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**QUANTITATIVE AND STRUCTURAL ANALYSIS OF KALABAGH IRON ORE BY
PHYSICO-CHEMICAL METHODS WITH REFERENCE TO ITS BENEFICIATION**

Part I.—Calibration of X-ray Spectrometer for the Estimation of Iron

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1. Introduction

As the iron ore from Kalabagh (West Pakistan) has been generally recognized to be the most practicable source of iron for the steel industry of the country, it was considered of importance to undertake detailed analytical and structural studies on this ore by a combination of chemical and physical techniques, with a view to determining the optimum conditions for its beneficiation. Among the physical techniques, X-ray methods have been extensively employed, because of the ease and reliability they offer in providing information on the structural characteristics of minerals.

The use of X-rays in the investigation of minerals can be divided into three distinct categories, namely (i) quantitative estimation of different elements in the sample, (ii) identification of the various constituent crystalline phases in the sample, and (iii) detailed examination of the structural relationships of these various phases. Studies in all these respects, have been carried out on the Kalabagh ore, and the results will be presented in a series of communications on the subject. The X-ray fluorescence spectrometer has been extensively used during these investigations and the present paper describes the standardization of this instrument for an accurate estimation of iron in the raw ore and in the beneficiated samples.

X-ray spectroscopy utilises the characteristic

secondary X-radiation from the elements in the test samples for their identification and quantitative estimation. The secondary X-rays, the K and L series lines of which are principally useful, are selectively reflected by a crystal grating which, when set in a position satisfying the Bragg relation, $\sin\theta = n\lambda/2d$, reflects the radiation of wave length λ on to the other side, where it can be picked up and its intensity measured by a Geiger counter (inset to Fig. 1(a)). Thus the glancing angle θ for the crystal setting identifies the radiation completely, and this in turn identifies the element producing it, while the intensity of this characteristic radiation is a measure of the quantity of the element present. Such a technique can therefore be used with advantage for both qualitative and quantitative analyses, especially for mineralogical and ore samples.

2. Basic Desiderata for the Analytical Work

The absolute value of intensity of a given reflection depends on various factors, such as, the intensity of the primary radiation, the thickness of the sample, its surface area exposed to X-rays, the particle size, and the composition of the matrix of the sample. The first four conditions can be standardised in a particular set-up but allowance for the composition of the matrix of samples presents a very considerable problem. In principle, a calibration curve can be drawn with standard samples containing known quantities of the test element and having essentially the

same matrix as the test material, and this curve can then be used for the analysis of the test samples. But in practice, this method is not suited for ore samples because of their complex and variable matrix, and for such cases the use of internal standards has been suggested.¹ The internal standard element has to satisfy two essential conditions: (i) that its emission line (the one that has to be used as its reference line) be close to the emission line of the test element, so that the disturbing effects due to the matrix of the sample will be identical for both the lines, and (ii) that the absorption edges of the standard and the test elements do not interact seriously with either of the reference lines. After the internal standard element has been selected, a calibration curve can be prepared with standard samples containing known percentages of the test element and the standard element. This calibration curve can then be used for the analysis of the test element in unknown samples.

3. Experimental Details

Equipment: A "Seifert" fluorescence spectrometer was used for this study, and a copper tube was used as the source of primary X-rays because it gives a higher sensitivity than other available tubes (Fig. 1). The surface area of the samples exposed to X-rays was maintained constant by keeping the relative position of the sample holder and the X-ray tube fixed. A lithium fluoride crystal, with planes of d -value equal to 2.00865 A.U. in the reflecting position, was used for analysing the characteristic secondary X-radiation given out by the elements in the sample. The spectrometer provided for scanning and automatic recording of the entire excited X-ray spectrum of the test sample, and also for the direct reading of the intensity of the lines in counts per second. The sensitivity of the Geiger counter could be varied with the help of the sensitivity selector switch to cover a full scale deflection of 10-30,000 c.p.s.

Sample Preparation: The sample was used in the powdered form, ground so that nearly all of it passed through a 100 B.S. sieve. Because the specimen had to be mounted vertically in the spectrometer used, it was first made into a paste with the help of a dilute amyl acetate solution of household cement, a commercial material used for joining plastic materials. This paste was then spread to a depth of approximately one millimetre on a glass slide about one inch square, thus providing enough material to receive the full spread of the incident beam. The slide dried fully in half an hour or so, and was then mounted in place on the spectrometer.

