X-ray Techniques: Overview

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The use of X-ray methods in the field of materials analysis is now entering its seventh decade. While the broad definition of X-ray methods covers many techniques based on the scatter, emission and absorption properties of X-radiation, the two most common are X-ray fluorescence (XRF) spectrometry and X-ray powder diffractometry (XRD). When a sample of material is bombarded with energetic radiation (X-rays, γ-rays, electrons, protons, etc.) vacancies may arise from the removal of inner orbital electrons. One of the processes by which the atom regains stability is by transference of electrons from outer to inner electron shells. Each of these transitions is accompanied by the emission of an X-ray photon having an energy equal to the energy difference between the two states. The X-ray emission wavelengths are characteristic of the atom in question and there is a simple relationship (Moseley's law) between the wavelength of the emission line and the atomic number of the atom. Thus when a sample is made up of many different types of atoms, each atom will produce a series of wavelengths, and all of the contributions add up to become the total X-ray emission from the sample. XRF is a technique which utilizes the diffracting power of a single crystal, or the proportional characteristics of a photon detector, to separate the polychromatic beam of radiation from the sample into separate wavelengths, thus allowing qualitative and quantitative elemental measurements to be made.

A beam of monochromatic radiation may also be scattered when X-ray photons collide with atomic electrons. Where the scattered wavelengths interfere with one another diffraction of X-rays occurs. All substances are built up of individual atoms and nearly all substances have some degree of order of periodicity in the arrangement of these atoms. It is the scattering from these periodic arrays that leads to the diffraction effect, and there is a simple relationship (Bragg's law) between the scattering

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angle, the wavelength of the radiation and the spacings between the planes of atoms. Since the distances between the atomic planes are dependent on the size and distribution of atoms – i.e. the structure of the material, XRD can be used for qualitative and quantitative phase identification.

1 INTRODUCTION

1.1 Brief History of the Development of X-ray Fluorescence and Powder Diffraction Methods

X-ray photons are a form of electromagnetic radiation produced following the ejection of an inner orbital electron and subsequent transition of atomic orbital electrons from states of high to low energy. When a monochromatic beam of X-ray photons falls onto a given specimen three basic phenomena may result, namely absorption, scatter or fluorescence. The coherently scattered photons may undergo subsequent interference leading in turn to the generation of diffraction maxima. These three basic phenomena form the bases of three important X-ray methods: the absorption technique, which is the basis of radiographic analysis; the scattering effect, which is the basis of X-ray diffraction; and the fluorescence effect, which is the basis of XRF spectrometry.

X-rays were discovered by Wilhelm Roentgen in 1895[1] and the property of the atomic number dependence of the absorption of X-ray photons was quickly established and applied for medical diagnostic purposes. Following the discovery of the diffraction of X-rays by Max von Laue in 1913, two major fields of materials analysis have developed. XRF spectrometry uses either the diffracting power of a single crystal to isolate narrow wavelength bands, or a proportional detector to isolate narrow energy bands, from the polychromatic beam characteristic radiation excited in the sample. The first of these methods is called wavelength-dispersive spectrometry and the second, energy-dispersive spectrometry. Because of the known relationship between emission wavelength and atomic number, isolation of individual characteristic lines allows the unique identification of an element to be made and elemental concentrations can be estimated from characteristic line intensities. Thus this technique is a means of materials characterization in terms of chemical composition. X-ray spectrometric techniques provided important information for the theoretical physicist in the first half of this century and since the early 1950s they have found an increasing use in the field of materials characterization. While most of the early work in X-ray spectrometry was carried out using electron excitation,[2] today most stand-alone X-ray spectrometers use X-ray excitation sources rather than electron excitation. XRF spectrometry typically uses a polychromatic beam of short wavelength X-radiation to excite longer wavelength characteristic lines from the sample to be analyzed. Modern X-ray spectrometers use either the diffracting power of a single crystal to isolate narrow wavelength bands, or a proportional detector to isolate narrow energy bands, from the polychromatic radiation (including characteristic radiation) excited in the sample.[3]

The second field of materials analysis involves characterization by means of atomic arrangement in the crystal lattice. XRD uses single or multiphase specimens comprising a random orientation of small crystallites, each of the order of 1–50 µm in diameter. Each crystallite in turn is made up of a regular, ordered array of atoms. An ordered arrangement of atoms (the crystal lattice) contains planes of high atomic density which in turn means planes of high electron density. A monochromatic beam of X-ray photons will be scattered by these atomic electrons and if the scattered photons interfere with each other, diffraction maxima may occur. In general, one diffracted line will occur for each unique set of planes in the lattice. A diffraction pattern is typically in the form of a graph of diffraction angle (or interplanar spacing) against diffracted line intensity. The pattern is thus made up of a series of superimposed diffractograms, one for each unique phase in the specimen. Each of these unique patterns can act as an empirical "fingerprint" for the identification of the various phases, using pattern recognition techniques based on a file of standard single-phase patterns. Quantitative phase analysis is also possible, albeit with some difficulty because of various experimental and other problems, not the least of which is of the large number of diffraction lines occurring from multiphase materials.

1.2 Role of X-ray Methods in the Modern Analytical Laboratory

Wavelength-dispersive spectrometers have been commercially available since the early 1950s and there are probably about 20 000 units in use in the world today. Energy-dispersive spectrometer systems became available in the early 1970s, and there are probably about 8000 stand-alone spectrometers in use, with perhaps slightly more than this number attached to scanning electron microscopes. XRF analysis finds a wide range of application since it allows the quantitation of all elements in the periodic table from F (atomic number 9) upwards.[4] Newer developments allow the determination of the ultralow atomic number elements including B, C, O and N. Accuracies of a few tenths of one percent are possible for most of the atomic number range, and elements are detectable in many cases to the low parts per million level. Excellent data treatment software is available allowing the rapid application of quantitative and semi-quantitative procedures.

X-ray powder diffractometers have been available in their modern form since the late 1940s, although camera systems were available back to the 1920s. There are probably of the order of 30 000 powder diffractometers in use – about half of these being automated to some degree. XRD is applicable to any ordered (crystalline) material and although much less accurate or sensitive than the fluorescence method, is almost unique in its ability to differentiate phases. Quantitative phase analysis is possible, but the accuracy of a determination is often compromised by preferred orientation of the specimen.

The fluorescence and diffraction techniques are to a large extent complementary, since one allows accurate quantitation of elements to be made and the other allows qualitative and semiquantitative estimations to be made of the way in which the matrix elements are combined to make up the phases in the specimen. Thus a combination of the two techniques will often allow the accurate determination of the material balance of a sample.

2 PROPERTIES OF X-RADIATION

2.1 Continuous and Characteristic Radiation

When a high-energy electron beam is incident upon a specimen, one of the products of the interaction is an emission of a broad-wavelength band of radiation called continuum, also referred to as white radiation or bremsstrahlung. This white radiation is produced as the impinging high-energy electrons are decelerated by the atomic electrons of the elements making up the specimen. The intensity/wavelength distribution of this radiation is typified by a minimum wavelength λ_{min} which is inversely proportional to the maximum accelerating potential V of the electrons. The intensity distribution of the continuum reaches a maximum at a wavelength 1.5 to 2 times greater than λ_{min}. Increasing the accelerating potential causes the intensity distribution of the continuum to shift towards shorter wavelengths. Most commercially available spectrometers utilize a sealed X-ray tube as an excitation source, and these tubes typically employ a heated tungsten filament as a source of electrons, and a layer of pure metal, such as chromium, rhodium or tungsten, as the anode. The broad band of white radiation produced by this type of tube is ideal for the excitation of the characteristic lines from a wide range of atomic numbers. In general, the higher the atomic number of the anode material, the more intense the beam of radiation produced by the tube. X-ray diffractometers typically employ a more focused filament assembly (12×0.05 mm) and run at a somewhat lower loading than the XRF tube. A key factor in the design of an X-ray tube for powder diffraction is the *specific loading* (watts per mm^2) of the tube.

2.2 X-ray Spectra

In addition to electron interactions leading to the production of white radiation, there are also electron interactions which produce characteristic radiation. If a high-energy particle, such as an electron, strikes a bound atomic electron, and the energy of the particle is greater than the binding energy of the atomic electron, it is possible that the atomic electron will be ejected from its atomic position, departing from the atom with a kinetic energy $(E - \phi)$ equivalent to the difference between the energy E of the initial particle and the binding energy ϕ of the atomic electron. Where the exciting particles are X-ray photons, the ejected electron is called a photoelectron and the interaction between primary X-ray photons and atomic electrons is called the photoelectric effect. As long as the vacancy in the shell exists, the atom is in an unstable state and can regain stability by transference of an electron from one of the outer orbitals to fill the vacancy. The energy difference between the initial and final states of the transferred electron may be given off in the form of an X-ray photon. Since all emitted X-ray photons have energies proportional to the differences in the energy states of atomic electrons, the lines from a given element will be characteristic of that element. The relationship (Equation 1) between the wavelength of a characteristic X-ray photon and the atomic number Z of the excited element was first established by Moseley.[5]

$$\frac{1}{\lambda} = K(Z - \sigma)^2 \tag{1}$$

in which K is a constant that takes on different values for each spectral series. σ is the shielding constant that has a value of just less than unity. The wavelength of the X-ray photon is inversely related to the energy E of the photon according to Equation (2):

