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Chapter 10

X-Ray Techniques

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Abstract

This chapter reviewed existing X-ray techniques that can be used for the analysis of materials, inclusive of those used as engineering and structural components. These techniques are X-ray fluorescence (XRF) spectrometry, proton-induced X-ray emission (PIXE) spectrometry, and X-ray diffraction (XRD). These analytical techniques provide qualitative and quantitative information on the composition and structure of materials with precision. XRD gives information on the crystalline forms and amorphous content of materials, which could be quite useful in failure analysis if the type of failure brings about morphological changes in the material under investigation. PIXE and XRF provide information on the types of elements present in a sample material and their concentrations. PIXE is however preferable to XRF due to its higher sensitivity to trace elements and lower atomic number elements as well as its faster analysis. XRF and XRD are more commonly used than PIXE which is a powerful, high-tech method that is relatively new in the field of chemical research. In this chapter, the theory and principles of these analytical techniques are explained, and diagrams showing the components of spectrometers and diffractometers are provided with descriptions of how they function.

Keywords: X-rays, X-ray fluorescence (XRF), proton-induced X-ray emission (PIXE) spectrometry, X-ray diffraction (XRD), spectrometer, diffractometer

1. Introduction

Metallic and polymeric materials used as engineering and structural components can undergo mechanical failure due to a number of factors which include misuse, design errors or deficiencies, inadequate maintenance, overloading, and manufacturing defects [1]. The different types of failure a material can undergo include wear, fracture, fatigue, creep, stress, and corrosion [1], all of which affect the structural integrity and possibly the morphology of the material. Analyses of materials generally can be carried out using X-ray techniques, such as X-ray fluorescence (XRF) spectrometry, proton-induced X-ray emission (PIXE) spectrometry, and X-ray

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diffraction (XRD). A vast amount of information on elemental composition and concentration (XRF, PIXE), material morphology (XRD) can be obtained from X-ray techniques which make them very helpful in the analysis of materials generally.

X-rays were discovered in 1895 by the German physicist, Wilhelm Conrad Röntgen (1845–1923) who was later awarded the Nobel prize for physics in 1901 [2]. X-rays are invisible, highly penetrating electromagnetic radiation of much shorter wavelength (but higher frequency and energy) than visible light. The wavelength (λ) range for X-rays is from about 10^{-8} to 10^{-11} m [3, 4] and the corresponding frequency (ν) range is from about 10^{16} to 10^{19} s^{-1} [4]. The advantages of using X-rays in analysis are: (i) it is the cheapest and most convenient method. (ii) X-rays are not absorbed very much by air, so the specimen need not be in an evacuated chamber [3]. The disadvantage is that they do not interact very strongly with lighter elements, so this could impose a limitation on the elements detectable by X-ray techniques.

1.1. X-ray emission theory

When samples are bombarded (irradiated) with high-energy protons (or X-rays in the case of XRF and XRD), the interaction of the protons with the electrons of the atoms in the sample causes ejection of the electrons in the innermost shells in atoms of the specimen [4, 5]. This creates a hole (vacancy) in the inner shell, converting it to an ion thereby putting it in an unstable state. To restore the atoms to more stable states, i.e., their original configurations, the holes in the inner shells (or orbitals) are filled by electrons from outer shells. Such transitions from higher to lower energy levels are accompanied by energy emission in the form of X-ray photon, [4, 6] for instance an L-shell electron fills the hole in the K-shell. Since an L-shell electron has a higher energy than a K-shell electron, the surplus energy is emitted as X-rays. In a spectrum, this is seen as a line. The energy of the X-ray emitted when the vacancies are refilled depends on the difference in the energy of the inner shell with the initial hole and the energy of the electron that fills the hole. The emitted X-ray radiation is characteristic of the element from which they originate since each atom has its specific energy levels. The number of X-rays is proportional to the amount of the corresponding element within the sample. An energy dispersive detector is used to record and measure these X-rays and their intensities are then converted to elemental concentrations. An atom can have several lines due to electronic transitions and subsequent refilling of vacant holes by different electrons within the atom. This collection of lines is unique to that element and is like a fingerprint of the element.

1.2. X-ray fluorescence spectrometry

X-ray fluorescence (XRF) is a non-destructive analytical technique used for the identification of elements and determination of their concentrations in solid, powdered, and liquid samples [7, 8]. Elements present in samples are detectable by XRF up to 100% and at trace levels, usually below 1 part per million (ppm) [8]. The elements detectable by XRF range from Sodium to Uranium. XRF has inherent design limitations, which has reduced its sensitivity to lower atomic number elements making it unable to detect elements lighter than sodium. XRF is based on X-ray emission theory.

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The wide application of XRF in industry and research is attributable to its ability to carry out accurate, reproducible analyses at very high speed. With modern, computer-controlled systems, operation is fully automatic and results are typically delivered within minutes or even seconds [8]. XRF analyzers are able to detect the elements present in a sample by measuring the secondary X-rays emitted from a sample irradiated with a primary X-ray source. Since a sample contains several elements, each of these elements produces a unique set of lines ("fingerprint") which is used in the identification of the element. This is why XRF spectrometry is a good technique for the analysis of the elemental composition of a material [9]. There are two types of XRF techniques: energy dispersive XRF (EDXRF), which has high accuracy and is sensitive for heavy metal analysis; and wavelength dispersive XRF (WDXRF), which is more suitable for the detection of light elements and rare earths [9].

1.2.1. How X-ray fluorescence works

X-ray fluorescence functions as follows [3, 7–9]:

1. The sample, which may be in the solid or liquid form, is bombarded with high-energy X-ray photons (primary X-rays) from an X-ray tube.
2. When an atom of an element in the sample is struck with an X-ray of sufficient energy (i.e., greater than the binding energy of the atom's K or L shell), an electron from one of the atom's innermost shells (K or L) is dislodged. This creates "holes" or vacancies in one or more of the orbitals, thereby, converting the atoms into ions which are unstable.
3. To restore stability to the atoms, the vacancies in the inner orbitals of lower energy levels are filled by electrons from outer orbitals, which are at higher energy levels. This transition from a higher to a lower energy orbital shell may be accompanied by an energy emission in the form of a secondary X-ray photon, a phenomenon known as "fluorescence." This is as a result of the release of excess energy by the higher orbital electron.
4. The energy (E) of the emitted fluorescence photons is determined by the difference in energies between the initial (higher) energy level (Ei) and final (lower) energy level (Ef) for the individual transitions. This energy difference (energy of the emitted photon) is related to the frequency (ν) of the photon by the mathematical expression:

$$\text{Energy (E) of emitted X} - \text{ray photon} = \text{Ei} - \text{Ef} = h\nu, \tag{1}$$

i.e., $E = h\nu$, but $c = \lambda\nu$, so $\nu = {}^{c}/_{\lambda}$

When the expression $\nu = {}^{c}/_{\lambda}$ is substituted into $E = h\nu$, we obtain the formula.

$$E = {}^{hc}/_{\lambda} \tag{2}$$

where h is Planck's constant = 6.62608×10^{-34} J s, c is the velocity of light = 2.9979×10^{8} m s^{-1}, and λ is the wavelength of the photon.

