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ACCURATE X-RAY FLUORESCENCE ANALYSIS WITHOUT INTERNAL STANDARD

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ACCURATE X-RAY FLUORESCENCE ANALYSIS WITHOUT INTERNAL STANDARD

by

FERNAND CLAISSE

QUÉBEC

1956

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by

Fernand Claisse

SUMMARY

This paper describes the preparation of ores, minerals and other chemical compounds for the analysis by an X-ray fluorescence method in which no internal standard is used. The method is rapid, accurate and almost universal in that it can be used for most elements without any difference in the procedure.

The description of the method is preceded by theoretical considerations and followed by examples of results obtained.

INTRODUCTION

It is the opinion of the writer that relatively complete theoretical study of the problems that arise in the analysis of ores and rocks by X-ray fluorescence has not been published.

Yet, such a study would be beneficial in that it would indicate how samples should be prepared to obtain any desired accuracy and even suggest ways to simplify the analytical procedures.

A paper written by Adler and Axelrod (1) on the use of an internal standard in X-ray fluorescence analysis gives a good discussion of sample matrix effects on line intensities. However, factors such as grain size and chemical combinations, which also affect line intensities to a comparable extent, are ignored by most writers.

The object of this paper is to make a study of these factors that determine line intensities in X-ray fluorescence analysis. A sample preparation technique in which absolute line intensities give true percentages of elements with accuracies comparable to that of routine chemical analyses for ores, minerals and other chemical compounds will be proposed.

THEORETICAL

Homogeneous sample

Let us first determine the curve of the line intensity as a function of concentration in a perfectly homogeneous binary mixture where the grains are infinitely small.

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*Published by permission of the Deputy Minister of Mines of the Province of Quebec.

(1) Adler, I. and Axelrod, J.M., Spectrochimica Acta, (1955) 7, 91-99.

Take for example Fe in Si, a system which approximates the case for the analysis of Fe in silicates. The absorption curves for these two elements are shown in Figure 1.

Now, consider a small volume dv of this sample at a distance x below its surface (Figure 2). It will emit fluorescent X-rays with intensity given by:

$$d I_o = b C I_i \, dv \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where I_i is the primary radiation intensity just before it enters the volume dv, C is the Fe concentration and b is a proportionality constant.

Now, the intensity I_i will depend on the absorption characteristics of the sample which vary with the wavelength. This is given by:

$$I_i = \int_{\lambda=0}^{\lambda=\lambda_e} I_A e^{-\mu \rho \sqrt{2} x} \, d\lambda \quad \ldots\ldots\ldots (2)$$

where I_A is the intensity of the primary radiation of wavelength λ striking the sample, μ is the corresponding mass absorption coefficient, ρ is the density of the sample, λ_e is the wavelength of the absorption edge for the FeK lines, and $x\sqrt{2}$ is the length of sample traversed by the X-rays. Here, as is usually the case, the primary and secondary radiations are assumed to be at 45^o with the surface of the sample.

In Equation 2, I_A is not usually known. But since exact calculations are not necessary we may replace eq.2 by a simpler relation:

$$I_i = I_1 e^{-\mu_1 \rho \sqrt{2} x} \quad \ldots\ldots\ldots (3)$$

where μ_1 and I_1 refer to one wavelength λ_1, called the effective wavelength for excitation, which will be situated somewhere on the low wavelength side of the absorption edge (Figure 1).

The measured intensity $d I_m$ which is the emitted intensity corrected for the absorption by the medium between the volume dv and the surface of the sample is given by a relation similar to equation 2. The absorption coefficient μ_2 is now the one that corresponds to the excited wavelength, namely 1.93 Å in the example studied;

$$d I_m = d I_o e^{-\mu_2 \rho \sqrt{2} x} \quad \ldots\ldots\ldots (4)$$

Combining equations 1, 3 and 4, and integrating for X, from zero to infinity, we obtain

$$I_m = \frac{k C}{\mu_1 + \mu_2} \quad \ldots\ldots\ldots\ldots (5)$$

where k is a proportionality constant.