$$\lambda(\text{Å}) = \frac{12.4}{E(\text{keV})} \tag{2}$$

Not all vacancies result in the production of characteristic X-ray photons since there is a competing internal rearrangement process known as the Auger effect.[6] The ratio of the number of vacancies resulting in the production of characteristic X-ray photons to the total number of vacancies created in the excitation process is called the fluorescent yield. Fluorescent yield values are several orders of magnitude less for the very low atomic numbers. In practice this means that if, for example, one were to compare the intensities obtained from pure barium ($Z = 56$) and pure aluminum ($Z = 13$), all other things being equal, pure barium would give about 50 times more counts than would pure aluminum. The L fluorescent yield for a given atomic number is always less by about a factor of three than the corresponding K

fluorescent yield, where K and L refer to the first and second electron shells. An excited atom can revert to its original ground state by transferring an electron from an outer atomic level to fill the vacancy in the inner shell. An X-ray photon is emitted from the atom as part of this de-excitation step, the emitted photon having an energy equal to the energy difference between the initial and final states of the transferred electron. The selection rules for the production of normal (diagram) lines require that the principal quantum number n must change by at least one, the angular quantum number ℓ must change by ± 1, and the J quantum number (the total momentum 'J' of an electron is given by the vector sum of $\ell + s$ where s is the spin quantum number) must change by 0 or 1. In effect this means that for the K series only $p \rightarrow s$ transitions are allowed, yielding two lines for each principal level change. Vacancies in the L level follow similar rules and give rise to L series lines. There are more of the L lines since $p \rightarrow s$, $s \rightarrow p$ and $d \rightarrow p$ transitions are all allowed within the selection rules. Transition groups may now be constructed, based on the appropriate number of transition levels.

Figure 1 shows plots of the reciprocal of the square root of the wavelength, as a function of atomic number, for the K, L and M series. As indicated by Moseley's law such plots should be linear. A scale directly in wavelength is also shown, to indicate the range of wavelengths over which a given series occurs. In practice, the number of lines observed from a given element will depend upon the atomic number of the element, the excitation conditions and the wavelength range of the spectrometer employed.

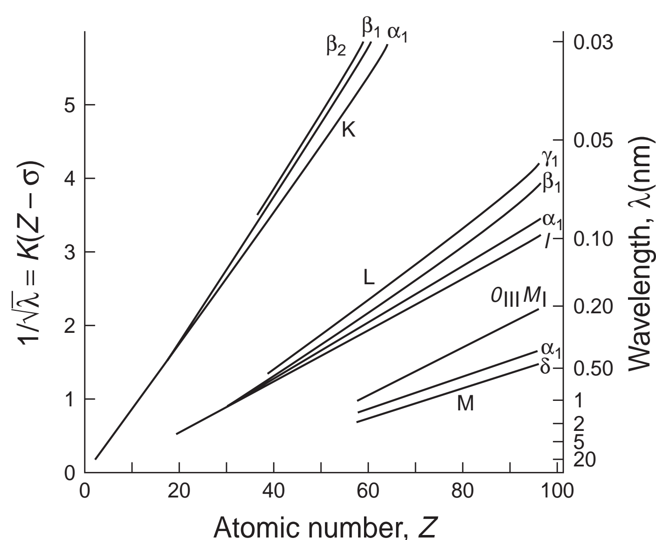

Figure 1 Moseley diagrams for the K, L and M series. (Reproduced from Jenkins, *X-ray Fluorescence Spectrometry*, 2nd edition, Wiley-Interscience, 1999. With permission from John Wiley & Sons.)

Generally, commercial spectrometers cover the K series, the L series and the M series, corresponding to transitions to K, L and M levels respectively. There are many more lines in the higher series and for a detailed list of all of the reported wavelengths the reader is referred to the work of Bearden.(7) In X-ray spectrometry most of the analytical work is carried out using either the K or the L series wavelengths.

While most of the observed fluorescent lines are normal, certain lines may also occur in X-ray spectra that do not at first sight fit the basic selection rules. These lines are called forbidden lines and are shown in the center portion of Figure 1. Forbidden lines typically arise from outer orbital levels where there is no sharp energy distinction between orbitals. A third type of line may also occur – called satellite lines – which arise from dual ionizations. Neither forbidden transitions nor satellite lines have great analytical significance; they may cause some confusion in qualitative interpretation of spectra and may even be misinterpreted as coming from trace elements. Most commercially available X-ray spectrometers have a range from about 0.2 to 20 Å (60–0.6 keV, $1\,\text{Å} = 10^{-10}\,\text{m} = 10^{-1}\,\text{nm}$) which will allow measurement of the K series from F ($Z = 9$) to Lu ($Z = 71$), and for the L series from Mn ($Z = 25$) to U ($Z = 92$). Other line series can occur from the M and N levels but these have little use in analytical X-ray spectrometry.

2.3 Absorption

When a beam of X-ray photons falls onto an absorber, a number of different processes may occur. The more important of these are illustrated in Figure 2. In this example, a monochromatic beam of radiation of wavelength λ_0 and intensity I_0, is incident on an absorber of thickness x_a and density ρ_a. The fate of each individual X-ray photon is governed by the following processes. Absorption occurs where only a certain fraction (I/I_0) of the radiation may pass through the absorber. Where

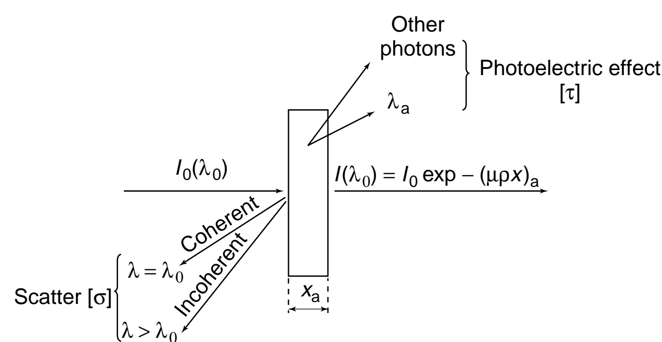

Figure 2 Interaction of X-ray photons with matter.

this happens the wavelength of the transmitted beam is unchanged and the intensity of the transmitted beam $I(\lambda_0)$ is given by Equation (3):

$$I(\lambda_0) = I_0 \exp -(\mu_a \rho_a x_a) \quad (3)$$

where μ_a is the mass attenuation coefficient of absorber a for the wavelength λ_0.

It will be apparent from the above that a number of photons equal to $(I_0 - I)$ have been lost in the absorption process, most of this loss being due to the photoelectric effect. Photoelectric absorption, usually designated τ, will occur at each of the energy levels of the atom. Thus the total photoelectric absorption will be determined by the sum of each individual absorption within a specific shell. The value of the mass attenuation μ referred to in Equation (3) is a function of both the photoelectric absorption and the scatter, Equation (4):

$$\mu = f(\tau) + f(\sigma) \quad (4)$$

However, $f(\tau)$ is usually large in comparison with $f(\sigma)$. Because the photoelectric absorption is made up of absorption in the various atomic levels, it is an atomic-number-dependent function. A plot of μ against λ contains a number of discontinuities called absorption edges, at wavelengths corresponding to the binding energies of the electrons in the various subshells. The absorption discontinuities are a major source of non-linearity between X-ray intensity and composition in both XRF and XRD.

2.4 Scattering

Scatter, σ, will occur when an X-ray photon collides with one of the electrons of the absorbing element. Where this collision is elastic, i.e. when no energy is lost in the collision process, the scatter is said to be coherent (Rayleigh) scatter. Since no energy change is involved, the coherently scattered radiation will retain exactly the same wavelength as the incident beam. As will be shown later, X-ray diffraction is a special case of coherent scatter, where the scattered photons interfere with each other. It can also happen that the scattered photon gives up a small part of its energy during the collision, especially where the electron with which the photon collides is only loosely bound. In this instance the scatter is said to be incoherent (Compton scatter) and the wavelength of the incoherently scattered photon will be greater than λ_0.

2.5 Role of Crystal Structure in X-ray Scattering and Diffraction

All substances are built up of individual atoms and nearly all substances have some degree of order of periodicity in the arrangement of these atoms. A crystal can be defined as a homogeneous, anisotropic body having the natural shape of a polyhedron. In practical terms, whether a substance is homogeneous or not can only be defined by the means that are available for measuring the crystallinity. In general, the shorter the wavelength, the smaller the crystalline region that is able to be recognized. Even noncrystalline materials have a degree of order and each will give some sort of a diffraction pattern. For example, glassy materials and liquids will give diffraction patterns of sorts, generally in the form of one or more broad diffuse peaks or halos. In XRD one is generally dealing exclusively with crystalline materials. The diffraction pattern can, moreover, be used to determine the degree of crystallinity, that is the dimensions of the crystalline regions in otherwise amorphous substances. A crystalline substance has a definite form which is retained no matter what the physical size of the crystal. A certain type of crystal can thus be defined in terms of specific physical characteristics which determine its shape. For example, a sodium chloride crystal has cubic symmetry and by definition the angles between all of the principal faces should be 90°. In fact there are other crystal classes which also have angles between faces of 90°, but the cube is unique in that the lengths of the sides are also equal. If our sodium chloride crystal were reduced in size until the smallest repeat unit was found (the so-called *unit cell*) it would indeed be found that all sides were equal. Hence it is apparent that a crystal type can be defined in terms of the lengths of the sides of its unit cell and the angles between the faces. Since every ordered material is made up of a unique arrangement and number of atoms, every ordered material will give a diffraction pattern which is, to all intents and purposes, also unique.

