α Fe [42], $c_{11} = 206$, $c_{12} = 133$, $c_{44} = 121$ for γ Fe [43]).

As a matter of importance, based on the basics for applying the $\sin^2\psi$ method, the following points are required for its application:

- A polycrystalline sample and continuous diffraction rings (not spotty) with sufficient intensity.
- Absence of a strongly preferred orientation sample
- An isotopically elastic sample.
- A measurement region with plane stress state.
- Absence of a stress gradient in the measurement region.

If these conditions are not satisfied, the $\sin^2\psi$ diagram may be curved, wavy, or irregular, so the stress value obtained from the slope of the diagram will be incorrect. Although the stress values are automatically generated once the measurement is performed by a commercial machine, it is recommended to check the diffraction line profile shape and $\sin^2\psi$ diagram to confirm the validity of the analysis and to prevent a miscalculation of the stress.

22.4 Summary

This chapter briefly introduces the general knowledge necessary for XSA, such as the principle of X-ray generation, diffraction theory, crystal structure of materials, and the relationship between stress and diffraction. In any case, XSA is an effective analytical method. The $\sin^2\psi$ method is a classic yet de facto standard and delivers significant results. Various applications have been assessed with XSA, including welding [7,44], surface treatments [3,5,6], mechanical processing [45], etc. Additive manufacturing is also expected to benefit from its application [46–48]. In addition to expanding applications, the measurement method has evolved from two-dimensional to three-dimensional [26,49–53].

It should be noted that correct measurements cannot be performed unless some requirements are satisfied, even though commercial measurement machines can easily perform measurements and display the results. Therefore, knowing the principles and basic theory is crucial for obtaining meaningful results before starting a measurement. It is also effective to receive support from a person who is proficient in XSA.

Finally, for a deeper understanding, must-read books are introduced. The book ‘Residual Stress Measurement by Diffraction and Interpretation’ [54] comprehensively introduces X-ray stress measurements. In addition to diffraction methods using X-rays and neutrons, ‘Structural and Residual Stress Analysis by Non-destructive Methods: Evaluation—Application—Assessment’ [27] includes non-diffraction, ultrasonic, and magnetic techniques. ‘Elements of X-ray Diffraction’ [23] remains an essential resource for X-ray users even though the first edition was published over half a century ago. In addition to X-rays, neutron is also an advantageous probe for measuring stresses. To this end, there are some books written on the neutron diffraction technique [55,56]. Many practical cases relating to residual stress on mechanical components are provided in the book ‘Residual Stress’ [44].

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CHAPTER 23

Non-destructive testing of ferromagnetic steel components based on their magnetic response

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23.1 Introduction

Magnetism entails many facets in contemporary non-destructive testing (NDT):

- A way to convey and transmit information like in eddy current testing [1].
- A source of a mechanical force like in magnetic particle inspection [2].
- The natural earth field is distorted by defects or properties to be assessed like in metal magnetic memory [3].
- An induced magnetic field is distorted by surface or subsurface defects like in magnetic flux leakages [4].

A new trend consists in exploiting magnetism differently, still for an NDT purpose, but the focus is set on the magnetization mechanisms of ferromagnetic components and their capability to indirectly convey information about targeted properties (mechanical, microstructural, etc.) [5].

Steel production is by far more extensive than any other metal production. Steel is used in domains as diverse as transportation (railway tracks, boat tanks, etc.), construction (concrete re-enforcing bars, bridges, etc.) [6], and energy (pipelines, turbines, etc.). In the steel industry, the demand for NDT is immense. Historically, surface defects (porosity, corrosion, cracks, etc.) were first targeted, but internal properties like residual stresses, plastic strains, internal dislocations, and the likelihood of failure due to creep or fatigue have grown in interest recently.

Every NDT method (ultrasound, magnetic particle inspection, X-Ray diffraction, etc.) can be applied to steel. Still, the techniques relying on magnetization mechanisms are unique to ferromagnetic materials, including steel [7].

The idea of developing NDT from the magnetization response is not new, and the first scientific publications on this topic can be found in the 60s [8,9]. First, developed at the academic level, it soon grew significant interest among steel companies. The first industrial machines dedicated to this topic were commercialized in the 1980s and found relative success [10]. Nowadays, devices like the Fraünofer IZFP 3MA or the Stresstech rollscan are relatively common [11–13].

The implementation and configuration of these devices are all based on the same protocols [14,15]. A large amount of experimental data is collected, then specific indicators evaluated on this data are defined. Eventually, complex mathematical correlations are established with targeted properties predetermined on well-known specimens. This method relies on meticulous experimental campaigns and leads to rejection thresholds setting acceptance limits. This configuration process is tedious, and not always reliable, and manufacturers are looking for alternatives.

Unfortunately, the configuration issue is not the only one mentioned by the end-users; the signal interpretation, indicators selection, and physical meaning are also recurrently stated as holding back this technological development [16].

Recently, researchers have proposed a new, fundamentally different approach. They are convinced that the sensitivity to the targeted properties differs from one magnetization mechanism to the other [5,17]. Progress in this domain comes from developing experimental situations where those mechanisms are separated. Once the targeted property is well defined, the final step consists of exploiting the most sensitive magnetization mechanism.

In this chapter, we will introduce in the first section what is nowadays considered in this domain as a targeted property. Then, the magnetization mechanisms will be described, such as the experimental situations where these mechanisms can be ideally observed. In the third section, correlations between the targeted properties and the magnetization mechanisms will be shown, and the last paragraph will include conclusions and perspectives.

23.2 Non-destructive testing based on the magnetization mechanisms: the targeted properties

In the domain of NDT based on the magnetization mechanisms, the targeted properties to be assessed can be classified into three categories:

- Internal mechanical stress
- Surface and subsurface heterogeneities
- Aging, creep, and microstructural variations versus time

23.2.1 The internal mechanical stress

In continuum mechanics, stress is defined as a physical quantity that expresses the internal forces that neighboring particles of a continuous material exert on each other. Internal mechanical stress is a critical factor in material performance, structural reliability, and the lifetime of industrial systems. Many techniques have been developed for their assessment [18,19]. The hole-drilling method [20], the contour method [21], the crack compliance method [22], and the stripping method [23] are mechanical techniques [19]. Chemical methods exist, too [24]. These techniques are destructive. NDT methods have also been developed [25], like diffraction methods (X-ray, Neutron), ultrasonic, or acoustic [24]. All these techniques can be applied independently from the tested specimens' nature. For ferromagnetic steel, methods based on the magnetization processes can be used as well. Eddy currents testing [26], magneto-acoustic emission [27,28], electromagnetic acoustic transducer [19], and Magnetic Barkhausen Noise (MBN) [29–31] are some of the most used magnetic methods, alone or in combination with other NDT techniques [32].

23.2.2 Surface and subsurface heterogeneities

Every metallic material contains heterogeneities. Inherent to the elaboration process, they spread all over the materials. These defects may be inclusions (metallic or nonmetallic), segregated or plastically deformed areas, cracks, precipitates of a second phase (iron carbide in steel), etc. [23,33]. These heterogeneities not only affect the mechanical properties. They are detrimental to the surface aspect and facilitate corrosion [34,35]. Furthermore, they can induce stress concentrations and thus cause premature failure of in-service components. The traditional NDT methods currently used to analyze the quality of new and in-service materials are mainly dedicated to detecting heterogeneities. These methods include

ultrasound [36], X-ray [37], eddy current [1], or electrostatic conductivity [38]. Successful results have been obtained using these techniques for non-metallic inclusions. However, metallic inclusions or heterogeneities are more complex to detect due to their similar physical properties to the host metal.

Surface defects are relatively easy to detect, and many existing techniques such as optical scanning can be used for this [39]. Subsurface damage observation is much more challenging. Subsurface damages are highly detrimental. They directly determine the performance and lifetime of a mechanical part, and their assessment is a priority [40].

23.2.3 Aging, creep, and microstructural variations versus time

In thermal power plants, ferromagnetic steels used in turbines and boilers are permanently exposed to high temperatures and pressures [41,42]. Similarly, in aeronautics, steel materials are exposed to extreme external conditions [43]. This continuous exposure can lead to irreversible microstructural changes. If not monitored on time, they can be followed by severe damages or even catastrophic incidents. Classical NDT techniques aim to identify material flaws at a later stage. Once a crack is initiated, it grows exponentially, and at the detection time, it is often too late to avoid irreversible harm. However, it has already been experimentally verified that a specimen undergoes local microstructural changes before crack initiation. If monitored on time, such microstructural clues can help anticipate failures. The concept of crack length versus time is shown in Fig. 23.1. Microscopic imaging methods can be used to observe microstructural variations. These methods include scanning electron microscopy (SEM) [44] and electron backscatter diffraction (EBSD) [45]. The tested specimens must undergo specific shape and size and require extensive sample preparation effort beyond the NDT's scope to obtain reliable data.

These methods find application at the laboratory scale, but in-situ applications are definitively unimaginable. Fig. 23.2 shows the microstructural evolution of creep on a strain versus time curve [46]. Initially, isolated cavities are created, eventually growing and forming larger oriented cavities. Under higher strain, oriented cavities result in crack formation and, finally, material rupture.

To replace SEM or EBSD in an industrial context, one promising solution is to use the magnetization signature and correlate it to the material microstructure. The magnetic response is strongly dependent on the

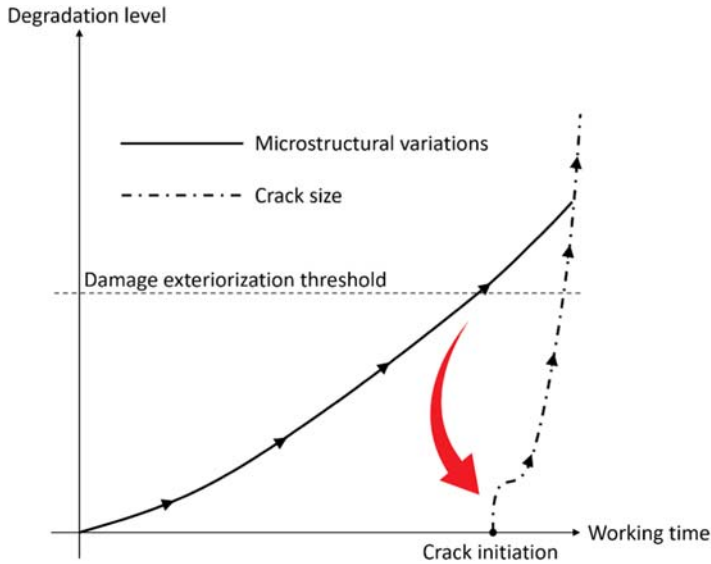


Figure 23.1 Comparison of crack size versus time, microstructural variation versus time.

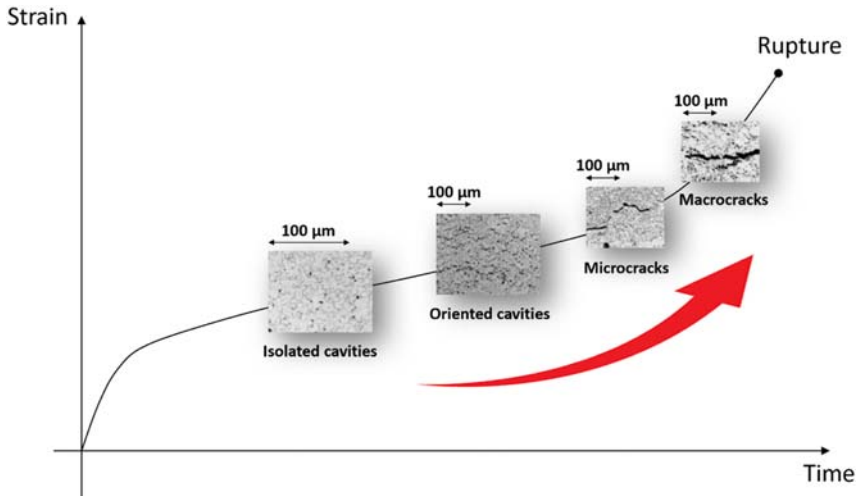


Figure 23.2 Strain versus time, illustration of the creep effect.

microstructural properties and distribution, and contemporary magnetic sensors can easily detect local information. Magnetic techniques have already been tried to identify creep, mostly on low-alloy steel, and a relatively poor correlation was found, as illustrated in Table 23.1 [41]. In this table, selectivity means the choice and effectiveness of the method.

Table 23.1 Comparison of non-destructive testing methods for creep detection.

Technique	Sensitivity	Selectivity	Damage type
Replication [41]	Surface only	++	Localized
Ultrasonic [48]	Average over thickness	++ (later stages) Surface sensitive	Localized/ volumetric
Magnetic properties [49]	Bulk	– / +	Volumetric
Barkhausen emission [50]	Thin subsurface layers	+ (Surface sensitive)	Localized
Eddy current [51]	Decays rapidly with depth	–	Volumetric

++ Good.
– Poor.

Quite surprisingly, opposite conclusions can be found in the literature about the selectivity of magnetic methods where Sposito et al. [41] rank it as poor, Tomas et al. result [47] in reliable applicability to detect early-stage fatigue and foresee lifespan.

23.3 The magnetization mechanisms

23.3.1 Ferromagnetism

Ferromagnetism occurs from atomic magnetic moments of electronic origin becoming ordered into small regions known as magnetic domains [52]. Each magnetic domain is typically composed of 10^{12} to 10^{18} magnetic moments aligned in the same direction and orientation. The size of the magnetic domains can vary from 10^{-4} to 10^{-6} m. At the domain boundaries, the atomic magnetic moments change their direction. These boundaries are called domain walls. As illustrated in Fig. 23.3, inside a domain wall, the change in direction progressively takes place over several hundred atoms (the exact number depends on energy minimization).

A fully saturated magnetic state characterizes every domain. Unless most of them are aligned in a given direction, the vector sum of all the domains is zero in a macroscopic demagnetized state. The domain direction of alignment typically follows the crystallographic axes. Due to the minimization of the magnetocrystalline anisotropy, some axes called “easy axes” are favored. The single-domain state being highly energetically unfavorable, an unmagnetized ferromagnetic material contains a large number of domains. The domain’s energy (known as magnetostatic)

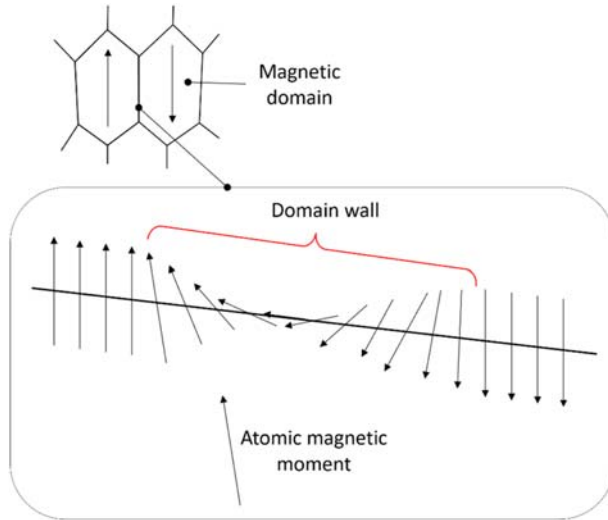


Figure 23.3 Orientation change of atomic magnetic moment in a Bloch type domain wall.

increases following an increase in the magnetic moment's number. Under a magnetic field stimulus, domains favorably aligned with the magnetic excitation grow at the expense of the unfavorable ones. The growth of a magnetic domain generates irreversible domain wall motions. The domain extension and the amount of domain wall motions depend on the intensity of the applied excitation, but microstructural, composition, and internal stresses are also highly influential.

As already discussed, the microstructural inhomogeneities include voids, cracks, nonferromagnetic inclusions, or impurities. These defects affect the mobility of the domain walls during the magnetization process. More specifically, two reasons can be listed:

- The reduction of the domain wall energy due to nonmagnetic regions.
- The generation of unusual domains called spike domains close to the nonmagnetic areas and the resulting reduction of the magnetostatic energy.

By reducing the domain wall area, an inclusion reduces the domain wall energy. It inhibits any motion, up to an applied field strong enough to push it through the following hooking defect. The creation of unconventional domains around inclusions was first suggested by Neel [53]. Inclusions produce a significant returning force. As a domain wall crosses

a defect, spike domains are generated in parallel to a reduction of the magnetostatic energy. Later, Neel's concept was experimentally confirmed by Williams [54,55], who studied iron-silicon crystals and checked the presence of spike domains.

The impending power of inclusions on the domain wall motion depends on their size. A large defect ($\approx 1 \mu\text{m}$, approximately the domain wall thickness) primarily hinders walls through spike domain formation and growth. More minor inclusions impede a wall mainly by reducing the domain wall energy. From the macroscopic point of view, a ferromagnetic material is constituted of multiple inclusions of randomly distributed sizes and shapes. On the first hand, this complex density makes it quasiimpossible to foresee the evolution of the magnetic parameters.

On the other hand, the effects of specific inclusions on the magnetization mechanisms can be studied and lead to conclusions. Significant non-magnetic defects will increase the coercivity and decrease the initial differential permeability (larger magnetostatic energy). Minor nonmagnetic flaws (second-phase precipitates or carbide inclusions) will also increase the coercivity and the initial differential permeability. Still, the reason is, in that case, linked to the reduction of the domain walls' surface energy [52].

The magnetization process in a ferromagnetic material is illustrated in a simplified way in Fig. 23.4. It can be summarized as follows: the magnetic domains with a magnetization oriented favorably to the applied magnetic field grow, while the domains unfavorably oriented decline in proportion. Then the magnetization of a magnetic domain, initially oriented along an easy axis, coherently rotates towards the direction of the applied magnetic field [56].

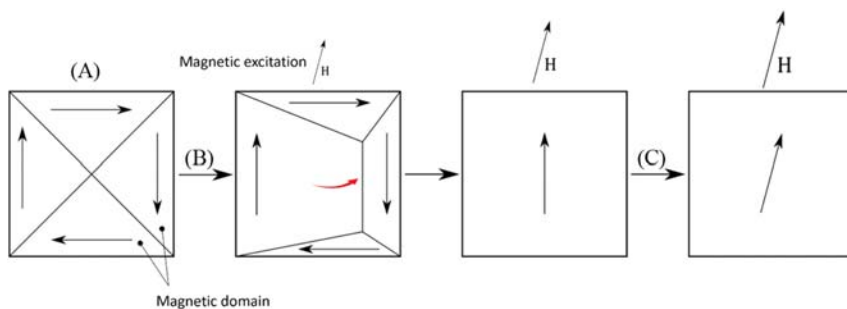


Figure 23.4 Schematic illustration of the magnetization process. (A) Demagnetized state (B) Domain wall motion (C) Magnetization rotation. In practice, the two mechanisms can occur simultaneously.