Thus, wavelengths are inversely proportional to the energies and are characteristic of each element.

5. The intensity of emission, i.e., number of photons is proportional to the concentration of the element responsible for the emission in a sample.

6. The measurement of the energy (E) of the emitted photons is the basis of X-ray fluorescence (XRF) analysis.

1.2.2. X-ray fluorescence spectrometer set-up

The set-up of the XRF spectrometer is shown in **Figure 1**. The major components are X-ray tube, diffractors (crystals), detectors, and counting electronics, which are described below.

1.2.2.1. X-ray tube

X rays can be produced in a highly evacuated glass bulb, called an X-ray tube, that contains two electrodes—an anode (positive electrode) and a cathode (negative electrode) [3]. The sealed X-ray tube is the primary radiation source and is powered by a high stability generator. The anode is usually made of platinum, tungsten, rhodium, or other heavy metals of high melting point [3, 8]. When a high voltage (about 40 KV) is applied between the electrodes, streams of electrons (cathode rays) are accelerated as they move from the cathode to the anode, producing X-rays as they strike the anode. The wavelength composition of the radiation from the X-ray tube depends upon the choice of anode material. For most applications, the optimal choice is a rhodium anode, although other options such as molybdenum, chromium, or gold may be preferable in certain circumstances [8].

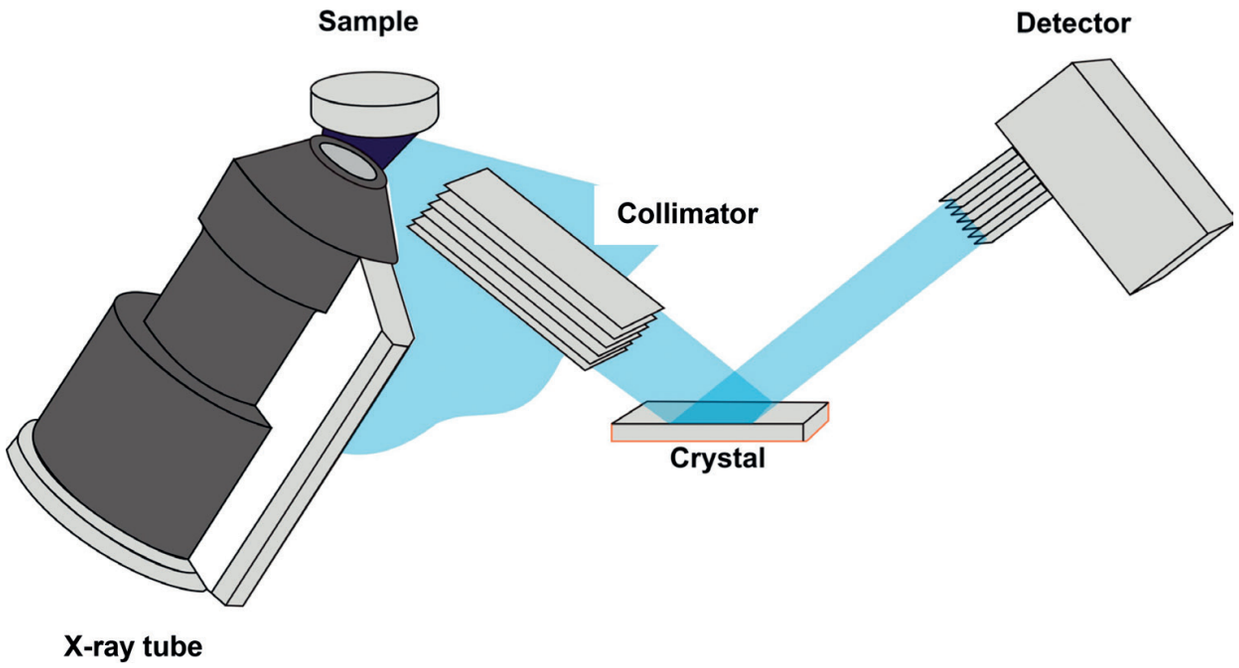


Figure 1. X-ray fluorescence spectrometer set-up (Source: PANalytical, the Analytical X-ray Company [8]).

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1.2.2.2. Diffractors (crystals)

The separation of fluorescent X-ray peaks depends upon the relationship between wavelength and the d-spacing of the diffraction medium; consequently, a number of different crystals must be used to cover the full measurable range. Single crystals, such as germanium, lithum fluoride, and indium antimonide, are ideal diffractors for many elements [8]. More recently, synthetic multilayers with very small d-spacings have been introduced to provide enhanced sensitivity for the lighter elements [8].

1.2.2.3. Detectors

The detection of fluorescent radiation emitted is based on an ionization effect similar to that described under sample excitation. For the longer wavelengths produced by light elements, gas-filled proportional detectors are employed while short wavelengths (heavy elements) are measured with a scintillation detector. Both convert the photon energies into measurable voltage pulses [7, 8].

1.2.2.4. Counting electronics

Counting electronics record the number of pulses produced by the detectors and the energy levels corresponding to their amplitude [8]. Although data collection must continue for long enough to minimize statistical errors, measurement times as short as 2 s usually suffice for many elements. Longer times are required for the lightest elements, which produce relatively small numbers of low-energy fluorescent photons.

1.2.3. Interpretation of XRF spectra

An XRF spectrum is made up of XRF peaks with varying intensities. It is a graphical representation of X-ray intensity peaks as a function of energy peaks. The peak energy identifies the element, while the peak height/intensity is generally indicative of its concentration. An automated routine peak search or match identifies the elements present in unknown samples (qualitative) and their concentrations (quantitative).

