Lecture No. 3

X-RAY FLUORESCENCE SPECTROMETRY
FOR MINERALS & METALS

by

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X-RAY FLUORESCENCE SPECTROMETRY
IN METALS AND MINERALS ANALYSIS

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During the last more than two decades, applications and uses of X-ray Emission Spectroscopy have multiplied many times. As because of the facts that the chemical methods require several hours and optical emission technique do not normally yield results of high absolute precision at high concentrations; the technique of X-ray fluorescence has, therefore, gained general acceptance. It has furnished the analyst a tool, which is capable of performing chemical analysis rapidly and non-destructively. X-ray fluorescence spectroscopy is more or less the X-ray emission spectroscopy.

When the target of an X-ray tube is struck by electrons these are retarded by the atoms of the target material and lose their energy in either of the two processes. Those that knock electrons out of the target atoms generate the characteristic line spectrum of the target element, while those that lose their energy by deceleration due to the interaction between the impinging electron and those of the target element, generates the continum of white radiation (Fig.1). The continuous broad band have a distribution that depends primarily on the voltage applied to the tube and a few sharp, intense characteristic lines whose wavelength depend on the target element.
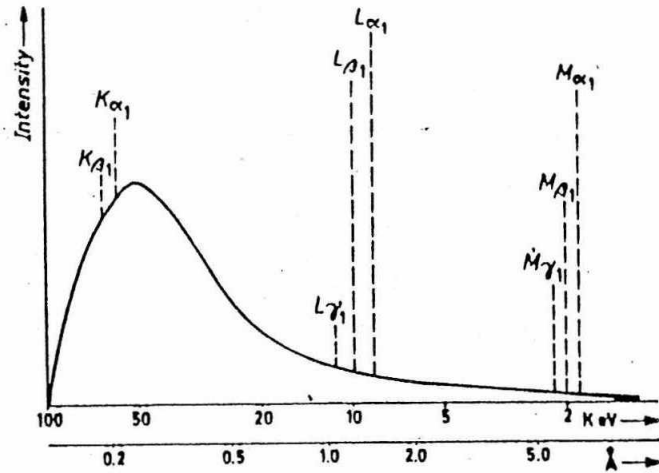
Fig. 1

The production of characteristic radiation arise from the energy transferences involved in the rearrangement of orbital electrons of the target element following ejection of one or more electrons in the excitation process (Fig.2). If the electron from the K-shell is ejected (i.e removed to infinity as far as that atom is involved, which may simply mean promotion to a conduction band). The atom becomes unstable due to the presence of a 'positive hole' in the K-shell. The stability of the atom can,
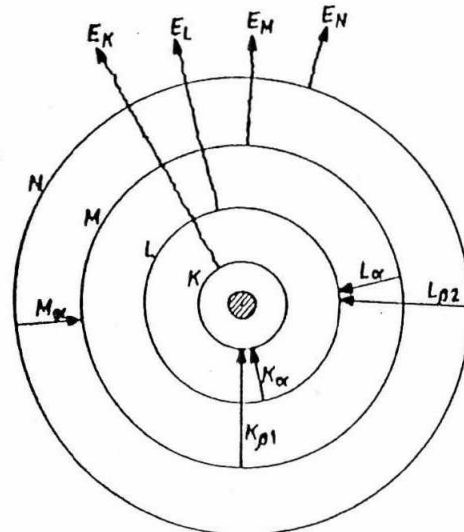

Fig.2

however, be regained by single or multiple transitions from outer orbitals, since in general, the potential instability due to the ionisation of an atom decreases in the order $K^+ > L^+ > M^+ > N^+$, etc. Each time an electron is transferred, the atom moves to a less energetic state and radiation is emitted at a wavelength corresponding to the difference in the energy between the initial and final states

of the transferred electron. The energy of the transferred electron will correspond to the potential required for its removal from its particular shell. For instance, if an electron is first ejected from the K-shell and this hole is filled by an L-electron the energy associated with this transference will be equivalent to (E_K-E_L); in fact the (K_α) line. The hole in the L-shell may then be filled by an M-electron with the emission of the L-line energy (E_L-E_M). This process will continue until the energy of the atom is lowered to a value approximating to that associated with normal electron vibration in the outer-orbitals, in general a few electron volt (eV).