Figure 3 illustrates in a simplified manner the diffraction patterns that would be obtained from (a) a single

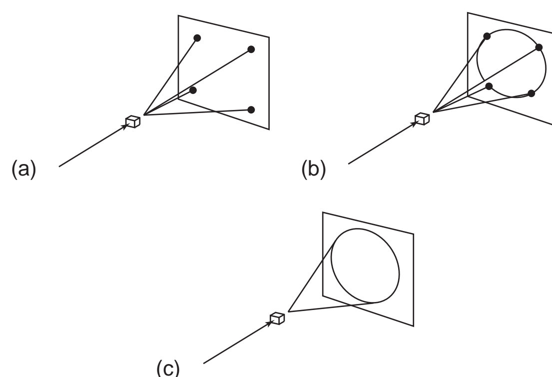

Figure 3 Diffraction patterns from (a) single crystal; (b) a random powder; and (c) an oriented powder. (Reproduced from Jenkins, Snyder, *Introduction to Powder Diffractometry*, Wiley-Interscience, 1996. With permission from John Wiley & Sons.)

crystal, (b) an oriented powder and (c) a random powder. In each instance the specimen is placed between a monochromatic beam of radiation and a piece of photographic film. In the case of the single crystal, because only certain crystal planes are in the position to diffract radiation onto the film, the pattern will appear as a series of spots on the film, the position of the spots being dependent upon the structure and orientation of the crystal. Changing the position of the crystal will bring other planes into diffracting position and the pattern of spots will change. In the case of a random powder, whatever the orientation of the specimen there is always a sufficient number of crystallites to diffract from the appropriate d-spacing(s) (see section 2.6). In the case of an oriented powder, however, there are more crystallites in certain orientations and less in others. Thus the pattern obtained is somewhere between the single-crystal and the random-powder patterns.

2.6 Interference and Diffraction Effects

As illustrated in Figure 4(a), a crystal lattice consists of a regular arrangement of atoms, with layers of high atomic density existing throughout the crystal structure. Planes of high atomic density means planes of high electron density. Since scattering occurs between impinging X-ray photons and the loosely bound outer orbital atomic electrons, when a monochromatic beam of radiation falls onto the high atomic density layers scattering will occur. In order to satisfy the requirement for constructive interference, it is necessary that the scattered waves originating from the individual atoms, the scattering points, be in phase with one another. The geometric conditions for this condition to occur are illustrated in Figure 4(b). Here, a series of parallel rays strike a set of crystal planes at an angle θ and are scattered as previously described. Reinforcement will occur when the difference in the path lengths of the two interfering waves is equal to a whole number of wavelengths. This path length difference is $2d\sin\theta$ where d is the inter-planar spacing; hence the overall condition (Equation 5) for reinforcement is that:

$$n\lambda = 2d\sin\theta \tag{5}$$

where n is an integer. Equation (5) is a statement of Bragg's law. Diffraction experiments are generally made at a fixed wavelength, thus a measure of the diffraction angles will allow the associated d-spacings to be calculated. Bragg's law is also important in wavelength-dispersive spectrometry since by using a crystal of fixed $2d$, each unique wavelength will be diffracted at a unique diffraction angle. Thus, measuring the diffraction angle 2θ allows the determination of the wavelength (inter-planar spacing) if the d-spacing of the crystal is known. Since there is a simple relationship between wavelength and atomic number, one can establish the atomic number(s) of the element(s) from which the wavelengths were emitted.

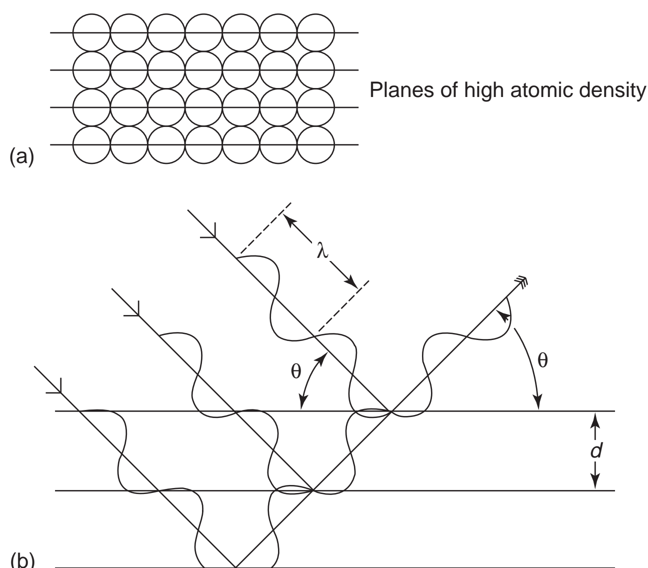

Figure 4 Scatter and diffraction from an ordered arrangement of atoms. (Reproduced from Jenkins, *X-ray Fluorescence Spectrometry*, 2nd edition, Wiley-Interscience, 1999. With permission from John Wiley & Sons.)

3 INSTRUMENTATION FOR X-RAY FLUORESCENCE ANALYSIS

X-ray spectrometers fall roughly into two categories: wavelength-dispersive instruments and energy-dispersive instruments. The wavelength-dispersive system was introduced commercially in the early 1950s and since the mid-1970s has developed into a widely accepted analytical tool. Analytical chemists have available to them a wide range of instruments for the qualitative and quantitative analysis of multielement samples, and in the choice of technique they will generally consider such factors as sensitivity, speed, accuracy, cost, range of applicability, and so on. Within the two major categories of X-ray spectrometers specified, there is of course a wide diversity of instruments available but most of these will fit the four basic types:

- simultaneous wavelength-dispersive
- sequential wavelength-dispersive
- bremsstrahlung source energy-dispersive
- secondary target energy-dispersive.

Although these different types of instrument may bear little physical resemblance to one another, for the purpose of comparison they differ only in the type of source used

for excitation, the number of elements which they are able to measure at one time, the speed at which they collect data and finally, their price range. All of the instruments listed above are, in principle at least, capable of measuring all elements in the periodic classification from $Z = 9°$(F) and upwards. All can be fitted with multisample handling facilities and all can be automated by use of minicomputers. All are capable of precision of the order of a few tenths of one percent and all have sensitivities down to the low parts per million level. As far as the analyst is concerned, they differ only in their speed, cost and number of elements measurable at the same time.

Single-channel wavelength-dispersive spectrometers are typically employed for both routine and nonroutine analysis of a wide range of products, including ferrous and nonferrous alloys, oils, slags and sinters, ores and minerals, thin films, and so on. These systems are very flexible but relative to multichannel spectrometers are somewhat slow. The multichannel wavelength-dispersive instruments are used solely for routine, high throughput, analyses where the great need is for fast accurate analysis, but where flexibility is of no importance. Energy-dispersive spectrometers have the great advantage of being able to display information on all elements at the same time. They lack somewhat in resolution over the wavelength-dispersive systems but also find great application in quality control, troubleshooting problems, and so on. They have been particularly effective in the fields of scrap alloy sorting, in forensic science and in the provision of elemental data to supplement X-ray powder diffraction data.

3.1 Basis of the Method

All conventional X-ray spectrometers comprise three basic parts: the primary source unit, the spectrometer itself and the measuring electronics. The primary source unit consists of a very stable high-voltage generator, capable of providing up to around 3 kW of power at a potential of typically 60–80 kV, plus a sealed X-ray tube. The sealed X-ray tube has an anode of Cr, Rh, W, Ag, Au or Mo and delivers an intense source of continuous radiation which then impinges on the analyzed specimen where characteristic radiation is generated. A portion of the characteristic ‘fluorescence’ radiation is then collected by the actual spectrometer where the beam is passed via a collimator or slit onto the surface of an analyzing crystal, where individual wavelengths are diffracted in accordance with the Bragg law. A photon detector, typically a gas flow or a scintillation counter, is then used to convert the diffracted characteristic photons into voltage pulses which are integrated and displayed as a measure of the characteristic line intensity.

3.2 X-ray Sources

Several different types of source have been employed for the excitation of characteristic X-radiation, including those based on electrons, X-rays, γ-rays, protons and synchrotron radiation. Sometimes a bremsstrahlung X-ray source is used to generate specific X-radiation from an intermediate pure element sample called a secondary fluorescer. By far the most common source today is the X-ray photon source. This source is used in primary mode in the wavelength- and primary energy-dispersive systems, and in secondary fluorescer mode in secondary target energy-dispersive spectrometers. A γ-source is typically a radioisotope that is used either directly, or in a mode equivalent to the secondary fluorescer mode in energy-dispersive spectrometry. Most conventional wavelength-dispersive X-ray spectrometers use a high power (2–4 kW) X-ray bremsstrahlung source. Energy-dispersive spectrometers use either a high-power or low-power (0.5–1.0 kW) primary source, depending on whether the spectrometer is used in the secondary or primary mode. In all cases, the primary source unit consists of a very stable high-voltage generator, capable of providing a potential of typically 40–100 kV. The current from the generator is fed to the filament of the X-ray tube, which is typically a coil of tungsten wire. The applied current causes the filament to glow, emitting electrons. A portion of this electron cloud is accelerated to the anode of the X-ray tube, which is typically a water-cooled block of copper with the required anode material plated or cemented to its surface. The impinging electrons produce X-radiation, a significant portion of which passes through a thin beryllium window to the specimen.

