X-Ray Fluorescence Analysis

A Review

By F. BROWN

(*Research Department, Imperial Chemical Industries Ltd., Billingham Division, Billingham, Co. Durham*)

When an element is irradiated with X-rays of sufficiently high energy, secondary, or fluorescence, X-rays are emitted that are characteristic of the element. Measurement of the intensity and wavelength of fluorescence radiation is now a well established method of analysis and has been applied to the determination of the elements from sodium (11) to uranium (92) in powder, liquid or metal samples. Coefficients of variation of about 1 per cent. in the concentration range 5 to 100 per cent. and of 5 per cent. in the 0·1 to 1 per cent. range can usually be obtained, and, in favourable instances, determinations at the parts per million level can be made. The method is rapid, independent of the chemical combination of the element and non-destructive in the sense that the specimen examined is not destroyed, although some specimen preparation may be necessary.

X-RAY SPECTRA

THE origin and general characteristics of X-ray spectra are well known; the features of particular importance to X-ray spectrometry may be summarised as follows.

When a stream of electrons is stopped by the target of an X-ray tube, part of the primary X-radiation emitted is in the form of a continuous spectrum covering a broad wavelength range (see Fig. 1).[1]   The kinetic energy of the incident electrons is dissipated by successive collisions with the atoms of the target material and part of the energy lost in each collision is re-emitted as an X-ray photon of definite frequency.
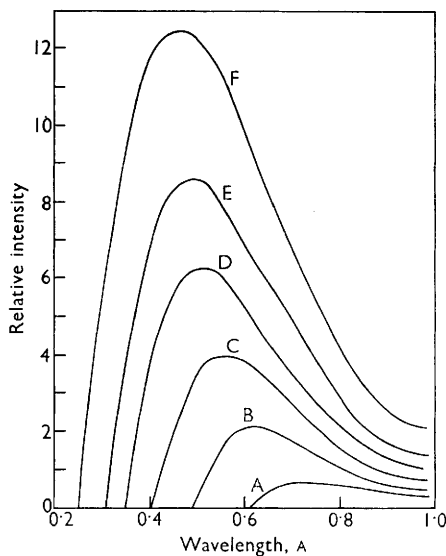

Fig. 1.   Variation in the spectral distribution of tungsten continuous radiation with tube voltage[1]: curve A, 20 kV; curve B, 25 kV; curve C, 30 kV; curve D, 35 kV; curve E, 40 kV; curve F, 50 kV

The continuum terminates abruptly on the short-wavelength side and this limiting radiation is emitted when an electron loses all its energy in a single collision.   The wavelength of

the spectral limit is related to the accelerating voltage applied to the X-ray tube, which limits the kinetic energy of the electrons, by the equation—

$$Ve = \frac{hc}{\lambda_{min.}} \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad (1)$$

where V is the X-ray tube voltage, e is the charge on the electron, h is Planck's constant, c is the velocity of light and $\lambda_{min.}$ is the wavelength of the spectral limit.

An increase in tube voltage results in an increase in the total energy emitted and a movement of the spectral distribution towards shorter wavelengths; the total energy emitted also increases with increasing atomic number of the target material.

The primary characteristic spectrum is made up of radiations, or lines, that have discrete wavelengths and is obtained in addition to, and superimposed on, the continuum when the incident electrons have sufficient energy to eject an electron from one of the inner shells of a target atom.   The resulting ionised atom regains stability by successive electron transitions from states of higher to lower energy, and the energy released by each transition appears as a spectral line having a frequency dependent on the difference in energy of the electron in the initial and final states.

K-series lines are obtained when a K electron is ejected and arise by electron transitions from outer shells to the K shell.   The L electrons are grouped according to their binding energy into three sub-shells, L_I, L_{II} and L_{III}, and each sub-shell has an associated spectral series.   The complete M spectrum is made up of five series corresponding to the five sub-shells.

The relative simplicity of characteristic X-ray spectra is explained by the limited number of energy levels in the atom, together with certain prohibited transitions.   From Fig. 2,[2] which shows the permitted transitions between energy levels in a uranium atom, it is evident that the complexity of a complete spectral series depends on the number of energy levels in the main shell and therefore increases in the order $K \rightarrow L \rightarrow M$.   As the atomic number decreases, the outer shells successively disappear and the characteristic X-ray spectrum becomes simpler.

The frequency, ν, of a spectral line belonging to a particular series varies regularly with atomic number, Z.   This relationship is expressed by Moseley's law—

$$\nu^{\frac{1}{2}} = K(Z - \sigma) \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad (2)$$

where K is a proportionality constant and σ is another constant, the value of which depends on the series.

The characteristic X-ray spectrum of an element can also be excited by X-rays if this primary X-radiation is sufficiently energetic to ionise an inner shell.   The energy needed to eject an electron completely from the atom is greater than that liberated as secondary X-radiation by an electron transition from the outermost shell to the ionised shell.   Since this transition gives rise to the line of highest frequency in the series, it follows that all the emitted lines will be of lower frequency, or longer wavelength, than that of the absorbed radiation. The phenomenon is therefore termed fluorescence.

If the wavelength of X-radiation incident on an element is gradually decreased, the X-ray photons become progressively more energetic until, at a certain wavelength, they are able to ionise one of the inner shells and produce the characteristic lines of a spectral series.   At this critical wavelength there is a sharp rise (the absorption edge) in the absorption of X-radiation by the element.   There is one absorption edge associated with each energy level, and, as the wavelength of the incident radiation is decreased, there is successive ionisation of the M_V to M_I, L_{III}, L_{II}, L_I and, finally, the K shell, with the appearance of lines of the corresponding spectral series (see Fig. 3).[3]   The wavelengths of some spectral lines and absorption edges of several elements are shown in Table I.[4]

A spectral series will be excited by primary continuous radiation only when the wavelength limit, $\lambda_{min.}$, equation (1), is shorter than the absorption edge of the series.   Since $\lambda_{min.}$ depends on the voltage applied to the X-ray tube, there is a critical excitation potential below which the lines of a spectral series will not be excited by primary radiation.   This critical value can be calculated for any series by substituting the appropriate absorption-edge wavelength for $\lambda_{min.}$ in equation (1).