23.3.2 The magnetization mechanisms and their associated experimental situations

Each magnetization mechanism is characterized by its own time constant, its own sensitivity to magnetic excitation, and the targeted properties listed in the second section of this chapter. It is complex to establish a list of magnetization mechanisms, most of which overlap or even happen simultaneously. Five of them can, however, clearly be distinguished:

- The domain wall bulging:

The domain wall bulging is a high time constant, reversible local distortion of the magnetic domain walls, happening in the low magnetic field amplitude excitation range [56,57]. The so-called magnetic incremental permeability is the best way to observe domain wall bulging and its variations versus the targeted properties (For a practical example, refer to Fig. 23.5). Magnetic incremental permeability is defined as the magnetic response of a ferromagnetic specimen exposed to a steady, high amplitude quasistatic magnetic field (0.1 Hz , $H_{\max} > 5 \cdot H_c$) superimposed to a small amplitude alternative magnetic excitation (50 kHz , $H > H_c/2$). The mathematical expression of magnetic incremental permeability μ_Δ is:

$$\mu_\Delta = \frac{1}{\mu_0} \cdot \frac{\Delta B}{\Delta H} \quad (23.1)$$

Two options can be used to measure the magnetic incremental permeability:

- The flat coil solution, where the coil impedance is monitored along the whole magnetization process [58].

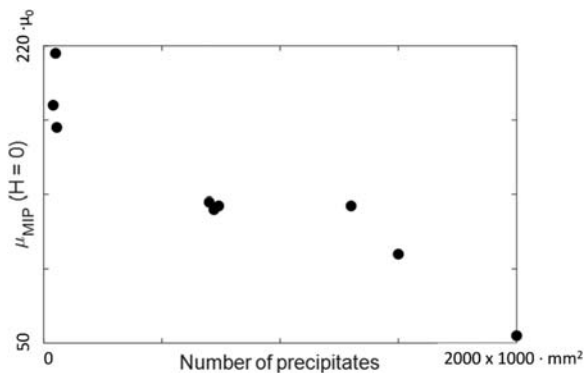


Figure 23.5 Typical evolution of the magnetic incremental permeability at $H = 0$ as a function of the number of precipitates.

- The transmitter/receiver coil solution see [59].
- The domain wall irreversible motions:

The magnetic domain wall's irreversible motions are a middle-range time constant and amplitude magnetization mechanism. It is due to the irreversible motions of the magnetic domain walls when they break away from pinning sites under the influence of magnetic excitation. The best way to observe the domain wall's irreversible motions and its variations versus the targeted properties is through the so-called MBN technique [31,60].

Every domain wall motion generates local flux variations that trigger discontinuous magnetic flux density displayed as a series of electrical pulses induced in an inductive magnetic sensor [61]. Among the large variety of magnetic sensors for MBN measurement, the pickup coil is the most popular in use.

Inside a material, the domain number is vast, the wall motions can be assimilated to a stochastic process, and the MBN raw signal is erratic and not reproducible. To overcome this issue and to obtain repeatable results, time average indicators are used for the MBN analysis. This includes for instant the MBN energy (MBN_{energy}) [61–64] (For illustration, refer to Fig. 23.6 top right-hand side corner):

$$MBN_{energy}(t) = \int_0^t \text{sign} \left[\frac{dH}{dt}(s) \right] V_{BK}^2(s) ds \quad (23.2)$$

Where V_{BK} is the sensor coil electromotive force, MBN_{energy} is not strictly energy but can be assimilated into an image of the kinetic energy of the domain walls [61,64].

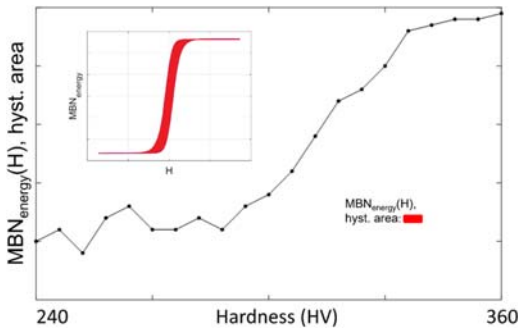


Figure 23.6 Typical evolution of the $MBN_{energy}(H)$ hysteresis loop area as a function of hardness.

- The magnetization rotation:

The magnetization rotation is a high time constant and amplitude magnetization mechanism. It corresponds to the rotation of the magnetic moment in a magnetic domain under the influence of very strong excitations. Among the magnetization mechanisms, the magnetization rotation has barely been studied and even less in an NDT context. Usually, this mechanism starts once the saturation elbow is reached and continues up to the magnetization saturation. Magnetization rotation can be observed experimentally when a tested specimen is excited with a high amplitude rotating magnetic field [56]. At sufficiently high excitation, the domains begin to merge and annihilate. Ideally, the domain structure converges toward a single-domain structure under an extremely high magnetic field. The disappearance of the magnetic domains and their kinetic reduces the hysteresis losses and the influence of the structural properties (dislocations, precipitates, etc.).

- The domain wall frequency dependence, ripples, and avalanches phenomena:

The magnetic energy losses in a ferromagnetic core have been studied for many years. It is a critical aspect of the definition of a new prototype as these losses affect the conversion efficiency and the temperature distribution highly. In this domain, Bertotti's statistical theory of losses [65,66] is still the most used method to evaluate the ferromagnetic losses in electromagnetic conversions. The statistical theory of losses is based on the concept of loss separation. It works under sinusoidal magnetization and assumes the absence of skin effect. The total loss per cycle W_{tot} is supposed to be the sum of three contributions (Eq. 23.3):

$$W_{\text{tot}} = W_{\text{hyst}} + W_{\text{clas}} + W_{\text{exc}} \quad (23.3)$$

W_{hyst} is the frequency-independent hysteresis loss contribution. W_{clas} (Eq. 23.4) is the classical eddy current loss term:

$$W_d = \frac{\sigma d^2}{12} \int_0^{1/f} \left(\frac{dB_a}{dt} \right)^2 dt \quad (23.4)$$

W_{clas} is derived from Maxwell's equations. It is due to the macroscopic eddy currents. B_a is the projection of the induction field $\mathbf{B}_a$ averaged through the sheet cross section in the thickness direction. σ is the electrical conductivity and d is the lamination thickness.

Finally, W_{exc} is the excess eddy current loss (Eq. 23.5), it is a direct image of the domain wall frequency dependence, ripples, and avalanches

phenomena (magnetic domains kinetic) as observed during the magnetization process.

$$W_{ex} = \sqrt{\sigma S G V_0} \int_0^{1/f} \left| \frac{dB_a}{dt} \right|^{1.5} dt \quad (23.5)$$

S is the cross section, $G = 0.1356$ is a dimensionless coefficient, and V_0 is a $\max(B_a)$ dependent statistical parameter linked to the microstructure [67].

This magnetization mechanism is frequency dependent and is happening under middle-range field amplitude. An illustration of the relationship between this mechanism and plastic strain is available in figure 4 of Ref. [68].

- The macroscopic eddy currents:

This magnetization mechanism is well identified in the NDT community, it is the fundament of the eddy current testing method [1], and it is observable through the W_{clas} term in the statistical theory of losses [66] (an example is given in Fig. 23.7). This mechanism is frequency-dependent and happens whatever the amplitude of the magnetic excitation. It is worth mentioning the skin effect associated with this mechanism [69–71] which reduces the volume of the magnetized mater as the frequency increases.

Table 23.2 summarizes the different magnetization mechanisms' properties (time constant, excitation level, geometrical scale).

Fig. 23.8 provides pictures of sensors (on the top), specimens, and examples of experimental setups (on the bottom) used at the academic scale to observe and isolate the magnetization mechanisms.

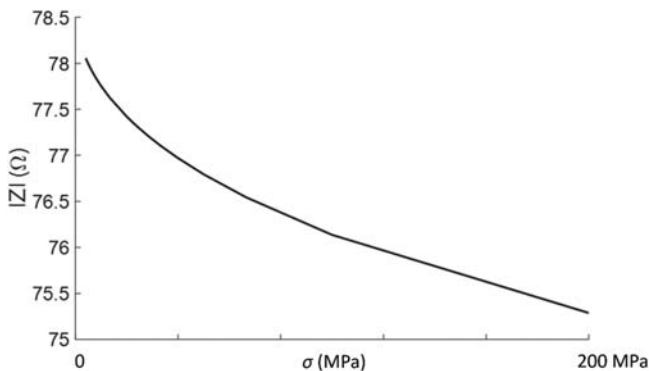
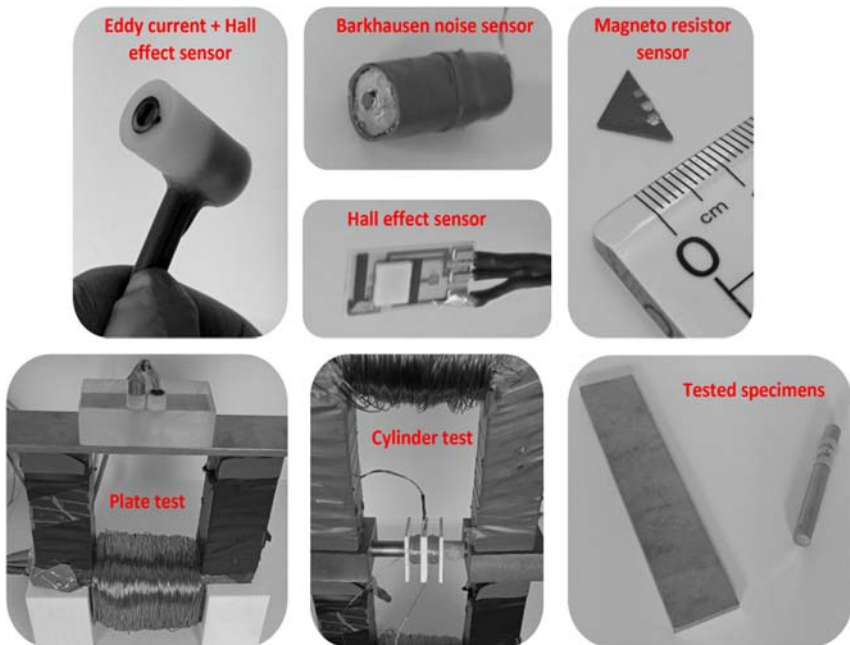


Figure 23.7 Illustration of a uniaxial homogeneous stress influence on the impedance modulus of an eddy current sensor.

Table 23.2 The magnetization mechanisms and properties.

Magnetization mechanism	Time constant	Magnetic excitation level	Geometrical scale
Domain wall bulging	Long	Low	Magnetic domain scale
Domain wall irreversible motions	Medium	Medium	Magnetic domain scale
Magnetization rotation	Short	High	Atomic scale
Domain wall frequency dependence	Medium	Medium	Magnetic domain scale
Macroscopic eddy currents	Medium	Medium	Macroscopic scale

**Figure 23.8** Illustration of sensors, specimens, and experimental setups used to observe the magnetization mechanisms at a laboratory scale.

23.4 Some examples of the link between the targeted properties and the magnetization mechanisms

Strong correlations have already been emphasized between the targeted properties described in the second section of this chapter and the

magnetization mechanisms. The influence of uniaxial compressive stresses on an eddy current testing measurement is, for instance, illustrated in Fig. 23.7. In ferritic steel, compression diminishes the magnetic permeability, which increases the penetration depth and reduces the sensor coil impedance for a given frequency. In this example, the coil characteristics are 3.3 mm inner diameter, 3.95 mm outer diameter, 3.0 mm height, 275 turns, and 0.05 mm wire thickness. The lift-off is 0.39 mm.

Similarly, the domain wall bulging observed from magnetic incremental permeability has already been demonstrated to be intensely dependent on the microstructural creep variations (see Fig. 23.5 for illustration) in high-chromium steel [17].

Also, the irreversible domain wall motion and the MBN measurement have been studied as a function of the three targeted properties [72]. Here again, as illustrated in Fig. 23.6, strong correlations were observed.

For the spontaneous rotation, since this magnetization mechanism is definitively more complex to isolate and observe, no study can be found in the scientific literature. Eventually, the influence of the targeted properties on the magnetic domain wall frequency dependence, ripples, and avalanches phenomena have been studied through the evolution of the magnetic losses and, more specifically, the excess losses. A good example can be seen in [73].

The experimental situations described in the third section of this chapter provide specific magnetic signatures ($MBN_{energy}(H)$ hysteresis cycles, MIP butterfly loops, etc.). However, it is essential to specify that even if those signatures were obtained in an ideal configuration, some indicators read on them can still be associated with multiple mechanisms. Let us mention coercivity, which depends on multiple magnetization mechanisms and in every experimental situation tested.

Another interesting fact comes from the combination of these signatures, which can reveal rich information on a given magnetization mechanism. By instant, the magnetization rotation can be observed from the difference of slopes at a saturated state of the usual $B_a(H)$ and $MBN_{energy}(H)$ hysteresis cycles.

23.5 Conclusion

Improvement in steel component quality controls has triggered strong efforts in developing consistent NDT methods. The final objective is reliability. Well-defined targeted properties can be scanned as precursors in

developing undesired cracks and potentially catastrophic failures. Those properties include internal stress, microstructural variations, etc. Unfortunately, there is no direct method to measure internal stress, and optical microstructural observations are unimaginable beyond the laboratory environment. Magnetization is the solution promoted in this chapter to reach the targeted properties indirectly.

The magnetization mechanisms are dependent on the targeted properties. These dependencies are not constant, and for physical reasons, a given targeted property will affect a given magnetization mechanism more.

Most of the magnetization mechanisms overlapped. One of the main challenges is to define experimental situations where the best magnetization mechanism can be isolated.

The future of this discipline relies upon the capability of developing magnetic sensors and experimental contexts able to provide reliable and reproducible images of the magnetization mechanisms. Printed electronics and sensors are an exciting solution [74,75]. By designing advanced parts, including permanent monitoring instruments, issues due to the positioning and the lift-off are overcome, and the reproducibility of the measurement is ensured.

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CHAPTER 24

Cloud-based non-destructive characterization

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24.1 Introduction

The platform of cloud computing is no longer the future, but it is in progress and has become an important part of our lives [1]. To form a large shared virtual resource pool, cloud computing links several computing services, resources, and software resources from which users can obtain corresponding services [2]. It has entered different areas, for example, scientific research, entertainment, education, development, consumption, and so on, with the fast popularization of cloud computing applications [3]. Cloud computing is a paradigm in which consumers are permitted to utilize cloud services as hosts through the Internet that can be dynamically scaled according to the needs of users [4]. In the cloud computing setting, the cloud service providers and the clients are the two key players [5]. In data centers, cloud service providers host cloud services and allow cloud users to browse and use these services on a rental basis (pay-per-use) [6]. Since cloud services have become very important, businesses, organizations, industries, and academia use some cloud services such as Cloud Non-destructive Characterization Testing (CNDCT), also known as Cloud Testing (CT). There is competition between vendors to provide services with high reliability, different specifications, and product characteristics. Therefore, asymmetric resources with diverse characteristics have been established [7].

Cloud computing attracts many companies and industries globally by proposing possible solutions for managing software applications and presenting convenient testing environments [8,9]. Cloud computing has improved the management methods of working with information networks and resources immensely [10]. Testing as a Service (TaaS) was

created because of cloud computing [3]. It has generated some problems and challenges, particularly in cloud-based, non-destructive test environments, considering the facilities provided by TaaS [11]. It is important to tackle and solve those problems [12]. Several challenges and advantages of CNDCT are also reviewed and addressed in this chapter, including a theoretical contrast between the cloud-based testing environment and conventional standard system testing [13].

CT can apply either testing the cloud-based systems or using the cloud for testing purposes: both strategies (and their mixture of cloud testing) have attracted interest in the study [14]. However, the acclaimed modern computing model comes with challenges, including “removal of mistakes in highly large-scale distributed systems” leading to a broad and hard research topic. CT refers to testing and measuring activities by utilizing cloud technologies and solutions. Scientists have actively researched the scientific and technological issues faced by CT in recent years and have provided various methods and resources to test cloud-based systems [15,16]. In addition to understanding the issue of cloud-based testing systems, scientists have also realized the cloud’s ability to reduce high testing costs. In reality, the cloud provides the ability to build and manage expensive test infrastructures and exploit flexible configuration and performance testing tools on-demand. Therefore, the word “cloud testing” has been utilized with two distinct meanings in the literature: CT or Testing in the Cloud (TiC) [17].

The following contents will be discussed in the rest of this chapter. Sections 24.2 and 24.3 discuss backgrounds and industrial cloud computing environments. The CNDCT techniques are presented in Section 24.4. Challenges and opportunities are presented in Section 24.5. Case studies and conclusions are presented in Sections 24.6 and 24.7, respectively. Moreover, the abbreviation used in this chapter is shown in Table 24.1.

24.2 Backgrounds and basic definition

In this section, the backgrounds and basic definitions of cloud computing are discussed.

24.2.1 Architecture and types

Cloud computing’s capabilities cover scalability, availability, and manageability. Furthermore, it has benefits of universality and economy such as service on-demand, stability, multitenancy, versatility, and comfort [18].

Table 24.1 Abbreviation table.

Abbreviation	Definition	Abbreviation	Definition
API	Application programming interface	PCI	Peripheral component interconnect
B2B	Business-to-business	SaaS	Software as a service
BaaS	Benchmark as a service	SIG	Special interest group
CNDCT	Cloud non-destructive characterization testing	SLAs	Service level agreements
CT	Cloud testing	TaaS	Testing as a service
DBSCAN	Density-based spatial clustering of applications with noise	TiC	Testing in the cloud
DSL	Domain-specific language	ToC	Testing of the cloud
GUI	Graphical user interface	ToiC	Testing of the cloud in the cloud
IaaS	Infrastructure as a service	UDP	User datagram protocol
NDT	Non-destructive testing	UML	Unified modeling language
NIST	National Institute of Standards and Technology	UTP	UML testing profile
IDS	Intrusion detection system	VM	Virtual machine
PaaS	Platform as a service	VPN	Virtual private network

Three service presentation standards (Infrastructure as a Service (IaaS), Platform as a Service (PaaS), and Software as a Service (SaaS)) and three architecture trends (hybrid cloud, public cloud, private cloud) are predominantly supported by cloud computing [19]. Different layers of the cloud computing model are shown in Fig. 24.1.

