

# RECENT TRENDS IN X-RAY FLUORESCENCE SPECTROMETRY AND ITS APPLICATIONS IN INSTRUMENTAL ANALYSIS

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## INTRODUCTION

X-Ray Fluorescence Spectrometry is now well established as a method for obtaining rapid qualitative and quantitative elemental analysis. Quantitative determinations are made by converting peak intensity into weight percentages of the element by means of proper calibration. Of major importance is the fact that the samples are not destroyed and the analyses can be performed on solid as well as liquid samples. The study is mainly regarded with the intensity measurements of the characteristic X-radiation at fixed wavelength for the elemental analysis in a sample. The changes in the valence state of a given element can produce shifts in the wavelengths of the characteristic radiation. L.G. Parrat resolved a shift of 2.85 XU for the sulphur  $K_p$  and  $K_a$  radiations when going from sulphide to sulphate sulphur. Also, the non-proportionality of X-ray Fluorescence intensity vs concentration of sulphur occurs in geological materials prepared as ground samples. Elshemier and Fabbi have found that samples containing sulphur as sulphate yield higher intensities than an equivalent amount of sulphur as the sulphide.

More so, the particle size of the powder sample affect the XRF intensity. It is considered that the fluorescent intensity of a pure material would increase as the particle size of the material in decreased. In the case of heterogeneous mixtures, it is the grains and surface irregularities of the specimen which have been found to introduce

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serious errors unless proper measures are taken to minimize or eliminate it. The presence of multigrade grains introduces problem in the measurement. The mineralogical differences contribute to the density, shape and size of the ground particles and it is the lack of practical means of reporting out of the measured grade of fine-ness of the sample which becomes major limitation of the process. Claisse explained the phenomenon through localized matrix effect caused due to the heterogeneity and showed that the fluorescent intensity increases with the decrease in the grain size. Bernstien attributed this to a decrease in the surface of the material which is possible with the reduction of the particle size. In a mixture of the multigrade particle size samples, the heterogeneity-effect has been seldom accounted for in determining the X-ray fluorescence intensity; whereas samples of different particulates are frequently encountered while dealing with minerals, ceramics, refractories materials.

Though the X-ray fluorescence spectrometry is the empirical method to produce accurate results, there is a great deal of uncertainty when the composition of the samples differ considerably. This problem arises most in the the quantitative analysis of slags and its products.

The present lecture would be mainly devoted to deal with, in brief, the X-ray fluorescence analysis of minerals & ores, slag samples, the analysis of priceless artifacts, radioactive materials and the analysis of trace elements present in the materials.

## **PRINCIPLE**

Fluorescence is a luminiscence phenomena. It is a term applied to the re-emission of previously absorbed light by the material. In the molecular photo-luminiscence photons of electromagnetic radiation excite molecules. The moleocules by absorbing light are in a higher electronic state and lose their excess energy to return back to the ground state. When the excited molecule returns to the ground state

by emitting light, it exhibits photo-luminescence. The decay time of fluorescence is of the same order of magnitude as the life-time of an excited singlet state ( $10^{-9}$  to  $10^{-7}$  sec.).

When an atom is excited by removal of an electron from an inner shell, it usually returns to its normal state by transferring an electron from some outer shell to the inner shell with consequent emission of energy as X-rays, that is, photons of high energy and short wavelengths in the order of tenths of angstrom to several angstroms. Eventually, a free electron will be captured by the ion. The X-ray emitted by an excited element have a wavelength characteristic of that element and an intensity proportional to the number of excited atoms.

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 ( $I_0$ ) of the incident beam would be cut down to value (I) according to the well-known law of absorption (Beer's Law) :

$$I = I_0 e^{-\mu d}$$

where  $\mu$  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 ( $\rho$ ) the density of the material. Consequently  $\mu$  the linear absorption coefficient must also be proportional to ( $\rho$ ) and their ratio  $(\mu/\rho)$  is, therefore, a constant which expresses the absorption in terms of mass traversed than the distance through the specimen. The equation relating to intensities of the transmitted and incident beams may therefore be written as :

$$I = I_0 e^{-(\mu/\rho) \cdot \rho \cdot d}$$

where  $(\mu/\rho)$  = is the mass absorption coefficient and  
 $\rho.d$  = 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 characteristic 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 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 in 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  $\lambda$  is:

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

where  $n$  is an integer,  $\theta$  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  $(\lambda/2)$  will be reflected at the same angle as a first order beam of wavelength  $(\lambda)$ .

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.

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

It is apparent from this that the dispersing power increases with increase of  $\theta$  or with decrease of 'd', in addition, the higher order of reflection the better is the dispersion.

## 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 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 known by elements fairly close together in the periodic table. Fig.1 illustrates the problem with specific reference to chromium, manganese, iron and nickel and shows

the absorption edges and  $K\alpha$  lines. It is seen that in the case of iron and manganese the absorption coefficients are relatively similar since the iron  $K\alpha$  - 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  $K\alpha$  - 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.2).

### **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.1 the nickel  $K\alpha$  line at  $1.659 \text{ \AA}$  lies very close to the iron absorption edge at  $1.743 \text{ \AA}$  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  $1.74 \text{ \AA}$  and that for Ni at  $1.49 \text{ \AA}$ . The intensity of iron  $K\alpha$  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. To overcome the errors due to matrix effect following techniques are adopted :

**(a) Comparison with a standard**

The usual practice to obtain the reliable results by XRF is to compare the unknown samples with the known standards, more specifically from the same origin. Also, the ultimate reliability is attained when an unknown and the standard are uniform 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  $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$  mixtures. Here the iron  $K\alpha$  line at  $1.937 \text{ \AA}$  is strongly absorbed by chromium whose absorption edge is at  $2.070 \text{ \AA}$ .

Cobalt has its characteristic  $K\alpha$  line at  $1.791 \text{ \AA}$  and since the absorption of iron and cobalt by chromium is similar a weighed quantity of, for example  $\text{Co}_2\text{O}_3$  could be added to  $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$  mixture as an internal standard. Since the absorption effects for iron and cobalt are similar and as concentration of cobalt is known (Fig.3) Fe % can be detected.



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

K = constant : could be determined by known Fe and Co percentage in a standard mixture  
 $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3 + \text{Co}_2\text{O}_3$ .

- 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 chosen. 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.

## 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.

$$I = I_0 \exp [ - ( \mu/\rho ). \rho .x ]$$

where,  $I_0$  is the incident intensity,  
 $I$  is the transmitted intensity  
 $\mu/\rho$  is the mass absorption coefficient and  
 $\rho$  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.

For better homogeneity the traditional method of fusing and grinding is desired, but the process is difficult and time consuming. It is therefore, imperative to employ the correction factors, which would be the function of particle size distribution and emitted intensities. Although the calibration standards obtained by dry mixing of components in appropriate proportions may be compositionally accurate, but they can be a major source of error in analytical results owing to the mis-match between the degree of heterogeneity and that of the sample.