The critical excitation potential for any given series increases progressively with atomic number.   The K-series lines of sodium (11) and uranium (92) appear at critical potentials of 1·07 and 115 kV, respectively; uranium L lines appear at 21·7 kV.   X-ray tubes currently

available have a maximum rating of 50 or 60 kV and are therefore unable to excite the K spectra of elements of high atomic number.   The K spectra are generally used for elements up to about barium (56) and the L spectra from lanthanum (57) to uranium (92).
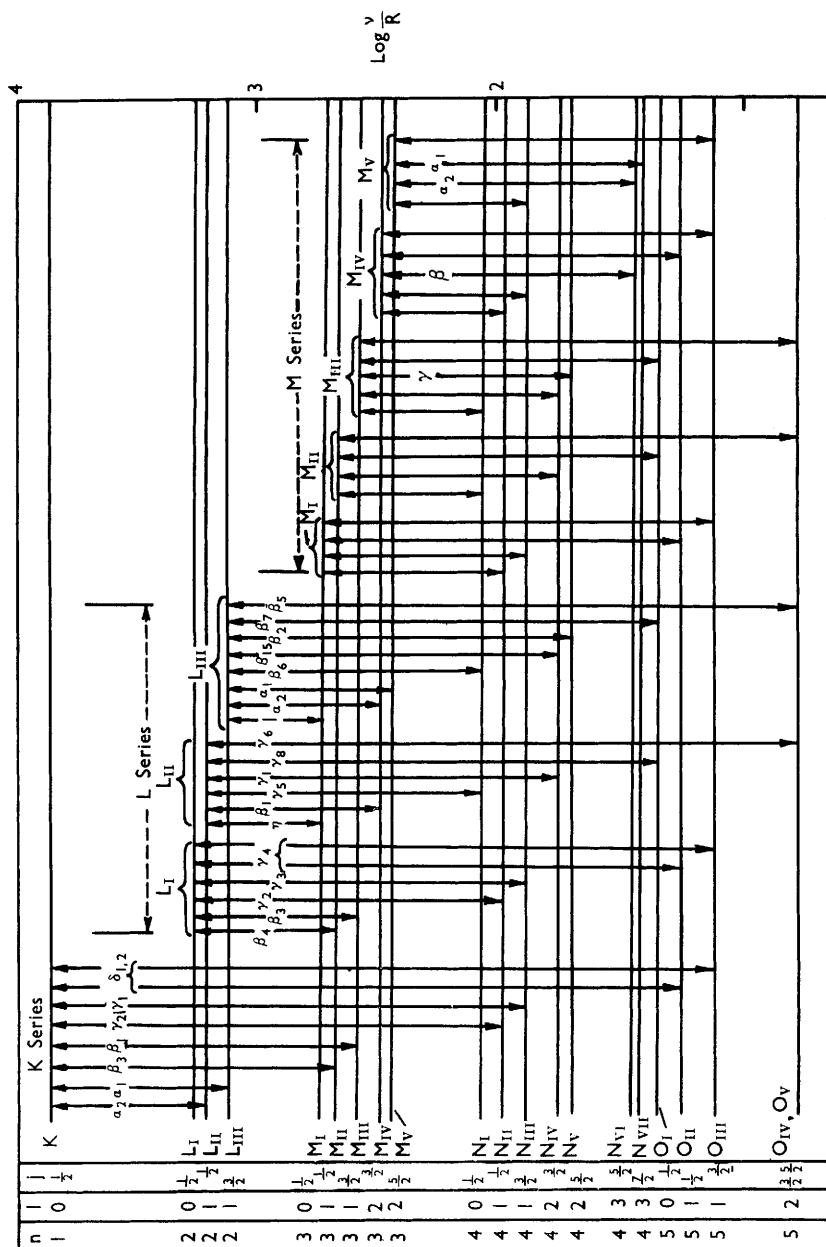

Fig. 2.   X-ray energy level diagram for uranium-92, showing the transitions permitted by the selection rules $\Delta l = \pm 1$; $\Delta j = \pm 1, 0$

DEVELOPMENT OF X-RAY SPECTROMETRY

In 1908, Barkla and Sadler[5] showed that secondary X-rays, which had a constant co-efficient of absorption and were therefore termed "homogeneous," were emitted when an element was bombarded with a beam of primary X-rays.

Friedrich, Knipping and Laue[6] demonstrated that a crystal could act as a grating for the diffraction of X-rays, and W. L. Bragg[7] suggested that such diffraction could be regarded as a

reflection of the electromagnetic radiation from well populated layers of atoms in the crystal. W. H. Bragg used the cleavage face of a rock salt crystal to reflect X-rays emitted from the platinum target of an X-ray tube. The crystal was placed on the prism table of a spectrometer and the radiation was detected by using an ionisation chamber mounted on the spectrometer arm. By rotating the crystal, in order to vary the angle of incidence, at half the angular speed of the ionisation chamber, he was able to obtain the first X-ray spectrum. Further work on the reflection of radiation from crystal planes led to Bragg's law—

$$n\lambda = 2d \sin \theta \quad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (3)$$

which relates the wavelength of the reflected radiation, λ, the angle of incidence, θ, on atomic planes of interplanar spacing d, and the order of reflection, n. Reflection will occur only when equation (3) is satisfied, so a heterogeneous beam of X-rays can be analysed by measuring the angles at which there is reflection from atomic layers of known interplanar spacing.