IaaS handles computer hardware such as data centers, memory, virtual server, processor, and network storage as a service. Without additional capital and time, it poses infrastructure provisioning and scalability problems [20]. Intrusion Detection Systems (IDS), Virtual Machine (VM)

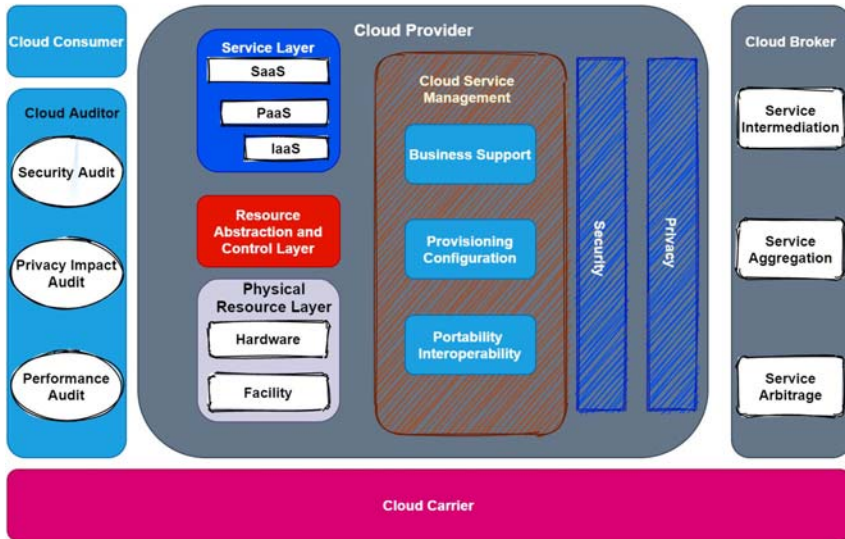


Figure 24.1 Cloud computing model.

monitoring, firewalls, and other security areas are also the subject of IaaS [21]. PaaS is placed in the service model's middleware and contributes in the form of architectures, frameworks, programs for integrated development environments, and tools for development. PaaS faces several challenges, such as underlying infrastructure security, lifecycle growth, and relationships with third parties. Also, SaaS is a set of remote computing services that allow applications to be deployed remotely by third-party vendors. A client can utilize the Internet for cloud service provider applications on the cloud infrastructure [22].

The service brokers' target is to route user requests to the most performant data center. The service broker policy determines which data center is the best for the user application based on factors like availability, cost, and time. In resource management, resources must be distributed at all times to efficiently address workload variability while ensuring Quality of Service (QoS) to end-users. Computing and network resources are restricted and must be shared efficiently among users in a virtual environment. We must consider issues including the adaptation, provisioning, distribution, and mapping of resources to conduct successful resource management [23]. A cloud customer is also an individual or company that has a contractual relationship with a cloud provider and uses its services. A cloud user searches a cloud provider's service catalog, orders the service

they want, sets up service contracts with the cloud provider, and uses the service. Also, A Service Level Agreement (SLA) is an arrangement between a customer and a service provider. The service provider and the service customer negotiate on specific aspects of the service, such as efficiency, availability, and responsibilities [24].

A private cloud is a kind of cloud computing controlled and operated in an organization's data center, classified as a private cloud. This type of cloud is simpler to define customer and supplier relationships since the system is managed and controlled by the same partnership. Also, academia, companies, or government agencies often use a type of cloud network known as the public cloud, which can create several issues because users do not know the resource owners or locations, which raises the complexity of defending resources against attacks [25]. Plus, the community cloud is a type of organization's cloud infrastructure of an entity with traditional client concerns. One or more organizations that operate and maintain neighborhood organizations or third parties are driving this cloud. The hybrid cloud is a mixture of two or more clouds. A hybrid cloud offers the benefits of various cloud deployment models; however, it is more structured and stable than a public cloud when accessing organizations through the Internet. In the end, the virtual private cloud is a semi-private cloud consisting of a Virtual Private Network (VPN) with fewer resources.

24.3 Industrial cloud computing

The area of industrial systems is evolving rapidly as new Internet-based ideas, technologies, tools, and methodologies are adopted. Rapid advancements in computing resources, combined with the advantages of the cloud and its applications, can lead to a new wave of service-based industrial networks with on-device and cloud functionalities. Their realization opens up new possibilities but also creates new challenges. Enterprise and industrial cloud computing concentrate on optimizing the usage of computing services and incorporating resources essential to the optimization and operations of the business [26]. Enterprise cloud connectivity is primarily done via the intranet, but the Internet may also be used. The enterprise itself owns and operates the hardware. Hardware problems are still present, albeit to a lesser degree [27]. The use of hardware can be enhanced by virtualization; however, it may cover only certain parts of the business's data center. The platform is assigned to a particular function and can support the key

operations of the business. Enterprise cloud will help the business economically, but it needs upfront investment and does not include billing of the operating expense form. Management, protection, and privacy are not a problem (beyond what is currently required), as the organization itself stores data. More importantly, the level of protection may increase centralization dramatically. There may be several strategic concerns in the case of the centralization of global sourcing. There is no major lock-in danger from the provider. Dependence on software vendors that offer cloud features is more or less the same as on software currently used. The public cloud implementation by large corporations or businesses was also addressed [28].

24.3.1 Cloud deployment for enterprises

With many deployment models, cloud services are pervasive as single-point access [29]. Each model has its trade-offs. The private cloud includes enterprise businesses deploying their core technology to build private data centers, for example, multitenant applications and virtualization. By negotiated charge-back mechanisms, individual companies may pay for utilizing standardized services. This strategy is more appealing for many businesses than transferring to the public cloud [30].

24.3.2 Service level agreement

The mutual agreements between customers and suppliers are generally referred to as SLAs, that is, the ability to deliver the services under predefined agreements. Many cloud providers currently provide SLAs, but these are fairly weak for user outage compensation [31]. Users still want secure and efficient services from the system. The cloud architecture is known to be highly open, running 24 hours a day for 7 days. Many cloud providers have made tremendous investments in making their systems as secure as they can offer their system size. Today, most cloud providers do not guarantee high availability; this is especially a problem with enterprise Mashups that need a collection of web services hosted in different cloud environments [32]. If, for whatever cause, service goes down, what can users do? How do users access their cloud-stored documents? In those cases, based on SLAs, the supplier can agree to pay the customer a fine as compensation.

24.3.3 Definition and architecture

The industrial cloud is an automation and collaboration platform for industrial digital knowledge [33]. It links unified data standards and common

ontologies with open and shared architectures [34]. It should be governed by an association composed of industry members in the form of, for example, a Special Interest Group (SIG) to ensure the creation, evolution, and acceptance of standards. SIG should comply with the international body responsible for standardization. Fig. 24.2 shows the industrial cloud. It ties businesses in the sector and even service companies together. Enterprises are the industry's heart, service companies typically offer services to other companies and are much more involved than in the industry.

Semantics and metadata are settled upon in advance in standard Business-to-Business (B2B) frameworks and are encapsulated in the systems [35]. The trend, however, is moving towards a more transparent atmosphere where contact partners are not provided in advance. It includes solutions where there is standardized and explicit semantics. Application integration, information integration, and information management include semantically defining and handling the underlying data and processes. Collaboration and communication within an industrial cloud rely on a common understanding of concepts. Unified data specifications, universal ontologies, open and shared architecture, and stable and efficient infrastructure are the fundamental factors of the industrial cloud. Simple data sharing between businesses is possible with unified data standards. Popular ontologies ensure a common perspective on the nature of knowledge [36]. Therefore, metadata must be shared between applications, and it must be possible to define applications within the cloud in a semantic

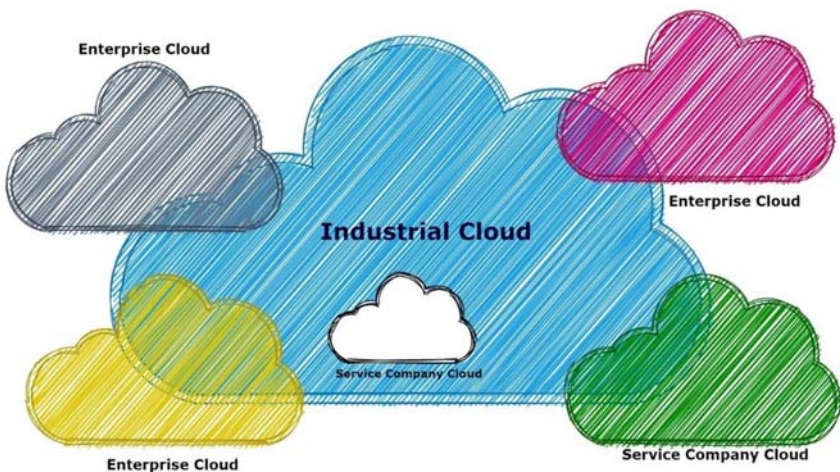


Figure 24.2 Industrial cloud scheme.

way [37]. Accessible and shared architecture is a means of interconnecting participants in the industrial cloud effectively [38].

An ontology is a framework that explains related concepts and the interactions between these concepts and collects semantic information about a certain domain. It is possible to communicate knowledge through systems and domains with a common ontology. This process allows for an automated and seamless flow of data where information can be accessed in the same way as stored locally, from its original location [39]. There are many explanations for creating and applying ontologies, such as simple sharing of information, easier extraction and aggregation of information from different structures by a third-party, easier change of world assumptions, and examination of domain-knowledge. The development of ontology should primarily be a process based on industry. It could be beneficial to use the cross-industry approach; however, it is not likely to be on a broader scale. They would still have access to the more general ontologies, however. A stable and reliable infrastructure creates trust between all participants and the network [40]. Adding new applications to the cloud should be simple, and apps should be easy to find based on their services. It would be easy to search for specific services within them by providing applications as semantically defined web services based on the widely accepted ontology. Domain-knowledge is derived from the applications; the programs are not hard-coded. The provision of new services is then simpler, and the operations rendered by these services are automatically interpreted [41].

To allow on-the-fly and automated subcontracting and outsourcing to lower operational costs, increase the level of innovation, and generate new opportunities, the industry should form an industrial cloud. The cloud method can be used to ensure an abstraction layer over all underlying technical integration and solutions processes [42]. The industrial cloud is the missing element that connects and structures current technologies on the road to functional implementation. Also, in Fig. 24.3, the industrial cloud's key goals are summarized, that is, sharing information, decision support, and service composition. In terms of its general purpose and technology used, the industrial cloud has been identified for the time being. Besides, it is important to position it compared to existing cloud kinds [43].

In Fig. 24.4, all three cloud forms are viewed in the form of a stack of functionality that they have. A cloud provider provides an Application Programming Interface (API) that cloud adopters can later use. Enterprise cloud develops based on a public cloud. Besides, it adds the potential of

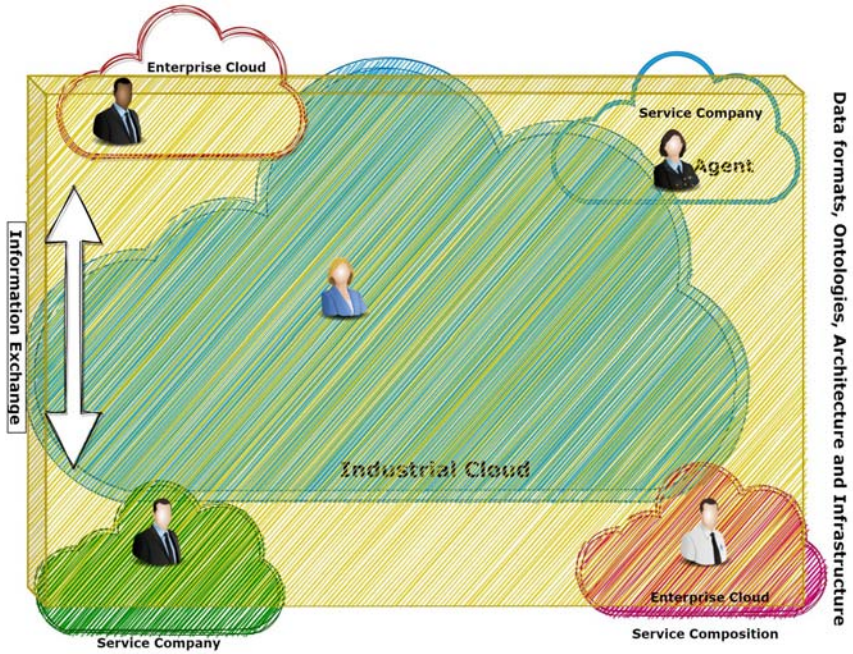


Figure 24.3 Industrial cloud integration, partnership, and composition.

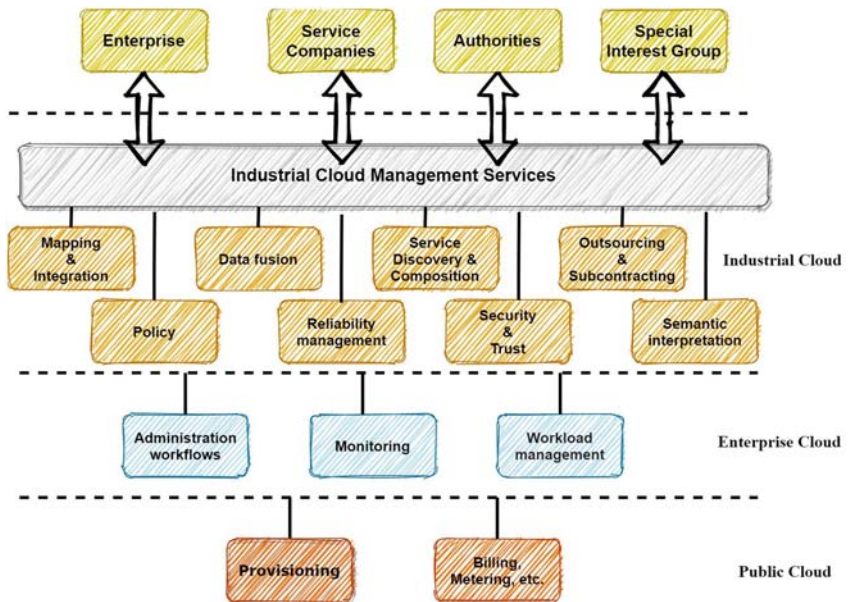


Figure 24.4 Cloud and industry integration.

controlling cloud workflows, managing workloads, and monitoring that goes beyond basic public cloud metering. Enterprise cloud is less common in this way but offers greater support for large enterprise users simultaneously [44]. Based on public and enterprise clouds, the industrial cloud is created. It provides simpler hardware provisioning through virtualization, administration of workflows, management of workloads, and monitoring [45]. However, integration tasks such as regulations, reliability management, protection and confidence, subcontracting, and outsourcing are further facilitated. It supports data semantic analysis, visualization, composition, data fusion, and service discovery [46]. Also, Fig. 24.4 visualizes that the idea of interenterprise collaboration provided in this section is part of cloud computing. It builds on and adds extensions to existing cloud models based on the real needs of industries. Some of the latest industrial cloud functions can migrate to lower-level clouds over time [47]. Small and medium-sized businesses, especially startups, are the primary users of the public cloud. This is because it allows for easy hardware management and versatility without incurring any major upfront costs. The internet is used to access the public cloud. A third-party corporation owns and operates the hardware. Companies who use it are unconcerned with hardware problems. Virtualization allows for a high degree of hardware utilization. Enterprise cloud relies on better use of computing resources and on incorporating and leveraging services essential to a company's operations. The most common method of accessing the enterprise cloud is via the intranet, but the internet can also be used. The company owns and operates its hardware. As a result, hardware problems still exist, albeit to a lesser degree. Virtualization may increase hardware utilization, but it can only apply to certain areas of a company's data center. The platform was developed with a particular objective in mind and is capable of providing for the company's core operations. Enterprise cloud appears to be a viable option for large-scale integration. Conversely, today's businesses face additional obstacles as a result of working with other businesses in the sector. To stay competitive, such cooperation is needed, but it necessitates the implementation of new technological solutions [48].

24.4 Cloud-based non-destructive testing and evaluation techniques

A modern paradigm of Non-destructive Testing (NDT) is CT or CNDCT. It is based on integrated research techniques from cloud computing and

NDT. It incorporates testing methods, knowledge exchange, and techniques for remote control [49]. A sign of CNDCT is the advent of NDT-integrated technology. It analyses the current status and future growth of integrated NDT technology. Also, CNDCT addresses the possibility and key issues of developing CT techniques. The CNDCT technology gathers, stores, and processes data from the client-side of the cloud. NDT signal processing, saving, assessment, prediction, and information feedback are clients' functions in the cloud. Software and hardware resources may be shared by users [50]. Users in different locations enjoy high efficiency and comfort with CNDCT. It is noted that the development of NDT and evaluation techniques is a trend in CT. Also, some useful research and practice are performed in the production and implementation of CNDT's integrated technology, based on the advancement of cloud computing technology and the actual situation of the development of NDT technology. CNDT's concept is that all data obtained by sensors/transducers are sent to the cloud side, where the data is to be analyzed, saved, processed, evaluated, projected, and fed back. The cloud side, which brings together a collection of non-destructive testing technology hardware and software tools, is a cloud computing services platform followed by the related NDT stand. In the detection method, the client-side can share all cloud resources and perform remote control and knowledge sharing, enjoying the convenient service and high productivity offered by detecting the cloud [51].

24.4.1 Background and history

The notion of integrated disruptive technology has started to draw substantial industry interest [52]. It is the principle of integrated innovation because, on each particular technique itself, there was nothing innovation other than the new product as a whole that integrated a large number of functions [53]. Former CEO Steve Jobs, the soul of Apple, led his team to take full advantage of the integrated technologies of innovation. They incorporated many fresh features such as movies, sports, music, and telephone into their products and streamlined the product design. Several experiments have been conducted for integrated innovation in the field of NDT, such as [54]. Industrial products dependent on composite or engineered testing techniques have recently been produced by NDT manufacturers worldwide. Ultrasonic and flux leakage integrated Bowring International Company has developed test systems for online steel pipe quality inspection [53].

Also, WorkStation 2000 and PowerStation testing systems have been developed by Olympus Corporation that combines ultrasonic testing and eddy current. It includes three main components: the core components, the control panel, and the regular components of the front-end. By replacing the corresponding front-end modules, users can easily swap the eddy current and ultrasonic functions. In the same rail detection system, the ultrasonic and eddy current testing techniques were used to detect various components' defects. The results obtained for the same defect by these two testing methods can be used as proof to help each other. Fortunately, the above-mentioned devices or facilities are just basically cobbled together with the hardware or have struggled to coordinate data acquisition, so they can not obtain real integration and multidata fusion [53].