1.2.4. Energy dispersive X-ray fluorescence (EDXRF)

EDXRF is the analytical technology commonly used in portable analyzers [9]. EDXRF is designed to analyze groups of elements simultaneously in order to rapidly determine those elements present in the sample and their relative concentrations. To understand how this method can be used, consider scrap metal. People in the business of recycling scrap metals need to positively identify numerous alloy grades, rapidly analyze their chemical composition at material transfer points, and guarantee the quality of their product to their customers [9]. This is important because metal alloys are designed for specific functions and are not interchangeable because small variations in composition can result in significantly different mechanical properties. However, hand-held XRF analyzers can easily separate these grades. Typical uses of EDXRF include the analysis of metals and alloys, petroleum oils and fuels, plastic, rubber and textiles, pharmaceutical products, foodstuffs, cosmetics, body care products, geological materials, cement, ceramics, etc. [9].

2. Particle induced X-ray emission (PIXE) spectrometry

2.1. Introduction

PIXE is an analytical method based on X-ray emission theory. Particle-induced X-ray emission or proton-induced X-ray emission (PIXE) spectrometry is a powerful, non-destructive analytical technique used to determine the elemental composition of a solid, liquid, thin film, and aerosol filter samples [5]. PIXE can detect all elements from sodium to uranium, giving a total of 72 elements (excluding Po, At, Fr, Ra, Ac, Pa, and the inert gases) detectable using this method [10]. PIXE technique relies on the analysis of the energy spectra of characteristic X-rays emitted by the de-excitation of the atoms in the sample bombarded with high-energy (1–3 MeV) protons with the aid of a suitable energy dispersive detector.

This technique was first proposed in 1970 by Sven Johansson at Lund University, Sweden, and developed over the next few years with his colleagues, Roland Akselsson and Thomas B. Johansson. PIXE is similar to other spectrometric technique used in elemental analysis as it is based on excitation of electrons in the atoms of the elements and electronic transitions that produce characteristic X-rays which by measurement of their intensities, the elements can be identified and their concentrations quantified [8]. The X-ray spectrum is initiated by energetic protons which excite the inner shell electrons in the target atoms. The expulsion of these inner shell electrons and re-filling of their vacant positions results in the emission of X-rays. The energies of the emitted X-rays are unique characteristic of the elements from which they originate, and the number of X-rays emitted is proportional to the mass/concentration of that corresponding element in the sample being analyzed [3, 5, 7, 8]. The generation of X-rays in a sample is very strongly influenced by the bombarding proton.

The use of proton beams for excitation has several advantages over other X-ray techniques. These are [5]:

i. Higher sensitivity to trace elements.

ii. Faster analysis due to higher rate of data accumulation across the entire spectrum.

iii. Better sensitivity, especially for the lower atomic number elements.

The high sensitivity of PIXE in trace elements determination is due to a lower Bremstrahlung background, which is as a result of the deceleration of dislodged electrons when compared to electron excitation and the lack of a background continuum when compared with XRF analysis. The increasing need for elemental analysis of very small samples (0.1–1 mg) as in aerosol filters has made PIXE gain wide acceptance as a valuable analytical tool [5]. Samples (or materials) whose elemental make-up can be determined using the PIXE technique include oils and fuels, plastics, rubbers, textiles, pharmaceutical products, foodstuffs, cosmetics, fertilizers, minerals, ores, coals, rocks and sediments, cements, ceramics, polymers, inks, resins, papers, soils, ash, leaves, films, tissues, forensics, catalysts, etc. [10]. The most extensive use of the PIXE method, however, is in the elemental analyses of atmospheric aerosol samples, dust and fly ash samples, different biological materials, and archeological and artistic artifacts. The need for small accelerators in nuclear physics research laboratories four decades ago, has largely confined PIXE to such laboratories; it is yet to be widely used for analytical purposes.

2.2. Development of PIXE analytical technique

This new analytical method, which became known under the acronym PIXE, was tested and applied in many nuclear physics laboratories during the 1970s [5]. The development of PIXE has been quite rapid. There were several reasons for its rapid development; first, the growing global interest in environmental protection issues created a need for efficient methods of elemental analysis for air pollution studies and the determination of toxic elements in the environment and in humans. Because, PIXE is well suited for the determination of trace elements in a matrix of light elements, it is ideal for studies of this kind. Second, as a consequence of the early days of fundamental nuclear physics research, small accelerators became available in many nuclear physics laboratories, where they were the standard equipment. However, interest soon shifted to higher energies and the small machines became obsolete, as far as nuclear physics was concerned. An alternative to scrapping them was to use them for research in applied science, and PIXE was one of the most popular options. A contributory factor was that not only the accelerator, but also auxiliary equipment such as detectors, electronics, and computer facilities were available in most laboratories making it possible for feasibility tests to be carried out in many laboratories. PIXE is capable of detecting elemental concentrations down to parts per million; however, the technology is still relatively new and untested in wider avenues of chemical research.

2.3. Ion beam analysis (IBA) principles

PIXE is one out of the four ion beam analysis (IBA) methods. IBA consists of whole methods of studying materials based on the interaction at both atomic and the nuclear level, between accelerated charged particles (ions) and the bombarded material (sample) [11]. When a charged particle moving at high speed strikes a material, a number of events can take place. The ion can interact with the electrons and nuclei of the material atoms, slows down and possibly deviates from its initial trajectory. This can lead to the emission of particles and/or radiations (*X*- and γ-rays), whose energy is characteristic of the elements that constitute the sample.

2.3.1. Ion beam analysis methods

The spectrometric analysis of the various secondary emissions leads to the various IBA techniques [5, 11, 12]:

1. **PIXE (particle-induced X-ray emission)** is based on atomic fluorescence and the analysis is performed with characteristic X-rays. PIXE is well adapted for the analysis of trace elements ranging from Na to U.
2. **PIGE (particle-induced Gamma-ray emission)** is based on nuclear reaction and the analysis is performed with characteristic Gamma-ray. PIGE is particularly useful for analyzing light elements such as F and lighter elements, which are inaccessible by PIXE
3. **NRA (nuclear reaction analysis)** is based on nuclear reaction and the analysis is performed with charged particles. NRA has demonstrated its usefulness in the study of the oxidation and deposition of hydrocarbon residue on metallic surfaces.