3.3 X-ray Detectors

An X-ray detector is a transducer for converting X-ray photon energy into voltage pulses. Detectors work through a process of photoionization in which interaction between the entering X-ray photon and the active detector material produces a number of electrons. The current produced by these electrons is converted to a voltage pulse, by a capacitor and resistor, such that one digital voltage pulse is produced for each entering X-ray photon. In addition to being sensitive to the appropriate photon energies, which means being applicable to a given range of wavelengths or energies, there are two other important properties that an ideal detector should possess. These properties are proportionality and linearity. Each X-ray photon entering the detector produces a voltage pulse, and where the size of the voltage pulse is proportional to the photon energy, the detector is said to be proportional. Proportionality is needed where the technique of pulse height selection is to be used. Pulse height selection is a means of electronically rejecting

pulses of voltage levels other than those corresponding to the characteristic line being measured. X-ray photons enter the detector at a certain rate and where the output pulses are produced at this same rate the detector is said to be linear. Linearity is important where the various count rates produced by the detector are to be used as measures of the photon intensity for each measured line.

In the case of wavelength-dispersive spectrometers, the gas flow proportional counter is generally employed for the measurement of longer wavelengths and the scintillation counter is used for the measurement of shorter wavelengths. Neither of these detectors has sufficient resolution to separate multiple wavelengths on its own, and so they have to be employed along with an analyzing crystal. However, in the case of energy-dispersive spectrometry, where no dispersing crystal is employed, a detector of higher resolution must be used.

3.4 The Wavelength-dispersive Spectrometer

In order to maintain the required geometric conditions a goniometer is used to ensure that the angle between source and crystal, and crystal and detector, is kept the same. The output from a wavelength-dispersive spectrometer may be either analog or digital. For qualitative work an analog output is traditionally used, and in this instance a rate meter is used to integrate the pulses over short time intervals, typically of the order of a second or so. The output from the rate meter is fed to an x/t recorder which scans at a speed which is conveniently coupled with the goniometer scan speed. The recorder thus displays an intensity/time diagram, which becomes an intensity/2θ diagram. Tables are then used to interpret the wavelengths. For quantitative work it is more convenient to employ digital counting, and a timer/scaler combination is provided which will allow pulses to be integrated over a period of several tens of seconds and then displayed as count or count rate.

Most modern wavelength-dispersive spectrometers are controlled in some way by a minicomputer or microprocessor and by use of specimen changers are capable of very high specimen throughput. Once they are set up the spectrometers will run virtually unattended for several hours.

3.5 The Energy-dispersive Spectrometer

Like the wavelength-dispersive spectrometer, the energy-dispersive spectrometer also consists of the three basic units – excitation source, spectrometer and detection system. In this case, however, the detector itself acts as the dispersion agent. The detector generally employed in this context is the Si(Li) detector. The Si(Li) detector consists of a small cylinder (about 1 cm diameter and 3 mm thick) of p-type silicon that has been compensated by lithium to increase its electrical resistivity. A Schottky barrier contact on the front of the silicon disk produces a p-i-n type diode (one with p-doped, isolating and n-doped layers). In order to inhibit the mobility of the lithium ions and to reduce electronic noise, the diode and its pre-amplifier are cooled to the temperature of liquid nitrogen. Incident X-ray photons interact to produce a specific number of electron hole pairs. The charge produced is swept from the diode by the bias voltage to a charge-sensitive pre-amplifier. A charge loop integrates the charge on a capacitor to produce an output pulse. A pre-amplifier is responsible for collecting this charge on a feedback capacitor to produce a voltage pulse proportional to the original X-ray photon energy. Thus when a range of photon energies are incident upon the detector, an equivalent range of voltage pulses is produced as a detector output. A multichannel analyzer is used to sort the arriving pulses at its input in the same fashion as to produce a histogram representation of the X-ray energy spectrum.

The output from an energy-dispersive spectrometer is generally displayed on some sort of visual display unit. The operator is able to dynamically display the contents of the various channels as an energy spectrum and provision is generally made to allow zooming in on portions of the spectrum of special interest, to overlay spectra, to subtract background, and so on, in a rather interactive manner. As in the case of the modern wavelength-dispersive systems, nearly all energy-dispersive spectrometers will incorporate some form of minicomputer which is available for spectral stripping, peak identification, quantitative analysis and a host of other useful functions.

4 ELEMENTAL ANALYSIS BY X-RAY FLUORESCENCE

4.1 Specimen Preparation Techniques for X-ray Fluorescence

Because X-ray spectrometry is essentially a comparative method of analysis, it is vital that all standards and unknowns be presented to the spectrometer in a reproducible and identical manner. Any method of specimen preparation must give specimens that are reproducible and which, for a certain calibration range, have similar physical properties including mass attenuation coefficient, density, particle size and particle homogeneity. In addition the specimen preparation method must be rapid and cheap and must not introduce extra significant systematic errors, for example the introduction of trace elements from contaminants in a diluent. Specimen preparation is an all important factor in the ultimate accuracy of any X-ray determination, and many papers have been published

describing a multitude of methods and recipes for sample handling.

In general samples fit into three main categories:

- Samples which can be handled directly following some simple pretreatment such as pelletizing or surfacing, for example homogeneous samples of powders, bulk metals or liquids.
- Samples which require significant pretreatment, for example heterogeneous samples, samples requiring matrix dilution to overcome inter-element effects and samples exhibiting particle size effects.
- Samples which require special handling treatment, for example samples of limited size, samples requiring concentration or prior separation and radioactive samples.

The ideal specimen for XRF analysis is one in which the analyzed volume of specimen is representative of the total specimen, which is, itself, representative of the sample submitted for analysis. There are many forms of specimen suitable for XRF analysis, and the form of the sample as received will generally determine the method of pretreatment. It is convenient to refer to the material received for analysis as the sample, and that which is actually analyzed in the spectrometer as the specimen. While the direct analysis of certain materials is certainly possible, more often than not some pretreatment is required to convert the sample to the specimen. This step is referred to as specimen preparation. In general, the analyst would prefer to analyze the sample directly, because if it is taken as received any problems arising from sample contamination that might occur during pretreatment are avoided. In practice, however, there are three major constraints that may prevent this ideal circumstance from being achieved: sample size, sample size homogeneity and sample composition heterogeneity. Problems of sample size are frequently severe in the case of bulk materials such as metals, large pieces of rock, etc.

Problems of sample composition heterogeneity will generally occur under these circumstances as well, and in the analysis of powdered materials, heterogeneity must almost always be considered. The sample as received may be either homogeneous or heterogeneous; in the latter case, it may be necessary to render the sample homogeneous before an analysis can be made. Heterogeneous bulk solids are generally the most difficult kind of sample to handle, and it may be necessary to dissolve or chemically react the material in some way to give a homogeneous preparation. Heterogeneous powders are either ground to a fine particle size and then pelletized, or fused with a glass-forming material such as borax. Solid material in liquids or gases must be filtered out and the filter analyzed as a solid. Where analyte concentrations in liquids or solutions are too high or too low, dilution or preconcentration techniques may be employed to bring the analyte concentration within an acceptable range.

4.2 Qualitative Analysis with the X-ray Spectrometer

Both the simultaneous wavelength-dispersive spectrometer and the energy-dispersive spectrometers lend themselves admirably to the qualitative analysis of materials. As was shown in Equation (1) there is a simple relationship between the wavelength or energy of a characteristic X-ray photon, and the atomic number of the element from which the characteristic emission line occurs. Thus by measuring the wavelengths, or energies, of a given series of lines from an unknown material the atomic numbers of the excited elements can be established. Because the characteristic X-ray spectra are so simple the actual process of allocating atomic numbers to the emission lines is a relatively simple process and the chance of making a gross error is rather small. In comparison, the procedures for the qualitative analysis of multiphase materials with the X-ray powder diffractometer is a much more complex business. There are after all only 100 or so elements, and within the range of the conventional spectrometer each element gives, on an average, only half a dozen lines. In diffraction on the other hand, there are perhaps as many as several million possible compounds, each of which can give on average 50 or so lines. Similarly if one compares the X-ray emission spectrum with the ultraviolet (UV) emission spectrum, the X-ray spectrum is much easier to interpret than the UV emission spectrum because the X-ray spectrum arises from inner orbital transitions, the number of which is of course rather limited, and the UV spectrum arises from transitions to unfilled levels, of which there can be many. A further benefit of the X-ray emission spectrum for qualitative analysis is that because transitions do arise from inner orbitals, the effect of chemical combination, i.e. valence, is almost negligible.

4.3 Development of Intensity/Concentration Algorithms

The great flexibility and range of the various types of XRF spectrometer, coupled with their high sensitivity and good inherent precision make them ideal for quantitative analysis. Like all instrumental methods of analysis the high precision can be translated into high accuracy only if the various systematic errors in the analysis process are taken care of. The precision of a well-designed X-ray spectrometer is typically of the order of one tenth of a percent or so, the major source of this random error being the X-ray source, the high voltage generator plus the X-ray tube. In addition there is an error arising from the statistics of the actual counting process.

Systematic errors in quantitative X-ray spectrometry arise mainly from absorption- and specimen-related phenomena, rather like in X-ray powder diffraction except that in the spectrometry case they are much more complicated. This is because in spectrometry many wavelengths are involved, whereas in diffraction one is dealing with a single wavelength, i.e. the diffracted, monochromatic tube line. This means, for example, that the equivalent absorption-effect expression becomes rather complex. Although these so-called matrix effects are somewhat complicated, many excellent methods have been developed over the past 30 years or so for handling them. The advent of the personal computer controlled spectrometer has done much to enhance the application of these correction procedures and today, in most cases, one is able to quantify most elements in the periodic table of atomic number 9 (F) and upwards to an accuracy of a few tenths of a percent. The areas of application of the XRF technique now cover almost all areas of inorganic analysis.