Eddysun corporation proposed a new concept for NDT integration technology in 2003. Eddysun corporation developed the SMART-2003 Magnetic Memory/Eddy Current Integration Testing System in the same year. The data acquisition for magnetic memory and eddy current testing could be carried out almost at the same place and at the same time by this system. Most software and hardware on the device share these two test mechanisms. The combination of both utilities and hardware plus software has resulted in the SMART-2003 being the first integrated multidata fusion NDT system in the industry. This equipment was commonly used to test armored cars and was increasingly widely used in manufacturing. Subsequently, the new kinds of integrated NDT equipment, the SMART-2004, and the SMART-2005 appeared at the times required, either with multi-NDT or mobile technology. In 2008, the word "integrated NDT technology" was introduced in the Chinese National Standards as NDT terminology, in which Eddysun Company played a major role [53].

An integrated Internet-based NDT system is also available on the market. The EEC-2008Net electrical/sound internet testing system and integrated technological advances by Eddysun corporation have been used in nuclear power stations. It has creative, high-efficiency, compact, and linked characters to the local network to ensure data security. The EEC-2008Net framework has the important elements of CT, the developed definition described above. The idea of CT is based on integrated testing technologies and cloud computing. Cloud computing has grown from idea to real action and has entered people's lives, and it can provide users with secure and personalized services and optimize the usage of resources.

However, CT based on cloud computing is a modern generic method of testing, which comprises various chemical and physical detection

mechanisms [55]. The NDT convergence technology trend is taking advantage of network technology, computer technology, and electronic technology growth. Various NDTs and control facilities have been connected to exchange information and resources and to offer users higher performance and lower costs of operation [56].

24.4.2 Innovation integrated by NDT

Using one single NDT method, it is difficult to evaluate an object in its entirety. Therefore, multi-NDT techniques are usually required. It is easier to implement the integrated NDT methodology, which combines multiple NDT methods, to improve reliability and performance, lower testing costs, and achieves testing fully. Five traditional NDT methods were called magnetic, eddy current, X-ray, penetration, and ultrasonic. Each of these methods has different principles of detection, leading to different features and limitations. For example, one of the most widely used ultrasonic test methods can be used to non-destructively assess the internal continuity of nonmetallic, metallic, and composite materials, and it is safe for humans and the environment. It can also be used for on-site testing. However, there are some shortcomings, such as coupling, surface preprocessing for parts with rough surfaces, dead-zones for testing, and so on.

The X-ray testing innovation adapts to various materials, surface, and structure inspections and does not require any special requirements. A variety of products can be applied to it. Moreover, the sensitivity of X-ray tests for plane defects is limited, and the X-ray test is hazardous to the human body and is expensive. The benefit of high speed, noncontact, and having no coupling is the new Eddy testing technique. It is, however, limited to testing conductive materials and can only identify subsurface and surface flaws, and complicated formed structures are difficult to test. The magnetic testing method can provide an intuitive, highly sensitive, transparent display of the shape, position, and defect size. With quick, convenient, and low-cost testing, there is almost no restriction on the specimen's size and shape. However, it is only sufficient for ferromagnetic materials to identify surface and near-surface flaws. Normally, the measurable depth is 1–2 mm. After testing, it requires demagnetization and cleaning in particular.

The penetration testing technique has the benefit of not restricting the specimen's geometry, scale, chemical composition, and internal structure. One operation can essentially identify all open defects on the surface. The

drawback is that it can diagnose surface defects opening up. With the advent of sophisticated objects, advanced technologies, and parts, it has become challenging to determine the magnitude of defects or carry out a complete and precise life assessment using single detection technology. Various cross-compound detection methods are also used to boost identification effectiveness, such as configurations of magnetic flux leakage and ultrasonic tests, endoscopy and eddy current, eddy current and magnetic flux leakage and magnetic memory, etc. In applying the integrated multi-NDT technique innovation, specific accomplishments were achieved [57].

The creative NDT integrations primarily incorporate a variety of techniques into three tiers, the first level such as integration of electromagnetic methods to integrate eddy current, leakage of magnetic flux and magnetic memory methods, acoustic pulse, integration of acoustic methods to integrate acoustic impedance, sound vibration and acoustic techniques of ultrasound. Then, in the mechatronics context, the second stage is to incorporate electrical and mechanical technology, such as the new train hollow shaft integration testing system, to integrate ultrasonically, eddy current, and magnetic memory methods. The third level is integrating internet networks and NDT technologies, data integration into the NDT service center or cloud for processing, analysis, and storage through Ethernet, the Internet, networking, or cloud platform.

24.4.3 The integrated technology development process for NDT

NDT integration technology development can be discussed briefly as three procedures: Initial integration of NDT is the first step. It was just to bring together two or more separate detection methods into one unit, neither data exchange nor any other interaction between and method of testing. The second stage focuses on modularization, which, through an NDT card, achieves integration [58]. The basic technique must be integrated by plugging its function module card into the Peripheral Component Interconnect (PCI) slot when a new function in the apparatus needs to be installed [59]. Now the second phase is in progress. Several of the circuits are shared by the various components and a fusion of test data. Various results can be viewed continuously on-screen when the findings have also been merged, that is, fusion findings gathered from multiple detection methods. The findings are fused in the data fusion center, allowing a detailed decision [60]. The use of the popular part of the various testing techniques, with Ethernet as the means of transport to

form an open digital information processing network, enabling signal management, data acquisition, system software, visualization, and sharing of other fundamental components, is a further stage of this step [61]. For high speed information transmission, it should have many connections. For instance, the 2008 network system built by EddySun Corporation has two key methods of communication, namely Ethernet network connections and USB.

Interface with Hi-Speed USB designed for a full transfer speed up to 480 Mbps, Plug and Play and hot-swap features, USB system link cable length up to 5 m, USB hubs for connecting tiered star topology. A host can link up to 127 USB devices and up to five topological connection phases as a communication interface between the host and the testing instrumentation, so it is very suitable. USB bus-based approach, combining several various evaluation testing methods, each tool may also have multiple channels consisting of a multichannel data acquisition method for detection 2. Modus of industrial Ethernet. Industrial Ethernet is theoretically compatible with commercial networks, but it should be possible to address the industrial sector's requirements by choosing materials, product intensity, and applicability. Ethernet technology is widely used; software and hardware have a wealth of resources; easy Internet access, office automation and industrial control networks, seamless networks; vast space for long-term development, and so on. Each plate supports multiple channels, using different detection network interface chips between the plates (100M/10M adaptive) and the software using TCP/IP or User Datagram Protocol (UDP) agreement via the multiblock test board through different Ethernet-connected hosts. 3G/4G/5G is either operating or preparing to run by contact, and its efficiency can be further enhanced.

The NDT-integrated network-based testing framework architecture is shown in Fig. 24.5. Each detector has a network interface and could be made up of Ethernet LANs. It uses a network switch or router to access the Internet. As a control bus and as an internet subnet, LAN is both. The network cable and hub are linked to various monitoring devices. The monitoring host may be either a computer on a LAN or an Internet-connected remote host.

Network-based NDT integration technology allows data collection, evaluation, and other multiplatforms to operate simultaneously. It combines the sharing of hardware, software, and data resources and achieves quick, long-distance real-time transport for raw data, application analysis software, and file archives, such as inspection reports. It can update online

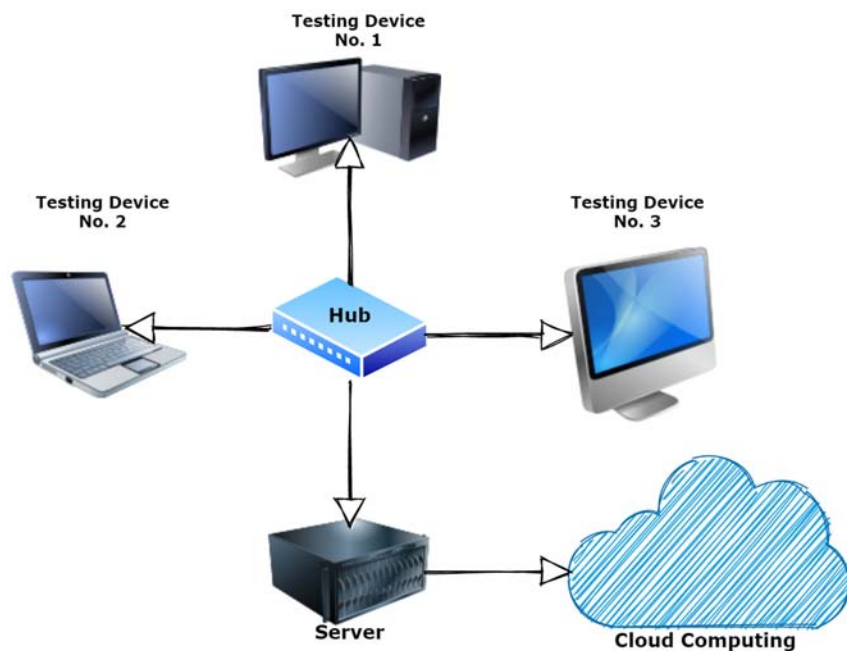


Figure 24.5 Integrated network NDT model.

applications in time for equipment and present technical personnel with remote training facilities and technical support, network testing and application, commissioning guidance, and installation. On-site identification precision and inspection performance are greatly enhanced. Specifically, the database is set up to enable identification. It is essential for the monitoring of health and the assessment of essential elements. The detection system can completely meet real needs and obtain accurate test results with fast test speed. Also, the EEC-2008net system is an integrated web-based NDT system developed for Daya Bay Nuclear Power Station by EddySun Corporation. There are great opportunities and benefits in integrating the network with NDT equipment.

Cloud will contribute to the further advancement of NDT integration technology. As described above, cloud computing refers to the building data center through distributed computing and virtualization technologies, offering free on-demand rent through the network and scalable access to technology developers, data storage, analytics, scientific computing, and other services for enterprise customers. By establishing a cluster of servers, data storage, hardware leasing, measurement, and review of various types

of services, cloud computing provides clients with different types of online services. Cloud services tend to be indefinitely elastic from the user's perspective and can be used pay-per-use on-demand. The CNDCT is that distributed computing is analogous to data center operations and the Internet over many devices, rather than local computers or remote servers. The CNDCT is the client's smart sensor to obtain storage, computation, processing, database, and interactive resources via near, long-range connections. Fig. 24.6 is an integrated system diagram of an Ethernet-based NDT. The CNDCT diagram is Fig. 24.7. It can be shown that more hardware resources are saved through cloud detection. To a large degree, the user can be streamlined, and customer service makes cloud requests without thinking about how. From the viewpoint of the instrument, NDT and the evaluation system will no longer be a small and complete system but "clouds" with limited wireless hardware. The test data is sent to the cloud, analyzed, and returned to the terminal. Features of the cloud include reception, identification, filtering, information fusion, storage, evaluation of expert systems, feedback, communication, sharing, etc.

Also, CNDCT is an extraordinary testing and assessment methodology to enhance work productivity and quality and prevent duplication of work, aggregating all the strength and support of mankind, and projecting the so-called root spirit by gaining knowledge to keep up with the times.

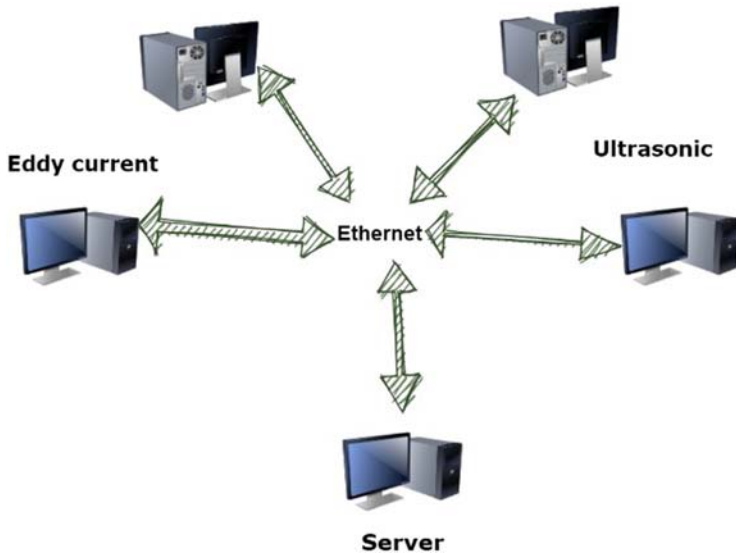


Figure 24.6 Optimized network Ethernet-based NDT.

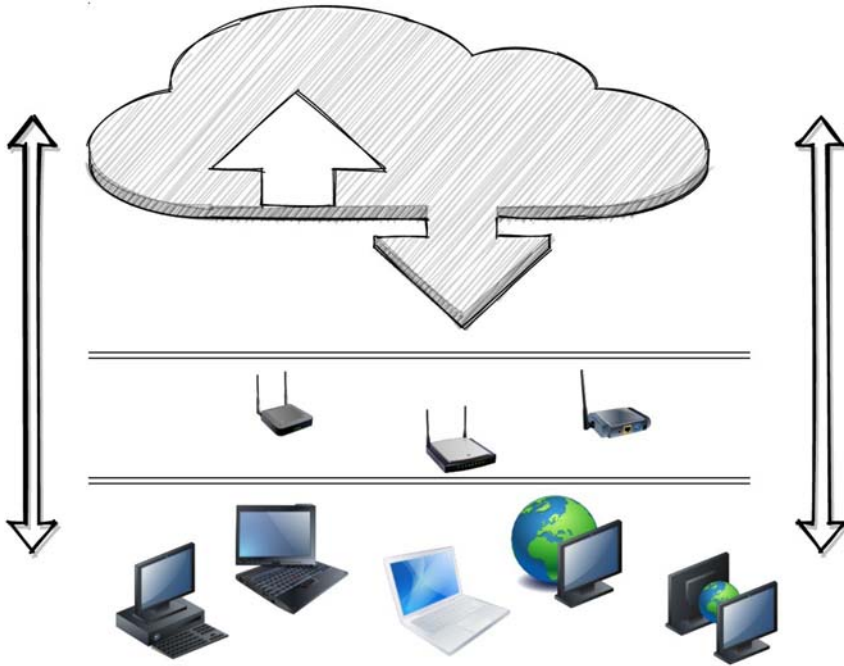


Figure 24.7 The CNDCT overall diagram.

Besides, it will optimize testing equipment hardware, and dramatically reduce costs, enabling users to experience quicker, more direct, and better. It is going to overthrow the people's history of testing thought. In several cases, the cloud testing method, including a multidisciplinary one, would be a gene that will lead to a breakthrough in the research industry.

24.4.4 The characteristics and difficulties of CNDCT

The CNDCT could provide a resource on-demand service within a short time. The CNDCT can prevent the overuse of resources. It consists of a parallel distributed system and virtualization of computing resources [62]. It is defined by a pool of resources, a network resource, computation, and storage, dynamically distributed according to customer requirements through virtualization technology. Customers can buy service services flexibly and easily, expanding processing capacity at any time based on real needs. Using several client applications and broadband networks, cloud detection resources are named. Based on the type of usage, the number of active users, storage, bandwidth, and so on, the resource

service can be tracked, reported to the customer and service provider, and paid. Faulty nodes can be automatically found; the device can continue to run through data replication and provide high-quality services to satisfy the service level agreement's requirements [63].

Security problems are the first challenge to be solved in CNDCT. As tasks are allocated to each calculation node, intensive data processing by a single instrument will be reduced, and performance will be increased. The protection of confidential data transmitted by users to the cloud end is of greater concern. The second is the issue of reliability. Utilizing the resource leasing service will minimize the expense of physical hardware and the risk of early-stage capital expenditure. The trust to hire user CNDCT refers to the standard of CNDCT itself, although users do not need to pay attention to hardware and software maintenance [60]. Maintainability is the third issue. Professional management and maintenance services are provided by CNDCT tools, reducing users' average daily maintenance and management software application expenses. Are all application software appropriate for the cloud environment for production and testing? It will be a long-term cycle when it comes to migrating previous software applications to the CNDCT environment. The fourth one is interacting. Users dynamically request CNDCT services based on business requirements, peak load handling, and resource release during off-peak hours. Cloud computing service providers can extend the limited number of CNDCT services, and the coordination between CNDCT services is weak. How to coordinate? For the establishment and implementation of CNDCT, these main technical problems must first be considered and resolved.

The position of the NDT staff is irreplaceable. For rain inspectors, CNDCT technology plays an important role. Potential customers will be more worried about the service, which requires accurate detection of conclusions in terms of the system and equipment used. Moreover, hardware costs are increasingly smaller than the proportion of test evaluation facilities, as is the case with smartphone production. To meet the needs of different users, researchers may build different grades or a special CNDCT terminal. Innovation management, such as the digital telephone marketing model, and integrated NDT sensor terminal, should be considered at "zero cost" to provide property owners and then demand inspection fees [64]. However, technology for NDT integration is an applied application. It can increase the efficiency of identification, reliability, and resource conservation and enhance the findings' integrity. So, CNDCT is an NDT-integrated

technology trend. Cloud integrates communication technology, network technology, sensor technology, and device technology with NDT integration technology and the latest development data and provides customers with a more convenient and more effective service. Using cloud computing, users can share hardware and software systems and take advantage of the benefits of network services and experience [65].

24.5 Challenges and opportunities in CNDCT

In Fig. 24.8, we present the structure developed to define and classify the CNDCT study methods [17]. We identify the six fields and their subjects.

- Perspective test: Novel perspectives on CNDCT are present in the methods belonging to this field. It discusses topics such as fundamental principles, terminology, challenges, and, among others, future research directions for CNDCT.