4. **RBS (Rutherford backscattering analysis)** is based on nuclear scattering and the analysis is performed by charged particles. RBS has proved its efficacy in identifying and localizing thin layers.

2.4. PIXE analysis

2.4.1. Basic principles

As a charged particle (proton) moves through a material, it loses energy primarily by exciting electrons in the atoms that it passes by. Electrons in the inner shells of the atom (predominantly the K and L shells) are given enough energy to cause them to be ejected, resulting in an unstable atom (ion). Electrons from higher shells in the atom then "drop down" to fill the vacancies and in so doing, give off excess energy in the form of X-rays. The energies of these X-rays are characteristic of the element and therefore can be used to identify elemental composition. Also, by measuring intensities of characteristic X-ray lines, one can determine concentrations of almost all elements in the sample down to approximately 1 ppm (part per million).

2.4.2. Sample preparation

No special sample preparation is required in PIXE analysis as is the case in spectroscopic techniques (UV, IR). This minimizes the potential for error resulting from sample preparation. Most samples are usually analyzed in their original states, e.g., aerosol filter, archeological samples, soil, ash, and biological samples. However, it is very important that the area/volume of the sample irradiated by the beam (usually a circular area with the diameter of 1–10 mm) is representative of the whole sample. PIXE technique probes only the top 10–50 μm of the sample (depending on the material, energy of the incident beam, and most importantly, on the energy of characteristic X-rays), therefore if the sample is not homogeneous, as is the case with some pottery and geological samples, it is advisable to grind the sample to a fine powder (with particle size less than 1–2 μm), thoroughly mix it with 20% analytical grade carbon powder and press into pellets. Samples for PIXE analysis may be in the form of solids, liquids, aerosol filters, and thin membranes. The samples which usually come in different forms are handled in different ways, the details of which are described below [10].

Solid materials such as plastics, papers, or metals are analyzed in their "as received" condition, while materials in powdered form such as fly ash, activated carbon, catalysts, and corrosion products are first ground to reduce the particle size to about 200 mesh or lower and pressed into pellets before analysis.

Liquid samples such as oils, process waters, and solutions are analyzed using a plastic cup of either 8 or 3 ml in capacity with a 0.3 mil Kapton front surface window and can be analyzed as received by this method without modification. However, some liquids that are highly caustic or highly acidic may require pre-dilution or neutralization before analysis.

Aerosol filters and thin-film membrane samples are prepared on a clean bench and environment then immediately transferred to the target chamber for analysis in order to eliminate

chances of sample contamination. Sample preparation is done by simply placing the filters or membranes as they are received, into snap-together plastic holders, which are then placed in the sample carousel. Since no permanent mounting is used, samples may be returned intact to clients upon request for archiving or for further analysis.

2.5. CERD ion beam analysis (IBA) set-up (accelerator room)

The Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria, acquired a 1.7 MeV Tandem Pelletron accelerator a few years ago. It is the first ion beam facility in Nigeria, and the only one in the West African sub-region [11]. This facility has provided the opportunity for CERD to apply ion beam analysis techniques in the accelerator laboratory, particularly, particle-induced X-ray emission (PIXE), Rutherford backscattering spectroscopy (RBS), particle-induced Gamma-ray emission (PIGE), and elastic recoil detection analysis (ERDA). However, the focus of this chapter is only on PIXE since it is based on the theory of X-ray emission, which makes it an X-ray technique that can be used in the analysis of materials.

The ion beam analysis (IBA) setup, generally known as the accelerator room, is presented in **Figure 2** The major components of the setup are the accelerator, end station, and detector [5, 11, 12].

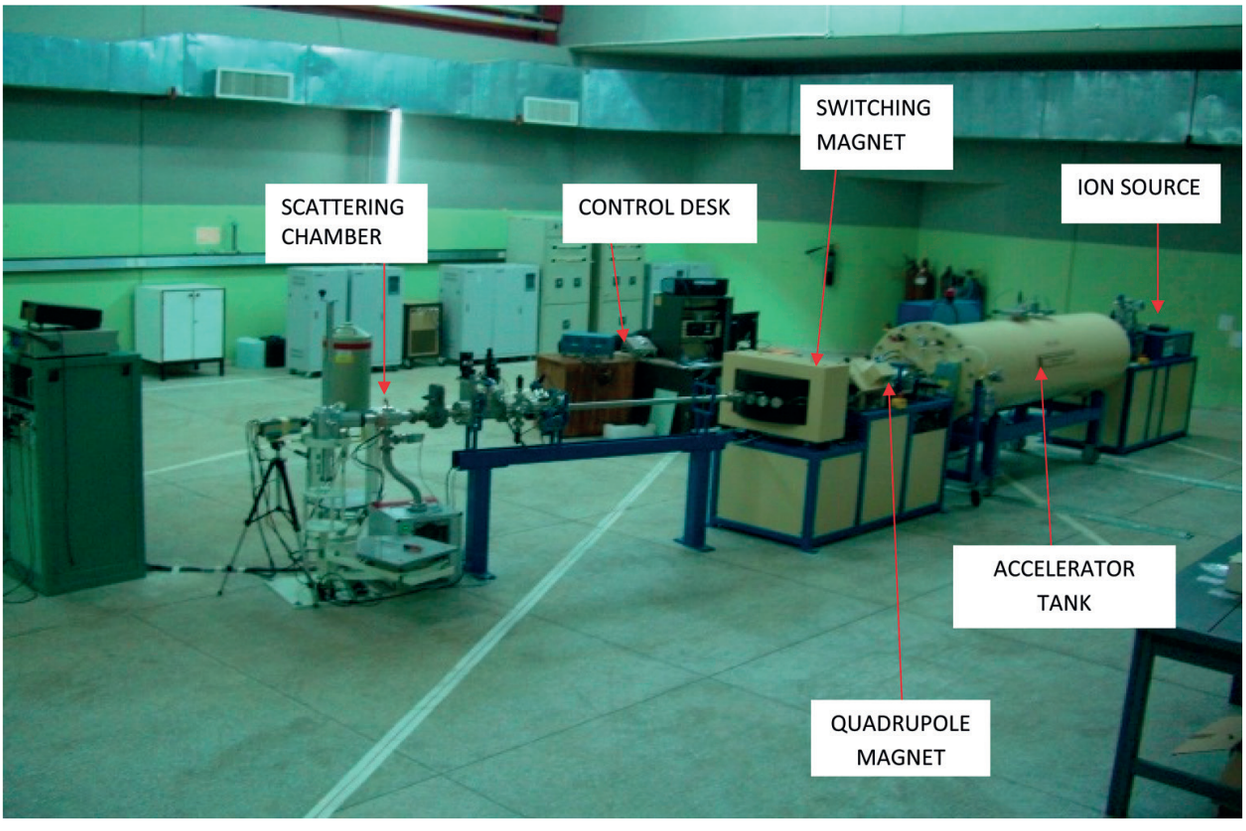


Figure 2. General view of ion beam analysis (IBA) setup at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria (Source: [11, 13]).