If we allow strictly monochromatic radiation (i.e X-ray of one wavelength only) to pass through a sheet of material of thickness 'd' cms the intensity (I_o) of the incident beam would be cut down to value (I) according to the well-known law of absorption (Beer's Law):

$$I = I_o\, e^{-\mu d}$$

where μ is the linear absorption coefficient. Now, the extent of absorption must be governed by the number of atoms through which the radiation must pass through rather than by the distance traversed through the material. For a given thickness of material the number of atoms traversed must be proportional to (ρ) the density of the material. Consequently μ the linear absorption coefficient must also be proportional to (ρ) and their ratio $(\frac{\mu}{\rho})$ is, therefore, a constant which expresses the absorption in terms of mass traversed than the distance through the specimen. The equation relating the intensities of the transmitted and incident beams may therefore be written:

$$I = I_o\, e^{-(\frac{\mu}{\rho})\cdot \rho \cdot d}$$

where ($\frac{\mu}{\rho}$) = is the mass absorption coefficient and

ρ.d = is the mass per square centimeter presented by the specimen to the incident beam

The process of absorption is itself somewhat complex. During the passage of X-ray beam through the specimen, energy is lost by the ejection of photoelectrons from the atoms of the irradiated material. Part of the radiation is converted to fluorescence X-rays which are caracteristic of the atoms of the irradiated substance. These rays are invariably of longer wavelength than the incident beam and are consequently less penetrating.

The single crystals have been found to act as natural three dimensional gratings and can be very efficiently, used as the dispersing material. For all the practical purposes we can imagine a crystal as made up of a set of parallel, equally spaced reflecting planes perpendicular to the direction we choose. The 2d-spacing (i.e, the perpendicular distance between the planes) being different for different sets of such planes, is used according to the need of our range for the analysis. Imagining a crystal is the above form, when a polychromatic X-ray beam is incident at a particular incident angle each wavelength will be reflected by different sets of planes depending on 2d-spacing of that sets.

According to Bragg, the relation between the 2d-value and the λ is:

$$n \lambda = 2d \sin \theta$$

where n is an integer, θ is the angle of diffraction or incidence for that set of plane and 'n' gives the order of reflection.

A second-order beam of wavelength ($\frac{\lambda}{2}$) will be reflected at the same angle as a first order beam of wavelength (λ):

The dispersion efficiency of a spectrometer is fixed. It is proportional to the spacing of the dispersing media i.e, 'd' spacing of the crystal. The dispersion of the analysing crystal can be derived by differentiating the Bragg's equation.

$$\frac{d\theta}{d\lambda} = \frac{n\lambda}{2d} \quad \frac{1}{\cos\theta}$$

It is apparent from this that the dispersing power increases with increase of θ or decreases of 'd' and in addition, the higher order of reflection the better is the dispersion.

An X-ray spectrometer as distinguished from an X-ray emission spectrograph is an instrument primarily intended to measure X-ray wavelength and intensity as a function of wavelength. The elements of a spectrometer are the source, the collimator, the crystal manochromator and the detector (Fig.3). The choice of a suitable analysing crystal is of utmost importance. Because, Sin θ cannot exceed unity, the Bragg's law limits the lines that can be sorted out by a crystal
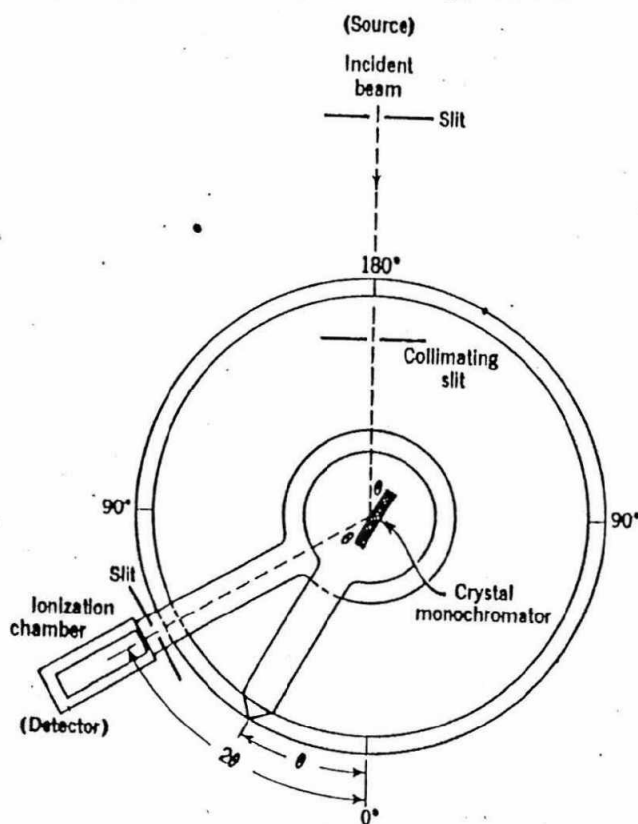

Fig.3

to those of wavelength 2d or less. The more commonly used analysing crystals alongwith their useful ranges are given in table.