A simplistic system of the binary mixtures of silicon dioxide and calcium carbonate is undertaken in various concentration ranges and

particle size as also done by Bernstein. As seen in the Fig.4, the intensity of Si K $\alpha$  radiation increases with the decrease in the particle size of silica in the binary mixture of silicon dioxide in the calcium carbonate matrix. The 5% silicon dioxide of 30 $\mu$ m fineness produces the same intensity as 15% silicon dioxide of 200 $\mu$ m size. Figures (2) and (3) are the results of the variation in the calcium carbonate particle size over SiK $\alpha$  intensities and the variations in silicon dioxide particle size over CaK $\alpha$  intensities respectively. These were seen in four different sets of possible mixtures by varying the fineness of the other component in both the system.

It is observed from the Fig.5 that with the decrease in the particle size of fixed silicon dioxide in the mixture the response for SiK $\alpha$  intensity is intense with the fine particles of silicon dioxide in a decreasing CaCO<sub>3</sub> size in the mixture. But, in the case of fixed CaCO<sub>3</sub> mixtures with the decrease in silicon dioxide particle size the Ca K $\alpha$  response is not similar as seen from Fig.6. The mechanism of the phenomenon can be explained by considering the shielding of a part of the particle of one component by the other component of the mixture. If the size of one component is kept constant and the other component size is decreased then the intensity of the first component decreases and that of the second component increases because of the exposition of the larger surface area of the component in a binary mixture. The different observations seen in the case of CaCO<sub>3</sub> can also be understood by considering the variation in mass absorption coefficients. It is seen that when the particle size of both the components are reduced uniformly the intensity for Ca-K $\alpha$  falls and the intensity of Si-K $\alpha$  increases. The absorption coefficient of calcium-carbonate ( $\mu = 2540$ ) for Si-K $\alpha$  radiation is about 1 $\frac{1}{2}$  times more than the absorption coefficient of silicon dioxide ( $\mu=1655$ ) for Si K $\alpha$  radiation. Also, the absorption coefficient of silicon dioxide ( $\mu=919$ ) for Ca K $\alpha$  radiation is almost three times that of the absorption coefficient of calcium carbonate ( $\mu=339$ ) for Ca-K $\alpha$  radiation. This explains the steep fall in the Si K $\alpha$  intensity in Fig.5 and also the change in CaK $\alpha$  intensity in Fig.6.

It is found, in general, that for binary mixtures a sixth order polynomial yielded satisfactory result. Table-I shows the results of bivariate analysis for the polynomial.

$$Z = a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4 + a_5x^5 + a_6x^6$$

It may be observed that in most cases coefficients upto  $a_4$  (i.e. fourth order) are adequate in relating the variables. The variance and correlation coefficients also indicate a responsible degree polynomial. It may be observed that for the case ( $\text{SiO}_2$  85% and  $\text{CaCO}_3$  15%) the relationship is almost linear, whilst for ( $\text{CaCO}_3$  85% and  $\text{SiO}_2$  15%) it is quadratic.

The multivariate analyses of the data depicted in Figs.(4-6) were carried out and are shown in Table-II. The polynomial employed in this case was also of 6th order viz.

$$Z = a_0 + a_1x + a_2y + a_3x^2 + a_4xy + a_5y^2 + a_6x^3 + a_7x^2y + a_8xy^2 + a_9y^3 + a_{10}y^6$$

It may be noticed that for ( $\text{CaCO}_3$  85% and  $\text{SiO}_2$  15%) and ( $\text{SiO}_2$  85% and  $\text{CaCO}_3$  15%) a third degree polynomial gave a satisfactory fit for the experimental data. However, for ( $\text{SiO}_2$ - $\text{CaCO}_3$  30 to 130  $\mu\text{m}$ ) a fourth order is essential to obtain a satisfactory fit of the data, indicating a slightly more complex relationship between Si  $K\alpha$  and the particle size of silica and the composition of the specimen.

The approach gives an idea about proceeding for mixture samples of higher order.

## APPLICATIONS

The technique of X-ray fluorescence spectrometry has wider scope of usefulness mainly depending on the practical problems. Categori-

cally, 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
3. Slag materials
4. Study about valance state
5. Highly radio-active material
6. Trace detection of the elements, etc.

**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 resolution 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  $K\alpha$ -radiations from nickel or the heavier elements. However, it was found by Gehrke and Cole using 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 characteristics 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 occurrence 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 with Eddt-crystal. For analysing lighter elements crystals of large spacings were advised as  $\sin \theta$  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 overcome 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 avoid 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.

**Analysis of Wolframite Ore :** The powdered samples of Wolframite Tungsten Ore showed interesting result while analysing with X-ray Fluorescence Spectrometry. It was observed that the problem of heterogeneity in the particle size is not the only concern, it is the change in the composition of the constituents with the mesh size became more effective in disturbing the reproducibility of the results. Fig.7(i-iv) show the XRF scan for  $WO_3$  content in wolframite at various mesh size of the samples ranging from -150 to -300 mesh, briquetted at three different pressures of 5, 10, and 20 tons/cm<sup>2</sup>. For the sake of comparison un-briquetted samples have also been studied under similar conditions. The tungsten ( $L\alpha$ ) at  $43^\circ(2\theta)$  is found to behave differently in all these cases as regards the shape and its peak height is concerned. Of-course, the un-briquetted powdered samples behaved randomly.

Some similar results have also been observed with the silicon peak (Fig.8 i-iv). It may be noted that the different peak intensities might be due to different level of grinding which exists in two major constituents  $WO_3$  and  $SiO_2$  of the ore. The percentage of  $WO_3$  has been found to increase while going from coarse to finer grinding and reverse is for  $SiO_2$ .

The specific gravity measurements supports this finding as shown in Table-III

As such in order to get reproducible results by XRF spectrometry optimum condition regarding grinding and briquetting needs to be achieved.

**Analysis of the Blast Furnace Slag Cements :** Although in X-ray fluorescence analysis the empirical method is found to produce accurate results but there is great deal of uncertainty when the composition of the samples differs considerable from place to place in some specimen. This problem arises most in the quantitative analysis of slags and its products. It is desired in such samples to fuse, dissolve and re-evaporated to get subsequently resolidified samples or fused glass beads by mixing the sample with  $\text{Na}_2\text{B}_4\text{O}_7$  for the X-ray fluorescence analysis. But, all these techniques are extremely time consuing. A different process is chosen, therefore, which includes the usual double briquetting technique and the use of  $\alpha$ -correction constants both for enhancement and absorption effect. This could give accurate and reproducible analysis for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$  within the acceptable limit of accuracy.

The study of the interelemental effect is based on the concept of the  $\alpha$ -factor as proposed by LaChance and Trail. By restricting the effect of one element over the other, the proportionality between the X-ray intensity and concentration is appropriately adjusted by the correction factor  $\alpha$  which may be written as

$$\frac{C_A^x \cdot I_A^S}{I_A^x \cdot C_A^S} = 1 + \alpha_{AB} (C_B^x - C_B^S)$$

Where,  $C_A$  is the concentration of element A

$C_B$  is the concentration of element B

$I_A$  is the intensity of element A

$I_B$  is the intensity of element B.

$\alpha_{AB}$  is the correction factor respectively the matrix effect on the element 'A' by the presence of element 'B' and the superscripts 'X', 'S' refer to the unknown and standard respectively.