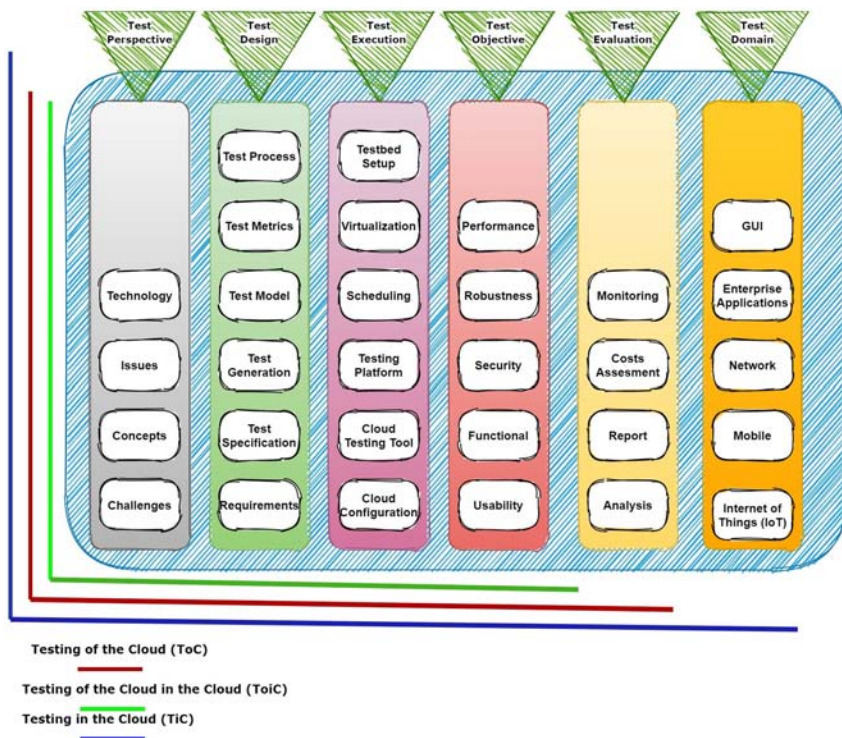


Figure 24.8 Cloud testing taxonomy.

- **Tests design:** The documents connected to this field include solutions that target the testing activity design phase. In particular, it examines the performance of design specifications, the definition of a test model or test metric, various test strategies for the generation or selection of test cases, the reduction of test cases, and the test suite's evaluation. Also, papers defining a cloud test process are included in the field.
- **Test execution:** Objects involved in the testing operation's execution process are involved in the techniques according to this field. Specifically, they present CNDCT frameworks, infrastructures, tools or facilities, visualization, cloud configuration methods, and testbed setup solutions.
- **Objective test:** The techniques in this area discuss key CNDCT intended purpose, including verifying that the systems comply with functional specifications or displaying specific nonfunctional properties, such as usability, robustness, reliability, performance, etc.
- **Evaluation test:** Strategies for this field cover the assessment of the testing activity and findings, the provision of support for test reports, the observation of test costs, or the quality assessment of the various testing methods.
- **Domain test:** Cloud-based testing solutions for the requirements arising from specific application domains, such as web or mobile applications, are present in the methods belonging to this area.

Overall, as shown by the colored frames in [Fig. 24.8](#), the methods are classified into three different categories spanning the above areas:

- *TiC* refers to software testing conducted to verify noncloud software/applications by utilizing flexible cloud technology, solutions, and computing resources. This category involves testing technologies tested using large-scale simulations and elastic tools provided by the cloud for various application domains, such as web or mobile environments. The key advantages of these technologies are (1) cost savings through the use of seemingly infinite cloud computing resources; (2) avoidance of the construction and maintenance of test infrastructure (scaffolding); (3) on-demand testing services offered by third parties for online evaluation of large-scale software systems [17].
- *Testing of the cloud* (ToC) refers to validating the quality of software and infrastructures implemented in the cloud, such as functional and nonfunctional properties. The emphasis is on the specific testing problems presented by cloud-based systems, so papers in this category aim to verify the automated cloud-based functional services offered and

validate their elasticity, scalability, performance, and safety. Besides, software applications can be deployed on various clouds, such as hybrid, private, or public, so testing can also concentrate on consistency and interoperability between heterogeneous cloud resources [17].

- *Testing of the cloud in the cloud* (ToiC) applies to cloud-deployed infrastructure and applications that are tested by leveraging cloud platforms. The intersection area between Testing of the cloud and Testing in the TiC is packed with papers belonging to this group [17].

24.5.1 Testing in the cloud

As has been mentioned, the cloud solves the limitations of conventional solutions to testing: indeed, the readiness of enormous quantities of capital, the capacity to handle vast amounts of data, and the availability of scalable, elastic environments enable testing goals to be tackled until they are rendered unworkable. Among them, is the ability to conduct huge combinatorial testing, assess efficiency in multiple-use scenarios, and evaluate attributes such as reliability, scalability, and elasticity most conveniently by scaling up and down resources [60]. Several functional testing techniques are transferred to the cloud because of these motivating factors, including model-based testing based on formal specifications, coverage testing, and combinatorial methodologies. In terms of direction, the TaaS paradigm opens up new points of view for functional testing, specifically for mobile or Graphical User Interface (GUI) testing purposes.

The availability of many relatively affordable cloud tools makes performance testing simpler, so many efforts have been conducted to address the performance testing objective. Fortunately, performance assessment involves rigorous preparation and setting up complex configurations to optimize test effectiveness. Thus, in this direction, authors have established a range of research suggestions that support load testing; evaluate consumption scenarios for generating performance test cases; concentrate on guaranteeing particular SLAs; target the management of broad test jobs; monitor and evaluate a large number of events. Among the key factors that make cloud computing an evolving trend is elasticity. Elasticity testing, in turn, may have various goals, also including monitoring different behaviors, defining the resources to be (un)allocated, organizing events in parallel, and, of course, targeting scalability. The focus of reliability testing is on observing the device test under the profile of operational use. Methods concentrate on calculating the degree of reliability or achieving

a particular reliability attribute through API testing. The improvement in the complexity of omnipresent software-intensive systems is accompanied by increasing concern about such systems' security, especially for mobile applications. Many other recent cloud research proposals include methods to virtualize, simulate, and detect network attacks, the vulnerability of protocols, and other security issues [61].

24.5.1.1 Pay-per-use business policy

Cloud resources are used to achieve test cost savings, scalability, and effective usage of the test resources, thus guaranteeing a standard of QoS according to an agreed SLA. To optimize the use of test resources and balance the load between them, test scheduling solutions and efficient resource allocation approaches are proposed by Jun-Ming [51]. Different methods are suggested for (1) partitioning the research tasks; (2) allocating them for simultaneous execution to different cloud processors; (3) and gathering data. To minimize the testing time, some plans concentrate on task scheduling algorithms and task decomposition methods. The aim is to balance the number of test cases or test suites necessary for each decomposed task or the execution time needed for each task to be performed. CNDCT allows for large-scale combinatorial testing by exploiting enormous computing resources that were not possible in conventional test systems. Via concurrent test execution and analysis, large numbers of processors are utilized to detect defective interactions and parallel test execution. To effectively conduct interoperability and compatibility testing, cloud-based testing infrastructures are also suggested.

Also, to manage cloud resources, dynamic resource adaptation methods are specified to dynamically add or remove VMs depending on the CNDCT platform's workload and the number of devices available. To maximize their use and reduce testing time, the goal is to balance the workload between many similar devices. To manage cloud resources, dynamic resource adaptation methods are specified to dynamically add or remove VMs based on the CNDCT platform's workload and the number of devices available. To maximize their use and reduce testing time, the goal is to balance the workload between many similar devices. Eventually, cloud tools are used in heavy testing methods, such as search-based software testing employing genetic algorithms. The most often used model for processing distributed data on multiple devices is MapReduce. The aim is to take advantage of easy-to-use parallelization mechanisms to

extend the solution spaces concerning sequential search-based methods and to achieve greater scalability and efficiency, thus enhancing the cost-effectiveness of these methods [51].

24.5.1.2 Model-based testing

Model-based testing helps, starting from an abstraction of the software-under-test, to create many test cases to be performed on the cloud. Various model-based testing frameworks are provided, for example, AUTOMATIC, which generates many different QoS configurations for CNDCT [66]; and ATCloud, which generates API model-based test cases [67]. MIDAS [68] is a model-oriented, scalable testing framework based on the Unified Modeling Language (UML) and the UML Testing Profile (UTP) based on a Domain-Specific Language (DSL). Another model-based architecture that analyses an app's source code and automatically extracts both a behavioral model and the APIs of externally referred applications is EvoDroid [69]. EvoDroid then uses these models to automatically create the tests performed on multiple Android emulators simultaneously in the cloud. Various testing systems leverage combinatorial testing methods, and test algebra and adaptive test configuration generation algorithms are used to classify defective interactions. Particularly, the test results are combined by different processors thanks to testing algebra rules that define certain interactions that do not need to be checked. The challenge of defining the configurations to be implemented and tested on a cloud platform to minimize their number and save testing effort is addressed by various solutions [67]. Also, compatibility testing is one of the fields of the mobile device domain that has been most investigated. Testing the same application running on many types of mobile devices emulated in the cloud is a common contribution to the papers on this subject [70].

24.5.2 Testing of the cloud

Analyzing this chapter's outcomes, we infer that the main objective for evaluating cloud-based systems is results. In CNDCT studies, some performance metrics are examined, such as average latency, execution time, and response time. There are other distinct targets for carrying out CNDCT, but these goals appear secondary compared to success in the light of the survey results. From the highest to the lowest order of appearance, these objectives are described as follows: (1) Functional aspects; (2) Security; (3) Elasticity; and (4) Reliability.

24.5.2.1 *Testing metrics*

Testing metrics are also commonly used; for example, Zhang et al. [70] provided an eCAD cloud system for detecting anomalies. To detect cloud anomalies, track various performance metrics, such as memory, CPU, or input/output. This tool internally uses an evolutionary data-clustering algorithm called Density-Based Spatial Clustering of Applications with Noise (DBSCAN). Kuo et al. [71] presented a generic cloud performance model for the evaluation of SaaS, PaaS, IaaS, and hybrid clouds as another example of the use of metrics. This work utilized various metrics of performance, such as speed, quality, latency, or bandwidth. Finally, a method to test IaaS elasticity on mixed workloads is proposed by Hu et al. [72]. To that end, the authors built a workload using various infrastructure cloud patterns and then extracted aggregate elasticity performance metrics, including resource, operation, and cost aspects. The test methods, techniques, and instruments are used over various approaches for evaluating the cloud range. For example, Abramova et al. [73] analyzed the Cassandra NoSQL database's scalability using the Yahoo Cloud Serving Benchmark. To start with, various types of cloud configurations are possible. The authors conclude that scaling the number of nodes, even for massive data sets, does not ensure performance improvements.

In several papers, CT tools and services are presented. A tool to derive test cases from a formal specification expressed as a DSXM model is presented by Lefticaru and Simons [74]. Gambi et al. [75] presented AUTOCLES, a TaaS tool for cloud-based elastic systems: AUTOCLES instantiates the software-under-test, configures the test environment, generates test input data, and executes the test cases from the JOpera (i.e., Visual composition language) specification of the software-under-test and a set of test cases defined using JMeter. Zech et al. [76] suggest a model-based and change-driven security testing alternative: by trying to apply malicious user methodologies to the system interface, the analysis describes possible intrusion points. CloudBench, an open-source IaaS cloud benchmark that is compatible with several cloud providers, including Google Compute Engine, and Amazon EC2, is presented by Silva et al. [77].

24.5.2.2 *Testbed setup*

In some studies, the setup of testbeds is distributed. Turner et al. [78] present, for example, the C-MART benchmark, capable of emulating modern web cloud applications. The tool is capable of generating workloads that emulate website access. Measurement of QoS performance using response

time is suggested. Also, the testing cost is another component of test results for applications deployed in the cloud. Similarly, Liu et al. [79] studied the effect of sequential vs. parallel execution on cloud infrastructures on testing costs. The information produced by tests is also collected as test reports. Usually, these results are produced by testing frameworks or instruments.

24.5.3 Testing of the cloud in the cloud

Performance and practical motivation are the key objectives for bringing CT into the cloud. The objective of several methods is security, while several methods cover several aspects: efficiency, elasticity, robustness, and reliability. Stub cloud models are used for the latest generation to achieve high structural coverage for cloud-based applications. Using fake stubs that offer user-defined return values, these models allow the simulation of real environmental conditions [80]. In various research, CT methods and services are dealt with. For example, Gao et al. [81] proposed a cloud-based TaaS (CtaaS) environment designed to support performance and scalability testing in SaaS. The PEESOS-Cloud, an architecture for performing experiments on services employing the characteristics of workloads, is provided by Ferreira et al. [82]. Fox et al. [83] provided an API called IoT-Cloud that enables developers to construct scalable, high-performance IoT applications. Finally, De Francesco et al. [84] explore the cloud-based computing infrastructure of Amazon AWS in the MIDAS project. Aspects of research infrastructure are explored in various ways.

24.5.4 Test perspective challenges

As mentioned above, CNDCT is a novel area that brings together many new basic principles, problems, and technologies related to a range of test aspects, ranging from resource management, performance evaluation and risk assessment, computational technology management, and maintenance. As has been said, the cloud platform is very complex and continuously changing. Therefore, the major challenge is that any proposed TiC solution needs to be continually updated and adapted to this evolution. Besides, the complexity of applications and infrastructures deployed and tested in the cloud is growing. This continuous update, development, and revision of the cloud environment go hand-in-hand with the continuous exploration of new problems, insights, and cloud research challenges. One of the key challenges of ToC due to the rising complexity is the ability to analyze the cloud framework as a whole through end-to-end evaluations.

As long as the testing applications increase, they become more challenging to set up and configure. Automation and maintenance of the proper setup to enable end-to-end research is a problem for practitioners. Besides, the end-to-end testing of cloud applications is typically a time-consuming operation that produces high costs. Elasticity is widely defined as a key benefit offered by cloud-based systems and is one of the common challenges across regions. In this regard, a possible ToC problem is the use of proper workloads to test the elasticity of the application deployed on a cloud solution. This challenge is generally divided into different sections: generation of workloads, scheduling and carrying out load tests, measurement/monitoring, and, finally, follow-up activities.

24.5.5 Test design challenges

Current techniques do not take unique cloud environment features such as load balancing, heterogeneity, connectivity, recurrent failures, scalability, and synchronization between distributed components properly into account concerning test design challenges in the cloud. Parallel test data generation algorithms, such as parallel Concolic execution, graph search heuristics, or combinatorial solutions, exploit powerful distributed computing frameworks such as Apache Hadoop MapReduce to spread public cloud test generation tasks, minimizing explosion of both event series and data value explosion. Identifying an abstract representation of the evolving cloud environment is an important challenge in this respect. Model-driven engineering and generative programming techniques are used to help application developers identify an abstract representation of the test scenario and identify the correct combinations of configuration choices for their applications to be deployed and evaluated. However, there is a scarcity of well-defined test models and coverage requirements to resolve the shortcomings of the various cloud technologies or providers [85].

It is typically defined as a challenge to optimize the efficacy of various types of tests for cloud applications. To achieve this optimization, various strategies are implemented, for example, using test collection, prioritization, or reduction approaches. Metaheuristic search algorithms are another popular research technique in this field. Engineers usually incorporate various SaaS and applications based on cloud infrastructures their APIs and networking protocols are provided. Due to the additional costs and challenges that directly affect the design and execution of the underlying experiments, this integration is challenging from a testing point of view [86].

Given the complex and heterogeneous cloud environments, providing a rigorous test plan that can consider the costs of using a cloud environment from consumption times through disassembly remains a challenge. Public cloud providers provide operating models and pricing structures, but they provide very little interpretability when testers need to modify vendors. Besides, before transferring tests to a cloud environment, a successful test strategy should also consider related hidden costs, such as the cost of encrypting data and the cost of tracking the use of cloud resources to avoid overuse and over-payment. Another important factor to be addressed in the test plan is the management of test data, particularly the implementation of acceptable security policies regulating the provision to third parties of sensitive or production data, while some techniques should be foreseen for filtering or scrutinizing data before cloud testing [87].

24.5.6 Test execution challenges

According to test engineers' feedback, the design of a test environment in the cloud is time-consuming and requires high costs and complexity. More attention should be paid to making test execution cost-effective in the cloud and reducing costs due to the configuration of the test environment on all cloud nodes. Indeed, improper sizes or unbalanced loads of the VMs allocated will result in low utilization of resources or increased response time. Efficient strategies are also required to execute complex test scenarios by utilizing dynamic scalability and elasticity of underlying computational resources. Test decomposition policies, test allocation, and test scheduling methods are important aspects being further explored [88]. These are required to decompose the test jobs into more test tasks that can be performed simultaneously to enhance the use of resources and calculation time. About TiC, the configuration of the cloud-based test environment is still difficult to understand. According to the offered APIs and connectivity protocols, testers need to deal with different SaaS applications. When legacy test software is migrated to the cloud, this task appears even more complex. Traditional test configuration practices do not consider the heterogeneity and complexity of the cloud. In this direction, the obstacle is investigating the creation of a holistic testing framework as an integrated solution with a core TaaS infrastructure, allowing extra capabilities such as nonfunctional testing or test planning methods to be easily added and scaled. This testing framework could support the construction and deployment of TaaS

infrastructure on-demand virtual test laboratories, enabling efficient test execution as well as sharing of resources and tool licenses. It enables some cloud providers to overcome the limitations of offering only a reduced set of configurations, bandwidth, networking, storage, and technology. A lack of standard interfaces and links to test tools and third-party solutions and the complexity of connectivity with other clouds remain the main obstacles to realizing this framework.

During large-scale test execution, a further critical problem is the absence of automated facilities to deal with test failures or detected bugs. To process and support any test failures during automated test execution, effective test execution solutions, and self-re-settable and auto-recoverable test scripts are needed. Multitenancy is a common aspect of cloud-based applications concerning ToC. An open challenge continues to be dynamic scenarios involving SaaS multitenancy. Usually, load-balancing technology aimed at decoupling client traffic from application resources is used to avoid data loss and network outages. Finally, the use of resources (e.g., CPU, memory, and disc) and related expenses are relevant to cloud technologies. Resource contention required for a given test suite execution on the various cloud providers is a potential challenge in this domain, particularly for ToIC [51].

24.5.7 Test objective challenges

The need to provide a viable approach to satisfy the testing needs of industries and organizations will drive research into more efficient ways of assisting practitioners in growth and testing activities and will increase interest in TiC solutions. The decision-making processes and cloud-based research management would require new priorities in this direction. Other essential aspects stem from the need to increase trust in the cloud system and its components, from its architecture to the applications it hosts. In our vision, in the TiC sense, certification, accuracy, assurance, and evaluation of the cloud environment can become the future keywords for the test target. In the testing environment, protection has become a hot research subject. Evaluating security aspects is particularly difficult when the device under test is installed in the cloud. In this domain, several open questions will lead to further investigation. For example, how to ensure and analyze privacy for users or privacy for business data hosted in cloud infrastructures. In the current state-of-the-art of CNDCT, achieving greater scalability and efficiency of ToIC approaches

is a common challenge. These two quality attributes are closely linked to various problems, for example, multitenancy, load balancing, or elasticity, that have already been raised.