Table

Crystal	Reflection plane	2d-spacing (A)	Lowest detectable	At.No.	Reflection efficiency
Topaz	(303)	2.712	V(23)	Cr(58)	Average
Lithium fluoride (LiF)	(220)	2.848	V(23)	Ce(58)	High
LiF	(200)	4.028	K(19)	In(49)	Intense
Sodium chloride	(200)	5.639	S(16)	Ru(44)	High
Quartz	(10$\bar{1}$1)	6.686	P(15)	Zn(40)	High
Penta erythritol	(002)	8.742	Al(13)	Rb(37)	High
Ethylenediamine d-tartrate	(020)	8.808	Al(13)	Br(35)	Average
Ammonium dihydrogen phosphate	(110)	10.65	Mg(12)	As(23)	Low
Gypsum	(020)	15.19	Na(11)	Cu(20)	Average
Mica	(00$\bar{2}$)	19.8	F(9)	Fe(26)	Low
Potassium hydrogen phthalate	(10$\bar{1}$1)	26.4	O(8)	V(23)	Average
Lead stearate	—	100.0	B(5)	Ca(20)	Average

For the larger wavelengths of radiations (soft X-ray) the analysing crystals must have larger d-spacings. To have such crystals, organic layers are deposited on transparent substrates. These are made on highly polished microscope slides (1"x3") or freshly cleaned mica sheets (these were cleaned by chromic acid and distilled water). Then it is dipped in and out of the solution in the tray by suspending it by a string attached to a motor driven eccentric, at a rate of once every minute. The tray is filled with a dilute solution of barium chloride, several drops of a dilute solution of stearic acid in n-hexane is spread on the surface of the solution between the barriers at the ends of the tray. The n-hexane rapidly evaporates, leaving monolayer of stearic acid which immediately reacts with the barium ions in solution to form an insoluble layer of barium stearate, the 'd' spacing of which is twice that of the length of the stearate molecule. As the stearate chain is roughly 25 Å long, the distance between successive rows of metal atoms is about 50 Å giving a pseudo-crystal with 2d-spacing of approximately 100 Å.

DETECTION

The basic problem of X-ray detection is that of converting the X-rays into a form of energy which can be measured and integrated over a finite period of time. Each method depends upon the ability of X-rays to ionise the matter. We are using here in our case the scintillation counter and for greater accuracy a gas-flow proportional counter. The P-10 gas (a mixture of 90% argon and 10% methane) is used as a flow-gas in the counter at a pressure of 10^{-2} to 10^{-3} torr. The detector's heads are fixed in the goniometer arm of the spectrometer (goniometer is the device which links the crystal and detector shaft in such a way so that detector shaft always has double span than the crystal shaft).

Primarily the analysis is followed with the identification of certain elements in a matrix with a measurement of the intensity of one of its characteristics lines, then to use this intensity to estimate the concentration of that element. By use of a range of standard materials a calibration curve can be constructed in which the peak response of a suitable characteristic line is correlated with the concentration of the element. But this all can stand in an ideal condition when there is no possibility of any mistake due to random or systematic errors.

Usually the random errors are due to the counting statistics, generator and X-ray tube's stability or any other defect in the unit. This is mostly avoided to a higher degree by the manufacturer. The systematic errors, which are mostly concerned with the sample may be categorically placed under two heads:

(a) Elemental Interactions
(i) Absorption - primary and secondary
(ii) Enhancement

(b)   Physical Effects

(i)   Particle size
(ii) Effects due to chemical state

These are also known as 'Matrix effect'.

When characteristic radiation is produced from an element in a matrix the number of characteristic photons actually leaving the sample, will be significantly less than the number initially produced. This is because most of the excited atoms of the element lie deep within the sample matrix and the characteristic radiation which is produced has to travel through the volume of the matrix in order to leave the sample. The contribution of the outer layers of the sample will be much greater than that of the inner layers. As the characteristic radiation is always produced to a finite depth below the sample surface, absorption effect will always be present. The magnitude of these effects will simply be dependent upon the differences in the absorption coefficients to the matrix. This is more observed in case of a heavy element in a very light matrix (as metals in lubricating oil, petrols, etc).