A plot of the left hand side of the above equation against  $(C_B^x - C_B^s)$ , therefore, gives a straight line with the slope yielding to " $\alpha_{AB}$ ". By assuming no interelemental effect, the intensity obtained through dilution by the additives gives  $I_{\text{theor}}$ , and the experimental intensity observed is the  $I_{\text{Exper}}$ . The ratio of  $I_{\text{theor}}$  to  $I_{\text{Exper}}$  has been calculated and plotted against the added percentage of the constituent. As discussed by Anderson et. al the  $\alpha$  factor is found directly from the slope of the line plot as shown in Fig.9.

The  $\alpha$  factor, thus obtained is used to correct the X-ray intensities.

$$I_{\text{corrected}}^A = I_{\text{uncorrected}}^A (1 + \alpha_{AB} \%B + \alpha_{AC} \%C + \alpha_{AD} \%D)$$

The corrected intensities are then plotted against concentration. It can be seen from the Fig.10 that the scatter of the points have markedly improved.

**Study of the Valance State by XRF Peak Shifts :** The wavelength of the characteristic X-radiation for the higher elements is not constant but is a function of valence state and to much lesser extent is a function of co-ordination number. The changes in the valence state of a given element can produce shifts in the wavelengths of the characteristic radiation. The Fig.11 shows the shift in peak position which results chiefly as a function of valence state of the element chlorine. The first order  $K\alpha$  peak, shifts nearly  $0.10^\circ$  ( $2\theta$ ) when going from the chloride ( $Cl^{-1}$ ) to the perchlorate ( $Cl^{+7}$ ). The peak for the chlorine in the chlorate ( $Cl^{+5}$ ) is between those for the chloride and perchlorate chlorine and lies closer to that of the perchlorate.

In case of the sulphur similar shifts has also been observed with  $K_p$  radiation for sulphide and sulphate sulphur. These shifts can, therefore, be related directly to valence state changes.

**Priceless Artifacts :** The non-destructive nature of X-ray spectroscopy make it more valuable as the priceless relics (artifacts) cannot be destroyed for wet chemical or emission spectroscopic analysis. To determine the alloy composition, little amount of the drillings obtained from the artifact is taken and dissolved. This is then absorbed on a weighed amount of cellulose powder which is dried and briquetted subsequently. Similarly the standards are also prepared with known percentage of the probable chemical and are mixed with weighed portions of the cellulose powder. They are dried and pressed under similar conditions. The intensity of the  $K\alpha$  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 sample with extra care to the health hazardous caused due to the stray radiation in handling them. The presence of Beta ( $\beta$ ) and Gamma ( $\gamma$ ) 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 less for gamma rays. Most suitable in this is the sodium-iodide scintillation counter with a very thin ( $\sim 0.012$ " ) scintillation crystal in it. The background effect is avoided by measuring the background without 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 :

$$\sigma_{\%} = \frac{(N_1 + N_b)^{1/2}}{(N_1 - N_b)}$$

where,  $N_1$  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 the 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. Zeman and coworkers have used the method of ion exchange membrane for the preconcentrations. The membrane is then dried and subjected to 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 24hours 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.

Progress in the field of instrumentation to accommodate the maximum number of elements for analysis is in 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 verstality is being supported much in the Research and Development activities.

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**Table-I**

Polynomial coefficients evaluated from Bivariate analysis of experimental data

Trial	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	Var- lance	Corr. Coeff.
IA	6.4	-4.2	1.13	-.155	.011	-.0004	*	0.0384	0.994
IB	1.336	-0.91	.272	-.039	.003	*	*	0.0334	0.9999
IC	-3.99	2.75	-.75	.106	-.008	*	*	0.0146	0.9999
ID	1.232	-.799	.217	-.029	.002	*	*	0.0044	.9998
-----									
IIA	.335	.00499	*	*	*	*	*	.0669	.9998
IIB	.319	-.005	*	*	*	*	*	.0734	.9988
IIC	.101	-.0019	*	*	*	*	*	.0097	.99952
IID	.056	.00013	*	*	*	*	*	0.0086	.9992
-----									
IIIA	.745	.013	-.00058	*	*	*	*	0.0049	.9992
			*						
IIIB	.739	.0051	-.00017	*	*	*	*	.0081	.9999
IIC	.581	0.163	-.0007	*	*	*	*	0.0109	.9995
			*						
IIID	.284	0.421	-.00181	*	*	*	*	.0161	.9993

\* Indicated as negligibly small

**Table-II**

Polynomial coefficients evaluated from the multivariate analysis of experimental data

CaCO <sub>3</sub> 85% - SiO <sub>2</sub> 15%	SiO <sub>2</sub> 85% - CaCO <sub>3</sub> 15%	SiO <sub>2</sub> -CaCO <sub>3</sub> 30/130 μm
a <sub>0</sub> 11.51	a <sub>0</sub> -9.1	a <sub>0</sub> 24.8
a <sub>1</sub> -.84	a <sub>1</sub> .688	a <sub>1</sub> -11.37
a <sub>2</sub> .011	a <sub>2</sub> .078	a <sub>2</sub> -5.2
a <sub>3</sub> .017	a <sub>3</sub> -.001	a <sub>3</sub> .018
a <sub>4</sub> -.00001	a <sub>4</sub> -.0054	a <sub>4</sub> .147
a <sub>5</sub> -.0006	a <sub>5</sub> -.0013	a <sub>5</sub> .844
a <sub>6</sub> -.0000999	a <sub>6</sub> .000015	a <sub>6</sub> .00003
a <sub>7</sub> .0001	a <sub>7</sub> .0001	a <sub>7</sub> -.0026
a <sub>8</sub> *	a <sub>8</sub> -.000003	a <sub>8</sub> .0034
a <sub>9</sub> *	a <sub>9</sub> .000002	a <sub>9</sub> -.124
Variance *	Variance 0.10005	a <sub>10</sub> 0.0
Corr.Coeff. *	Corr.Coeff. .9999	a <sub>11</sub> .00001
		a <sub>12</sub> .00006
		a <sub>13</sub> -.00003
		a <sub>14</sub> .0095
		Variance .0455
		Corr.Coeff. .9998

**Table-III**

*The specific gravity of Tungsten Ore sample with sieve fractions*

Sample No,	Particle size( $\mu$ )	Sieve Fraction (mesh size)	Specific Gravity
1	-106	150	3.400
2	-106 + 75	200	3.454
3	-75 + 63	250	3.566
4	-63 + 53	275	3.650
5	-53	300	3.750