TABLE I

WAVELENGTHS OF SOME SPECTRAL LINES AND ABSORPTION EDGES OF CERTAIN ELEMENTS

These wavelengths have been taken from Compton and Allison's Tables[4] and converted from kXU to A by using the factor 1·00202

		K series				L series				
Element	Atomic number	α_1, A	α_2, A	β_1, A	$\lambda_{abs.}$, A	α_1, A	α_2, A	β_1, A	γ_1, A	$\lambda_{abs.}(L_{III})$ A
Magnesium ..	12	9·889		9·558	9·515	—	—	—	—	—
Sulphur ..	16	5·372	5·375	5·031	5·019	—	—	—	—	—
Titanium ..	22	2·749	2·752	2·514	2·496	—	—	—	—	—
Copper ..	29	1·541	1·544	1·392	1·380	—	—	—	—	—
Niobium ..	41	0·746	0·750	0·666	0·653	5·724	5·730	5·491	5·035	5·223
Iodine ..	53	0·433	0·438	0·384	0·374	3·148	3·157	2·937	2·583	2·719
Tungsten ..	74	0·209	0·214	0·184	0·179	1·476	1·487	1·282	1·099	1·214
Uranium ..	92	0·127	0·131	0·112	0·107	0·911	0·922	0·720	0·615	0·722

The next stage in the development of X-ray spectrometry was due to Moseley,[8] who investigated the spectra emitted by several elements that, in turn, were used as the target of an X-ray tube. The radiation was dispersed by using a crystal of potassium ferrocyanide and was recorded on a photographic plate. The relationship he found between the frequency of a spectral line of a particular series and the atomic number of the element was referred to in the previous section, equation (2).

The potentialities of X-ray emission spectrometry as an analytical method were evident from Moseley's work, and X-ray spectra were later used to identify the elements masurium (43), illinium (61), hafnium (72) and rhenium (75).

In order to use primary X-ray spectra for analysis, the specimen must be plated or smeared on to the target of the X-ray tube. This has several disadvantages: the tube must be re-evacuated when the specimen is changed; the heating effect of the electron stream may cause chemical reaction, selective volatilisation or melting; when photographic recording is used, weak lines may be difficult to detect because of the blackening effect of the continuous radiation. However, in spite of these drawbacks the technique did achieve some success[9 to 14] and is still used to-day.

Analysis by using fluorescence spectra avoids these difficulties because the specimen is placed outside the X-ray tube and no secondary continuum is obtained. The disadvantage is that fluorescence lines are much weaker than primary lines, and, since photographic recording was almost universally used in the early days, long exposures were often necessary. von Hevesy and his co-workers[15] first used fluorescence spectra for analysis, and other successful applications[14,16,17] have been reported.

The widespread application of X-ray fluorescence analysis is the direct result of improvements in X-ray tubes and the development of counter tubes as detectors. It has been found particularly useful in routine analysis and for determining closely related elements, for example, the rare earths, the noble metals, niobium and tantalum, and hafnium and zirconium, when other methods of analysis are difficult or time-consuming.

GENERAL PRINCIPLES

The following description of a plane-crystal spectrograph, which is most generally used for analysis, is based on the instrument made by Philips Electrical Ltd., The Netherlands, and shown in Fig. 4.
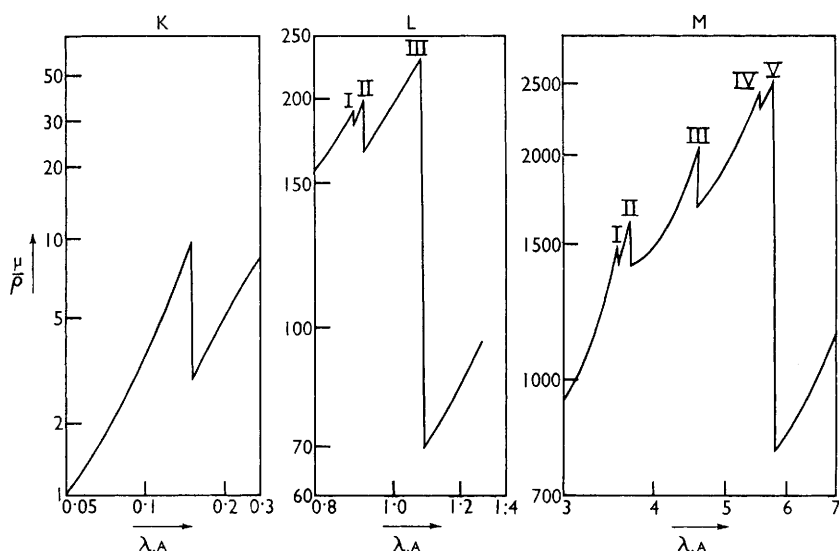

Fig. 3.   Variation in the mass absorption coefficient (μ/ρ) with wavelength (λ) in the regions of the K, L and M absorption edges[3]
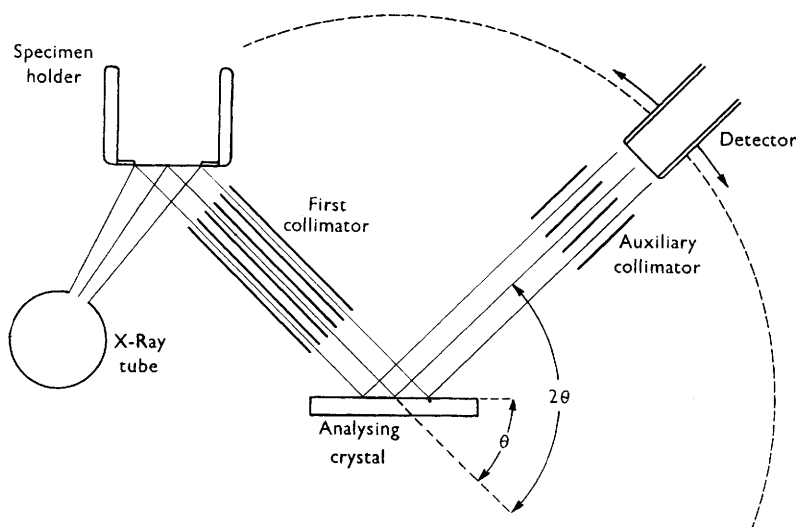