ABSORPTION

In general absorption effects are shown by elements fairly close together in the periodic table. Fig.4 illustrates the problem with specific reference to chromium, manganese, iron and nickel and shows the absorption edges and K α lines. It is seen that in the case of iron and manganese the absorption
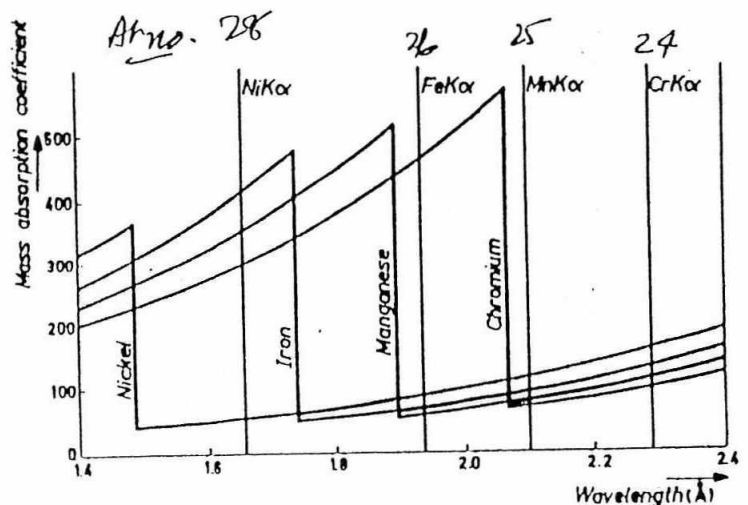

Fig.4

coefficients are relatively similar since the iron K_α -line lies to the long wavelength side of both its own absorption edge and that of Mn. In the case of iron/chromium however, a rather different situation occurs since the iron K_α -line lies very close to the chromium absorption edge. Hence one would expect that as more iron were added to a binary mixture of iron and chromium the absorption coefficient would decrease showing a negative deviation (in the Fig.5)
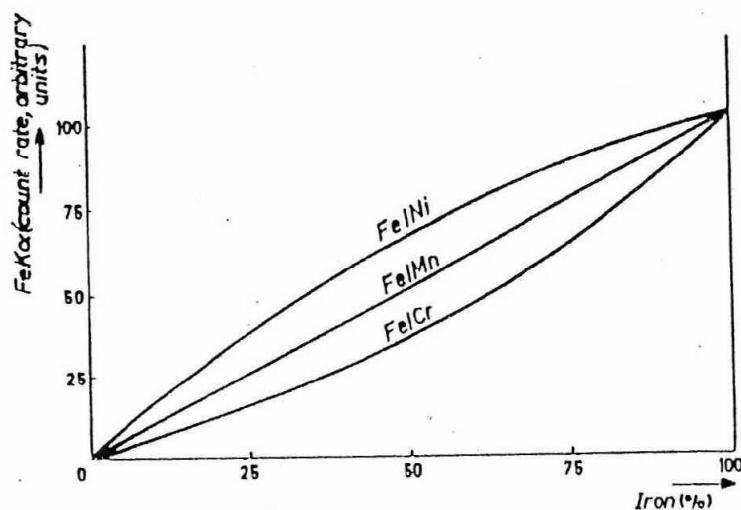

Fig.5

ENHANCEMENT

In the enhancement effect, one element is strongly absorbed by another. As for example in the case of iron-Cr, the measured intensity of the absorbed element will be low by an amount depending on the fraction of photons actually absorbed. Thus, in general, where a characteristic line of element A lies just to the energy side of element B. 'A' is said to be strongly absorbed by B and B is in turn enhanced by A. In Fig.4 the nickel K_α line at 1.659 Å lies very close to the iron absorption edge at 1.743 Å and to its high energy side. The X-rays with the highest absorption probability for iron, are those having a wavelength slightly shorter than the iron absorption edge. However, these rays

are heavily absorbed by iron, the absorption by nickel for these rays being quite small, since the absorption edge for iron is situated at 1.74 Å and that for Ni at 1.49 Å. The intensity of iron K_α is, therefore, relatively higher in an iron/nickel alloy than in pure iron.

It is difficult to give a hard and fast rule as to the range over which absorption and enhancement effects (also known as interelemental effect) can be considered negligible, but in very general terms, if the range in mass absorption coefficient for the required wavelength does not exceed 5% or so and provided that variation in the concentration of possible enhancing element is also less than 5%, linear curves can be obtained.

The effect due to the physical reasons (grain size and surface irregularities) on the X-ray fluorescence is well known and is recognised as a property which may produce serious errors unless proper measures are taken to minimise or to eliminate it. Normally, when the specimen is a metal the surface irradiated by the X-ray beam is polished to a smooth finish. If the specimen is a powder, the particles are reduced in fineness by an appropriate grinding technique to a point where further reduction provides no additional increase in intensity.