In the conversion of net line intensity to analyte concentration it may be necessary to correct for any absorption and/or enhancement effects which occur. Absorption effects include both primary and secondary absorption. Primary absorption occurs because all atoms of the specimen matrix will absorb photons from the primary source. Since there is a competition for these primary photons by the atoms making up the specimen, the intensity/wavelength distribution of these photons available for the excitation of a given analyte element may be modified by other matrix elements. Secondary absorption refers to the effect of the absorption of characteristic analyte radiation by the specimen matrix. As characteristic radiation passes out from the specimen in which it was generated, it will be absorbed by all matrix elements, by amounts relative to the mass attenuation coefficients of these elements. The total absorption of a specimen is dependent on both primary and secondary absorption. Enhancement effects occur when a nonanalyte matrix element A emits a characteristic line that has an energy just in excess of the absorption edge of the analyte element. This means that the nonanalyte element in question is able to excite the analyte, giving characteristic photons over and above those produced by the primary continuum. This gives an increased, or enhanced, signal from the analyte.

Since the early work of Sherman[8] there has been a growing interest in the provision of an intensity/concentration algorithm which would allow the calculation of the concentration values without recourse to the use of standards. Sherman's work was improved upon first by the Japanese team of Shiraiwa and Fujino[9] and later, by Criss and Birks[10,11] with their Naval Research Laboratory X-ray Fluorescence program (NRLXRF). The same group also solved the problem of describing the intensity distribution from the X-ray tube.[12] The problem for the average analyst in the late 1960s and early 1970s, however, remained that of finding sufficient computational power to apply these methods. In the early 1970s, de Jongh suggested an elegant solution[13] in which he proposed the use of a large mainframe computer for the calculation of the influence coefficients, then use of a minicomputer for their actual application using a concentration correction influence model.

4.4 Quantitative Methods

The simplest quantitative analysis situation to handle is the determination of a single element in a known matrix. In this instance, a simple calibration curve of analyte concentration vs line intensity is sufficient for quantitative determination. A slightly more difficult case might be the determination of a single element where the matrix is unknown. Three basic methods are commonly employed in this situation; use of internal standards, use of standard addition or use of a scattered line from the X-ray source. The most complex case is the analysis of all, or most, of the elements in a sample, about which little or nothing is known. In this case a full qualitative analysis would be required before any attempt is made to quantitate the matrix elements. Once the qualitative composition of the sample is known, again, one of three general techniques is typically applied; use of type standardization, use of an influence coefficient method or use of a fundamental parameter technique. Both the influence coefficient method and the fundamental parameter technique require a computer for their application. In principle, an empirical correction procedure can be described as the correction of an analyte element intensity for the influence of an interfering element(s) using the product of the intensity from the interfering element line and a constant factor as the correction term.[14] This constant factor is generally referred to as an influence coefficient, since it is assumed to represent the influence of the interfering element on the analyte. Commonly employed influence coefficient methods may use either the intensity or the concentration of the interfering element as the correction term. These methods are referred to as intensity correction and concentration correction methods, respectively. Intensity correction models give a series of linear equations which do not require much computation, but they are generally not applicable to wide ranges of analyte concentration. Various versions of the intensity correction models found initial application in the analysis of nonferrous metals where correction constants were applied as look-up tables. Later versions[15] were supplied on commercially available computer controlled spectrometers and were used for a wider range of application. A concentration

model[16] requires the solving of a series of simultaneous equations, by regression analysis or matrix inversion techniques. This approach is more rigorous than the intensity models, and so they became popular in the early 1970s as suitable low-cost minicomputers became available.

Influence coefficient correction procedures can be divided into three basic types: fundamental, derived and regression. Fundamental models are those which require starting with concentrations, then calculating the intensities. Derived models are those which are based on some simplification of a fundamental method but which still allow concentrations to be calculated from intensities. Regression models are those which are semi-empirical in nature, and which allow the determination of influence coefficients by regression analysis of data sets obtained from standards. All regression models have essentially the same form and consist of a weight fraction term, W (or concentration, C); an intensity (or intensity ratio) term, I; an instrument-dependent term which essentially defines the sensitivity of the spectrometer for the analyte in question, and a correction term which corrects the instrument sensitivity for the effect of the matrix. The general form is given by Equation (6):

$$W = I\langle \text{instrument} \rangle [1 + \{\text{model}\}] \tag{6}$$

Equation (6) shows that the weight fraction W of an analyte is proportional to the product of measured intensity I from the analyte, corrected for instrumental effects; and a matrix correction term. Different models vary only in the form of this correction term.

The major advantage to be gained by use of influence coefficient methods is that a wide range of concentration ranges can be covered using a relatively inexpensive computer for the calculations. A major disadvantage is that a large number of well-analyzed standards may be required for the initial determination of the coefficients. However, where adequate precautions have been taken to ensure correct separation of instrument- and matrix-dependent terms, the correction constants are transportable from one spectrometer to another and, in principle, need only be determined once.

4.5 Trace Analysis

The XRF method is particularly applicable to the qualitative and quantitative analysis of low concentrations of elements in a wide range of samples, as well as allowing the analysis of elements at higher concentrations in limited quantities of materials. A measurement of a line at peak position gives a counting rate which, in those cases where the background is insignificant, can be used as a measure of the analyte concentration. However, where the background is significant the measured value of the analyte line at the peak position now includes a count rate contribution from the background. The analyte concentration in this case is related to the net counting rate. Since both peak and background count rates are subject to statistical counting errors, the question now arises as to the point at which the net peak signal is statistically significant. The generally accepted definition for the lower limit of detection (LLD) is that concentration equivalent to two standard deviations of the background counting rate. A formula (Equation 7) for the LLD can now be derived:[17]

$$\text{LLD} = \frac{3/m}{R_\mathrm{b}/t_\mathrm{b}} \tag{7}$$

In Equation (7) R_b is the count rate at the background, t_b is the time spent counting the background and m is the sensitivity of the spectrometer in c/s/%. Even though we are using two standard deviations, two measurements, peak and background, must be made. This increases the error by $\sqrt{2}$. It is the practice to assume that $2\sqrt{2} \sim 3$, hence the '3' in Equation (7). It is important to note that not only does the sensitivity of the spectrometer vary significantly over the wavelength range of the spectrometer, but so too does the background counting rate. In general, the background varies by about two orders of magnitude over the range of the spectrometer. It will be seen that the detection limit will be best when the sensitivity is high and the background is low. Both the spectrometer sensitivity and the measured background vary with the average atomic number of the sample. While detection limits over most of the atomic number range lie in the low parts per million range, the sensitivity of the X-ray spectrometer falls off quite dramatically towards the long wavelength limit of the spectrometer owing mainly to low fluorescence yields and the increased influence of absorption. As a result, poorer detection limits are found at the long wavelength extreme of the spectrometer, which corresponds to the lower atomic numbers. Thus the detection limits for elements such as fluorine and sodium are at the levels of hundredths of one percent rather than parts per million. The detection limits for the very low atomic number elements such as carbon ($Z = 6$) and oxygen ($Z = 7$) are very poor, typically of the order of 3 to 5%.

5 INSTRUMENTATION FOR POWDER DIFFRACTION

5.1 Basis of the Method

The powder method derives its name from the fact that the specimen is typically in the form of a microcrystalline powder, although as has been indicated, any material

which is made up of an ordered array of atoms will give a diffraction pattern. The possibility of using a diffraction pattern as a means of phase identification was recognized over 50 years ago but it was not until the late 1930s that a systematic means of unscrambling the superimposed diffraction patterns was proposed.[18] The technique was based on the use of a file of single phase patterns, characterized in the first stage by their three strongest reflections and a search technique based on matching strong lines in the unknown pattern with these standard pattern lines. A potential match was then confirmed by a check using the full pattern in question. The identified pattern was then subtracted from the experimental pattern and the procedure repeated on the residue pattern until all lines were identified. Techniques for this "search/matching" process have changed little over the years and, although in the hands of experts manual search/matching is an extremely powerful tool, for the less experienced user it can be rather time-consuming. Round robin tests have indicated that 2–4 hours are typically required for the complete identification of a four-phase mixture.[19] A growing complication is that the file of standard patterns increases by about 1500 each year and currently stands at about 118 000 entries. The responsibility for the maintenance of the Powder Data File (PDF) lies with the International Centre for Diffraction Data (ICDD) which is a not-for-profit organization located in Newtown Square, Pennsylvania. This group is made up of a staff of permanent officers along with a number of academic and industrial scientists who are active in the field of XRD. The PDF is a unique assembly of good-quality single-phase patterns and is used by thousands of chemists, geologists, materials scientists, etc. all over the world.

5.2 Production of Monochromatic Radiation

With the growing need for high-quality X-ray powder diffraction data, one especially important parameter is the method by which the analytical wavelength is treated. Problems can occur in data treatment because of the polychromatic nature of the diffracted beam and the variability in the angular dispersion of the diffractometer. A combination of these two facts can lead to difficulty in manually assessing where the maximum of a peak occurs, especially in the range of angles from 30° to 60° 2θ. Of the many methods commonly employed to render the radiation monochromatic (or bichromatic), most will fit into two broad categories – instrumental methods and computer methods. The more common instrumental methods of monochromatization include the following:

- use of a β-filter
- use of a proportional detector and pulse height selection
- use of a Si(Li) solid-state detector
- use of a diffracted-beam monochromator
- use of a primary beam monochromator.