4. Semi-quantitative Calibration Curve for Elements Heavier than Titanium

An approximate calibration curve was initially prepared to obtain a rough measure of the sensitivity of the instrument for the different elements of the periodic table, the sensitivity being expressed as counts per second for one per cent element by

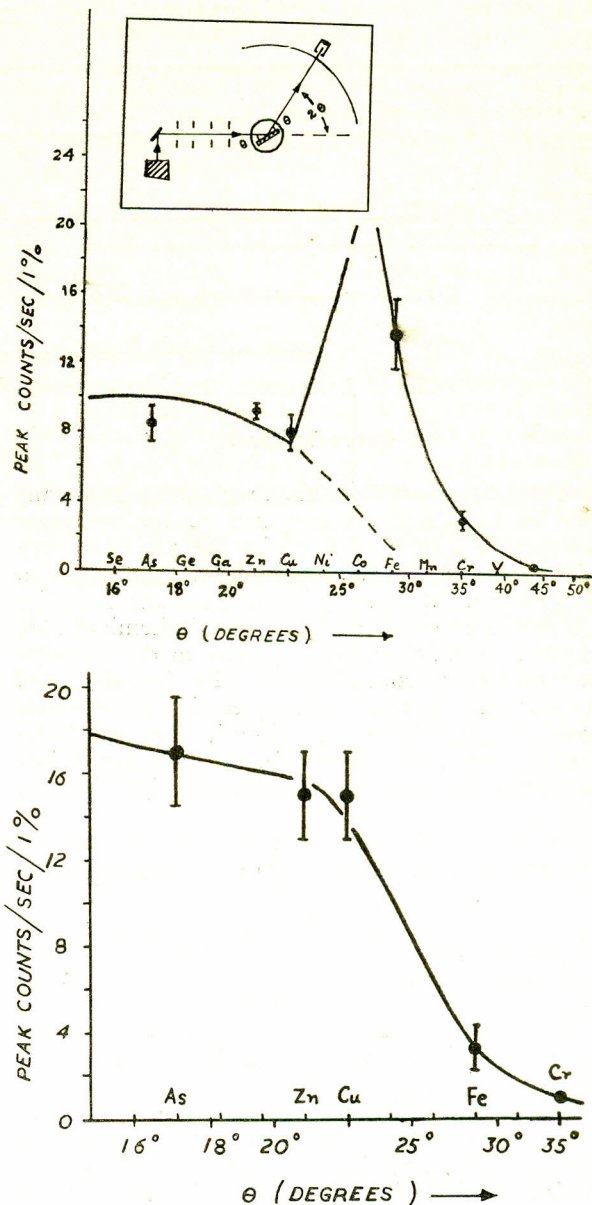


Fig. 1.—Semi-quantitative calibration curves from titanium to selenium with (a) copper tube (top) and (b) molybdenum tube, both run at 45 kV and 20 mA. The short vertical lines indicate the variation of the experimental points with the matrix of the mixture, and the inset shows a schematic diagram of the spectrometer.

weight in a mixture composed of several compounds. A portion of this curve, covering the elements from titanium (atomic number 22) to selenium (atomic number 34) is shown in Fig. 1(a) and 1(b), that in Fig. 1(a) being obtained with a copper tube as the primary source of X-rays, whereas Fig. 1(b) shows the curve obtained with a molybdenum tube, both the tubes being run at 45 kV and 20 mA. These curves were obtained with standard calibrating samples prepared by mixing several compounds containing known quantities of test elements, different samples being prepared separately for the different parts of the periodic table, and the results finally checked by using a composite sample containing about fifteen elements spread over the full range, from $Z=20$ to $Z=92$. As expected, a considerable variation was found in the number of counts per second (for one per cent element by weight) when the composition of the matrix was changed, but the mean values plotted in Fig. 1 may be taken to be correct to within their standard deviations, which are shown by the short vertical lines in the figure. These curves can, therefore, be used for a preliminary semi-quantitative estimate of the constituent elements of a mineral sample. This analysis is then used to define the optimum experimental conditions to be used for an accurate quantitative measurement, as described below for the Kalabagh iron ore samples.

It should be mentioned that in the present study the peak heights from the recorded traces of the various characteristic X-ray lines have been used. This procedure is justifiable provided that the operating conditions are kept constant, particularly with regard to scanning speed and time-constant of the rate-meter smoothing circuit. For the work described herein a scanning speed of 1° per minute was used, the capacitor of the smoothing circuit being kept fixed at a moderate value.