PARTICLE SIZE EFFECT

The particle size effect can be expressed in terms of the fundamental property of the element, viz. the characteristic absorption length (x) by the earlier expression

$$ I = I_0 \exp \left[- \left(\frac{\mu}{\rho} \right) . \rho . x \right] $$

where, I_o is the incident intensity,
I is the transmitted intensity,
$\frac{\mu}{\rho}$ is the mass absorption coefficient
and ρ is the density

The absorption length for a particular system is calculated from the above expression. Ordinarily powder samples are briquetted with or without a binder under high pressure, which varies with the material and the particle size. The finer particles requiring a lower pressure and the coarse to a high pressure. The binders which are usually employed are starch, ethyl-cellulose, lucite or urea. But this method can be used if the one has a constant mineralogical composition. In case of non-homogeneous samples, fusion method is adopted which includes the dissolution of the mineral sample in a matrix of molten borax. It is then allowed to solidify into a bead.

In a binary system, if one component of a two component mixture is held constant in particle size and the second varied, the intensity for the component whose particle size is constant will decrease and the intensity for the component whose particle size is reduced will increase. The mechanism can be explained by considering the geometry involved in the excitation of the particles in which the incident beam makes an angle 60° with the sample surface and the emission direction is 30° (Fig.6). It can be seen in case-1 that almost all of the particle 'A' is irradiated by the incident beam, but only 50% of this irradiated volume can be seen by the analysing crystal without its being filtered by an adjacent particle 'B'. This unobstructed portion of particle 'A' is

Case I
Particle Size A=B
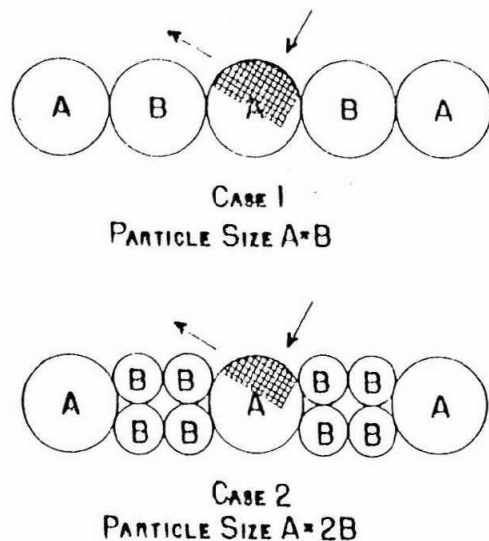
Case 2
Particle Size A=2B

Fig.6

indicated in the figure by the shaded portion of the excited area. In case-2 it can be seen that component 'B' now limits both the exciting and the emitted radiations to a greater extent than was true in case-1. Thus the unobstructed portion represented by the shaded area in case-2 can be considerably smaller than in case-1. In addition, as was apparent in the experimental data the intensity observed from the component A, which has the constant particle size, will decrease regardless of the relative absorption coefficients of the components A & B in the mixture. It is similarly evident that the intensity of radiation emitted by component B will increase as its particle size is reduced.

After many such observations, it can be concluded that to obtain better results in the analysis of ores and minerals, fine grinding and homogenising of the sample is needed as is also seen in Fig.7 (of Cu-ore) for grounded and ungrounded samples.

To overcome all these four types of errors which arise due to the matrix effect, various techniques
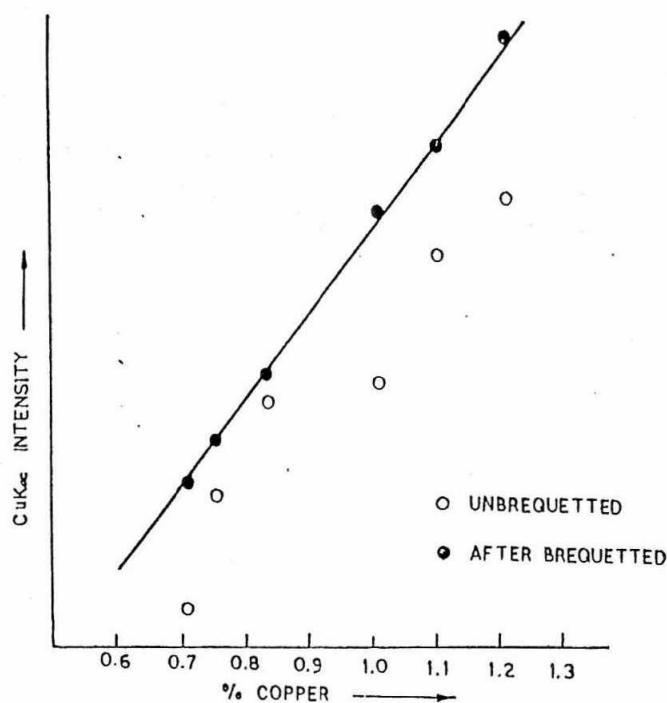

Fig.7

have been adopted to ensure the reliable results. These are:

(a) **Comparison with a standard**

In this, ultimate reliability is attained when an unknown and the standard are uniform, identical in composition and identically prepared.