24.5.8 Test evaluation challenges

Factors such as network latency or workload conditions that can influence the validation must be addressed in nonfunctional testing. Thus, it is necessary to be able to properly monitor and trace such influencing conditions to achieve meaningful test evaluation. Also, SLAs are not always appropriate, that is, structured contracts that guarantee a negotiated QoS. While SLAs are not supposed to be broken, some breaches can occur and affect the TiC session's outcome. In conclusion, more focus should be put on linking the cloud test reports with information/metrics that could assist testers. Most primary studies include support for canonical IaaS indicators such as memory or CPU used to be evaluated and summary information to be recorded. Native support for customizable aggregation of the controlled indexes offers an interesting guideline for reporting capabilities in TiC. The state of practice in TiC exposes the broad adoption of ad hoc solutions for measuring/certifying various quality attributes. Such a practice may lead to some sort of technical debt for customers relying on TiC in the long run (e.g., vendor lock-in). The lack of structured reporting approaches could also restrict the possibility of moving towards developing a concrete cloud brokerage ecosystem for TiC as an additional consequence. In structuring/scripting solutions explicitly designed to handle the outcomes generated by a particular TaaS system, further effort should be spent encouraging the application of well-known design patterns.

The upload of software-under-test on third-party premises concerns confidentiality, a well-known obstacle to the adoption of TiC. From our point of view, it is important to remember that both public and private cloud confidentiality and security should be linked to the entire collection of testing objects. In this context, technical or legal means should not be limited to the objects to be executed that are loaded in the cloud, but rather to the whole collection of historical reports resulting from their execution. The data obtained during testing and monitoring can be used to learn the similarities between the predicted test behavior and the observed one. Certain similarities can be used to identify bottlenecks and flaws in the device under evaluation. Facilitating decision-making based on test results and metrics through various machine-learning approaches will lead to promising research for evaluating cloud-based applications.

In the ToiC arena, similar problems related to data processing testing are also likely to occur. The inherent complexity of the cloud testing testbed is an additional issue in this domain, and as a result, the data volume can be increasingly higher. All in all, in the assessment of test results, current big data systems may be useful for data discovery, integration, or advanced research.

24.5.9 Test domain challenges

The effect of costs is typically under-estimated when implementing CNDCT solutions. Sometimes, but not with appropriate thought, the pay-as-you-go business model is alluded to. For example, a staging phase is needed to upload the code that will be executed remotely with all its required dependencies to launch testing sessions on new environments allocated to the cloud. Moreover, to properly configure the environment, further computational resources are required. Often, with the use of the monitoring and logging tools of the particular TiC solution, there are hidden testing costs (e.g., due to packages set up across the network) that increase. As a result, the requested degree of detail in the test analysis should be best suited to a clear understanding of its relevant costs and how such quantities of information can be properly consulted and collected. The rapid growth of cloud technology and the absence of standards often make it impossible for unique application domains to be ported to various cloud providers. For example, following TaaS or Benchmark as a Service (BaaS) on-demand methods this issue typically forces practitioners to build custom testing solutions. Typically, testing complex cloud scenarios in particular domains (e.g., mobile apps) require tremendous effort to have the correct infrastructure and configuration needed for testing. The challenges are twofold in this arena. On the one hand, the lack of automation can lead to high maintenance and operational costs of the correct testbeds for testing. The lack of open-source solutions, on the other hand, may pose a potential issue, especially for small or medium-sized projects aimed at developing and testing specific applications [17].

24.6 Case studies

CNDCT has faced unparalleled difficulties with the continuous growth of software size and sophistication of hardware facilities. These issues could be addressed by the dynamic allocation, self-service requirement, and

transparent cloud computing services functionality. CNDCT is a modern testing framework that can easily manage users' distributed testing tools in a single platform or service and provide business organizations with a shared and accessible automated testing environment delivery platform. Enterprises and academia do not need to buy test servers, test applications, and deploy a complex testing environment when CNDCT is applied to testing. Besides, the CNDCT shortens the time before items enter the market and guarantee the Web systems' consistency. For CNDCT, not all applications are accepted. The cost of relocation, for instance, is much greater than the return. The test program's features decide if the program's testing phase is sufficient for migrating to the cloud. Factors of control are as follows. The first consideration is that test tasks are mutually exclusive or have clear interdependencies to perform simultaneous task execution. The second aspect is that the operating environment that realizes cloud testing automation is independent and simple to define. The last consideration is that CNDCT is sufficient to achieve test scalability for automated testing. The types of testing are determined by the features of the execution engine in CNDCT. In general, high-capacity automated and performance testing in the cloud area is very complex. The following functions are included in a mature CNDCT system: testing monitoring, digital testing management, tracking, scalable testing environment, automated testing and control services, multitenant testing module, integrated solutions, and combinations.

24.6.1 The overall design of the testing system

In this section, we will look at the overall design of the testing method as well as a meaningful case study.

24.6.1.1 The step of cloud testing

The user first sends the test request to machines in the process of CNDCT, and then the system accepts the testing tasks. Besides, virtual and middleware tools are deployed to conduct the execution and supervision of the testing. Finally, the results of the research are gathered. The CNDCT phase is shown in [Fig. 24.9](#).

24.6.1.2 The system architecture

The principle of cloud computing could be linked back to the process of computers saving time. Individuals conducted measurements and programming via the terminal and PC during that time, monitored their

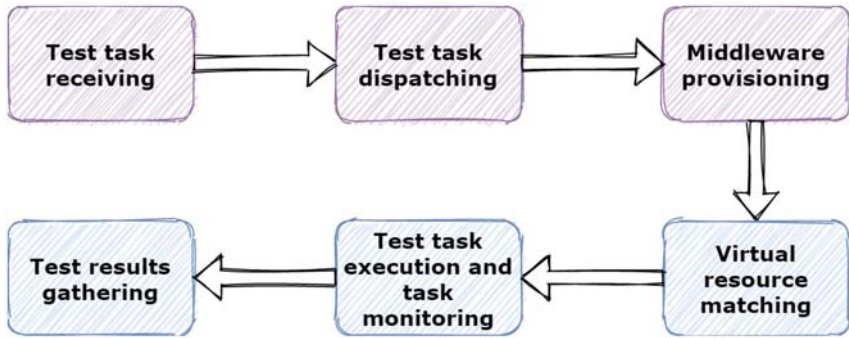


Figure 24.9 The step of cloud testing.

computing environment, and chose a computer software and personalized device following their requirements. Data and programs vanish from the desktop after entering the cloud era, and the entire user interface can rely on a web browser-based window.

24.6.1.3 Design

Due to the scheduling and deployment of VMs and the complex deployment of testing tasks, the deployment strategy of parallel testing tasks in the testing management module is very important in CNDCT. After the user has submitted the test tasks, it is important to forecast the number of VMs in conjunction with the number of tasks and the review of test objects, which may minimize requests due to unnecessary VM waste. Furthermore, the inadequacy of testing machines may prevent the loss of testing time. The test cases necessary for CNDCT are autonomous from each other. There is no need to consider the dependencies between tasks in the testing task scheduling phase of the CNDCT platform, simplifying the algorithm used in the scheduling process. The scheduling system uses a high-priority scheduling algorithm based on a dynamic priority, that is, the priority of the testing tasks alternates with the execution of the tasks or the tasks' waiting period. The priority tasks are performed first.

24.7 Conclusion and viewpoints

The NDT integration technology can boost the efficacy of identification, reliability, and resource conservation and increase test results' integrity.

A trend for NDT-integrated technology is CNDCT. The CNDCT integrates sensor technology, network technology, communication technology, and computer technology with NDT integration technology and the latest development performance and provides customers with a more convenient and more effective service. Users can share cloud service hardware and software resources and appreciate the comfort of network services and experience.

In particular, the most actively examined field is test execution. Indeed, the cloud provides the ability to build and manage expensive test infrastructures and to exploit flexible on-demand tools for testing configuration (using cloud virtualization) and performance (using cloud elasticity). In this order, the second most researched area is the test objective, with performance, functionality, protection, reliability, and elasticity being the most frequently covered in the primary studies surveyed. Indeed, the cloud's flexibility, performance, and computing capacity open up new, fascinating testing possibilities that were previously thought impossible: large combinatorial testing, a huge number of simultaneous executions, simulation and emulation, dynamic scheduling, resource allocation, and adaptation, as well as a more effective and efficient evaluation of quality characteristics such as scalability. Not surprisingly, the areas in which this occurs most frequently are smartphones and web apps, given the transfer of testing to the cloud. IoT and networking are other areas that will benefit from the cloud opportunity but have not yet done so in significant measure. The area also lacks proper conceptualization: a minority of papers covered test viewpoints, within which the most covered subjects are, paradigmatically, by far the open issues and problems.

In recent years, much research has been consecrated to TiC, ToC, and testing of the cloud in the cloud. Research related to testing activities is constantly developing in all three categories. New approaches, methods, and infrastructures are still being proposed, especially in the context of mobile systems and web applications. Authors have built a classification that represents the key areas of research in recent years through construction, namely, test perspective, test design, test execution, test purpose, test assessment, and test domain. We have also listed those subjects within each of these areas that have drawn the greatest attention and in which several solutions have been suggested. The most actively examined field is test execution. Indeed, the cloud provides the ability to build and manage expensive test infrastructures and exploit flexible on-demand tools for configuration and performance testing.

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CHAPTER 25

Complementary results of non-destructive elemental assay and liberation analysis of waste printed circuit boards

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25.1 Introduction

Printed circuit boards (PCBs) are the main component of almost all electrical and electronic equipment (EEE) systems. When these EEEs end up with their lives, they become waste and named waste electrical and electronic equipment (WEEE) or E-waste [1]. Although PCBs form 3% by weight of total electronic waste these are the most valuable components of E-wastes. Thus, the recycling of PCBs makes economic and strategic sense [2,3].

PCB is a thin board on which microelectronic components are mounted. These components behave as electrical conductors (ECs) which provide interconnections between different components of PCBs [4]. Thus, PCBs mechanically assist the connection among ECs in electrical equipment. This connection is established using conductive paths, tracks, signals, and traces from laminated Cu sheets on the nonconductive membrane of PCB. Furthermore, it becomes the reason for the connection between software and hardware in EEEs [1].

25.1.1 Classification of printed circuit boards

Based on the versatility of EEEs, PCBs are used in various applications. According to Ref. [1], the PCBs from E-waste were classified into four major categories:

- Small and Large Home Appliances
- Office Appliances
- Medical Instruments
- Industrial Machineries

In addition, according to the European Directive 2002/96/EC, the European Commission further divided the PCBs into ten different categories. These categories are listed in [Table 25.1](#).

In addition to valuable metals/materials, they also contain some hazardous heavy metals which can be harmful to the environment and our health. These include batteries containing mercury, cadmium, and lead, cathode ray tubes containing lead in cone glass, and asbestos waste, toner cartridges, lead, and cadmium solders, polychlorinated biphenyl containing capacitors, and halogenated flame retardants plastics in PCBs [6].

25.1.1.1 Types of printed circuit boards

Besides the classification of PCBs according to their applications, they are also categorized based on their composition which is further divided into three types.

1. *Single-layered board*: A circuit board made of a single copper layer without metallization holes.
2. *Double-layered board*: A circuit board made of a double lamination of copper and unified by metallic holes.
3. *Multilayered board*: A circuit board having multiple layers of copper for better efficiency with metalized connections.

According to market and economic analysis, it is very important to know if those PCBs are recyclable or not. Thus, PCBs are further experimented with and divided into rich, or poor boards based on their metallic compositions. The PCBs having large cylindrical capacitors and polymers, or a smaller number or larger diameter of processors and IC chips are categorized as poor boards. It is due to their low metallic quantity such as audio instruments, television, and printers. While the PCBs have a huge number of components such as processors, conductive chips, less capacitors, and are thinner than poor boards, are categorized as rich boards. They have a large number of metals such as PCBs from mobile phones, computers, laptops, etc. [7,8].

25.1.1.2 Composition

The composition of EEES has various components and substances. These include ferrous and nonferrous metals, in which base metals (BMs), PMs, rare-

Table 25.1 Classifications of PCBs by European Commission under the European Directive 2002/96/EC [5,6].

Categories	Major EEEs
Large household appliances	Refrigerators and freezers, washing machines and dryers dish washing and cooking machines, electrical stoves and hot plates, microwaves, electric heaters and radiators, electric fans, air conditioners, other fanning, exhaust ventilation and conditioning equipment
Small household Appliances	Vacuum cleaners and carpet sweepers, sewing, knitting, other textile Equipment, ironing, mangling and other clothing appliances, toaster, fryers, grinders, coffee machine and opening or sealing equipment, electric knives, hair cutting, hair dryer, shaving, massage, and body care machines, clock and watches
IT and telecommunication equipment	Data Processing frames, minicomputers and printers, personal computers (CPU, mouse, keyboard, screens), laptops, notepads, typewriters and copying machines, calculators, telephones, and facsimile
Consumer equipment	Radio, Television, Video cameras and Video recorders, Hi-fi recorders, Audio amplifiers and Musical instrument
Lighting equipment	Luminaries for fluorescent lamps, straight fluorescent, and compact fluorescent lamps, high-intensity discharge, and low-pressure sodium lamps
Electrical and electronic tools	Drills, saws, and sewing machines, milling, turning, sanding, shearing, welding, soldering, and riveting equipment, etc.
Toys, leisure, and sports equipment	Electric trains and car racing sets, video games and its consoles, computer for biking, diving, and rowing, etc. electrical and electronic sports equipment, coin slot machines
Medical instruments	Radiotherapy, cardiology, dialysis, and pulmonary ventilator equipment, nuclear medicine, laboratory equipment, analyzers, freezers, and fertilization test equipment
Monitoring and Control Equipment	Smoke detector, heating regulator, and thermostats, measuring, weighting, adjusting, monitoring and control instruments
Automatic dispensers	Automatic dispensers for hot drinks, hot or cold bottles, solid products, money, and others

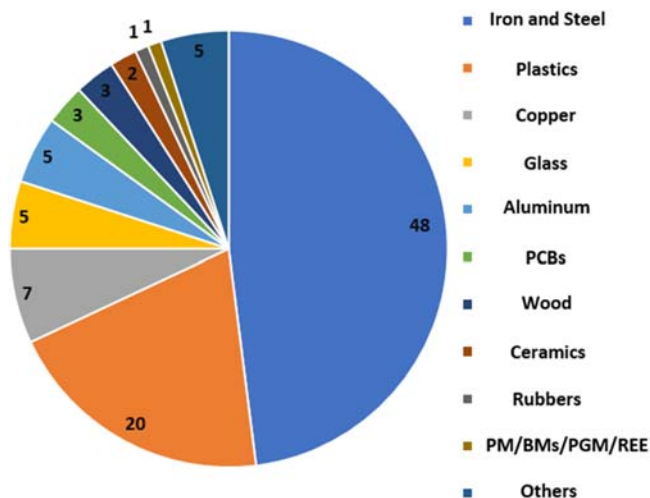


Figure 25.1 General main composition of waste electrical and electronic equipment [1].

earth elements (REEs), platinum group of metals, scarce metals, and some hazardous substances such as heavy metals, plastics, and other hazardous substances are included. As the compositions of WEEE are shown in Fig. 25.1, the chemical composition of metals always varies with respect to the type and application of electronic waste, even more specifically in WPCBs [1].

The bare/mother boards of PCBs are made up of epoxy resins, and fiberglass which is laminated with a thin Cu layer. This arrangement is formed by mechanical interlocking such as etching technologies or chemical bonding mostly Black-oxide treatment [9]. Thus, electronic components such as resistors, connectors, relays, solders, capacitors, transistors, heat sinks, IC chips, connecting pins, and many other components [1]. These electronic components of PCBs contain almost 60 or more valuable metals/nonmetals and hazardous elements [10]. The overall composition is classified into 23%–30% polymers, 30%–49% ceramics and glass, and 28%–40% metals in PCBs [6,11].

25.1.1.3 Valuable elements

The valuable elements include some BMs, PMs, platinum groups of metals, and REEs. The list of these elements with general composing quantities in PCBs is shown in Table 25.2.

Copper is normally found in the foliated membrane of fiber, lead, and tin are the base of solders, and gold is found in IC chips, connecting pins, processors, and conductive chips. Furthermore, silver is found in

Table 25.2 Valuable and nonhazardous elemental composition of PCBs by weight percentage [6,11,12].

Elements	Amount (wt.%)	Elements	Amount (wt.%)	Elements	Amount (wt.%)
Copper	10–26.8	Lead	1.8–4	Sodium	0.175
Iron	5.3–10	Calcium	1.8	Zirconium	0.074
Silicon	8	Nickel	0.47–0.8	Beryllium	0.061
Aluminum	1.9–7	Zinc	0.8	Palladium	0.062
Titanium	3.3	Manganese	0.65	Gold	0.008–0.04
Vanadium	2.4	Magnesium	0.28	Sulphur	0.034
Tin	2–4	Silver	0.25–0.33	Bismuth	0.029
Molybdenum	0.029	Phosphorus	0.004	Hafnium	0.0008
Tantalum	0.016	Lanthanum	0.0028	Scandium	0.00014
Cobalt	0.006	Strontium	0.0024	Europium	0.0001
Potassium	0.0055	Platinum	0.0023	Selenium	0.0001

Table 25.3 Percentage compositions of some hazardous substances in printed circuit boards [12].

Elements	Amount (wt.%)	Elements	Amount (wt.%)
Bromine	3.4	Cerium	0.0114
Lead Oxides	1.8	Cadmium	0.007
Antimony	0.3	Arsenic	0.0015
Chlorine	0.19	Thorium	0.00034
Chromium	0.13	Mercury	0.0001
Cesium	0.0001		

connectors and capacitors. The other elements are found in different electronic components [11,12]. There are some other trace elements such as indium, tellurium, and germanium in composition with brominated flame retardants (BFRs) in epoxy resin matrix [6].

25.1.1.4 Hazardous substances

Besides valuable elements, there are some hazardous elements and substances which are harmful to health as well as the environment. These harmful substances include Bromine, Lead Oxides, Antimony, Chlorinated polymers, Chromium, Cerium, Cadmium, Arsenic, Thorium, Mercury, Cesium, and organic hazardous substances such as BFRs and Polychlorinated dibenzo-p-dioxin/furans (PCDD/Fs) [12–14]. The percentage composition of some of these hazardous substances is mentioned in Table 25.3.