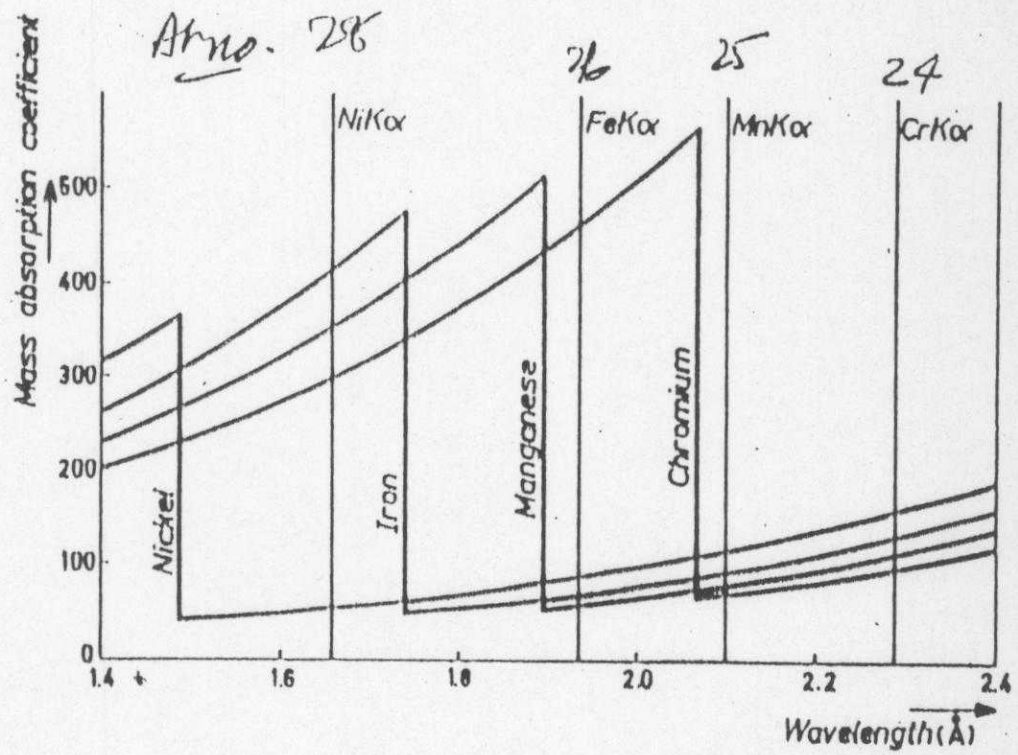


FIG.1 ORIGIN OF ABSORPTION AND ENHANCEMENT EFFECTS



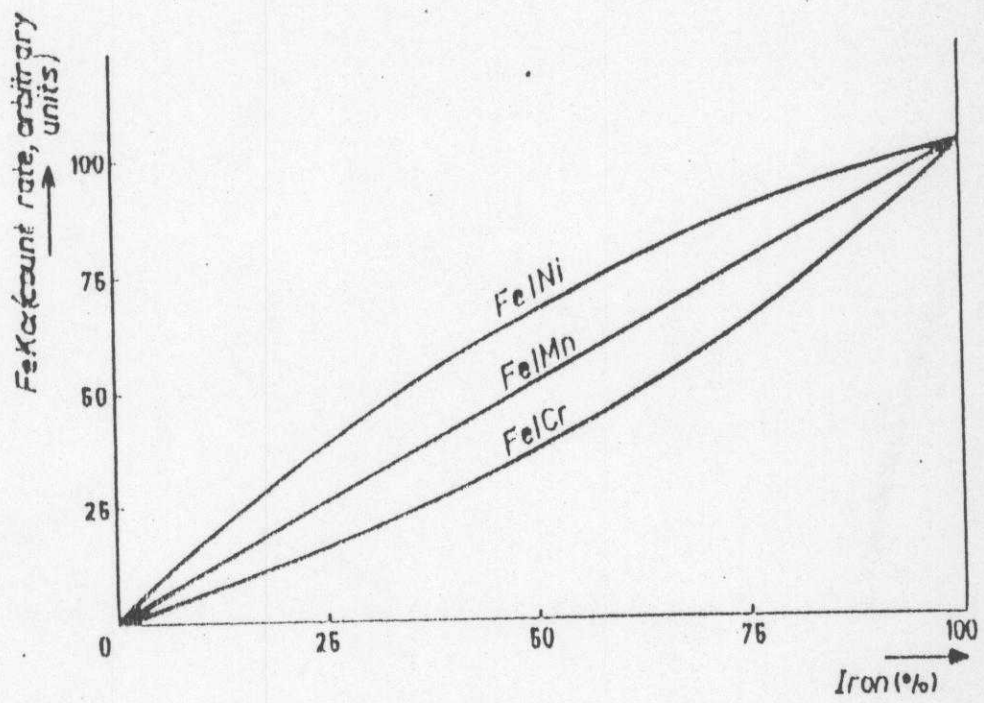


FIG.2 EFFECT OF ABSORPTION AND ENHANCEMENT EFFECT

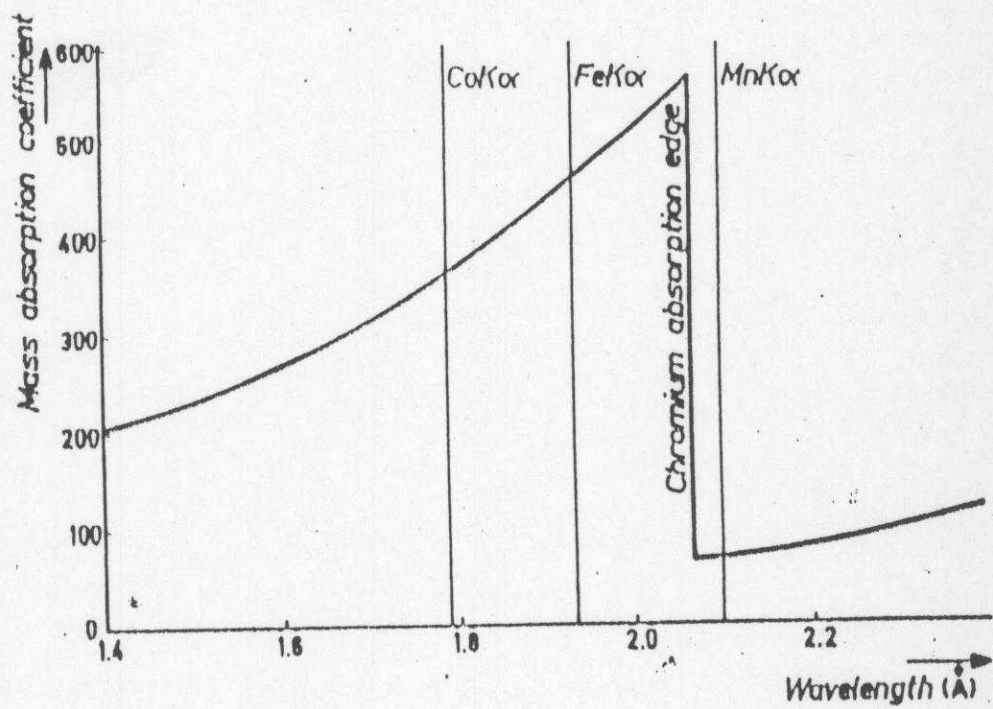


FIG.3 CHOICE OF INTERNAL STANDARD

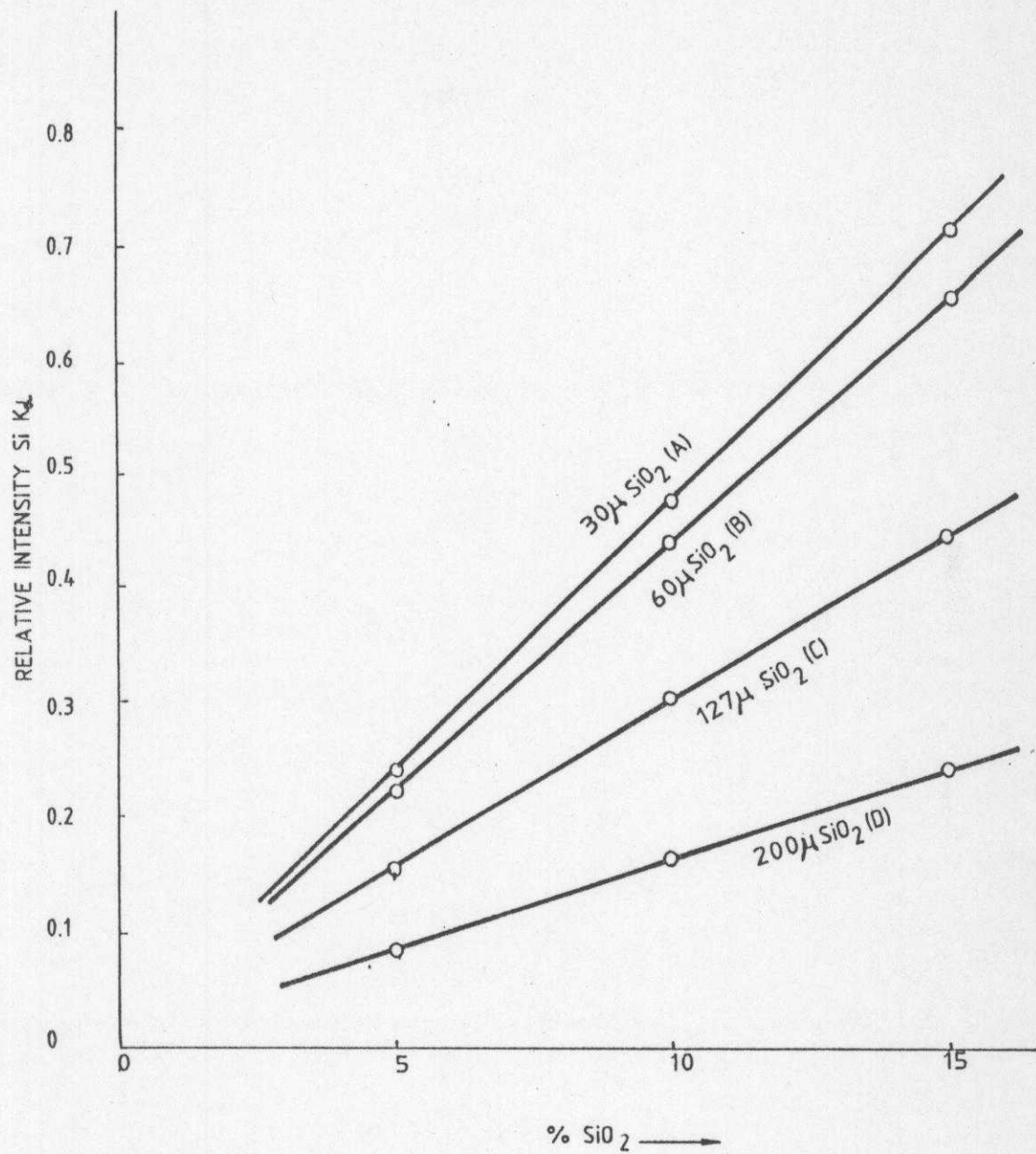