(b) **Use of internal standard**

(i) An added internal standard is properly chosen and uniformly distributed in the mixture.

In this method a known percentage of the internal standard is mixed homogeneously with the sample. For example, the determination of iron in Fe_2O_3/Cr_2O_3 mixtures. Here the iron K_α line at 1.937 Å is strongly absorbed by chromium whose absorption edge is at 2.070 Å.

Cobalt has its characteristic K_α line at 1.791 Å and since the absorption of iron and cobalt by chromium is similar a weighed quantity of, for example Co_2O_3 could be added to Fe_2O_3/Cr_2O_3 mixture as an internal standard. Since the absorption effects for iron and cobalt are similar and as concentration of cobalt is known (Fig.8) Fe% can be detected.
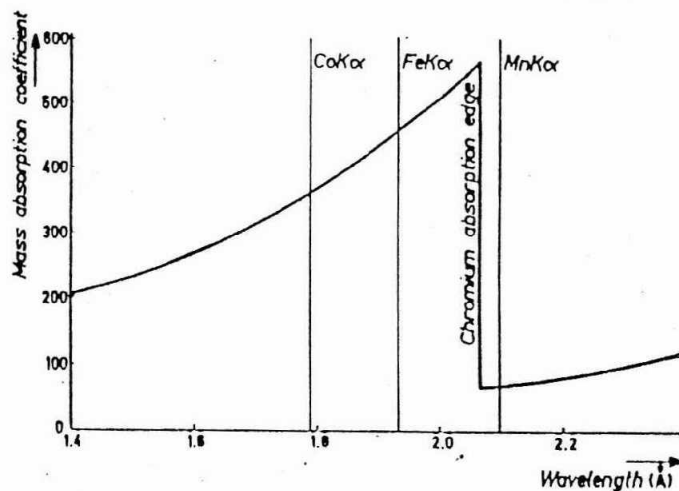
Fig.8

$$\frac{\text{Count rate due to } Fe(K_\alpha)}{\text{Count rate due to } Co(K_\alpha)} = K \cdot \frac{\text{Concentration of Fe}}{\text{Concentration of Co}}$$

K = constant: could be determined by known Fe and Co percentage in a standard mixture $Fe_2O_3/Cr_2O_3 + Co_2O_3$.

(ii) An element of known-weight fraction in the sample may sometimes serve as a built in standard for the analysis when suitable standards are not found.

A scattered line in the background may serve as a reference in some cases.

(c) Dilution

The dilution, in general, with a relatively transparent material is useful in dealing with the absorption and enhancement effects. This is done either in briquetting the samples or in fusion. If the solvent contains light atoms only, then absorption and enhancement effects due to heavy elements in the original sample will both be negligible in the highly dilute solution. Also, this procedure reduces the intensity of the analytical line and may cause enhancement if the diluent is improperly choosen. This has been employed with great success over a wide range of its applications but have been found most successful in the analysis of geological samples where elemental concentration ranges can be enormous. Using a diluent as a solvent for the sample, either an aqueous or acid solutions in determining both trace and major constituents have found its versatility in X-ray fluorescence research. This is completely independent of the need for the chemically analysed reference materials. Standards are easily prepared from the solutions of pure metals or oxides, which may be combined in varying proportions to cover any anticipated analytical range.

APPLICATIONS

The technique of X-ray fluorescence spectrometry has wider scope of usefulness mainly depending on the practical problems. Categorically, this may be divided into six major groups and many subgroups according to the physical-state of the specimen and the concentration of the elements present therein:

1. Metals and alloys
2. Minerals and ores: (a) Geological material and museum objects
   (b) Glass and ceramic
3. Highly radio-active material
4. Trace detection in plants, blook tissues etc.
5. Petroleum products, crude oil & hydrocarbons; and in the
6. R & D purposes.

In brief, the individual headsare discussed below:

Metals and Alloys

Diverse varieties of the sample of a large number of alloys appear in practice. Obviously, it needs many modifications and improvements as and when needed to suit the requirements. Generally, the specimen are prepared first by sawing or cutting to size and then abrazing the surface down to about 100 emery paper or to 30 to 50 microinch finish. They are rotated, while excited by the radiations to average out the slight inhomogenities in the specimen.