Fig. 5.   Diagrammatic arrangement of the plane-crystal X-ray spectrograph

The arrangement for exciting, dispersing and detecting fluorescence radiation is shown diagrammatically in Fig. 5.   The specimen in the specimen holder is irradiated from below with an unfiltered beam of primary X-rays, which causes the elements present to emit their characteristic fluorescence lines.   Part of the fluorescence beam is collimated by a Soller slit system and directed on to the plane surface of the analysing crystal.   The line radiations are reflected according to Bragg's law and pass through an auxiliary collimator to the detector, where the energy of the X-ray photons is converted into electrical impulses, or "counts." The impulses are then amplified and fed to an electronic counting panel, where they may be
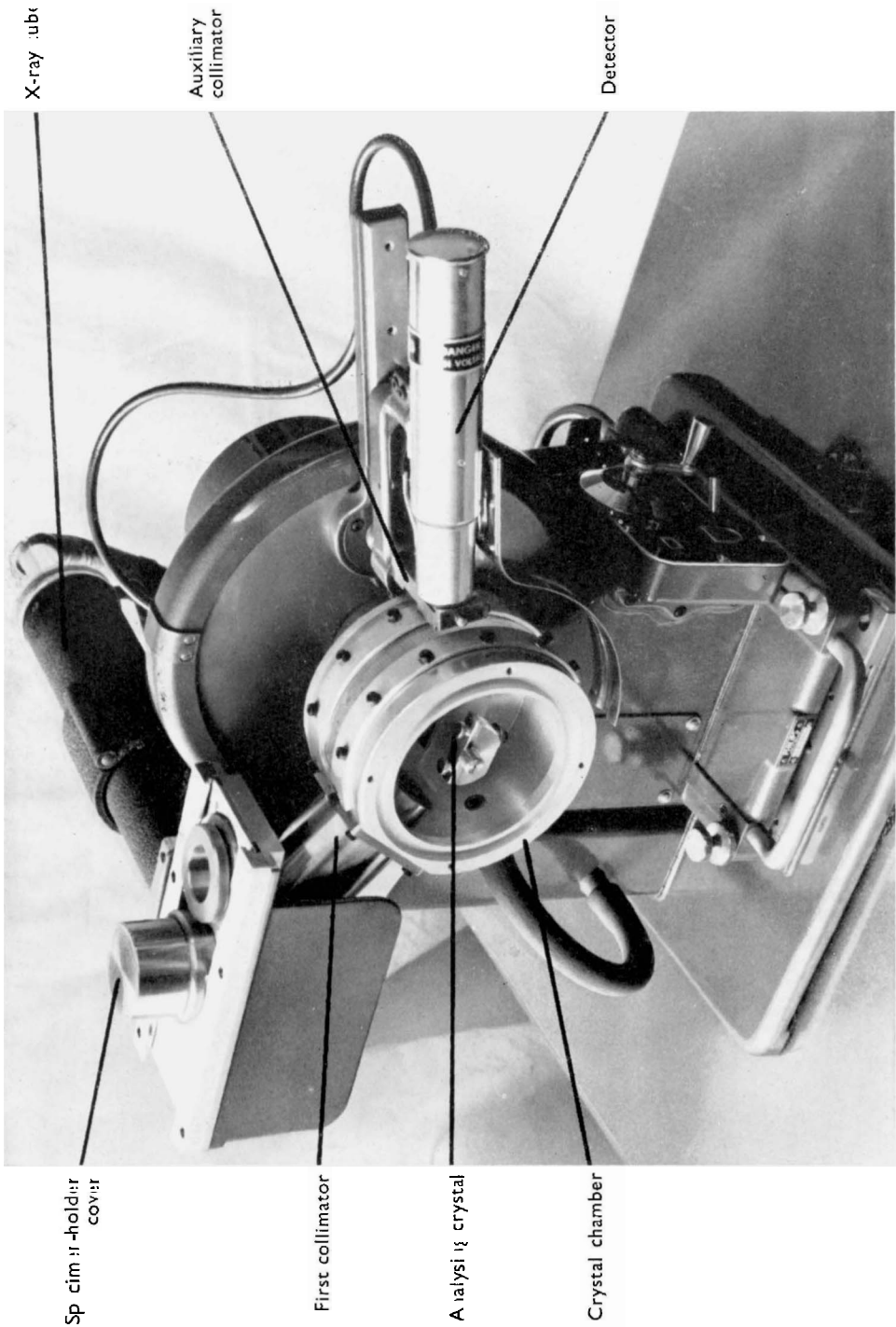
X-ray tube