5. Quantitative Calibration Curve for Iron by the Method of Dilution-cum-Internal Standard

It can be seen from Fig. 1 that the sensitivity obtained with the copper tube in this range of the periodic table is higher than with the molybdenum tube, the copper tube giving almost three times as many counts as the molybdenum tube for the same percentage of iron content in any sample. This made the copper tube the preferred choice as the source of primary X-rays for the present work.

From the semi-quantitative analysis, it was known that the mean iron content of the ore

sample was around 35%, and because the individual samples were expected to vary widely in iron content, therefore the calibration curve had to be drawn so as to cover a wide range, say from 15 to 60% iron. This meant (cf. the semi-quantitative calibration curve) that the peak heights of the Fe $K\alpha$ line would lie between 200 c.p.s. and 750 c.p.s. if the samples were used as such. Although the instrument counter is able to record such large counts accurately, yet the requirement that the calibration curve be prepared with standard calibrating samples having the same matrix as the test samples is impossible to meet, especially in view of the wide variations in the nature of the ore samples, which were from different areas and depths within the ore field. A partial solution of this difficulty is to dilute the test samples (by a large factor) with a suitable compound, and then to compare them with standard calibrating samples containing different quantities of the test element distributed in the same diluting agent. This method has its justification, because in this case the matrix of the test samples and the standard samples is essentially that of the diluting agent. The otherwise reliable method of incorporating a suitable element as an internal standard in the test samples and also in the calibrating standard samples for comparison, cannot by itself cope with the errors caused by a variable matrix.

Keeping in view the influence of a diluting agent in reducing the uncertain disturbing effects of the matrix, a method based on the combination of the dilution and the internal standard technique was developed for the present work. Calcium carbonate was used as the diluting agent and the dilution factor has been taken as ten. This dilution by a factor of ten will evidently reduce the intensity of the Fe $K\alpha$ line for the poorest standard calibrating sample to a low value of nearly 20 c.p.s., but this is no disadvantage since it can be accurately recorded by the counter. On the other hand, it will reduce the error caused by the presence of the variable matrix to a negligible value of less than 1%.* Cobalt was chosen as the internal standard element, because it is close enough to iron and its absorption and emission lines do not interact seriously either with the iron or the copper lines (from the exciting tube), as can be seen from the wavelengths given in Table 1.

Having thus made a choice of the diluting agent and the internal standard element, a standard "calibrating mixture" was prepared by

* This estimate is based on a dilution factor of 10 coupled with the variations in counting rate due to matrix variations seen in Fig. 1.

TABLE I.—K-SERIES EMISSION LINES AND ABSORPTION EDGES OF IRON, COBALT AND COPPER

Elements	K α_2 in A.U.	K α_1 in A.U.	K β_1 in A.U.	K-absorption edge in A.U.
Iron	1.9399	1.9359	1.7565	1.7433
Cobalt	1.7927	1.7889	1.6207	1.6081
Copper	1.5443	1.5405	1.3921	1.3804

mixing cobalt in the form of cobalt acetate in calcium carbonate, so as to have nearly a 10% content of cobalt acetate in the mixture. The calibrating samples were then prepared by taking a constant quantity (about 4.5 g.) of the standard calibrating mixture and mixing it with known quantities of ferric oxide (Fe_2O_3) so as to obtain concentrations of 0.16% to 6% iron in the total mixture. Because a small mechanical mixer was not available, the mixing of each sample was done manually for fifteen minutes, the technique used being to add the "calibrating mixture" in three or four successive instalments with thorough mixing for five minutes between additions. A specimen record of counting rate against the angle 2θ is shown in Fig. 2. The experimental values of peak counts have been determined from the mean of two observations on the peak heights of the Fe $K\alpha$ and Co $K\alpha$ lines from two successive records for each standard sample. A calibration curve with $\log [H(\text{Fe}K\alpha)/$

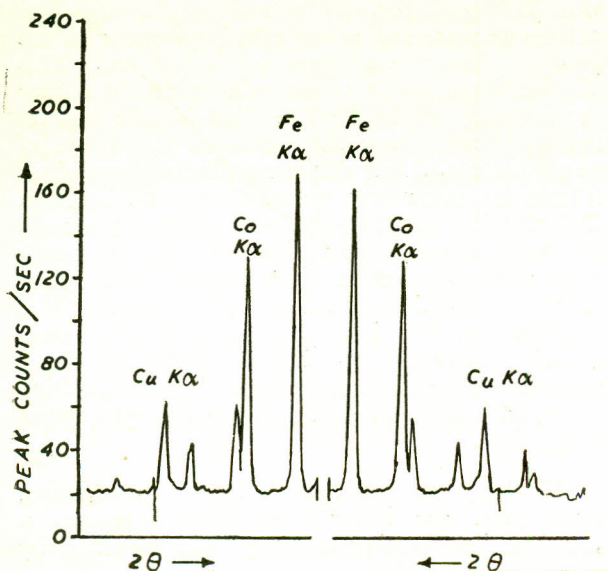


Fig. 2.—A typical record of the iron, cobalt and copper peaks obtained in two successive runs with a calibrating sample for iron estimation.