In plain carbon steels estimation of Mn (> 0.05%) was a problem due to the lack of energy resolutions using X-rays from the heavier elements. Because when $Fe(K_\alpha)$ peak, the

resolution has no meaning. This is always the case in the X-ray fluorescence spectrum of carbon steels excited by K -radiations from nickel or the heavier elements. However, it was found by Gehrke and Cole using the $Co(K_\alpha)$ radiation in exciting the Mn over the iron. The $Fe(K_\alpha)$ peak is then sufficiently reduced relative to $Mn(K_\alpha)$ in the X-ray fluorescence spectrum, so that these are sufficiently resolved. As the adding of the internal standards in the solid samples are not feasible, the metallic constituents which do not vary significantly are taken as the internal standards. Of-course, in some cases solutions of the samples were made and the desired internal standards were added to it.

Determination of lighter elements with XRF was of some problem as the phenomenon called 'the fluorescent yield' limits the intensity of the characteristic spectrum, when K-electron is knocked out of an atom, another electron will replace it giving rise to one of the K-series emission lines. However, in some cases, the K-emission radiation do not leave the atom. They may instead knock-out the L-electrons and thus generate the L-series. This is also known as the 'Auger Effect' and the probability of its occurence increase as we go to the lower atomic numbers. Also the characteristic radiation (X-ray) of the lighter elements (11.9 to 2.7 Å) get strongly attenuated in air and is lost before reaching the detector unless helium or hydrogen gas or a vacuum path is used. Wagner and Bryan have used vacuum as well as helium path for the determination of aluminium in Fe-Al alloy. They have found that, using of the vacuum path gives 10% higher the intensity than that of the He-path using Eddt-crystal for analysing crystals of large spacings were advised as sin 0 cannot exceed unity in the Bragg's relation.

Minerals and Ores

Minerals and ores may be examined either as solids or as

powders. A great deal of work has been done in establishing standards and evaluating X-ray spectrochemical analysis for all types of minerals, ores, ceramics, and refractory materials. One of the simplest ways is to grind the sample and subsequently press it to a tablet. But this can be used if the ore has a constant mineralogical composition. This mineralogical effect can be overcomed by a well established sample preparation technique. In the other case, the sample is used with borate, destroying the original structure of the mineral and forming a glass. The glass disc, called the bead, can be analysed directly. In this the analytical line is almost linearly related to the concentration of the analyte. Sometimes, the intensity of the analytical line become less or more as they are absorbed or enhanced by the varying amounts of other elements in the specimen. If the bead composition is fairly constant the inter-elemental effect which is also known as 'matrix effect', is negligible. A method to the inter-elemental effect is the use of the internal standards which is added to the flux in a fixed quantity to both standards as well as the sample. The materials having same mineralogical composition for establishing the working curves, eliminates the necessity of internal standards or other treatment of the sample.

Priceless Artifects

The non-destructive nature of X-ray spectroscopy makes it more valuable as the priceless relics (artifects) cannot be destroyed for wet chemical or emission spectroscopy analysis. To determine the alloy composition, little amount of the drillings obtained from the artifect is taken and dissolved. This is then absorbed on a weighed amount of celluose powder which is dried and briquetted subsequently. Similarly the standards are also prepared with known percentage of the probable chemicals and are mixed with

weight portions of the cellulose powder. They are dried and pressed under the similar conditions. The intensity of the approximate (K_α) lines were measured for the calibration as well as to obtain the result.

Highly Radioactive Materials

Fluorescent X-ray analysis of highly radioactive samples require the same basic equipment and techniques as ordinarily used for non-radioactive samples with extra care to the health hazardous caused due to the stray radiation in handling them. The presence of Beta (β) and gamma (γ) rays are the problem with radioactive materials. It is to develop a technique which can eliminate the effects of these rays. It can be done in either of the two ways: (a) to reduce the concentration of the radioactive sample by dilution; (b) to reduce mechanically the effect of these rays and their secondary effects on the X-rays detector. The magnitude of which depends to a large extent upon the type and the magnitude of the activity of the sample. This obviously alters the geometry of the spectrometer. Also a detector is to be so chosen such that the efficiency of its detection for the X-rays are more and low for gamma rays. Most suitable in this is the sodium-iodide scintillation counter with a very thin ($\simeq 0.012''$) scintillation crystal in it. The background effect is avoided by measuring the background counts without the X-rays.