FIG.4 SILICON-K $\alpha$  INTENSITY IN SiO $_2$ -CaCO $_3$  MIXTURES  
(CaCO $_3$  PARTICLE SIZE-325 MESH)

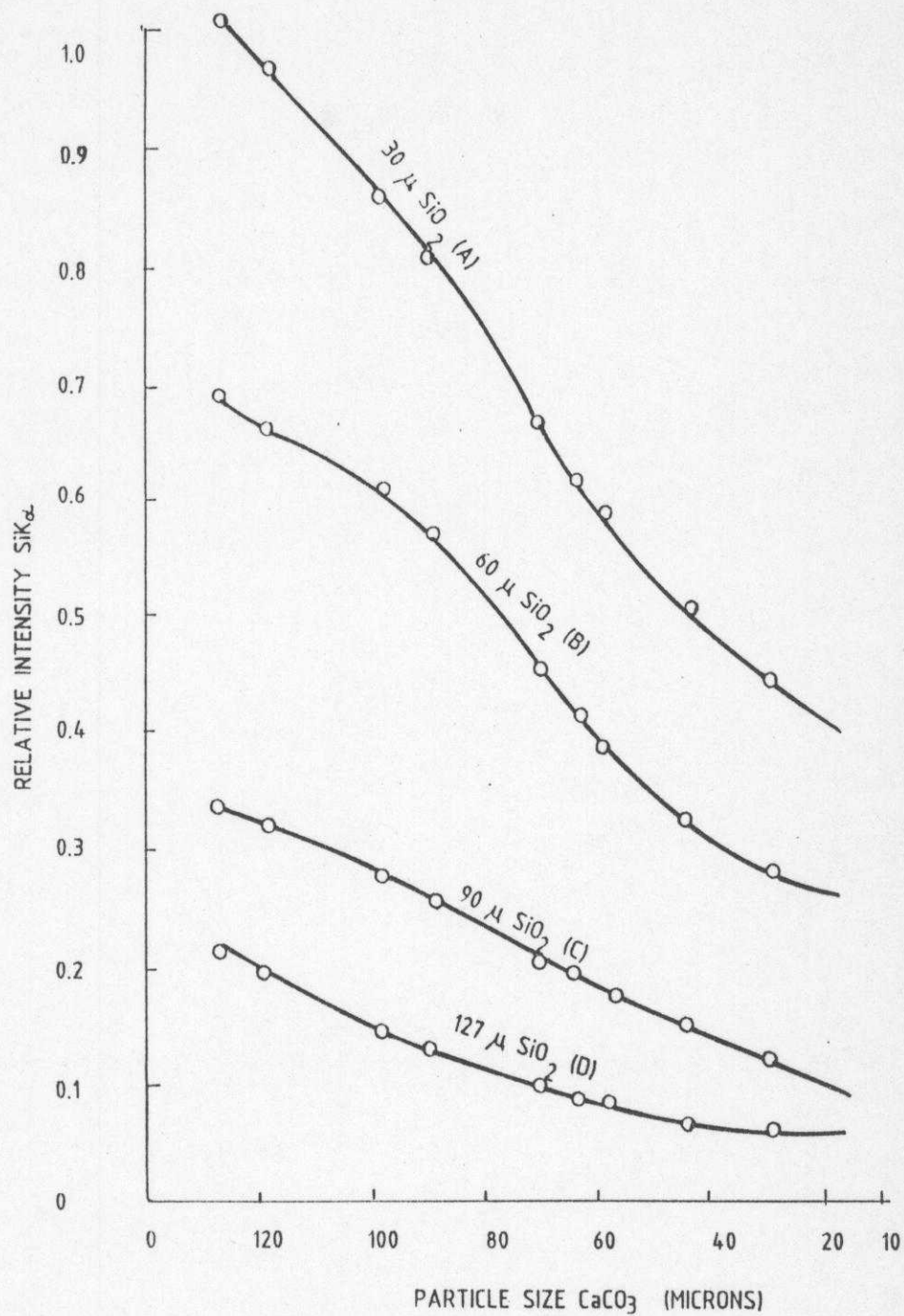


FIG.5 EFFECT OF LIMESTONE PARTICLE SIZE ON THE RELATIVE INTENSITY OF SiK $\alpha$  [85% SiO<sub>2</sub> + 15% CaCO<sub>3</sub>]