2.5.1. The accelerator

The IBA facility is centered on a Tandem Pelletron Accelerator, Model 5SDH, built by the National Electrostatics Corporation (NEC), USA. It is equipped with an RF charge exchange ion source (Alphatross) to provide both proton and helium ions [12]. Positive ion beam is extracted from a plasma in the RF source and accelerated at 4.6 KeV for protons (6 KeV for alphas) into the charge exchange cell, where a portion (1–2%) is converted to negative ions by means of rubidium vapor. These negative ions are extracted and then accelerated to the desired energy by the Tandem Pelletron accelerator, which has a maximum terminal voltage of 1.7 MV [11]. At the terminal, in the center of the accelerator, a nitrogen stripper gas converts the negative ions to positive ions and they undergo a second-stage of acceleration. Thus the accelerator can deliver a proton beam of 0.6–3.4 MeV or an alpha beam of up to 5.1 MeV. The accelerator tank is filled with SF_6 insulating gas at a pressure of 80 psig. Two ultrahigh vacuum turbo molecular pumps rated at 3001/s, one at the low energy (LE) end and the other at the high energy (HE) end of the accelerator maintain the ultrahigh vacuum which could reach 2×10^8 Torr inside the accelerator tube and ~10^{-7} Torr in the beam line extension [5, 11]. Control of the accelerator is facilitated by a computerized control panel with digital and analog displays. The accelerator has provision for five beam lines, but only PIXE is in use. The beam line in use (+15°) is equipped with a multi-purpose end-station for broad beam IBA analysis.

2.5.2. The end station

The general view of the end-station in CERD is shown in **Figure 3**. The end-station was designed and built by the Materials Research Group (MRG) at iThemba Labs, Sommerset West, South Africa [11].

The end-station consists of an Aluminum chamber of about 150 cm diameter and 180 cm height. At 90 cm height, the chamber has four ports and a window. Port 1 at 165° is for the RBS detector, Port 2 at 135° is for the PIXE detector, Port 3 at 30° is for the ERDA detector, the window at 0° is for observing the beam position and size, while port 4 at 225° is for PIGE [5, 11]. The chamber has a sample ladder that can accommodate eleven 13 mm samples. The chamber has a sample ladder that can accommodate 11 samples. The end-station has a turbo pump and a variable tantalum beam collimator (1, 2, 4, and 8 mm diameter) to regulate beam size and an isolation value.

2.5.3. The detector

The PIXE detector is a canberra Si (Li) detector (model ESLX30-150) with 30 mm^2 active area, a 25-mm thick Be window, and 150 eV FWHM energy resolution at 5.9 KeV [11]. There is a wheel in front of the PIXE detector to hold up eight different absorbers (four are installed) to cut off low energy peaks if necessary and/or reduce the count rates of the low Z elements. Canberra Genie 2000 (3.1) software is used for the simultaneous acquisition of the PIXE and RBS data. GUPIXWIN is the computer code used for PIXE data analysis.

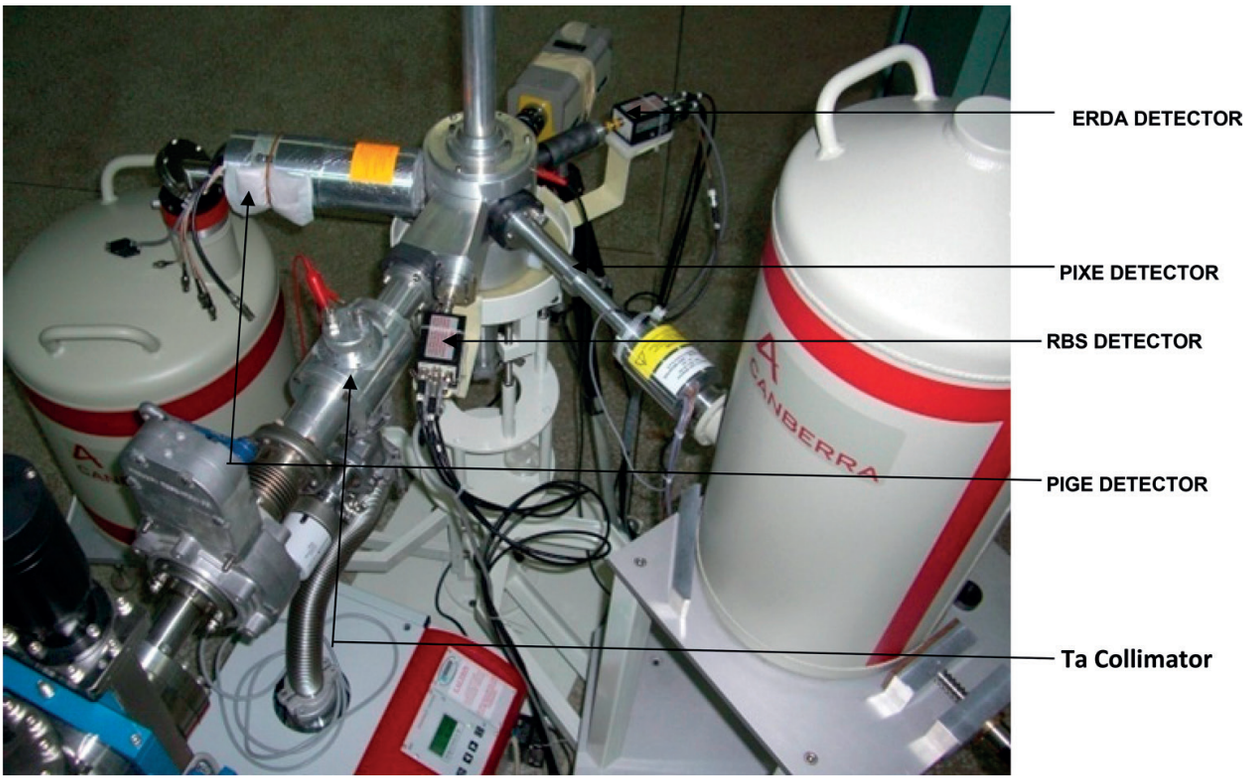


Figure 3. General view of the IBA End Station at CERD, OAU, Ife, Nigeria showing four ports and a window for RBS, PIXE, ERDA, and PIGE detectors (Source: [13]).