The basic purpose of the monochromatization of the diffracted radiation is to obtain an experimental pattern from a single, unique wavelength. Inspection of Bragg's law (Equation 5) reveals that each unique d-spacing will diffract different wavelengths at their own unique diffraction angles. Thus, if a pattern were measured using an X-ray beam containing two wavelengths, the observed pattern would, in fact, be two patterns (one for each wavelength) superimposed on one another, and clearly will be more difficult to interpret than a diffractogram from a single wavelength. While the problems associated with the interpretation of a diffractogram from two known wavelengths can be significant, much more of a problem occurs when additional wavelengths are diffracted. The characteristic K-radiation emission from typical X-ray tube anode materials is much more complex than the simple α-doublet and β-doublet model generally employed in classical powder diffractometry. For most practical purposes, however, the copper K spectrum is generally considered to consist simply of two pairs of lines, the α_1/α_2-doublet, occurring from a 2p → 1s transition; and the β_1/β_3-doublet from a 3p → 1s transition. The following table lists the values of the Kα and Kβ wavelengths for the more common X-ray tube target elements.

Anode	Kα_1(100)	Kα_2(50)	Kβ(15)
	Wavelength (Å)		
Cu	1.54060	1.54439	1.39222
Cr	2.28970	2.29361	2.08487
Fe	1.93604	1.93998	1.75661
Co	1.78897	1.79285	1.62079
Mo	0.70930	0.71359	0.63229

In most experimental work, the β-doublet intensity is typically reduced to less than a few percent of the α-doublet intensity by use of filtration, or it is removed by use of a diffracted beam monochromator or a high-resolution energy-resolving detector. In each case, what remains is essentially bichromatic X-radiation. The exception to this occurs with the primary beam monochromator where only the α_1 is directed onto the specimen. In applying the usual bichromatic radiation to the measurement of interplanar spacings, the main problems are the angle-dependent dispersion of the α_1/α_2-doublet, and differences in peak asymmetry between the two. It follows from Bragg's law that an error in d-spacing is linearly related to an error in wavelength. For manual qualitative phase identification, an accuracy of about 5 parts in 1000 for $\Delta d/d$ is sufficient;

and about twice this accuracy is required for computer search/matching. Provided that the true α_1-emission line is being used, i.e. either the diffracted beam is really monochromatic, or the contribution from the α_2 is effectively removed from the diffraction profile, then the wavelength need also be known only to about 2 parts per 1000. For accurate lattice parameter determination, it is common practice to use an internal standard and, in these cases, the wavelength value is, to all intents and purposes, redundant.

5.3 Use of Diffractometers in the Powder Method

A powder diffractometer is essentially a device which allows a range of θ values to be scanned, rotating the photon detector at twice the angular speed of the specimen thus maintaining the required geometrical condition. The specimen consists of a random distribution of crystallites so that the appropriate planes will be in the correct orientation to diffract the wavelength λ each time the Bragg condition is satisfied. Thus in X-ray diffraction each peak angle value corresponds to a certain d-spacing. In the wavelength-dispersive spectrometer a single crystal of known d-spacing is used to disperse the polychromatic beam of characteristic wavelengths coming from the sample, such that each wavelength will diffract at a discrete angle.

Figure 5 shows a schematic drawing of a typical vertical powder diffractometer system and illustrates the geometry of the system. This geometric arrangement is known as the Bragg–Brentano parafocusing system and is typified by a diverging beam from a line source F, falling onto the specimen S, being diffracted and passing through a receiving slit RS to the detector. Distances FS and SRS are equal. The amount of divergence is determined by the effective focal width of the source and the aperture of the divergence slit DS. Axial divergence is controlled by two sets of parallel plate collimators (Soller slits) SS1 and SS2 placed between focus and specimen, and specimen and scatter slit respectively. Use of the narrower divergence slit will give a smaller specimen coverage at a given diffraction angle, thus allowing the attainment of lower diffraction angles where the specimen has a larger apparent surface (thus larger values of d are attainable). This is achieved, however, only at the expense of intensity loss. Choice of the divergence slit, plus its matched scatter slit, is thus governed by the angular range to be covered. The decision as to whether or not the slit size should be increased at a given angle will be determined by the available intensity. A scintillation detector is typically placed behind the scatter slit and this converts the diffracted X-ray photons into voltage pulses. These pulses may be integrated in a rate meter to give an analog signal on an x/t recorder. By synchronizing the scanning speed of the goniometer with the recorder, a plot is obtained of degrees 2θ against intensity, called the diffractogram. A timer/scaler is also provided for quantitative work and this is used to obtain a measure of the integrated peak intensity of a selected line(s) from each analyte phase in the specimen. A diffracted beam monochromator may also be used in order to improve signal-to-noise characteristics.

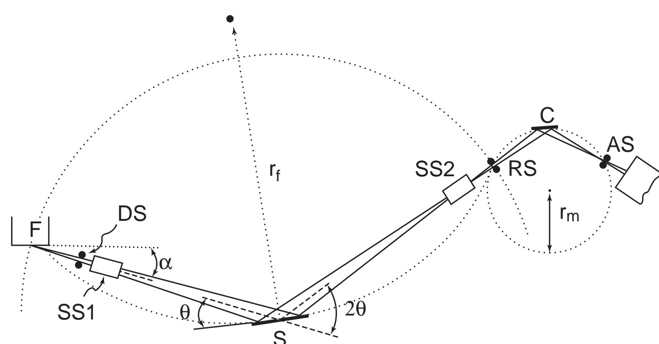

Figure 5 Bragg–Brentano parafocusing geometry. (Reproduced from Jenkins, Snyder, *Introduction to Powder Diffractometry*, Wiley-Interscience, 1996. With permission from John Wiley & Sons.)

5.4 Powder Cameras

The simplest device for the measurement of a powder diffraction diagram is the Debye–Scherrer powder camera. This consists of a cylindrical camera body carrying an entrance pinhole collimator and an exit beam collimator lying along the diameter of the camera. The specimen is mounted as a thin cylinder at the central axis of the camera. A piece of film is placed inside the cylindrical wall of the camera and small holes are cut in the film for the entrance and exit collimators. A beam of X-rays is directed onto the specimen via the entrance collimator and the diffracted X-rays fall onto the film. The film is then developed and laid flat for the interpretation. In order to make estimation of 2-θ values from the film easy, the diameter of the camera is made such that one or two mm of film corresponds to exactly $1° \ 2\theta$. The powder camera finds great application in the analysis of very small specimens and good patterns can be obtained from only a few milligrams of specimen. The camera technique has the disadvantage that it may be rather slow and exposure times are typically in the range of 1–6 hours. In addition to the Debye–Scherrer powder camera there are also available more specialized cameras for various applications. As an example, the Guinier camera is a powder camera which incorporates a focusing monochromator and works in a transmission mode. Although the intensities are rather unreliable and it is more difficult to align than the Debye–Scherrer camera, the Guinier camera can give

very high quality patterns in a relatively short period of time. Another useful camera is the Gandolphi camera which is essentially a Debye–Scherrer camera with an eccentric specimen rotation movement added, allowing the generation of a 'powder' pattern from a small single crystal.

6 PHASE CHARACTERIZATION BY X-RAY DIFFRACTION

6.1 Qualitative Analysis of Polycrystalline Material

Of all of the methods available to the analytical chemist only X-ray diffraction is capable of providing general purpose qualitative and quantitative information on the presence of phases (e.g. compounds) in an unknown mixture. While it is true that techniques such as differential thermal analysis will provide some information on specific phase systems, under certain circumstances such methods could not be classified as general purpose. A diffraction pattern contains a good deal of information of which three parameters are of special interest:

- the position of the diffraction maxima
- the peak intensities
- the intensity distribution as a function of diffraction angle.

The three pieces of information can, in principle, be used to identify and quantify the contents of the sample, as well as to calculate the material's crystallite size and distribution, crystallinity, stress and strain. The ideal specimen preparation for a given experiment depends largely on the information desired. A sample which is used only for the identification of its constituents may be quite different from a sample used to measure strain, which in turn may be different from a sample used in quantitative analysis.

A diffraction pattern is characteristic of the atomic arrangement within a given phase and to this extent it acts as a *fingerprint* of that particular phase. Thus by use of the ICDD PDF a series of potential matches can be obtained. A complication in the application of this method for the analysis of multiphase materials is that the patterns are superimposed and consequently there may be uncertainties as to which lines belong to which phases. As shown in Figure 6, it is common practice to "reduce" the *experimental* pattern to a *reduced* pattern. This process was first carried out because of problems with storage and replication of powder patterns, and the procedure persists today.