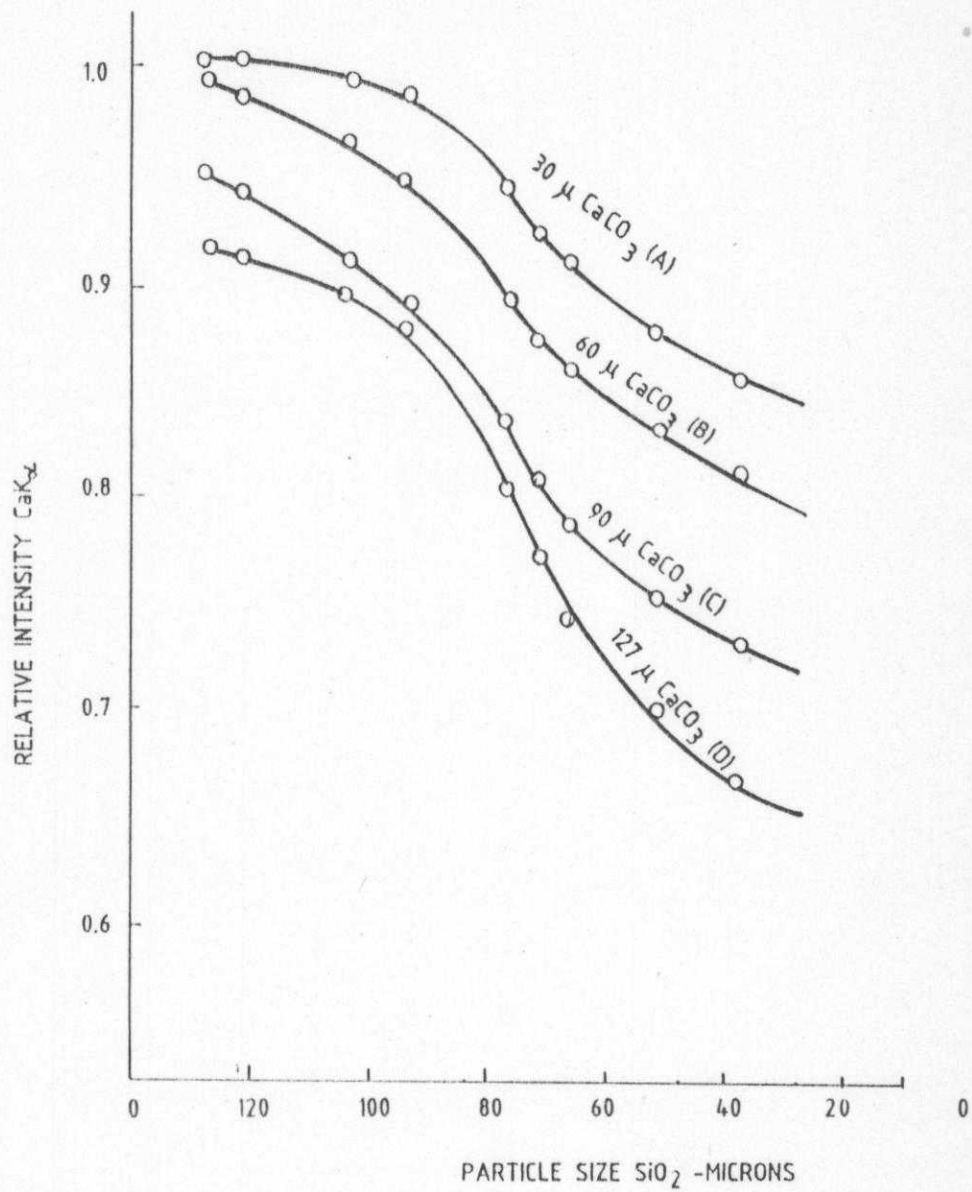


FIG.6 EFFECT OF PARTICLE SIZE OF SILICA ON THE RELATIVE INTENSITY OF CaK $\alpha$  (85% CaCO $_3$  + 15% SiO $_2$ )

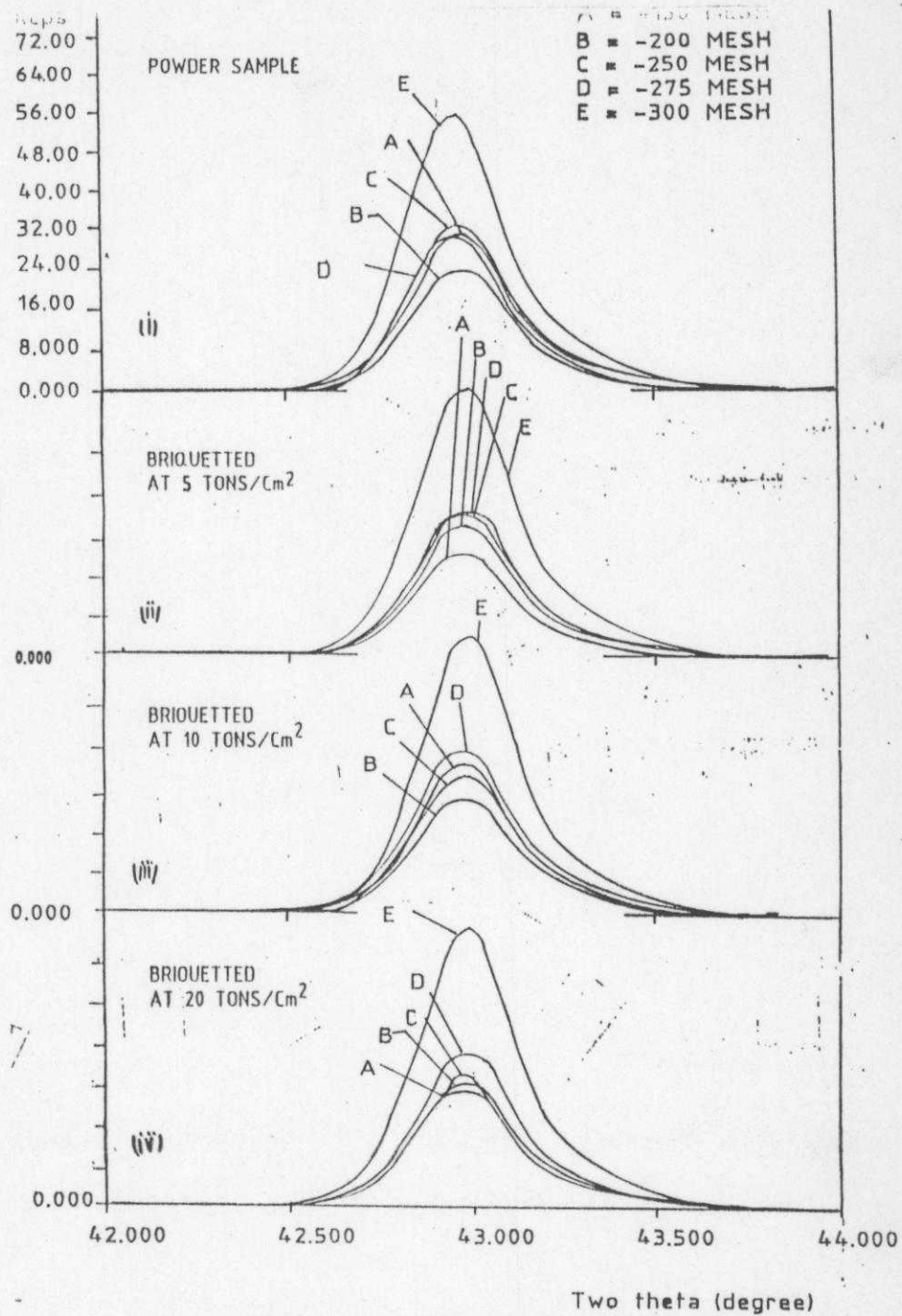


FIG. 7 XRF SCAN OF  $\text{WO}_3$  FOR VARIOUS PARTICLE SIZE AT DIFFERENT BRIQUETTING PRESSURES.