2.6. PIXE spectral results

PIXE spectra are generated in parts per million due to the sensitivity of the technique. The PIXE spectrum of rice husk ash heated at a combustion temperature of 600°C and duration of 5 h is presented in **Figure 4** as an example [13]. The corresponding concentrations values (ppm) of the elements in **Figure 4**, determined by computer software, are presented in **Table 1**.

A typical PIXE spectrum is composed of [11]:

1. Characteristic X-ray lines
2. Background
3. Spectrum artifacts

The X-ray energy spectrum consists of a continuous background together with the characteristic X-ray lines of the atoms present in the specimen. The X-rays are detected by means of a Si (Li) detector and the pulses from the detector are amplified and finally registered in a pulse height analyzer. Since a PIXE spectrum is usually quite complicated with many peaks, some of them overlapping, a computer is used for its deconvolution [5]. The number of pulses in each peak, which is a measure of the concentration of the corresponding element in the specimen, is calculated.

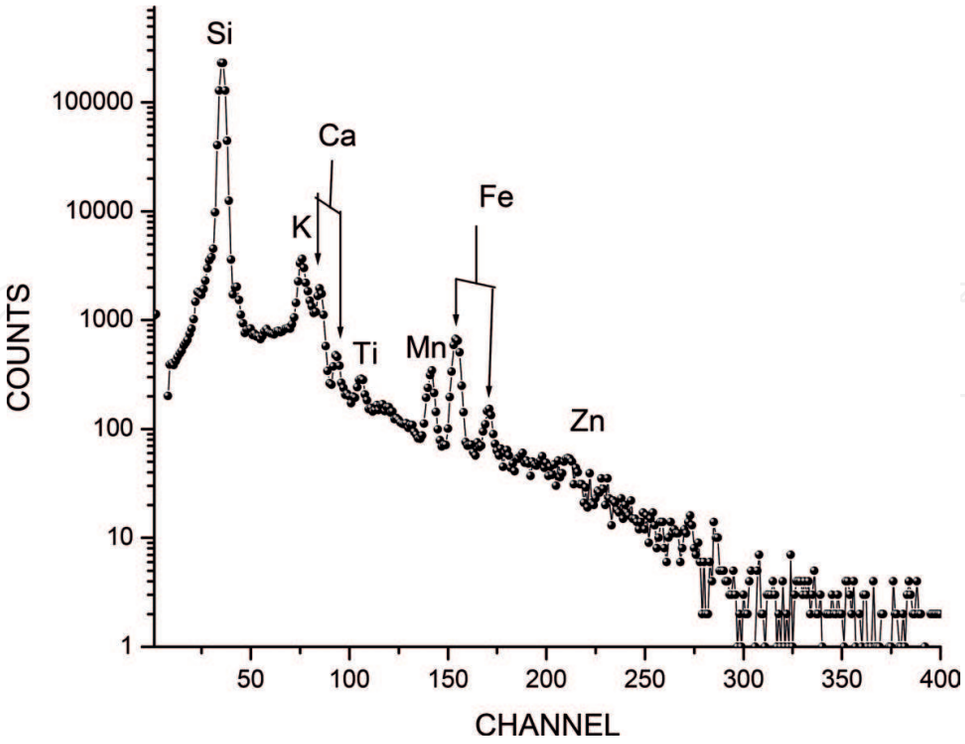


Figure 4. PIXE spectrum of rice husk ash obtained by heating rice husks at 600°C for 5 h. (Source: [14]).

Element (symbol)	Concentration (ppm)	Statistical error (ppm)
Mg	3344.4	245.48
Al	258.9	22.39
Si	358368.2	430.04
P	7995.4	410.96
S	201.0	93.36
Cl	279.9	56.85
K	2008.3	40.97
Ca	909.3	18.46
Ti	76.5	8.34
Mn	222.4	10.52
Fe	696.2	16.78
Zn	9.6	4.10

Table 1. PIXE concentration values (ppm) of the elements in rice husk ash obtained by heating rice husks at 600°C for 5 h [14].

2.6.1. PIXAN-PIXE analysis software

PIXAN, the software used for the analysis of PIXE, covers the following areas [11]:

i. Spectrum analysis—Determination of peak areas.

ii. Estimation of elemental concentrations from peak areas; thin target, thick target.

iii. System calibration against standards.

PIXAN consists of five executable programs.

2.6.2. Calculation of final concentrations

For thin samples, e.g., filters: Conc ($\mu g/cm^2$) = $\frac{PEAK\ AREA}{THIN}$

For thick samples, e.g., solid: Conc (mg/kg) = $\frac{PEAK\ AREA}{YIELD}$

Note: The spectrum of the elemental composition of rice husk ash shows a preponderance of silicon (present in the form of silica) in the ash as is evident from the peak height. Other elements present in small quantities are K, Ca, Mn, Fe, while Ti and Zn are present in minute quantities. With the aid of PIXAN software, the calculations of the concentrations of the elements shown in the spectrum were translated into figures in parts per million as shown in **Table 1**.

2.6.3. Conversion of concentration values of elements from parts per million (ppm) to percentage

It is often necessary, for practical purposes, to convert the PIXE concentration values from ppm to % concentration. This calculation is done as follows [13–16]:

$$1\ \text{ppm} = \frac{1}{1,000,000} \tag{3}$$

$$\text{In \%} = \frac{1}{1,000,000} \times 100 = \frac{1}{10,000} \tag{4}$$

$$\text{To convert X ppm to X \%} = \frac{Xppm}{10,000} \tag{5}$$

Example: If an element has a concentration value of 1354 ppm its concentration in % is 0.1354%.