Trace Detection of the Elements

X-ray fluorescence spectrometry is essentially a method which counts atoms. The minimum number of atoms which are required to give a measurable signal above the background is, therefore, the limit of the minimum detection. Low concentration measurements depend on both the absolute intensity

available and the line to background ratio. In most of the cases it is the detector statistics that determine the precision and the detectability rather than the other instrumental statistics. The coefficient of variation can be given as:

$$\sigma\% = \frac{(N_\ell + N_b)^{\frac{1}{2}}}{(N_\ell - N_b)}$$

where, N_ℓ and N_b are the total number of counts at the peak and background positions respectively. To reduce the background effect, sometime the pulse height analyser is used. Basically a pulse height analyser acts as an electronic gate. All the pulses coming from the detector are fed into it, but only pulses having predetermined energy ranges are allowed to pass through it to the counting circuits. This results to an improved signal to background ratio and makes quantitative measurements possible. Generally, in trace detection, preconcentration is needed to obtain a considerable response. Zemany and coworkers have used the method of ion exchange membrane for the preconcentrations. The membrane is then dried and subjected fluorescent radiation. Determinations of strontium in human serum and bone have also been made using XRF, by Hatelson and Shield by evaporating a preconcentrated solution on the filter paper in plants selenium is directly determined by Handley. He took the plant material and dried for 24 hours at 60°C and was ground and pressed into a disc. Fagel et.al have used an organic precipitant and briquetting to determine small amounts of metallic impurities in alkali-carbonates.

Petroleum Products, Crude Oils and Hydrocarbons

The use of X-ray fluorescence for the elemental analysis of various contaminates and additives associated with

petroleum products has minimised the problems of petroleum industries. With the handling difficulties of the liquid samples the crudes vary considerably in viscosity, volatility and organic composition. The heat from X-ray tube may also cause evaporation of the more volatile crudes and partial loss of sample through creeping. To avoid this, Lopp and Glaypool have designed a special type of sample holder which can accommodate 3-4 samples at a time so that sample can be moved into positions for analysing without opening the sample chamber. The sample level in each case is kept the same because the intensity of the fluorescent radiation varies with the distance between the sample and X-ray tube. While working in Humble Oil Refining Company Texas, Gunn pointed out that this variation in fluorescent intensity is due to absorption which appears in varying the depth of the elemental specimen in oil, depth of the solution containing the specimen and the obviously the amount of the element dissolved in it. As usual the analysis is accomplished by the ratio of the counts accommodated on a fixed time basis on the standard and the sample. To measure the concentration of 'vanadium' and 'nickel' in crude oil samples the intensities of $Ni(K_\alpha)$; $V(K_\alpha)$ and $W(L_{L_1})$ lines are obtained. As the scattering of the primary X-ray beam differs with variation in crude oil composition, it affects considerably the intensities due to nickel and vanadium in the sample. To compensate for this matrix effect and instrumental variations, the scattered radiation from the tube is used as an internal standard.

The tungsten L_1-line at 49.24° (2 θ) is chosen because of its proximity to the nickel line and also because of its intensity being of the same order as that of vanadium and nickel lines. The ratios

$$\frac{V_{K_\alpha}}{W_{L_1}} \quad \& \quad \frac{Ni_{K_\alpha}}{W_{L_1}}$$

rather than the absolute intensities are then used to determine concentration.

Crudes containing less than 5 ppm of V and Ni are coked with concentrated sulphuric acid and ignited at 500°C in a muffle furnace to concentrate the inorganic portions of the sample. A solution containing 25 ppm of cobalt is added as an internal standard to each oil before ashing is begun. After all carbon was burnt off, the ash is dissolved in hot HCl. The volume of the solution is reduced. The intensities of the nickel, cobalt and vanadium K_α lines are measured and the ratios $\frac{Ni_{K\alpha}}{Co_{K\alpha}}$ and $\frac{V_{K\alpha}}{Co_{K\alpha}}$ are used in determining the concentration from a calibration curve.

In measuring the content of impurities in liquid hydrocarbons it may not be possible that the elements are ideally dispersed in the organic substrate but may exist as suspended particle. It has been found by Gunn that the increase in particle size reduces the intensity of fluorescent emission to many fold. He took the specific case of zinc and iron and concluded that it should be less than 1μ in size and approximate the intensity of the element in solution. It is because the X-ray fluorescence emitted is lessened by the internal absorption loss within the particle. The loss decreases as the particle size is reduced, the extent of which depends on the absorption coefficient of the particle for both incident and emerging X-ray.

Progress in the field of instrumentation to accommodate the maximum number of elements for analysis is in the process. Its utility for the fundamental problems of bonding are also being considered so as to replace the X-ray emission spectrometry with the X-ray fluorescence spectrometry. Being more convenient to handle with the dependable results its versality is being supported much in the Research and Development activities.

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