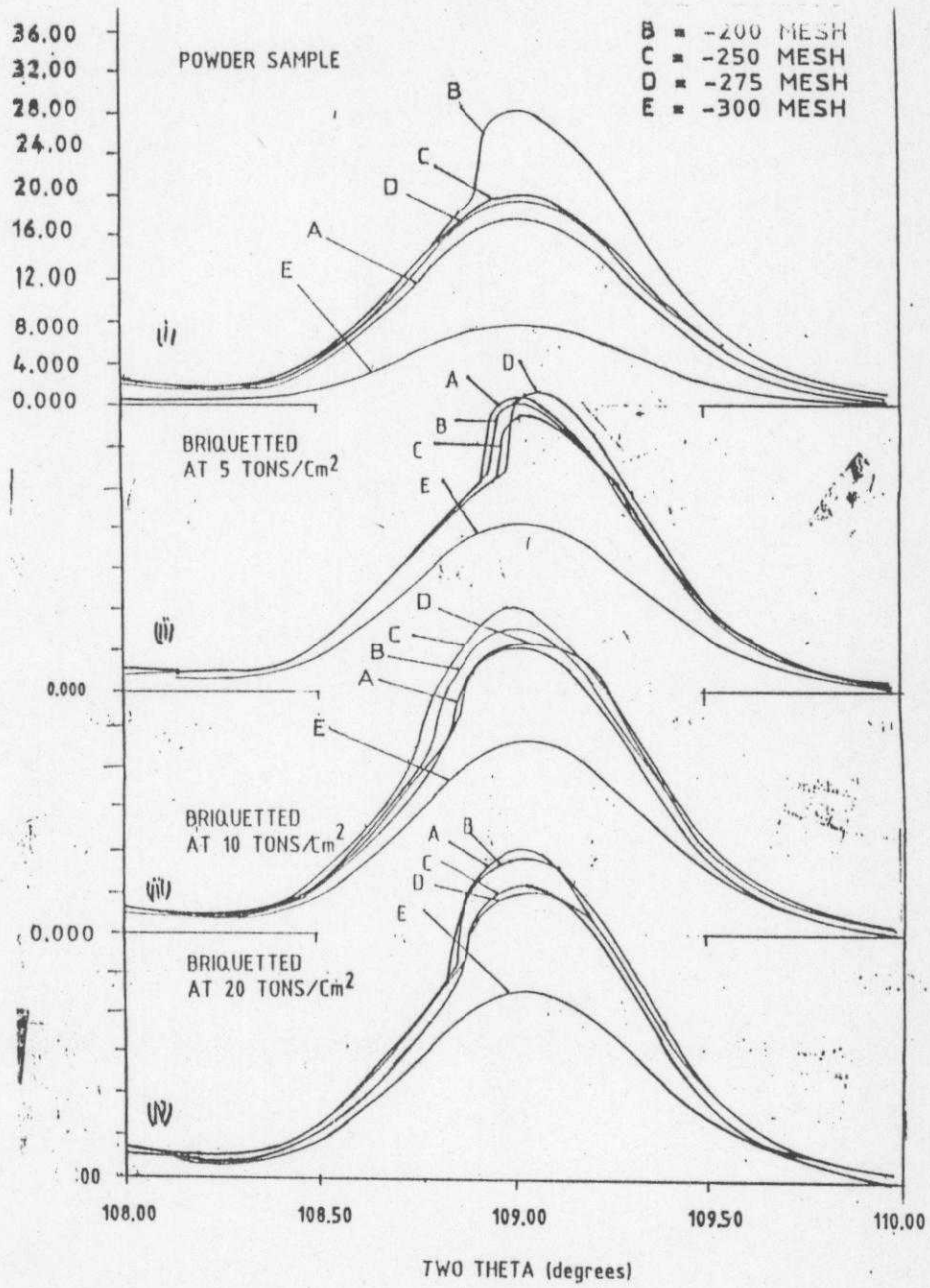


FIG. 8 XRF SCAN OF SiO<sub>2</sub> FOR VARIOUS PARTICLE SIZE AT DIFFERENT BRIQUETTING PRESSURES.