2.6.4. Conversion of concentration values of elements (in ppm) to their oxides in percentage

PIXE analysis gives the concentration of the elements in parts per million (ppm). However, if the samples are in the form of ash, it means the elements present are in the form of oxides. To convert the concentration of the elements expressed in ppm to their oxides (also in ppm), the former is divided by a conversion factor, which is obtained from a ratio of the element to its oxide as follows [13–15]:

$$\text{Oxide of element (in ppm)} = \frac{concentration\ of\ element\ in\ ppm}{Conversion\ factor} \tag{6}$$

However to convert concentration from ppm to percentage (%), the value obtained above is divided by 10,000. For example, to convert Mg with concentration value of 4164.5 ppm to MgO (in %)

$$\text{MgO Concentration (\%)} = \frac{4164.5\ ppm}{0.6031} \times \frac{1}{10000} \quad \text{where 0.6031 is the conversion factor} = \frac{6905.16}{10000} = 0.6905\,\% \text{ of MgO.} \tag{7}$$

The conversion factor is obtained from the ratios of the atomic weights of the pure elements to their oxides. Thus, the ratio of atomic weight of Mg to that of MgO = $\frac{24.31}{40.31}$, which gives the value of 0.6031.

3. X-ray diffraction technique

3.1. X-ray diffraction

The most commonly used device for X-ray generation is an X-ray tube, which consists of a cathode that emits electrons and an anode (the target). When electrons from the cathode are accelerated by a high voltage and bombard a metal target, usually a heavy metal such as copper or molybdenum, X-rays are generated. When X-rays irradiate a material sample, in cylindrical or pellet form, scattering occurs. The nature of scattering of the X-rays by the sample is determined by the morphology (degree of crystallinity and amorphousness) of the sample and could be *coherent* or *incoherent*. In coherent scattering, also known as *X-ray diffraction* there is no change in wavelength or phase between the incident and scattered rays [17]. Crystalline samples cause coherent scattering, while amorphous and semi-crystalline samples bring about incoherent scattering also known as diffuse scattering, in which there is change in both wavelength and phase. Every crystalline substance scatters X-rays in its own unique diffraction pattern due to differences in planar spacing of the crystals. The diffraction pattern of crystalline materials is composed of a series of concentric cones arising from scattering by the crystal planes. As the degree of crystallinity increases, the rings become more sharply defined. Consequently, for predominantly amorphous materials, the X-ray diffraction pattern is diffuse and a halo (characterized by a dark-shaded portion in the center) is observable. A great deal of information on the morphology and structure of a material is obtainable from the visual inspection and mathematical interpretation of the pattern and intensity of the scattered radiation, such as degree of crystallinity, dimensions of crystalline domains, bond distances and angles, and type of conformations in the crystalline regions. In the case of mechanical failure of a material, the morphology may involve a transformation from a high degree of crystallinity to a lower degree or even amorphousness which will be evident in the X-ray diffraction patterns of the material before and after failure.

3.2. X-ray diffraction as an analytical technique

X-ray diffraction (XRD) is a versatile, non-destructive analytical technique for the identification and quantitative determination of the various crystalline forms known as "phases" of

compounds present in powdered and solid samples [8]. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. Identification is achieved by comparing the X-ray diffraction pattern or "diffractogram" obtained from an unknown sample with an internationally recognized database containing reference patterns for more than 70,000 phases [8]. The most commonly used XRD methods involve the use of single crystals, but *powder diffraction* techniques are also used, especially for investigating solids with infinite lattice structures [18]. X-rays are chosen for these techniques because they have wavelengths of the same order of magnitude as typical inter-atomic distances in crystalline solids [19]. Consequently, diffraction is observed when X-rays interact with an array of atoms in a solid. The process involves generation of X-rays by a cathode ray tube, filtration to produce monochromatic radiation and collimation to concentrate the rays before it is directed towards the sample [3, 4]. The interaction of the incident X-rays with the sample produces constructive interference when conditions satisfy Bragg's law. Modern computer-controlled diffractometer systems use automatic routines to measure, record, and interpret the unique diffractograms produced by individual constituents in even highly complex mixtures.

The result of an XRD measurement is a *diffractogram* showing: (i) phases present (peak positions), (ii) phase concentrations (peak heights), (iii) amorphous content (background hump), and (iv) crystallite size/strain (peak widths) [8]. The widths of the peaks in a particular phase pattern provide an indication of the average crystallite size. Large crystallites give rise to sharp peaks, while the peak width increases as crystallite size reduces. XRD can also be used to measure texture of sample, stress in sample, and for analysis of thin films.

A crystal lattice has a regular structure with three-dimensional distribution of atoms in space, e.g., cubic, rhombic. The atoms are arranged in such a way that they form a series of parallel planes separated from one another by a distance d, which varies according to the nature of the material. [8]. For any crystal, planes exist in a number of different orientations, each with its own specific d-spacing. Defects in the lattice structures of crystalline solids have an important and sometimes dominating influence on the mechanical, electrical, and optical properties of solid materials [19]. XRD technique can be used to obtain information on the defects and imperfections in the crystal lattice of solids which could be natural or as a result of failure.

XRD is useful in analyzing a wide range of materials, from powders and thin films to nanomaterials and solid objects. In powders, chemical phases are identified qualitatively as well as quantitatively. High-resolution X-ray diffraction reveals the layer parameters, such as composition, thickness, roughness, and density in semiconductor thin films.

3.3. Diffraction and Bragg's Law

Diffraction is a wave phenomenon in which there is apparent bending and spreading of waves when they meet an obstruction. Diffraction occurs with electromagnetic waves, such as light and radio waves as well as sound and water waves. Light diffraction is caused by light bending around the edge of an object. To understand diffraction, we have to consider what happens when a wave interacts with a single particle. The particle scatters the incident beam uniformly in all directions. If the beam is incident on a solid crystalline material, the scattered beams may add together in a few directions and reinforce each other to give diffracted beams. By studying

the diffraction pattern of a beam of radiation incident on the crystal, the structure of the crystal can be determined. As light is diffracted by a grating, so does radiation beam take place only in a certain specific direction. Measurements of the directions of the diffraction and the corresponding intensities provide information on the crystal structure responsible for diffraction.

3.3.1. Bragg's Law equation

Bragg's Law states that when a monochromatic and coherent (in-phase) beam of X-rays is incident on a crystal surface at an angle θ, scattering occurs; constructive interference of the scattered rays also occurs at angle, θ to the planes if the path length (interplanar) difference, d, is equal to a whole number, n, of wavelengths. The angles of the crystal and detector can be varied so that a particular wavelength can be measured. The efficiency of the scattering depends on the number and distribution of the electrons at the lattice sites, which is determined by the structure of the molecules that occupy the lattice site. By varying the angle θ, the Bragg's Law conditions are satisfied by different d-spacings in polycrystalline materials.