Auxiliary collimator

Detector

Specimen-holder cover

First collimator

Analysis crystal

Crystal chamber

Fig. 4. Philips X-ray fluorescence spectrograph
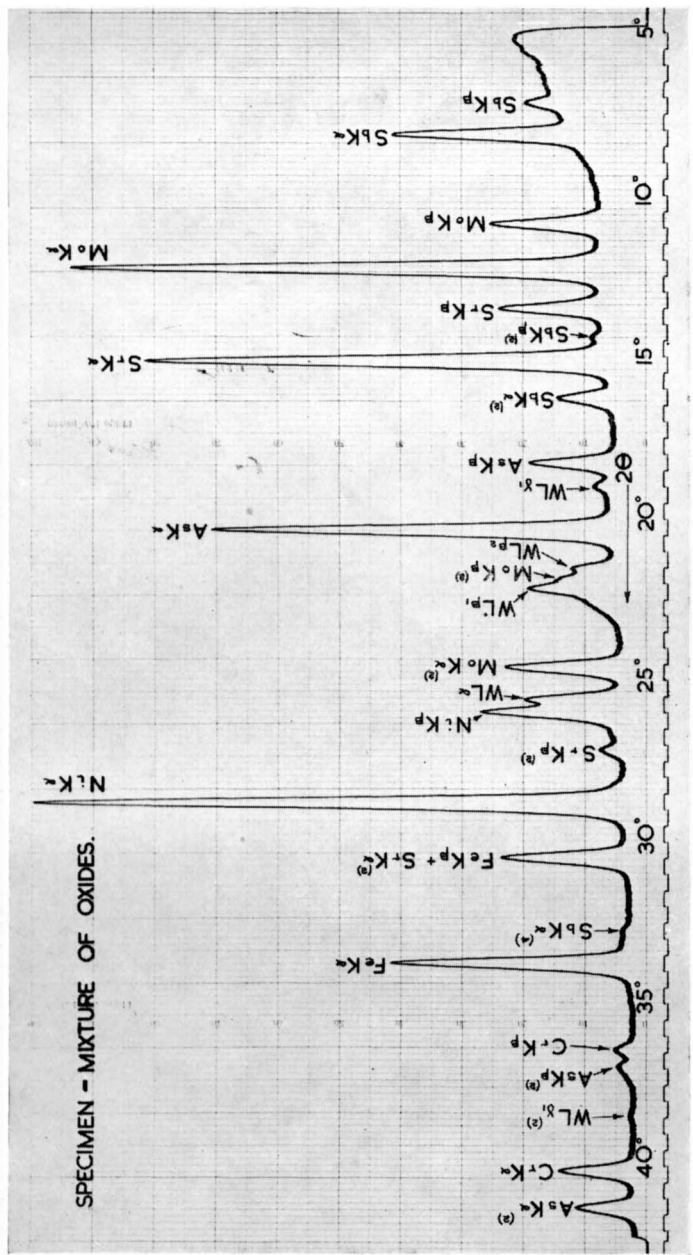
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Fig. 6, Spectral scan of specimen containing 1 per cent. each of antimony, molybdenum, strontium, arsenic, nickel, iron and chromium, as oxides, in a silica matrix. **Higher order reflections are shown by superscripts.** Conditions: tungsten tube; 50kV; 20 mA; quartz crystal; scintillation counter at 950 volts; scan speed 1° (2θ) per minute

either integrated in a rate meter and recorded on a strip chart or else scaled down to units that can be visually observed on decatron scalers.

Intensity losses caused by absorption of the longer wavelength, or soft, X-rays by air can be reduced by evacuating the crystal chamber shown in Fig. 4.   Absorption by air can be completely avoided by using a vacuum spectrograph, which permits the evacuation of the entire radiation path.   Alternatively, the radiation path can be enclosed in a rubber bag and the air displaced by helium, which has a low absorption for soft X-rays.[18]   Because of the shortage of helium, vacuum spectrographs are used in Europe for investigating radiation of longer wavelength (3 to 11 A).

Focusing spectrographs that involve reflection from[19] and transmission through[20] a curved crystal have been described.   Collimators are not required and the increase in intensity obtained by focusing the fluorescence lines makes the technique suitable for the analysis of small specimens ($\sim$1 mg).   Plane and curved crystal arrangements have been described by Birks, Brooks and Friedman.[21]

For qualitative analysis it is usual to make a chart record.   The angle, θ, between the plane surface of the crystal and the incident fluorescence beam is gradually increased, and at certain well-defined angles the appropriate fluorescence lines are reflected.   The detector and crystal are rotated, either manually or automatically, at angular speeds in the ratio 2 to 1 and the variation in the detected intensity is recorded on a moving chart as a series of peaks, corresponding to fluorescence lines, above a background, principally due to general scattering of the primary radiation by the specimen, as shown in Fig. 6.   The angular position of the detector, in degrees of 2θ, is also recorded on the chart, so that a peak can be identified from the angle at which it appears.   Tables have been published[22] listing characteristic lines, wavelengths and values of 2θ for use with various analysing crystals.   Additional evidence for identification may be obtained from relative peak heights and by determining the voltage at which the peak appears, *i.e.*, the critical excitation potential.

For quantitative analysis it is necessary to measure the intensity of a characteristic line of the element.   This can be done either by collecting counts for a certain period of time (fixed-time method) or by measuring the time necessary to collect a pre-set number of counts (fixed-count method).[23]   It is usual to measure intensities at the peak angle and at a suitable background position close to the peak, and the net line intensity (peak *minus* background), in counts per second, is then related to the concentration of the element.

EQUIPMENT

X-RAY TUBES—

X-ray tubes are usually of the sealed-off type having tungsten, molybdenum or gold targets.   They have power ratings of from 1 to 3 kW and operate with half- or full-wave rectification.   With Philips equipment, constant intensity of primary radiation is achieved by high stabilisation of the tube current and voltage.   The focus of the electron beam and the viewing angle are such that the primary beam is projected on to an area of about 500 sq. mm on the surface of the specimen.   The tube window is of thin ($\sim$1 mm) beryllium, which will transmit X-rays of wavelength up to 3 to 4 A.[3]

It has been stated previously that the excited secondary radiation does not include a continuous spectrum, but the primary continuum is scattered by the specimen and is chiefly responsible for the background radiation.   Characteristic primary radiation from the target material, and from any impurities present in the target, is also scattered and will be recorded, so it would be unwise to choose, for example, a tungsten tube for the determination of tungsten in a specimen.   The spectral purity of the primary beam can be investigated by scanning the complete spectral range, carbon or sugar, which give no recorded fluorescence lines, being used as a specimen.