$H(\text{Co}K\alpha)]$ against $\log [C(\text{Fe})/C(\text{calibrating mixture})]$ was drawn as in Fig. 3, where H denotes peak heights in counts per second, and C denotes percentage concentration by weight in mixture. A fairly good straight line plot results, but the points for low percentages of iron tend to be rather widely scattered. This was suspected to be due to incomplete mixing of the samples, because the standard samples for obtaining these points had been prepared in a single step by mixing only a few milligrams of ferric oxide in about 4.5 grams of calibrating mixture. In order to improve the accuracy in this region, fresh standard samples were prepared starting from a single standard calibrating sample containing 8.6% Fe_2O_3 , the weaker calibrating samples being made from this sample by successive dilution with the calibrating mixture. The results are given in Table 2. This technique gives better dispersal of the iron oxide, and a better calibration curve is obtained as shown in Fig. 4, thus confirming the importance of careful mixing. The previous calibration curve is also drawn in Fig. 4 (broken line) and is seen to be exactly parallel to the new curve for iron contents greater than 8%, which proves the accuracy of both sets of readings in this range.

6. Application and Discussion of the Calibration Curve

The deviations of the individual readings from the mean value are indicated by the circles around the points shown in Fig. 4, and a smooth curve has been drawn through them. It may be

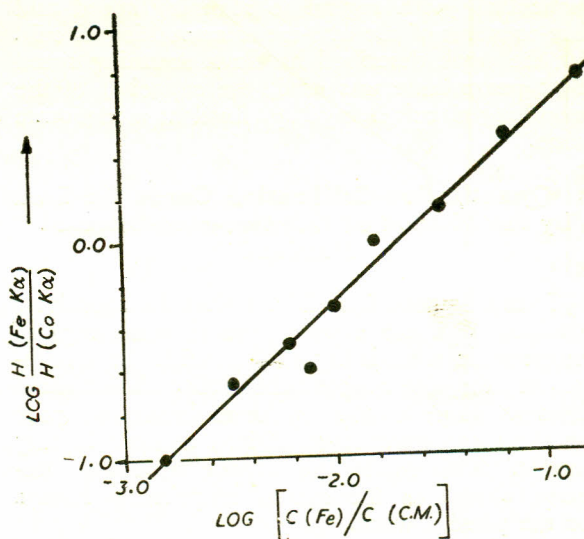


Fig. 3.—Logarithmic quantitative calibration curve for iron, showing large errors at small iron content due to imperfect mixing.

noted that this curve does not deviate far from a straight line. A number of analyses have been based on this curve and have given results in good agreement with the chemical analyses, the error being nearly $\pm 1\%$. The outstanding advantages of this analytical technique are its simplicity and

rapidity, which were of great value in following the course of ore beneficiation produced by various methods.

An attempt was also made to use the Cu $K\alpha$ line from the X-ray tube itself as an internal

TABLE 2.—CALIBRATION DATA FOR PLOTTING THE CURVES IN FIGS. 4 AND 5.

Sl. No.	Percentage of iron in the total mixture	Percentage of the calibration mixture in the total mixture	log $\frac{\% \text{ Fe in mixture}}{\% \text{ calib. mixt. in the mixture}}$	log $\frac{\% \text{ Fe in the mixture}}{\% \text{ calib. mixt. in the mixture}}$	Peak counting rate in counts/second			$\log \frac{H(\text{Fe}K\alpha)}{H(\text{Co}K\alpha)}$	$\log \frac{H(\text{Fe}K\alpha)}{H(\text{Cu}K\alpha)}$
					Cu $K\alpha$	Co $K\alpha$	Fe $K\alpha$		
1	6.00	90.0	$\bar{2}.824$	0.778	48.5	166	336	0.306	0.841
2	3.17	94.7	$\bar{2}.525$	0.501	39.2	106	142	0.127	0.559
3	1.71	97.2	$\bar{2}.245$	0.233	48.0	149	92.5	$\bar{1}.793$	0.285
4	0.938	98.4	$\bar{3}.979$	$\bar{1}.972$	37.8	118	42.6	$\bar{1}.558$	0.052
5	0.517	99.1	$\bar{3}.717$	$\bar{1}.714$	48.0	136	35.3	$\bar{1}.415$	$\bar{1}.867$
6	0.287	99.5	$\bar{3}.460$	$\bar{1}.458$	38.3	106	20.4	$\bar{1}.284$	$\bar{1}.726$
7	0.159	99.7	$\bar{3}.203$	$\bar{1}.202$	54.3	161	16.2	$\bar{1}.003$	$\bar{1}.475$