Thus, the diffraction process occurs when the Bragg's Law condition is satisfied [18]. It is mathematically expressed as:

$$n\lambda = 2d\sin\theta \tag{8}$$

where λ is the wavelength of incident X-rays, d is the interplanar spacing, θ is the X-ray angle of incidence, and n is an integer.

This means that the two waves, originally in phase, have to remain in phase as they are scattered. This relationship between the wavelength, λ of incident X-ray radiation and the lattice spacings, d of the crystal is *Bragg's law* and is the basis for the technique of X-ray diffraction [4] (**Figure 5**). The interplanar spacing of a crystal lattice determines the angles at which strong X-ray diffractions occur. These interplanar spacings (also called lattice spacings) are an inherent characteristic of the crystal, for they are determined by the size and arrangement of its atoms. Each crystalline compound has its set of interplanar spacings and thus its own characteristic set of X-ray diffraction angles that like a fingerprint can be used to identify the substance [19] as illustrated in **Figure 5**.

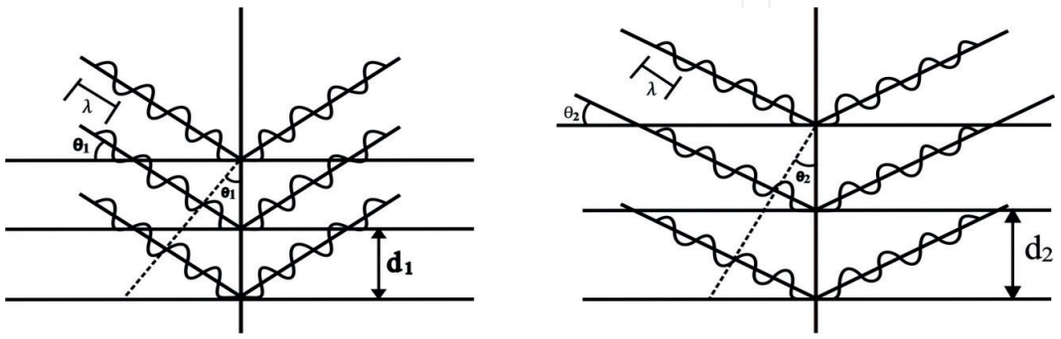


Figure 5. Diffraction: Bragg's Law [8].

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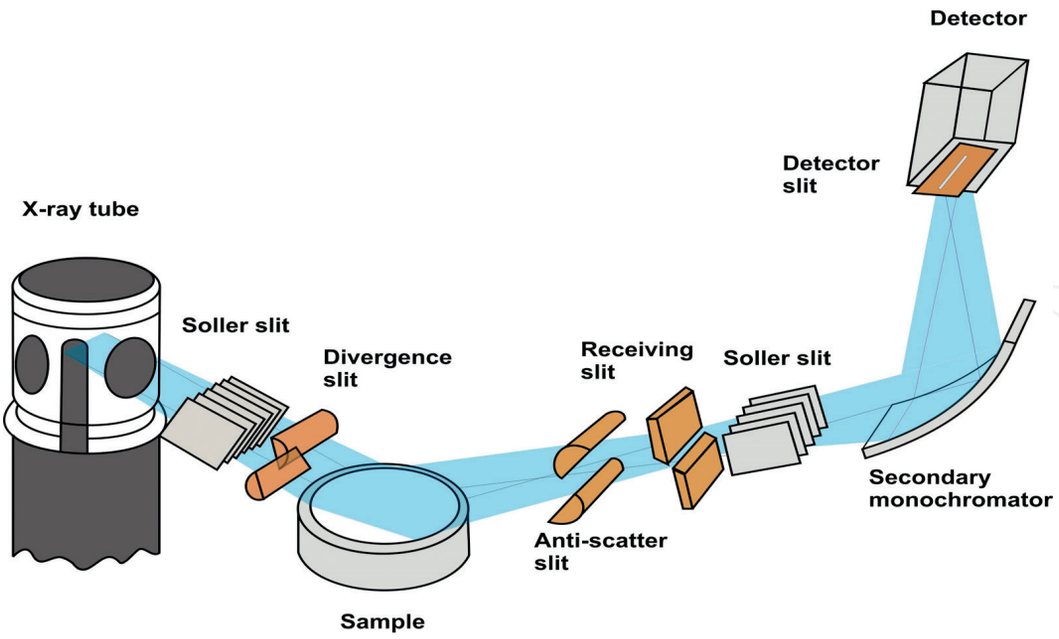


Figure 6. X-ray diffractometer set-up (Source: PANalytical, the analytical X-ray company [8]).

3.4. X-ray diffractometer set-up

An X-ray diffractometer typically consists of of an X-ray source, a mounting for the crystal, turntables to allow variation in the angles of the incident X-ray beam and crystal face, a slit arrangement, a monochromator and an X-ray detector [8, 18–20]. The setup of an X-ray diffractometer is shown in **Figure 6**.

Stresses and preferred orientation can be determined in a wide range of solid objects and engineered components. Many researchers in industrial as well as scientific laboratories rely on X-ray diffraction as a tool to develop new materials or to improve speed and efficiency of production processes. Fully automated X-ray diffraction analysis in mining and building materials production sites results in more cost-effective solutions for production control. Innovations in XRD closely follow research on new materials such as in semiconductor technologies and pharmaceutical investigations. XRD provides answers to many analytical questions related to the structure of material samples which makes it a useful tool in the analysis of failure in materials.

4. Conclusion

This review has shown that a great deal of information is obtainable with precision from the use of X-ray techniques in the analysis of materials. Analysis by XRD technique provides information for the identification and quantitative determination of the various crystalline forms of a material so it is useful in detecting the morphological changes that have occurred in a material after failure, if the crystal lattice structure has been affected. XRF and PIXE are both useful in the determination of the elemental components of a material and their concentrations.

However, PIXE, a powerful, high-tech analytical tool is preferable to XRF, due to its higher sensitivity to trace elements and lower atomic number elements as well as its faster analysis. However, if on-the-spot analysis is required as is sometimes the case in field work, EDXRF and WDXRF spectrometers would be preferred due to the advantage of portability.

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