In practice it is rather unusual to analyze specimens in which nothing at all is known. Generally one has access to

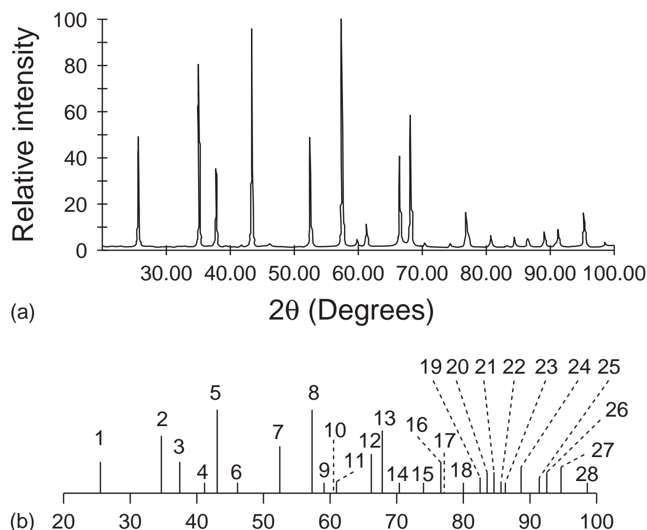

Figure 6 (a) The experimental pattern and (b) the reduced pattern of Al_2O_3. (Reproduced from Jenkins, Snyder, *Introduction to Powder Diffractometry*, Wiley-Interscience, 1996. With permission from John Wiley & Sons.)

information about sample history, environment, etc. and additional analytical information can be employed where available. As an example, in the routine analytical laboratory it is common to find the X-ray diffractometer and the X-ray spectrometer being used to give complementary information. Thus a more common means of identifying phases in an "unknown" mixture is to use the technique of preconceived. In this case educated guesses are made as to what phases may be present and these phases are sought first. As an example, if one were analyzing a specimen obtained by aspirating air through a filter paper, and the X-ray spectrometer indicated significant concentrations of silicon and iron, likely candidates to search for in the diffraction pattern would be SiO_2, Fe_2O_3 and $FeSiO_3$. In order to simplify the search procedure further the ICDD has subdivided the file of standard patterns into Mineral, Inorganic, Organic, Metals and Alloys, Common Phases, etc. XRD is an invaluable technique for qualitative phase identification but it is neither a sensitive nor a rapid means of analysis. The minimum detectable limit found by routine qualitative procedures would be of the order of several percent, compared, for example, with a few parts per million in XRF. A complete analysis would take several hours to complete, although this will of course depend to a very large extent on the experience of the analyst and the complexity of the problem in hand. The method is applicable to almost any crystalline material whether inorganic or organic.

6.2 Search Procedures

The PDF is described in section 5. Several different approaches are used to identify phases in an unknown

mixture. The first method is an analytical approach in which no basic assumptions are made about the sample being analyzed. The three strongest lines in the pattern are used to locate potential matches in the PDF index. Each time a potential candidate is found, a match is made with the complete pattern. If all lines agree, a phase confirmation is assumed and the lines for the match subtracted from the original pattern. This process is repeated until all significant lines in the pattern are identified. The second method is based on a series of guesses based in turn on preconceived ideas of what phases might be present. The two basic parameters being used in this search/match process are the "*d*" values which in turn have been calculated from the measured 2-θ values in the diffractogram, and the relative intensities of the lines in the pattern. Whereas the "*d*" value can be accurately measured – perhaps with an accuracy of better than 0.5% in routine analysis, the intensities are by comparison rather unreliable and can be subject to errors, sometimes running into tens of percent.

6.3 Modern Computer-based Methods

More than 90% of all new powder diffractometers now sold in the world are automated. Many excellent computer programs are provided with these instruments to aid the diffractionist in the reduction of powder data. Unfortunately, there can be pitfalls in the use of some of these programs, especially for the newcomer to the diffraction field. A popular misconception is that automated diffractometers are easier to use than manual systems. What, in fact, is true is that automated powder diffractometers (APD) can give many hours of unattended and reliable data collection and can greatly assist in the tedious and routine tasks of data analysis, provided one is careful to apply the programs in the correct manner.

During the 1960s, as mainframe computers evolved (e.g. IBM 7094, CDC 6600, etc.) crystallographic computing was performed in a noninteractive environment, where cards were input into a program operating in a batch stream. Owing to the very high cost of computers, laboratory automation was nearly nonexistent, so these early developments can be considered as the zeroth generation of laboratory computational software. One of the first APDs was developed by Rex[20] in the mid-1960s. However, it took the microelectronics revolution of the 1970s to initiate the general techniques which have led to today's automated instrumentation. Although the principal thrust in the early 1970s was to develop the hardware interfaces needed to allow a computer to control a diffractometer, this work rapidly gave way to the much more serious problems of devising algorithms for the control of the instrument and the processing of the digital data. The 1970s saw the evolution of the early laboratory computer (e.g. the Digital Equipment Corporation PDP-8, and PDP-11), and the first generation of process control software. Input to the program was first by paper tape and later by magnetic tape cassette, with programs written in low-level assembler language. Systems of this type were developed at Alfred University, Corning Glass Works and General Electric. The first commercial APD system in the USA was the Philips APD-3500[21] which developed from involvement in the NASA project for a Lunar Receiving Laboratory. This instrument utilized a 4000-word, 18-bit program logic controller (a forerunner of what was to become the microprocessor). Within the 4 K of core, routines were available for hardware control, data collection, data manipulation and sophisticated math – all without hardware arithmetic capability!

The second generation of laboratory software evolved on the next generation of laboratory computers (e.g. the PDP 11/34), with the introduction of floppy disks which permitted convenient use of high-level language compilers. The first of these systems was written in FORTRAN and allowed the user to conduct an interactive dialogue with the computer to set up and execute an automated experiment and analyze the data.[22] The development of the 5 and 10 Mbyte Phoenix and Winchester disk drives, allowed the development of the third generation of software involving extensive file structures with help screens on video terminals and default files containing the users' typical settings, rather than interactive dialogue.[23,24] A fourth generation of software is currently evolving where all interactions with the user are done through a "point and click" video interface with a mouse. The trend is to eliminate all keyboard activity and convert crystallographic methods, which used to rely on the user evaluating numbers, to visual examination of graphical data.

There are essentially four elements to the automation of a diffractometer:

- the replacement of the synchronous $\theta : 2\theta$ motor with a stepping motor and its associated electronics
- the replacement of a conventional scaler/timer with one which can be remotely set and read
- the conversion of the various alarms, limit switches and shutter controls to computer-readable signals
- the creation of an interface which will allow a computer to control 1 through 3.

These four items are easily obtained today by direct purchase of modules which often plug directly onto the bus of a modern minicomputer.

Today, nearly all laboratory APD systems are controlled by a personal computer. The major impact of computer automation on improving the accuracy of the measurement of diffraction angles has come from the algorithms which bring much more intelligence to the

process than has been conventionally used in manual measurements. There are two areas here which need to be considered; the first is the algorithms which control the collection of data, and the second, those which reduce the data to d values and intensities. The first generation of control algorithms were principally nonoptimizing, move and count methods. Although various attempts have been made to use the computer's decision-making capability to bring more "intelligence" to the data-collection process,[25] the algorithms in use today continue to be nonoptimizing. The fundamental problem is the determination of the intensity threshold above background, which limits the ability to detect small peaks that could be due to trace phases in the specimen. Thus, in the limit, an intelligent algorithm would spend all of its time counting where the peaks are not present. The key hindrance to the development of intelligent data-collection software remains our inability to predict or even accurately describe the diffractometer's background function.

6.4 Limitations Due to the Specimen

The aim of any diffraction experiment is to obtain the best possible data, within the appropriate constraints of the relevant circumstances, so that the data can be correctly interpreted and analyzed. One of the major problems in achieving this goal is the preparation of the specimen. Various methods of specimen preparation have been devised[26] and the success of a given diffraction experiment will invariably depend on the correct choice of preparation method for the sample being analyzed and for the instrument conditions being used for the analysis. Because of the many problems associated with the form of the analyzed material, it is useful to differentiate between the sample and the specimen. The sample is generally considered to be the material submitted for analysis. It is generally assumed that the sample has been correctly taken (sampled) by the submitter to give a representative measure of the problem at hand. It is now up to the diffractionist to take an aliquot of the sample and prepare a specimen for analysis. This specimen preparation may involve a number of steps such as drying, grinding, sieving, dilution, mounting, etc. It is tacitly assumed that the analysis of the specimen represents the analysis of the sample. While this assumption is generally true, it may not always be so, and the analyst must be on his guard to ensure that all reasonable precautions are taken to avoid contamination or phase changes during the process of specimen preparation.

The biggest overall problem in specimen preparation is that due to preferred orientation. Particle and crystallite size, sample size, sample position, crystallite orientation, and absorption will affect the quality and appearance of any diffraction pattern. As a rule of thumb, the best specimen preparation methods are those that allow the analyst to obtain the desired information with the least amount of sample treatment. This is especially important in the analysis of unknown materials, pharmaceuticals and organics where the materials being analyzed may be sensitive to grinding, humidity or atmospheric environment. Extensive specimen preparation may change the sample so that the analyst is no longer analyzing the original problem. A good example is the case of hydrates and polymorphs in pharmaceutical formulations. The presence of hydrates and/or polymorphs may change the melting, solubility and blending characteristics of the formulation. In such a case the analyst must ensure that the sample preparation method does not dehydrate the sample or change the polymorphic composition. This may eliminate specimen preparation methods involving grinding, spray drying and vacuum drying and may necessitate that the sample be sealed in a controlled environment.