25.2 Non-destructive characterization of the printed circuit board for selective liberation and enrichment of metals

The characterization of WPCBs is extremely important to assess the economic and beneficiation aspects for the recycling of metals due to the diversity, complexity, multiple laminations, and heterogeneity in the construction of WPCBs, and thus their recycling is very challenging [2]. Valuable metals such as Cu, Sn, and Ag are entrapped or embedded in the layers of epoxy resins and fiberglass, and this entrapment is the main hindrance to the recycling of those metals. Thus, the main factor is the degree of liberation which can be optimized by comminution performance (e.g., selection of appropriate comminution method, whereas rotation speed and impact of hammers in the case of a hammer mill), and it can strongly affect the recovery of valuable materials. On the contrary, it is very difficult to ground metals than nonmetals because of their ductility. The metals in PCBs are reinforced into glass and plastics, thus their brittleness causes them to be present in fine fractions more than metals [1,15].

Based on these issues, various non-destructive characterization methods such as Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS), X-Ray Fluorescence (XRF), X-Ray Computed Tomography, and Prompt-Gamma Activation Analysis have been evaluated in our previous studies. A series of our studies have been conducted to better understand the liberation, distribution, and enrichment of valuable metals in ground PCBs for downstream processes [2,15–17]. From these characterization techniques, our complementary results of XRF and SEM-EDS were summarized and compared in this chapter.

25.2.1 Non-destructive elemental assay of printed circuit boards by X-ray fluorescence

The hammer mill products were sieved, weighted, and sampled for non-destructive X-ray fluorescence analysis (XRF). A portable XRF machine (Niton XL3t GOLDD+, Thermo Scientific, Waltham, MA, United States) on a stand was operated through a personal computer with purpose build software. The mining Cu/Zu mode with the full fundamental parameter algorithm was used. The concentrations of the following metals can be detected: Mg, Al, Si, P, S, Cl, As, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, W, Pb, Bi, Zr, Nb, Mo, Sn, Ba, Sb, Cd, Pd, Sr, Rb, Se, and Ag and Au (Thermo Fisher Scientific Inc., 2019).

The hammer-milled particles were fed into a standard plastic container covered with X-ray thin film (TF-160–255, MYLAR, Port St. Lucie, FL, United States) window facing the X-ray beam and were measured for 120 s/point to detect and measure the elemental composition. Due to the heterogeneity of the samples, especially for coarser fractions, that is, +0.25 mm, we conducted at least five measurements for each size fraction (+2–4, +1–2, +0.5–1; +0.25–0.5 mm, +0.125–0.25, and –0.125 mm) in each milling condition. The average grade (element %) by size fraction for each metal and the 95% confidence interval were calculated and applied for further calculation to evaluate the milling performance [15].

From the XRF elemental assay, the back-calculated grade of the different metals of our interest in the feed material is given in Table 25.4, together with literature values [7,10]. Our measured values generally agree with literature values with some deviation that could be due to differences in the heterogeneity and preparation of samples and analytical methods. Since we used the same samples and methods, this deviation does not affect the evaluation and comparison among our products discussed in the series of our works.

25.2.1.1 Recovery and enrichment ratio of metals

The metal recovery was calculated as follows:

$$\text{Recovery} = \frac{C_i c_i}{Ff} \quad (25.1)$$

where C_i is the mass in the product particle size fraction “ i ” after hammer milling, c_i is the metal grade (element %) in the product particle size fraction “ i ” after hammer milling, F is the feed mass and f is the feed metal grade (element %).

The metal enrichment ratio can be defined as:

$$\text{Enrichment ratio} = \frac{\text{Element}\% \text{ in the concentrate}}{\text{Element}\% \text{ in the feed (f)}} \quad (25.2)$$

Table 25.4 Feed metal composition in comparison with literature values [15].

Sample	Au %	Pb %	Zn %	Cu %	Fe %	Al %
Feed 2–4 mm	0.03	0.54	0.62	4.40	5.25	7.33
Feed 1–2 mm	0.04	0.86	0.49	8.39	2.33	5.34
Data from [10]	0.03	0.2–0.3	0.5–3.0	7.0–36.0	2.0–12.0	1.0–22.0
Data from [7]	0.10	2.40	2.30	22.0	5.70	3.90

The metal recovery and enrichment ratio were calculated as a function of each milled particle fraction size as a concentrate to evaluate the presence and degree of selective/preferential metal concentrations to specific size fractions under different milling conditions.

25.2.1.2 Results on Cu behavior after hammer milling

Cu is one of our major interests due to the high demand for this commodity. The recovery and enrichment ratio of Cu after hammer milling were thus calculated and their plots are given in Figs. 25.2 and 25.3 as some examples, and the effects of the feed mass and milling time are discussed [15].

Fig. 25.2 shows the Cu recovery at a constant feed mass under different milling times (A–C) and a constant milling time with different feed masses (D–F). Generally, Cu is concentrated in coarse (+0.5–1 mm) and fine (–0.125 mm) size fractions with its absence/minimum concentration in the middle (+0.125–0.5 mm) size fraction after the hammer milling. Enrichment into fine size can be explained by selective Cu liberation while the enrichment in coarse size can be due to selective agglomeration [15]. The latter can be explained by the mechano-chemical reaction due to the heat generated inside the mill chamber. Literature reported similar agglomerate formations via ball milling [18].

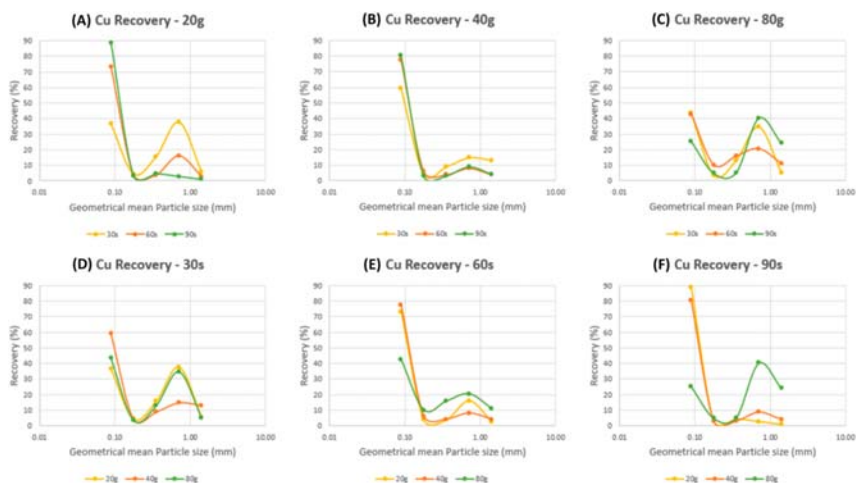


Figure 25.2 Cu recovery after hammer milling as a function of feed mass, milling time, and particle size. Feed size +1–2 mm (A) 20 g feed, (B) 40 g feed, (C) 80 g feed, (D) 30 s milling time, (E) 60 s milling time, and (F) 90 s milling time. Experimental data points are connected with lines for the purpose of visual aid only [15].

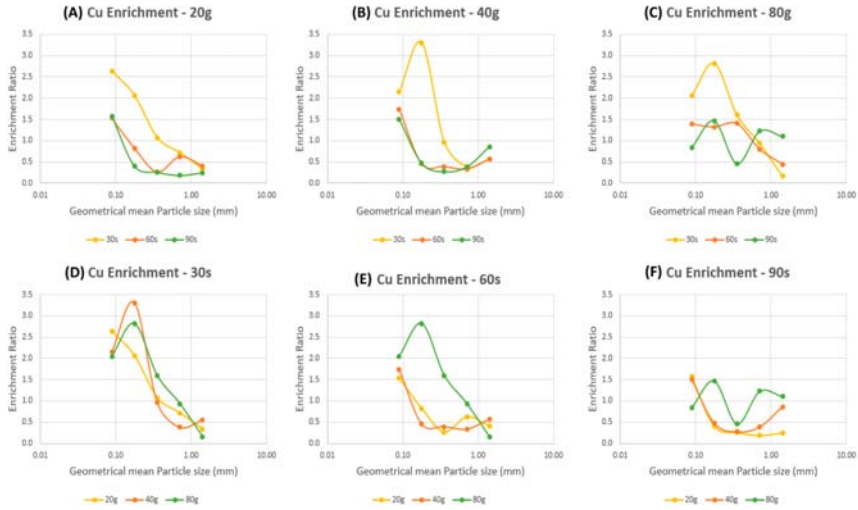


Figure 25.3 Cu enrichment ratio after hammer milling as a function of feed mass, milling time, and particle size. Feed size +1–2 mm (A) 20 g feed, (B) 40 g feed, (C) 80 g feed, (D) 30 s milling time, (E) 60 s milling time, and (F) 90 s milling time. Experimental data points are connected with lines for the purpose of visual aid only [15].

Fig. 25.2 shows that the Cu recovery for 30 seconds milling time is considerably high both in the finest (above 35% for all the feed mass) and a coarse fraction (+0.5–1 mm) for a feed mass of 20 g (38%) and 40 g (15%). For the feed mass of 80 g, the Cu recovery behavior was slightly different while its general trend is similar. Fig. 25.2C shows that with the increase in milling time the Cu recovery in the finest size fraction decreased to 26% (90 seconds) from 43% (60 seconds) while the Cu recovery in the coarse fraction (+0.5–1 mm) increased to 40% (90 seconds) from 20% (60 seconds). The latter indicates the Cu agglomeration enhanced more than the Cu size reduction, with increasing milling time. In general, a trend easily recognized is that for the intermediate fractions (+0.125–0.5 mm), regardless of feed mass and milling time, the Cu recoveries were considerably low, sometimes even close to 0%.

Fig. 25.3 shows the Cu enrichment ratio after hammer milling, using the same set of experimental conditions as shown in Fig. 25.2. In Fig. 25.3, the Cu enrichment is especially noticeable with the 30 seconds milling time in comparison with the other milling times at a fixed feed mass rate, and with an enrichment peak in the finer fractions (i.e., +0.125–0.25 mm and –0.125 mm). For example, the enrichment ratio

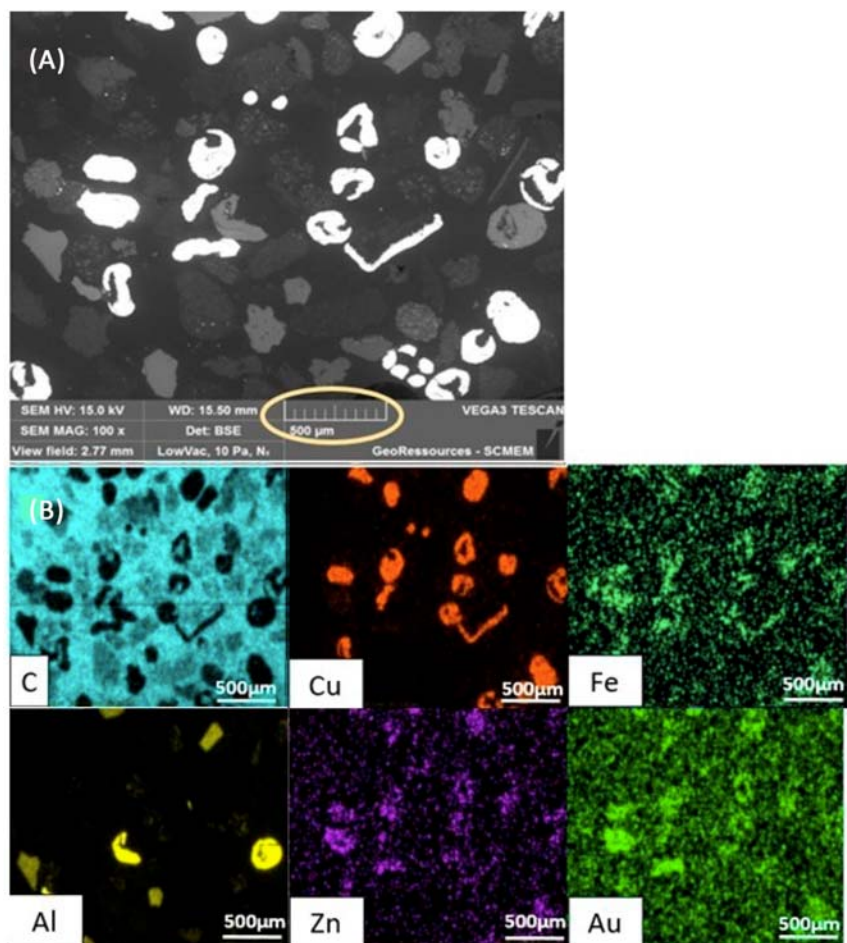


Figure 25.4 (A) Backscattered electron image obtained by SEM for the 80 g sample ground at 90 s to achieve the size fraction of + 0.125–0.25 mm [17]. (B) Elemental map obtained by the EDS detector showing the distribution of elements Carbon (light blue), Copper (orange), Iron (dark green), Aluminum (yellow), Zinc (purple), and Gold (light green) [17].

was 2.8 in +0.125–0.25 mm while 0.2 in +1–2 mm with 80 g feed mass and 30 seconds milling time. At a fixed grinding time (Fig. 25.3D–F), the variation in the feed mass rate is not as conclusive in terms of which feed mass rate provides the optimal enrichment ratios, although in general high enrichment into the finer fractions was obtained (e.g., 2.6 in –0.125 mm vs 0.3 in +1–2 mm with 20 g feed mass and 30 seconds milling time, Fig. 25.3A).

25.2.1.3 Scanning electron microscope-energy dispersive spectroscopy complementary results of liberated printed circuit boards

Gonçalves and Otsuki [17] conducted the SEM-EDS analysis on three fine-size fractions of WPCBs. The size fractions are $-0.5 + 0.25$, $-0.25 + 0.125$, and -0.125 mm for all samples ground by a hammer mill which conditions are described in Table 25.5. A representative sample of 0.2 g was obtained using coning and quartering methods and passed by the sample preparation protocols of SEM-EDS analysis.

The backscattered electron images were obtained by SEM and elemental maps of the sample were by energy dispersive X-ray spectroscopy (EDS). The dark region shows plastic and the bright regions show metallic particles as shown in Fig. 25.4A. The level of brightness distinguishes the composition based on atomic numbers. The elements having narrow-range atomic numbers show similar brightness such as Cu, Fe, Co, Ni, and Al [17]. Thus, the EDS detector provided the qualitative analysis as shown in Fig. 25.4B, with elemental peaks having a low peak-to-background ratio [19].

The degree of liberation for all the samples was studied by SEM-EDS results shown in Fig. 25.5. The sample with 20 g and 30 seconds milling time shows 40% Cu, 22% Al, and 8% other metals liberation in $-0.5 + 0.25$ mm fraction which has been increased in -0.125 mm fraction stating 68% Cu, 60% Al and 72% others. The same trend was observed in other results such as a sample with 80 g with 90 seconds liberation of Cu 50%, Al 45%, and other metals 40% in $-0.5 + 0.25$ mm fraction which is increased up to 88% Cu, 79% Al and 84% other metals in -0.125 mm fraction. This trend reveals that the degree of liberation increases with the decrease in particle size [17].

Another effect on selective liberation by the increase in sample mass was also interpreted by these results. In general, the liberation degree increases with a decrease in particle size. It can be attributed to the collision probability

Table 25.5 Grinding conditions including sample mass and milling time by hammer mill for four samples acquired for SEM-EDS analysis [17].

Sample no.	Sample mass (g)	Milling time (s)
1	20	30
2	40	30
3	40	90
4	80	90

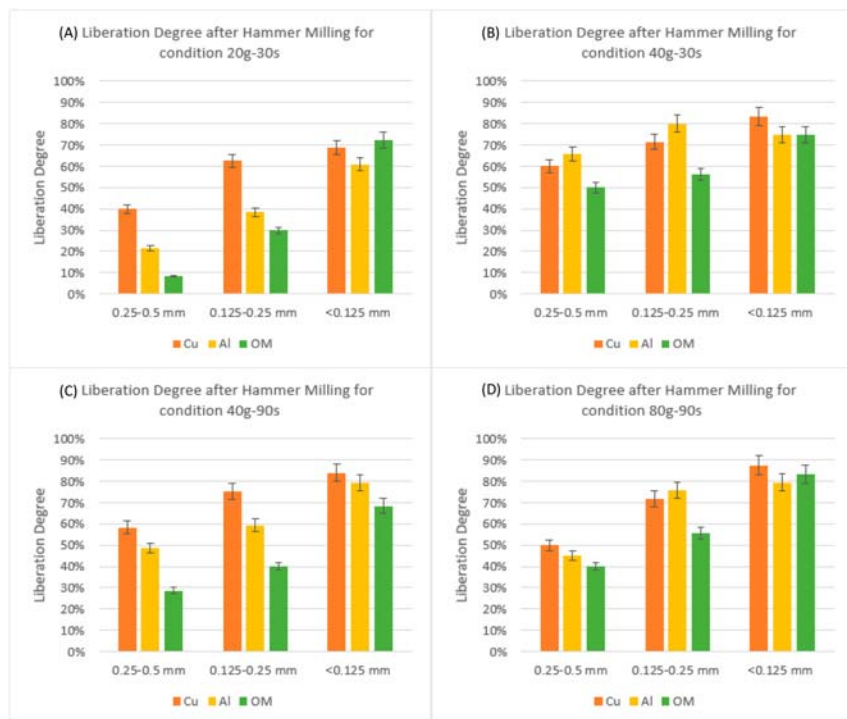


Figure 25.5 Degree of liberation for all the samples with their size fractions based on the SEM-EDS image analysis. (A) sample mass 20 g and 30 s milling time, (B) sample mass 40 g and 30 s milling time, (C) sample mass 40 g with 90 s milling time, and (D) sample mass 80 g with 90 s milling time.

among particles and hammers or an increase in attrition and abrasion factor during milling. Moreover, the increase in milling time from 30 to 90 seconds for the sample of 40 g in Fig. 25.5B and C reveals a little but the same effect on selective liberation. It achieved more selective liberation for Cu at coarser and intermediate-size fractions than fine-size fractions. It can be addressed due to selective agglomeration at coarser size fraction. However, in general, the liberation degree is more in the finest fractions. Correspondingly, it also effects the liberation parameter K which determines the trend of degree of liberation as shown in Fig. 25.6. It can be determined by linear regression of the plot among geometric mean of particle size (μm) and natural logarithm of degree of liberation. Thus, a large K indicates a huge change in liberation degree and fine-size fraction. While a small K indicates a little increase in liberation degree stating a coarser fraction. The general trend reveals that K increases with less feed mass and milling time [17].