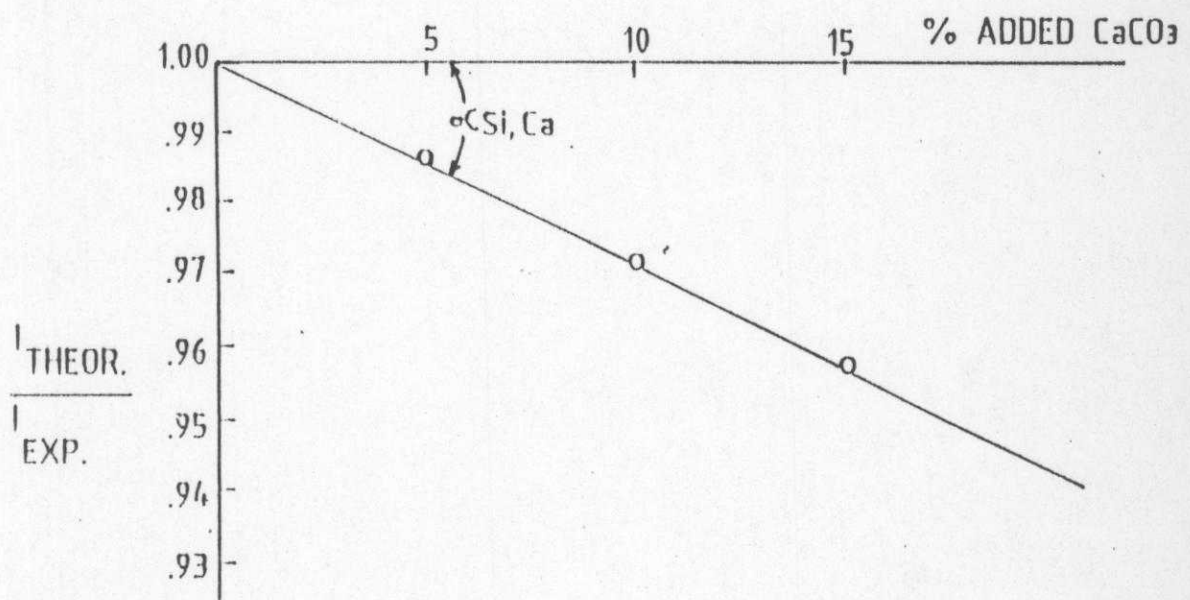


FIG.9 DETERMINATION OF  $\alpha_{\text{CSi, Ca}}$



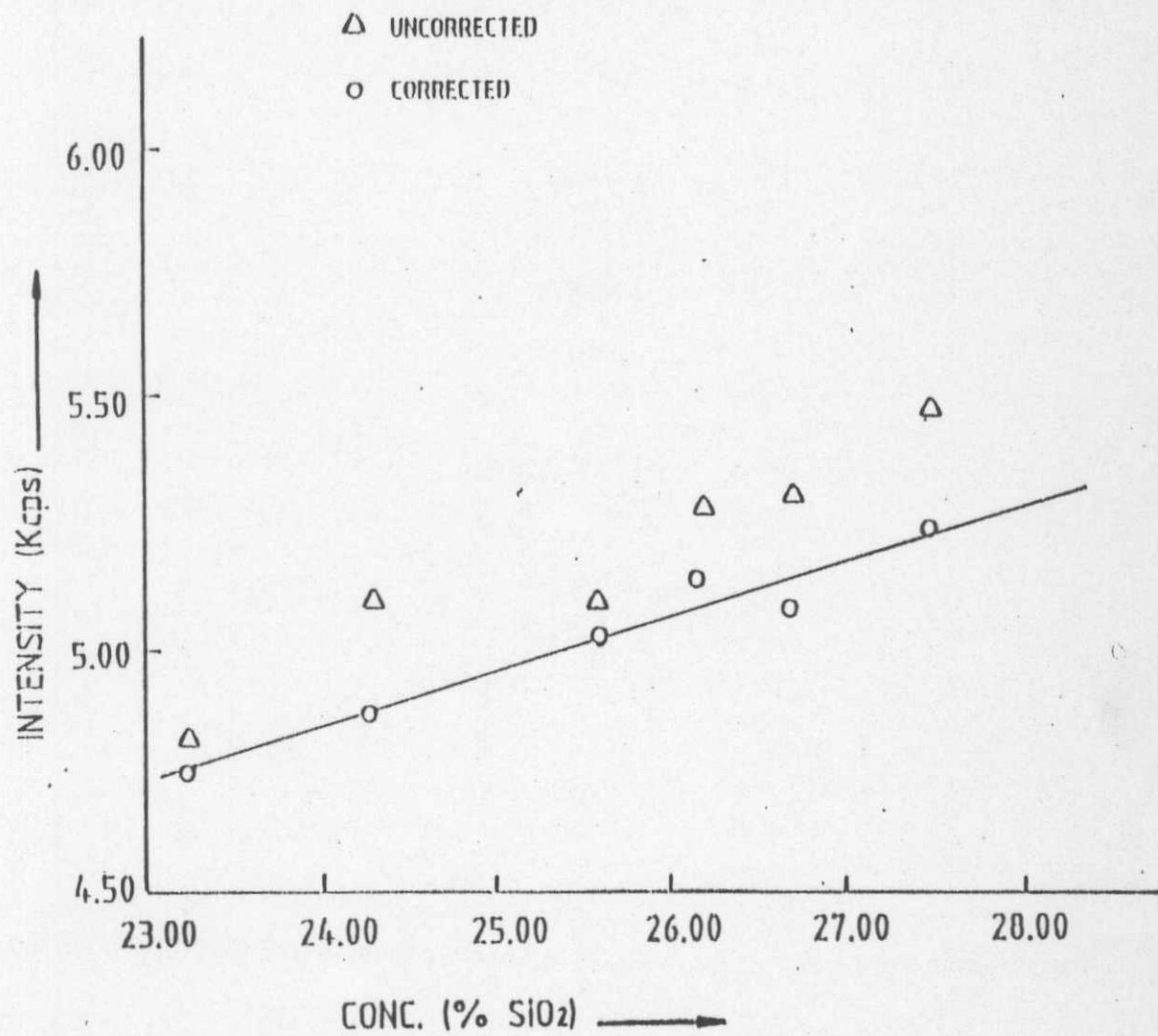


FIG. 10 SiO<sub>2</sub> CALIBRATION OF B.F. SLAG CEMENTS.

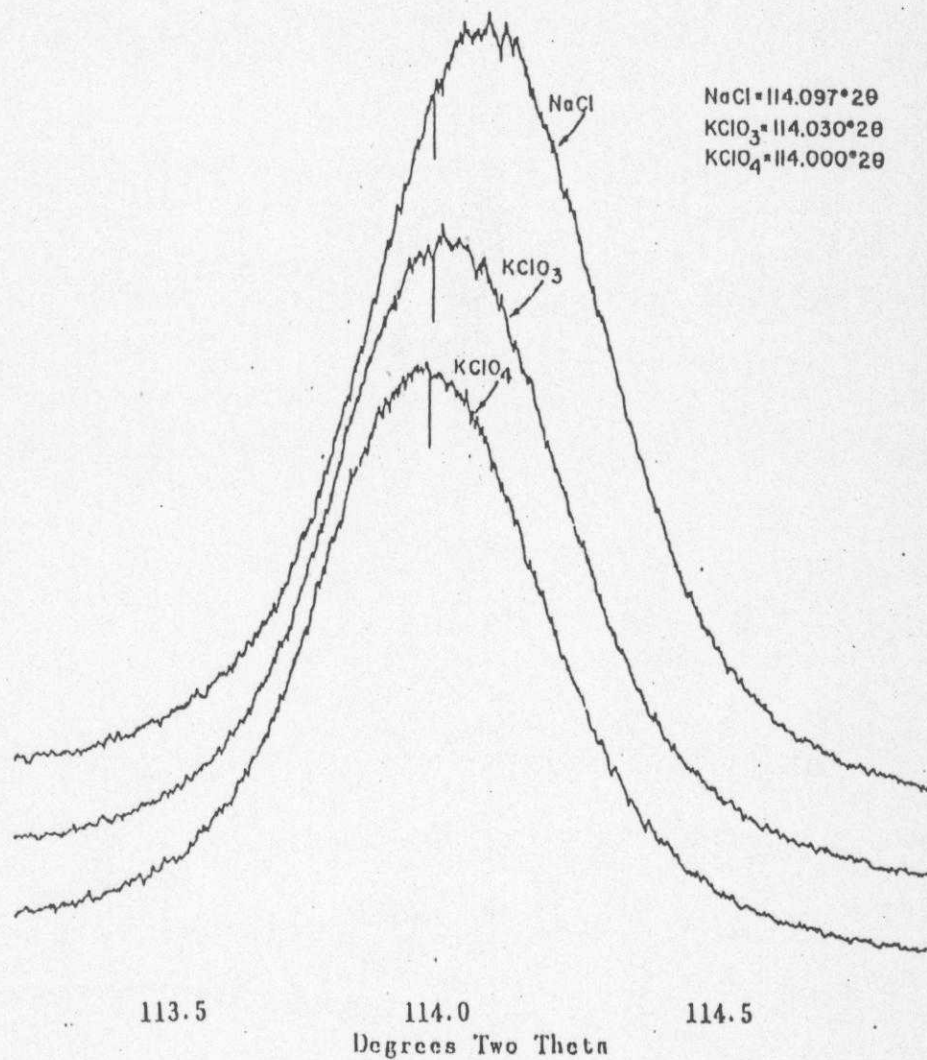


FIG. 11 Experimental curves showing variation of chlorine  $K_{\alpha}$  peaks with chemical combinations using NaCl analyzer.