SPECIMEN HOLDER—

The Philips specimen holder is an aluminium cylinder 32 mm in diameter and 29 mm deep. The specimen is supported by a thin film of Mylar, and an aluminium mask restricts the area of specimen illuminated to a rectangle 18 mm $\times$ 27 mm.   Specimen holders made from plastic material are available for the examination of acid or alkaline solutions.

COLLIMATORS—

The fluorescence radiation is collimated either by a series of narrowly spaced metal plates or a bundle of tubes. The angular divergence of the rays that reach the crystal is limited by the first collimator (see Fig. 5). The auxiliary collimator is coarser and is particularly useful at very low values of θ for preventing radiation that has not been reflected by the crystal from reaching the detector.

The width of a spectral line depends on the degree of collimation. Increased resolution can be obtained by decreasing the separation of the metal plates or by increasing the length of a collimator, but this is achieved at the expense of intensity. The effects of various collimating systems on line intensities, line profiles and line-to-background intensity ratios have been investigated by Campbell, Leon and Thatcher.[24]

ANALYSING CRYSTALS—

According to Bragg's law, there is a theoretical upper limit of 2d for the wavelength that can be reflected from a crystal of interplanar spacing d, and this limiting radiation will be reflected when 2θ is 180°. This angle is beyond the range of X-ray spectrographs, and, in addition, the intensity of reflected radiation decreases rapidly with increasing angle, so it is usual to select a crystal having an interplanar spacing such that the desired radiation is reflected in the angular (2θ) range 10° to 100°. The interplanar spacing of the crystal also determines the degree of dispersion of the spectral lines; for maximum dispersion, the crystal having the least spacing should be used.

The crystal should be large enough to accept at small angles all the radiation transmitted by the first collimator and must emit no fluorescence lines of its own that would overlap the spectral lines of interest.

Some examples of the crystals used as analysers are shown in Table II.

TABLE II

TYPICAL ANALYSING CRYSTALS

Crystal	Reflecting plane	Interplanar spacing (d), A
Topaz	303	1·356
Lithium fluoride	200	2·014
Sodium chloride	200	2·821
Calcium fluoride	111	3·16
Quartz	10$\bar{1}$1	3·343
Ethylenediamine D- tartrate	—	4·404
Ammonium dihydrogen orthophosphate	—	5·325
Gypsum	020	7·60
Mica	002	9·963

DETECTORS—

Geiger, proportional and scintillation counters[25 to 29] have replaced photographic film for the detection of fluorescence X-radiation. The spectral sensitivity of each type varies with wavelength, as shown in Fig. 7,[30] and the choice of a detector is governed primarily by the radiation to be detected.

The Geiger counter[31] is widely used for detecting radiation in the range 0·7 to 3 A, and, since it is relatively insensitive to scattered hard radiation, the background intensity is low. Its principal disadvantage is the long time needed for the counter to recover after a discharge has occurred (dead time). During this time, 200 to 300 microseconds, the counter is inactive and at moderately high intensities there are serious counting losses. A Geiger counter is not normally used for measuring intensities in excess of 1000 counts per second.

Proportional[32,33] and scintillation[34] counters have a short dead time ($\sim$0·2 microseconds), so that the response to X-ray photons is linear up to extremely high count rates. In addition, the amplitude of a pulse delivered by these counters is proportional to the energy, and therefore inversely proportional to the wavelength, of the absorbed X-ray photon, so it is possible to discriminate electronically against unwanted radiations. An important advantage of the scintillation counter is its high sensitivity over the range 0·3 to 2·5 A, but it is not used for detecting radiation softer than Ti Kα because the signal is then indistinguishable from detector noise.

A gas-flow proportional counter[18] is used with vacuum or helium-filled spectrographs for detecting soft X-radiation (3 to 11 A). The mixture of gases, usually 90 per cent. of argon and 10 per cent. of methane, flows continuously through the tube, so that a leak-proof window is not necessary. In consequence, the window can be made extremely thin and high transmittance for long wavelengths is obtained.
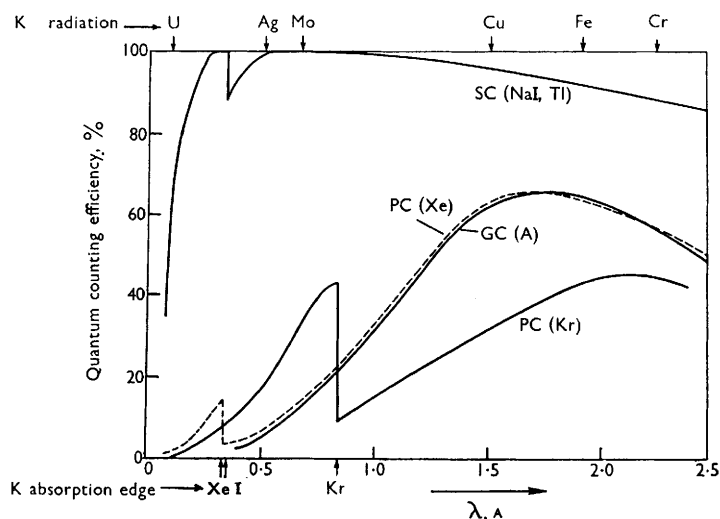

Fig. 7. Variation in calculated quantum counting efficiency with wavelength (λ) for typical scintillation (SC), krypton- or xenon-filled proportional (PC) and argon-filled Geiger (GC) counters[30]

QUANTITATIVE ANALYSIS

SPECIMEN PREPARATION—

The specimens examined are often the actual samples received for analysis, but some specimen preparation is occasionally necessary.