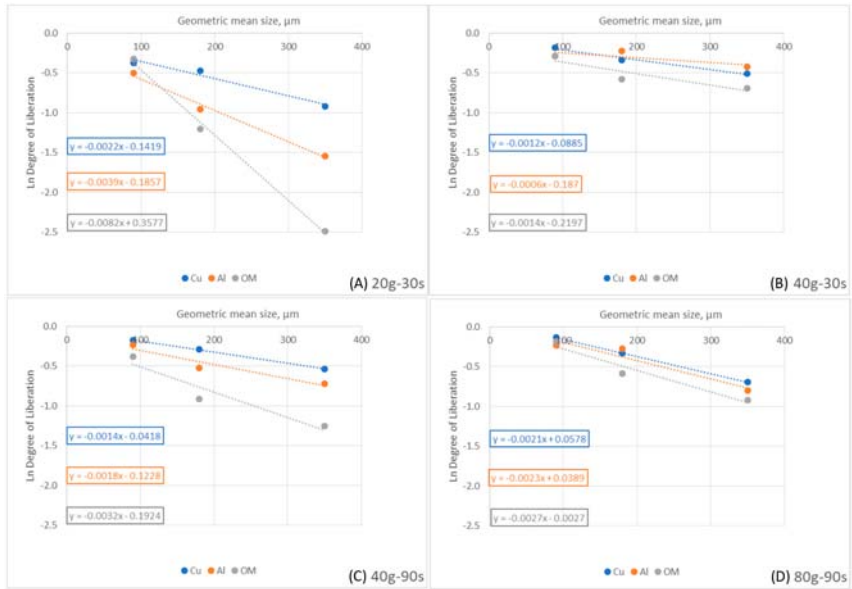


Figure 25.6 Degree of liberation determined by SEM-EDS image and elemental mapping analysis as a function of geometrical mean. (A) Cu, Al, and other metals—20 g feed and 30 s milling time; (B) Cu, Al and other metals—40 g feed and 30 s milling time; (C) Cu, Al, and other metals—40 g feed and 90 s milling time; and (D) Cu, Al, and other metals—80 g feed and 90 s milling time.

Based on the results of SEM-EDS and XRF analysis and literature review, some of their advantages and disadvantages are summarized in [Table 25.6](#).

25.3 Summary and future perspectives

This article summarized non-destructive characterization methods to evaluate the selective milling of PCBs by using a hammer mill in terms of elemental distribution and degree of liberation. A series of milling time and feed mass was investigated for understanding their effects on the behavior of metal deportment and enrichment as well as the change in the degree of liberation in different product size fractions, based on the characterization by the portable XRF and SEM-EDS.

The selective agglomeration led to the Cu and Al recovery in the coarse fraction, while the selective size reduction led to their recovery in the finest fraction. Our results clearly showed the usefulness of non-destructive characterization to evaluate the selective milling process and enhance the further beneficiation processes of the PCBs.

Table 25.6 Advantages and drawbacks of non-destructive characterization of mechanically processed PCB particles by using XRF and SEM-EDS [2,17,20–25].

Scanning electron microscopy and energy dispersive spectroscopy	
Advantages	Disadvantages
Able to use multiple detectors (e.g., SE, BSE, X-ray) and to provide information about complex associations using complementary information by using those detectors. Feasible to reveal information based on texture and chemical composition. Can detect elements having atomic number 4 or higher. Much better light element/low-energy line sensitivity than XRF. Large concentration range from 0.1 to higher than 10 wt.%. Data can be collected and analyzed simultaneously	It is an expensive setup, and should be housed in an area that is free from electrical, magnetic, and vibrational interference. Sensitive to operating parameters such as beam control. Careful sample preparation is necessary for precise analysis. Sample needs to be flat and electrically conductive. In other words, polishing and carbon/gold coating are required.
X-ray fluorescence	
Advantages	Disadvantages
Easy to access and operate. Fast multielemental and non-destructive analysis. On-site evaluation is possible. Can be applied to a large area sample as well as spot analysis on a small area. Analyzed volume ranges from μm to mm. Lower detection limit (10–150 ppm) than SEM-EDS. Easy or no sample preparation required. Sample does not need to be electrically conductive and polished. Data can be collected and analyzed simultaneously.	XRF gun reveals more uncertainty on large samples than small size spot analysis. Difficult to detect light elements having atomic number less than 12. The detection limit for heavy elements is greater than 20 ppm. The elements to be analyzed are based on the analysis mode selected before the measurements. Not flexible in this aspect.

Further research to develop a standard protocol for elemental deportment/concentration and degree of liberation analysis applicable to various complex/heterogeneous materials will be useful and worth conducting.

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CHAPTER 26

Future perspectives on non-destructive material characterization methods towards sustainability and circular economy

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26.1 Introduction

In 1972, the Club of Rome published “The Limits to Growth” [1], reported their global system modeling, and predicted that our growth will reach its limit by 2030 due to shortages of food and nonrenewable resources, and environmental pollution. Based on their prediction via this ground-breaking report, a large number of global initiatives have been developed. They include sustainable development goals (SDGs) and the Paris Agreement adopted in 2015.

Among many other potential contributions, the recycling of metals/materials can be a potential solution addressing many SDGs, including “12—Responsible consumption and production” via extended producer responsibility and relevant recycling system/technology developments. For example, selective material recovery is particularly challenging but important in metal/material recycling. It can be significantly advanced via the synergistic combination of material characterization, selective liberation, and selective separation [2,3]. Within this framework, non-destructive material characterization can be very helpful since a quick acquisition of material properties can properly optimize the recycling process based on the change in feed and processed materials and process performance. In addition, capturing material heterogeneity is of great help in addition to the average material properties from destructive characterization methods through acid digestion followed by chemical elemental assay.

To have a better insight into/opportunity of achieving sustainable utilization of our limited resources, the development of new methods and/or the combination of multiple supplemental (and/or other) characterization methods for the utilization of complex/functional materials in energy-saving and consumer electronics is particularly required. Proper utilization and characterization of such complex materials is still a complicated and challenging task, since the material/element spatial heterogeneity and thus their process and/or resultant products/services might be varied with time (e.g., Refs. [2–6]).

Fig. 26.1A shows the life cycle of a product [7] and Fig. 26.1B shows the relationship between product functionality and its complexity/heterogeneity as well as its difficulty in characterization and recyclability. As shown in Fig. 26.1A, in forward logistics, a product is created while in reverse logistics an end-of-life product is collected, dismantled, treated to recover the valuable materials, removed toxic substances, and otherwise disposed of via landfilling or incineration. The ratio between forward and reverse logistics and disposal depends on the regions/countries. In the case of e-waste in the United States, one report informed that the ratio was 20 vs 80 wt.% [8]. In relation to a product life cycle, the product functionality may significantly affect both forward logistics and reverse logistics. The better product functionality based on the increase in its complexity and heterogeneity, the more difficulty in product and material characterization while

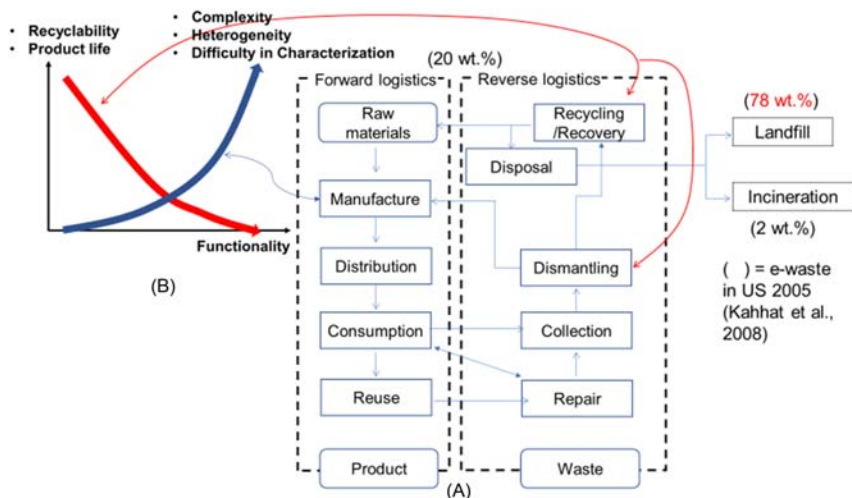


Figure 26.1 (A) Life cycle of a product and (B) relationship among product functionality and its complexity/heterogeneity as well as difficulty in characterization and recycling. *Part (A) modified from Zeng et al. (2013).*

the less product life and recyclability. In the view of recycling, dismantling and recycling/recovery phases can be more complex and time and cost-ineffective.

Within the above-mentioned framework, in the following sections, some of the previous studies and future perspectives in terms of complex/heterogeneous material characterization as well as coupling multiple characterization methods to capture such complexity/heterogeneity will be described and discussed.

26.2 Complexity and heterogeneity

A proper characterization of heterogeneous composite materials is a challenging task since the majority of characterization methods analyze either the average characteristics of the whole material or a narrow area of specific interest [e.g., 2–6]. In addition, those characterization methods often require the size reduction and dissolution of a material that averages the whole material and could overlook potential issues associated with spatially heterogeneous materials and values associated with fine grains/particles. This could also overlook the correlation between the microscopic structure of fine grains and the macroscopic mechanical behavior of metals/alloys, for example. Such correlations were found to be useful in many different aspects, while research gaps have been identified in terms of the advancement of characterization methods. On the other hand, gaining a better understanding of heterogeneous metals/alloys is of great importance from scientific and engineering points of view, since processing, producing, and applying these materials including advanced technologies (e.g., batteries, printed circuit boards) is vital to our high tech products and modern society.

Some potential contributions of non-destructive material characterization in this field are listed in [Fig. 26.2](#). There are multiple fields of studies should involve in the development of non-destructive material characterization methods towards complex/heterogeneous materials, as seen in [Fig. 26.2](#). Thus, synergistic collaboration and interaction among scientists and engineers from respective fields of studies are necessary to advance the significant development. One of them can be the characterization of industrial wastes for understanding the spatial distribution and liberation/association of key components to develop a proper recycling flowsheet. Such a synergistic correlation was found to be useful in many different respects, while there remain so many research gaps that have been identified. At the same time, a better understanding of heterogeneous composite materials is of great

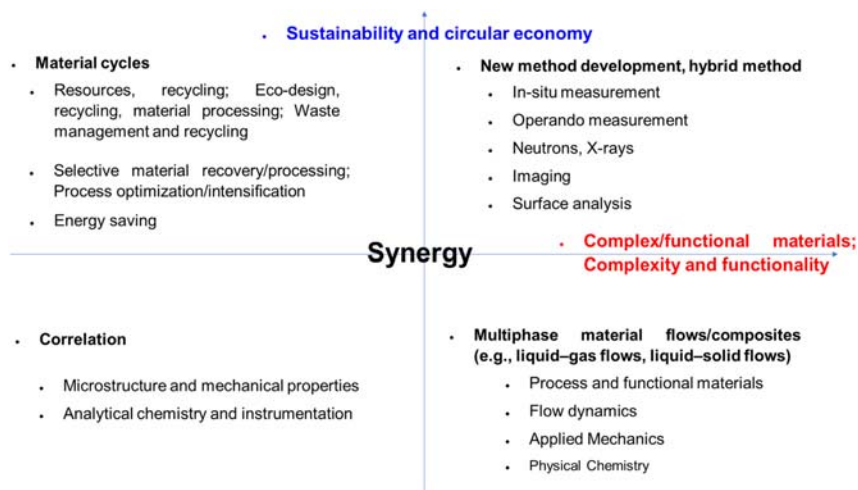


Figure 26.2 Some keywords associated with non-destructive material characterization methods in the context of complexity and functionality as well as sustainability and circular economy.

importance from scientific and engineering points of view, since the processing and production/application of composite materials are vital to our modern society, including raw materials (e.g., complex ores) and advanced technologies (e.g., batteries, printed circuit boards, [2–6]).

The other example can be multiphase material flows/composites (e.g., liquid–gas flows, liquid–solid flows) via the development of a new characterization method and/or process intensification. For example, a proper characterization of particle-laden fluids is still an extremely challenging task, since the majority of characterization methods and model analyses are usually developed for simple model systems [9,10]. On the other hand, actual systems are more complex and heterogeneous, and therefore those properties should be captured from a proper characterization.

26.3 Coupling multiple methods to capture material characteristics from different angles

The coupling of multiple characterization methods aims to provide scientists and engineers with a better understanding of material(s) of interest from different angles, for example, the correlation between the changes in (a) microscopic physical/chemical properties and (b) macroscopic properties of material(s) of interest. Further development on the coupling of

characterization of those two aspects towards the enhancement of process and application of material is particularly encouraged [9–11].

Within the above framework, some potential contributions to the non-destructive characterization of complex and heterogeneous materials are shown in Fig. 26.3. They can be bound with two keywords, that is scale difference and property difference/change that can bridge (1) external force-driven coupling phenomena and (2) change in material properties due to correlation in multiscale nature. Non-destructive material characterization can strongly help to better understand the relationship between the aspects of (1) and (2).

Changes in material properties can be external force-driven coupling phenomena whose examples can be mechanochemical [12–14], photocatalysis [15], electro/magneto-rheological fluids [16]. For example, metal/alloy mechanical properties can be strongly influenced by its microstructure that can be analyzed by various non-destructive characterization methods, such as SEM-EDS [13], EBSD [14]. The microstructure of an alloy (e.g., crystal structure/orientation, shear banding) can be arranged by external force application, including mechanochemical processing via ball milling, to optimize the macroscopic mechanical properties of the alloy (e.g., hardness). In addition, changes in microscopic interactions of colloidal particles by chemical/physical means can influence the macroscopic colloidal particle suspension/dispersion behavior [9–11,17] as described next.

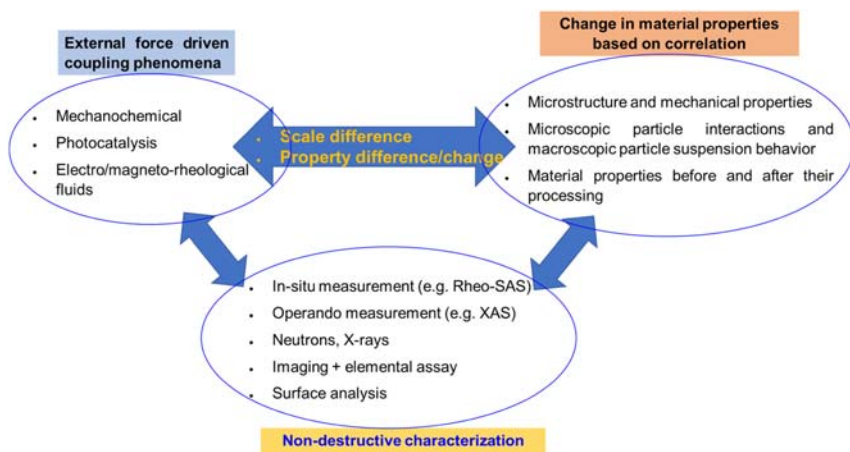


Figure 26.3 Relationship among external force-driven coupling phenomena, changes in material properties based on correlation, and non-destructive characterization.

One of the non-destructive material characterization couplings can be coupling suspension rheology and colloidal forces/interactions to further understand the influence of microscopic particle-particle interactions on the macroscopic suspension behavior under different chemical/physical environments. Such correlation has been reported in many different aspects while there are so many research gaps even in a focused area of this coupling, for example, correlation between particle-particle interactions and particle suspension yield stress [10,11]. At the same time, understanding the macroscopic behavior of a concentrated suspension is of great importance from scientific and engineering points of view since processing and application of colloidal particle suspensions are vital to our modern society, including daily life products (e.g., food, cosmetics) and advanced technologies (e.g., batteries).

A proper characterization of concentrated colloidal particle suspensions is still a challenging task since the majority of characterization methods usually require a dilute suspension of which analysis could overlook potential issues associated with enhanced particle-particle interactions leading to particle coagulation and thus increasing suspension viscosity and facing difficulty in handling such a suspension [9–11,17–20]. One non-destructive characterization coupling able to study multiscale property change is in-situ/Operando measurements that can be performed in neutron facilities, synchrotron X-ray facilities, or even with a laboratory scale with some limitations. Rheo-SAS (rheology-small angle scattering coupling) is one such in-situ measurement and is able to capture the correlation between microscopic particle interactions and macroscopic particle suspension behavior [17]. Not only scattering studies but also other characterization methods, such as imaging [21] and surface analysis [22], can be coupled with external force-driven phenomena. The further development of coupling non-destructive material characterization methods is particularly encouraged to properly capture the material complexity and heterogeneity towards our sustainability and circular economy.

26.4 Conclusions

In this chapter, some future perspectives on non-destructive material characterization methods were provided, in the context of sustainability and circular economy. In this framework, we focused on the following aspects: characterization of complex and heterogeneous materials. As a single characterization method capture specific material properties only, we would need to combine several complementary characterization methods to capture the complex and heterogeneous nature of modern materials in

a wide range of applications. In addition, synergistic collaboration and interaction among scientists and engineers from respective fields of study are highly encouraged to further develop a non-destructive characterization of complex and heterogeneous materials for our sustainable society.

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Non-Destructive Material Characterization Methods

EDITED BY AKIRA OTSUKI, SEIKO JOSE, MANASA MOHAN, SABU THOMAS

Non-Destructive Material Characterization Methods provides a wealth of knowledge, instruction, and theoretical and practical insight into how to implement different non-destructive testing methods for effective material characterization.

The book starts with a concise introduction to the field before progressing to coverage of a wide range of non-destructive characterization techniques that can be immediately implemented. Imaging and microscopy techniques are covered with step-by-step insight into characterization using a polarized microscope, an atomic force microscope, computed tomography, ultrasonography, magnetic resonance imaging, infrared tomography, and more. Spectroscopic, elemental assay, and mapping techniques are discussed next, including Raman spectroscopy, UV spectroscopy, atomic absorption spectroscopy, and neutron activation analysis. The book also covers displacement measurement techniques, large-scale facility techniques, and a combination of multiple characterization methods. Each chapter includes case studies, applications, and recent developments, and the book concludes with discussion of future opportunities for non-destructive material characterization methods toward sustainability and the circular economy.

Key Features

- Provides an overview of a wide-range of non-destructive material characterization methods, their strengths and weaknesses, when to apply them, measurement and data analysis considerations, and other practical tips
- Methods outlined include eddy current sensing and imaging, ultrasonic sensing and imaging, RF and THz imaging, internet and cloud-based methods, and more
- Case studies and applications are included throughout the book

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