6.5 Quantitative Methods

Once the presence of a phase has been established in a given specimen one can, at least in principle, determine how much of that phase is present by use of the intensities of one or more diffraction lines from the phase. However, as has been pointed out previously, it may be difficult to obtain an accurate value for these intensities. The intensities of the diffraction peaks are subject to a variety of random and systematic errors and the errors fall roughly into three categories:

- Structure-dependent: that is a function of atomic size and atomic arrangement, plus some dependence on the scattering angle and temperature.
- Instrument-dependent: that is a function of diffractometer conditions, source power, slit widths, detector efficiency, etc.
- Specimen-dependent: that is a function of phase composition, specimen absorption, particle size, distribution and orientation.

For a given phase, or selection of phases, all structure-dependent terms are fixed, and in this instance have no influence on the quantitative procedure. Provided that the diffractometer terms are constant, this effect can also be ignored. Thus if one calibrates the diffractometer with a sample of the pure phase of interest and then uses the same conditions for the analysis of the same phase in an unknown mixture, only the random errors associated with a given observation of intensity have to be considered. The biggest problem in the quantitative analysis of multiphase mixtures then remains the specimen-dependent terms, and specifically those dependent upon particle size and distribution, plus effects of absorption.

The absorption effect has already been mentioned and clearly, in a multiphase mixture, different phases will absorb the diffracted photons by different amounts. As an example, the mass attenuation coefficient for Cu Kα radiation is 308 ($cm^2\,g^{-1}$) for iron, but only 61 ($cm^2\,g^{-1}$) for silicon. Thus iron atoms are five times more efficient than silicon atoms for absorbing Cu Kα photons. There are a variety of standard procedures for correcting for the absorption problem of which by far the most common is the use of the internal standard. In this method a standard phase is chosen which has about the same mass absorption coefficient as the analyte phase, and a weighed amount of this material is added to the unknown sample. The intensities of a line from the analyte phase and the internal-standard phase are then used to estimate the relative concentrations of internal-standard and analyte phases. The relative sensitivity of the diffractometer for these two phases is determined by a separate experiment.

The handling of particle problems is unfortunately much more complex. As has been previously stated the powder method requires a specimen which is randomly oriented since the geometry of the system requires that an equal number of crystallites be in the correct position (i.e. orientation) to diffract at any diffraction angle where the goniometer happens to be. Where particles lie in a preferred orientation there will be more particles available to diffract at the angle corresponding to this orientation, and, what is equally important, less particles available to diffract at other diffraction angles. The overall effect is to enhance some intensities and to diminish others. In other words, the intensities are now dependent upon particle distribution and orientation. Some materials, just by virtue of their crystal habit, may become preferentially oriented during sample preparation. As an example, mica, being a rather "platy" material, will prefer to stack one plate on top of another rather than take up a random orientation. The overall effect of preferred orientation can vary from insignificance to the extent where errors of the order of tens of percent can accrue in cases where they are not taken care of. Careful specimen preparation is always called for and this may include grinding, sieving, spray-drying, and a host of other techniques. The areas of application of quantitative XRD are many and varied, and hundreds of analysts are using this technique on a daily basis. Some of the more common applications would include ore and mineral analysis, quality control of rutile/anatase mixtures, retained austenite in steels, determination of phases in airborne particulates, various thin-film applications, study of catalysts and analysis of cements. The current state of the art in the quantitative analysis of multiphase materials is that accuracy of the order of a percent or so can be obtained in those cases where the particle orientation effect is either nonexistent, or has been adequately compensated for.

6.6 Limitations of the Diffraction Method

There is little doubt that the diffraction method is without parallel as a general-purpose tool for phase identification but like all analytical techniques it is not without some shortcomings. Two of these are of particular importance. The first of these is related to the chance of misinterpretation during the course of a qualitative analysis procedure. Although, in principle, a diffraction pattern is "unique", in practice there are sufficient similarities between patterns as to cause confusion. This is particularly so in the case of multiphase specimens. In addition to this there are probably in excess of two million possible unique "phases", of which only 120 000 or so are on the ICDD file as single-phase patterns. There is as a result a certain chance of a given phase not being in the file. The second problem relates to the sensitivity of the powder diffraction method. As such, the diffraction method is not comparable in sensitivity (i.e. rate of change of measured signal per change in analyte-phase concentration) to the other X-ray-based techniques. Whereas in X-ray spectrometry one can obtain detection limits in the low parts per million region, the powder method has difficulty in identifying several tenths of one percent. To this extent it is less sensitive than the fluorescence method by about three orders of magnitude.

7 FUTURE TRENDS FOR X-RAY DIFFRACTION AND FLUORESCENCE

7.1 Analysis of Small Specimens and Thin Films

Conventional XRF spectrometers are generally designed to handle rather large specimens with surface areas of the order of several square centimeters, and problems occur where the sample to be analyzed is limited in size. The modern wavelength-dispersive system is especially inflexible in the area of sample handling, mainly because of geometric constraints arising from the need for close coupling of the sample to X-ray tube distance, and the need to use an airlock of some kind to bring the sample into the working vacuum. The sample to be analyzed is typically placed inside a cup of fixed external dimensions that is, in turn, placed in the carousel. This presentation system places constraints not only on the maximum dimensions of the sample cup, but also on the size and shape of samples that can be placed into the cup itself. Primary source energy-dispersive systems do not require the same high degree of focusing, and to this extent are more easily applicable to any sample shape or size,

provided that the specimen will fit into the radiation protected chamber. In some instances the spectrometer can even be brought to the object to be analyzed. Because of this flexibility, the analysis of oddly shaped specimens have been almost exclusively the purview of the energy-dispersive systems. In the case of secondary target energy-dispersive systems, while the geometric constraints are still less severe than the wavelength system, they are much more critical than in the case of primary systems. Where practicable, the best solution for the handling of limited amounts of material is invariable found in one of the specialized spectrometer systems.

One of the major problems that inhibits the obtaining of good detection limits in small samples is the high background due to scatter from the sample substrate support material. The suggestion to overcome this problem by using total reflection of the primary beam was made as long ago as 1971,(27) the technique being referred to as total reflection X-ray fluorescence (TRXRF) spectrometry. Unfortunately the absence of suitable instrumentation prevented real progress being made until the late 1970s.(28,29) The TRXRF method is essentially an energy-dispersive technique in which the Si(Li) detector is placed close to (about 5 mm), and directly above, the sample. Primary radiation enters the sample at a glancing angle of a few seconds of arc. The sample itself is typically presented as a thin film on the optically flat surface of a quartz plate. Here, a beam of radiation from a sealed X-ray tube passes through a fixed aperture onto a pair of reflectors that are placed very close to each other. Scattered radiation passes through the first aperture to impinge on the sample at a very low glancing angle. Because the primary radiation enters the sample at an angle barely less than the critical angle for total reflection, this radiation barely penetrates the substrate media; thus scatter and fluorescence from the substrate are minimal. Because the background is so low, picogram amounts can be measured or concentrations in the range of a few tenths of a ppb can be obtained without recourse to preconcentration.(30) Similar parallel-beam thin-film methods are finding increasing use in powder diffraction.

7.2 Impact of the Synchrotron

The availability of intense, linearly polarized synchrotron radiation beams(31) has prompted workers in the fields of XRF(32) to explore what the source has to offer over more conventional excitation media. An exciting new field developed in the early 1980s called synchrotron source X-ray fluorescence (SSXRF). In the synchrotron, electrons with kinetic energies of the order of several billion electron volts (typically 3 GeV at this time), orbit in a high-vacuum tube between the poles of a strong (about 10 000 Gauss) magnets. A vertical field accelerates the electrons horizontally, causing the emission of synchrotron radiation. Thus synchrotron source radiation can be considered as magnetic bremsstrahlung in contrast to normal electronic bremsstrahlung produced when electrons are decelerated by the electrons of an atom. It has been found that, because the primary source of radiation is so intense, it is possible to use a high degree of monochromatization between source and specimen, giving a source that is wavelength (and, therefore, energy) tunable, as well as being highly monochromatic. There are several different excitation modes that can be used using SSXRF including: direct excitation with continuum, excitation with absorber-modified continuum, excitation with source crystal monochromatized continuum, excitation with source radiation scattered by a mirror, and reflection and transmission modes. The intensity of the synchrotron beam is probably four to five orders of magnitude greater than the conventional bremsstrahlung source sealed X-ray tubes. This, in combination with its energy tunability and polarization in the plane of the synchrotron ring, allows very rapid bulk analyses to be obtained on small areas. Because the synchrotron beam has such a high intensity and small divergence, it is possible to use it as a microprobe of high spatial resolution (about 10 μm). Absolute limits of detection around 10^{-14} pg have been reported using such an arrangement.(33) SSXRF has also been used in combination with TRXRF. Very high signal/background ratios have been obtained employing this arrangement for the analysis of small quantities of aqueous solutions dried on the reflector, with detection limits of <1 ppb or 1 pg. Additional advantages accrue because synchrotron radiation is highly polarized and background due to scatter can be greatly reduced by placing the detector at 90° to the path of the incident beam and in the plane of polarization. A disadvantage of the SSXRF technique is that the source intensity decreases with time, but this can be overcome by bracketing analytical measurements between source standards and/or by continuously monitoring the primary beam.

ABBREVIATIONS AND ACRONYMS

APD	Automated Powder Diffractometer
ICDD	International Centre for Diffraction Data
LLD	Lower Limit of Detection
NRLXRF	Naval Research Laboratory X-ray Fluorescence
PDF	Powder Data File
SSXRF	Synchrotron Source X-ray Fluorescence
TRXRF	Total Reflection X-ray Fluorescence
UV	Ultraviolet
XRD	X-ray Powder Diffractometry
XRF	X-ray Fluorescence

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