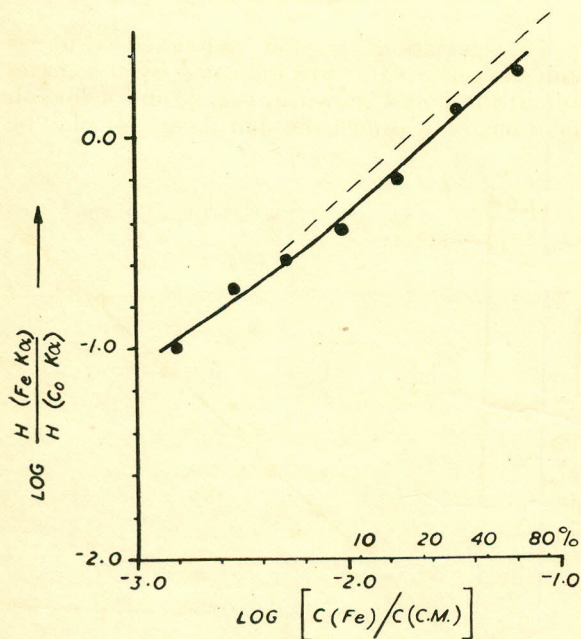


Fig. 4.—Logarithmic calibration curve for iron obtained from samples with improved mixing. The broken line corresponds to the curve of Fig. 3, and the per cent figures given along the abscissa denote the corresponding iron content for an unknown sample on the basis of 10% dilution.

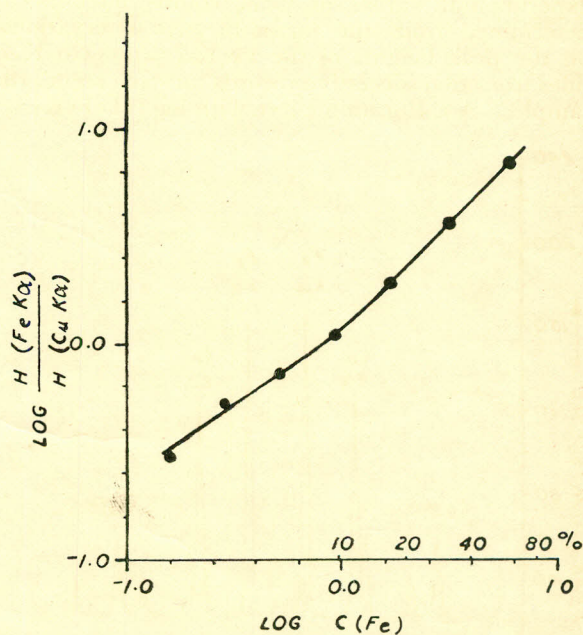


Fig. 5.—Logarithmic calibration curve obtained using the copper $K\alpha$ line from the tube as an internal standard. The per cent figures along the abscissa denote the corresponding iron content of an unknown sample on the basis of 10% dilution.

standard, first because the ore sample itself does not contain copper and secondly because the Cu $K\alpha$ line is also close to the Fe $K\alpha$ line. A calibration curve with $\log [H(\text{Fe } K\alpha)/H(\text{Cu } K\alpha)]$ against $\log C(\text{Fe})$ was drawn, and is given in Fig. 5. The deviations of individual points from the mean value have been estimated, as before, from measurements on two successive records, and are of the order of the radii of the circles shown in the figure. Although this calibration curve appears to be somewhat better than that shown in Fig. 4, the nature of the two curves is essentially the same. This indicates that the characteristic radiation of the tube itself can be very profitably used as an internal standard, provided, of course, that the test sample does not contain the target element in appreciable quantities. This method would have the added advantage that an external element does not need to be introduced into the sample, and thus the

uncertainties pertaining to its improper mixing are eliminated.

It must, however, be noted that the success of any method of calibration for analytical work will eventually be determined by the nature of the ore sample, and individual cases have to be studied on their own merits before choosing the most suitable method.

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Reference

1. John S. Stevenson, *Am. Mineralogist*, **39**, 436 (1954).