The effects due to differences in the sizes of the particles must be considered when powders are examined, because the absorption of fluorescence radiation increases with grain size. Methods for avoiding particle-size problems include (*i*) grinding the sample, either alone[35] or with an added abrasive, such as silicon carbide,[36,37] until the effect of particle-size differences is negligible, (*ii*) mixing the sample with a binder and pressing into briquette form,[38,39] and (*iii*) dissolving the sample in fused borax and casting the melt as a glass disc.[40]

Bulk metal samples must be of a size such that they will fit the specimen holder and should present a flat surface to the primary beam. Koh and Caugherty[41] found that surface finish, grain size and residual stresses do not greatly affect the intensity of characteristic radiation from alloys. If metallic samples are received as millings, drillings, filings or wire, it is necessary either to use the acid solution as a specimen or to evaporate the solution to dryness and examine the powder.[39]

The use of solutions as specimens[42,43,44,45] is particularly suitable for many internal-standard and addition methods of analysis. The heating effect of the X-ray beam may result in concentration errors, owing to expansion or vaporisation of the liquid, but such errors are usually small because of the short irradiation time.

The amount of specimen used is not important provided that the area defined by the aluminium mask is completely covered and a certain critical depth of penetration by X-rays is exceeded. (In some instances, *e.g.*, the determination of silver and bromine on photographic film, the critical depth is not exceeded.) This depth is about 0·03 mm for nickel, iron and chromium,[41] 0·25 mm for minerals[46] and several millimetres for liquid specimens.

EXCITATION—

A spectral series will be most effectively excited by radiation that has a wavelength coincident with the absorption edge of the series. When several elements in a specimen have

to be excited, it is impracticable to use a different monochromatic radiation of the ideal wavelength for exciting each element, so it is necessary to use the primary continuous radiation. The primary characteristic radiation will make an appreciable contribution to the excitation when a strong primary line has a wavelength just shorter than the absorption edge of the series.   Since the total energy emitted as primary radiation increases with the atomic number of the target material, it would be expected that radiation from a tungsten target would be more effective than that from a molybdenum target for exciting X-ray spectra.   Campbell, Carl and White[47] have found that primary radiation from tungsten is more generally useful but, for exciting the elements from germanium (32) to yttrium (39), a molybdenum tube is preferable because of the contribution of the molybdenum characteristic spectrum.

The optimum excitation voltage depends on the absorption edge of the series to be excited.   As the tube voltage increases, there is an increase in the intensity of the primary continuous spectrum and a decrease in the wavelength of the radiation having the maximum intensity (see Fig. 1).   The most effective component of the continuum for exciting a spectral series is that just on the short-wavelength side of the absorption edge, so for exciting short-wavelength spectra it is evident that the tube should be operated at its maximum voltage. For fluorescence radiation of longer wavelength, a voltage setting below maximum is better, because the most effective component is now in the long-wavelength region, where an increase in tube voltage results in a small increase in intensity relative to the integrated intensity of the continuum.   At higher voltages, therefore, the background intensity due to general scattering of the continuum will increase more rapidly than the intensity of the fluorescence line and the resulting decrease in the ratio of peak to background gives a lower sensitivity.[3] The optimum tube voltages for exciting the K spectra of iron and molybdenum are 35 and 60 kV, respectively.[29]

ABSORPTION EFFECTS—

Ideally, the intensity of a line would be independent of the matrix and would increase linearly with concentration over the range 0 to 100 per cent.   It would then be possible to determine the concentration of an element in any sample by using only the pure element as a standard.   Deviations from linearity are due to absorption of X-radiation, both primary and fluorescence, by the elements present in the sample.[48]

The absorption coefficient for X-radiation increases between absorption edges as approximately the fourth power of the atomic number,[4] so the composition of the specimen will influence the depth of penetration of the primary beam and therefore the number of atoms of the element being determined that will be excited.   The measured fluorescence radiation is affected by specimen composition in the same way.

The second type of absorption effect depends on the relative position of characteristic lines and edges.   For example, Fe Kα radiation ($\lambda = 1\cdot932$ A) is strongly absorbed by chromium ($\lambda_{abs.} = 2\cdot066$ A); Ni Kα radiation ($\lambda = 1\cdot655$ A) is strongly absorbed by and therefore excites iron ($\lambda_{abs.} = 1\cdot739$ A).   Thus, if iron is to be determined in a specimen containing iron, nickel and chromium, the intensity of Fe Kα radiation will depend not only on the iron content but also on the amounts of nickel and chromium present.[41]

METHODS OF QUANTITATIVE ANALYSIS—

For quantitative analysis it is necessary to obtain a relationship between line intensity and concentration of the element to be determined.

The simplest method is to prepare a calibration curve showing the variation in line intensity with concentration by using chemically analysed samples.   The curve will be linear only if the absorption effects described in the previous section are negligible, and any deviations from linearity may be minimised by using standards that are closely similar in composition.[49]   This method is particularly well suited to the analysis of routine samples, in which the concentration of each element is restricted to a fairly narrow range.

In the addition technique, the intensity of the analytical line is measured before and after the addition of a known amount of the element.[47]   The method is best suited to the determination of concentrations of less than 5 per cent. of an element, because it is necessary to assume a linear relationship between line intensity and concentration.

The internal-standard method, which has been widely used to avoid absorption problems,[50,51,52] involves the addition to the sample of a known amount of a reference element that will give a characteristic line close to the analytical line and is affected in the same way

by disturbances due to absorption.   Standards are used to determine the variation in the ratio of the analytical and reference-line intensities with concentration, and the calibration may be used to determine the element in variable matrices.   The choice of a reference element depends on the relative positions of the characteristic lines and absorption edges of the element to be determined, the reference element and the disturbing elements responsible for absorption effects.[37,53]   Preferential absorption of a line would occur if a disturbing element had an absorption edge between the comparison lines; one line would be preferentially enhanced by a strong disturbing line between the absorption edges of the comparison elements.   These circumstances must be avoided by choosing an appropriate reference element.

Matrix dilution will also avoid serious absorption effects.   The samples are heavily diluted with a material having a low absorption, so that the resulting specimens have about the same absorption for X-rays.   The concentration, and therefore the effect, of the disturbing elements is reduced, and although the intensity of the measured radiation is also reduced, a linear calibration graph can be obtained.   Gunn[54] used a $(1 + 1)$ mixture of lithium carbonate and corn starch as a diluent; the method of fusing the samples with borax and casting the melt as a glass disc has already been mentioned.[40]

Arithmetical correction factors have been used to overcome absorption problems.[55] These factors are calculated from a family of curves showing the variation of intensity with concentration of the element to be determined, each curve representing a different amount of the disturbing element.   Sherman[56] derived a set of equations relating intensity to concentration by using parameters obtained from the examination of standards, and Noakes[57] has described an absolute method for the analysis of multi-component alloys.

APPLICATIONS

Comprehensive bibliographies of the analytical applications of X-ray fluorescence spectrometry have been published by Mack[58] and Liebhafsky and Winslow.[59]   The following examples will illustrate the rapidity, versatility and precision of the technique.

The analysis of high-temperature alloys[49,60] and the investigation of oxidation and diffusion processes in metallic systems[41] have been described.   Molybdenum (0·7 to 5·8 per cent.) and ruthenium (0·5 to 4·6 per cent.) in uranium have been determined with average absolute errors of 0·03 and 0·05 per cent., respectively.[61]   Silverman, Houk and Moudy[62] obtained a coefficient of variation of 0·5 to 1·0 per cent. for the determination of 15 to 25 per cent. of uranium dioxide in stainless steel by using strontium as internal standard.   The counting time was about 12 minutes, and large amounts of iron, chromium and nickel were without effect on the result.

Methods for the analysis of various types of mineral have been discussed by Carl and Campbell.[46]   The determination of thorium in ores and rocks by using thallium[63] or selenium[36] as internal standard has been described, and Gulbransen[64] has determined barium in barite ores to within 0·5 per cent. of the result obtained by wet chemical methods.   After a calibration curve has been prepared and the sample ground, a determination can be made in 3 minutes.   The analysis of amphibolite rocks has been investigated by Chodos, Branco and Engel,[35] whose preliminary results indicate that iron, calcium, titanium, potassium, manganese, silicon, aluminium and magnesium can be determined with a relative error of 2 to 3 per cent. in 2 hours.   Methods for the determination of niobium and tantalum in ores,[46,51,52] yttrium. thorium and the rare-earth elements in bastnaesite ore[65] and yttrium in rare-earth mixtures[66] have been reported.

Marine sediments have been analysed for barium and titanium (0·01 to 2·0 per cent.) and zinc (0·004 to 0·6 per cent.),[67] and Campbell, Carl and White[47] have compared methods of X-ray fluorescence analysis for determining germanium in coal and coal ash.   By a preliminary chemical extraction of the germanium, concentrations above 0·001 per cent. could be determined to within 10 per cent. of the amount present.   Clark and Terford[68] have found that X-ray analysis is far more reliable than chemical analysis for determining 1 to 20 per cent. of iron in dust samples.   I have used a Geiger-counter spectrograph for determining strontium, as parts per million and parts per ten thousand, in samples of sodium chloride and limestone, respectively.   MacNevin and Hakkila[69] have described a method for the determination of palladium, platinum, rhodium and iridium, in which filter-paper impregnated with a solution of the elements is used as a specimen.

Other applications that have been described include the determination of lead[42,70] and bromine[42] in petrol, bromine in liquid hydrocarbons,[50] uranium in aqueous solutions,[43,71]

barium, calcium and zinc in lubricating oils,[44] vanadium and nickel in residual fuels and charging stocks[72] and potassium in potash concentrates and tailings.[73]

I have found that the X-ray technique greatly facilitates the routine analysis of a wide variety of catalysts, the analysis time often being a matter of minutes.   Absorption effects have been avoided by matrix dilution with borax.   Dyroff and Skiba[74] have reported the determination of iron, nickel and vanadium on cracking catalysts in an analysis time of 15 minutes, and Gunn[75] has determined platinum (0·05 to 1 per cent.) on re-forming catalyst with a standard deviation of $\pm 0·006$ per cent. of platinum at the 0·6-per cent. level.

The method has been used for the measurement of the plating thickness of metals,[76] and Rhodin[77] analysed thin ($\sim$100 A) films of iron, nickel, chromium and stainless steels prepared on a Mylar support by evaporation *in vacuo.*

FUTURE DEVELOPMENTS

Major developments in instrumentation to extend the range of elements that can be determined to those below sodium (11) do not appear to be imminent.   Improvements in X-ray tubes and detectors will increase the rapidity and precision of analyses, and automatic instruments, which are used in the U.S.A. for process control, are now being developed in Europe.   It seems certain that applications of the technique to routine and non-routine analytical problems will be extended and that X-ray fluorescence spectrometry will continue to grow in popularity and importance.

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