It is known that, for a mixture, the mass absorption coefficient μ is given by

$$\mu = a\mu_a + b\mu_b + \text{-----} n\mu_n \ldots (6)$$

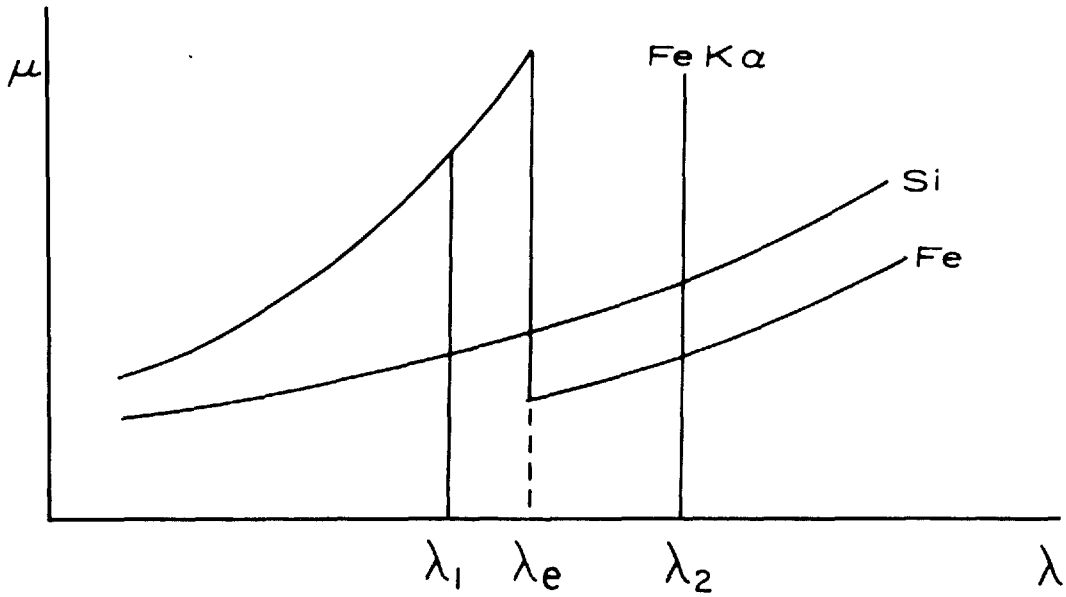

FIG. 1 ABSORPTION CURVES OF FE AND SI FOR X-RAYS.

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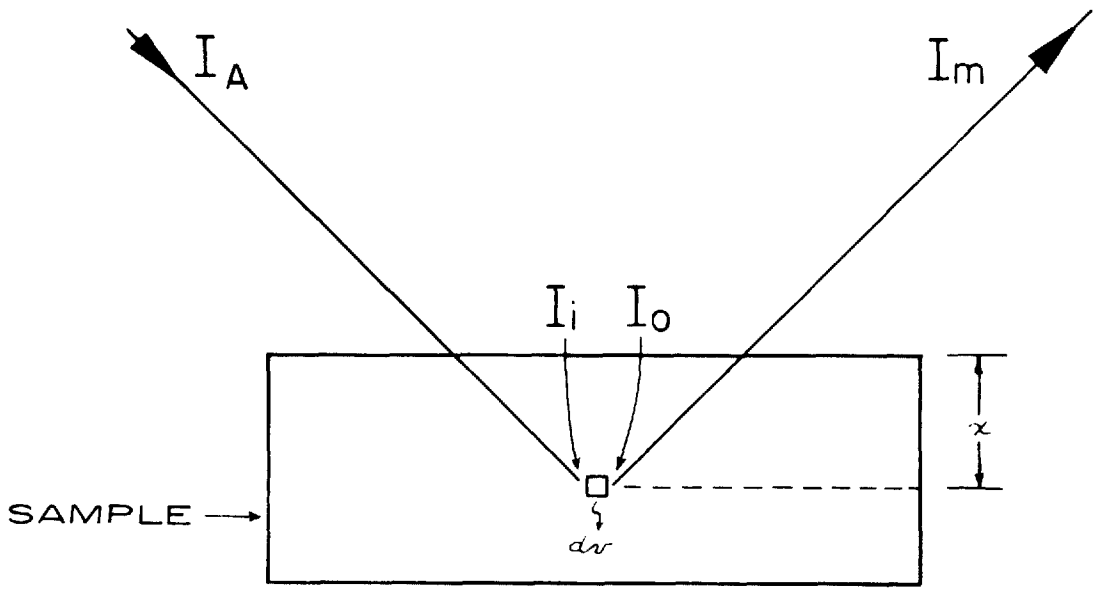

FIG. 2

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where $a, b, ----, n$ are the weight concentrations of the constituents, and $\mu_a, \mu_b, ---\mu_n$ are their respective mass absorption coefficients. Then we have for a binary mixture

$$I_m = \frac{k\ a}{a(\mu_1+\mu_2)_a + b(\mu_1+\mu_2)_b} \quad .. \ (7)$$

Applying equation 7 for a very dilute solution, that is with a very small, and b equal to 1, we find

$$\left(\frac{dI_m}{da}\right)_{a=o} = \frac{k}{(\mu_1+\mu_2)_b} \quad ..... \ (8)$$

We have, for very high concentrations, where b is very small and $a \cong 1$

$$\left(\frac{dI_m}{da}\right)_{a\approx 1} = \frac{k}{(\mu_1+\mu_2)_a} \quad ..... \ (9)$$

Since $(\mu_1)_a$ is usually much larger than $(\mu_2)_a$, $(\mu_1)_b$ and $(\mu_2)_b$, the curve of the intensity of the fluorescent radiation as a function of concentration will almost invariably show a decrease in slope as the concentration is increased (Figure 3).

Similar calculations for systems with more than two components give comparable results.

Some of the difficulties that arise in X-ray analysis are due to the slope of this curve (Figure 3), at low concentrations, and to its curvature at high concentrations. Both of these factors are dependent on sample matrix.

Heterogeneous samples

Most of the analyses made today by X-ray fluorescence are done on heterogeneous samples, that is, samples composed of grains which differ in their chemical composition. Calculations for a general case will not be given here on account of the difficulties involved. However, from the study made in the preceding section, additional information can be gained from these samples.

Let us imagine a sample composed of two kinds of grains which are assumed to be large compared to the depth of penetration of X-rays (Figure 4). The element to be analysed is present only in the dark grains and its concentration in these grains is represented by A (Figure 3). The concentration of the element in the whole sample is represented by B in the same illustration.

Let us now consider one dark grain on the surface of the sample. The presence of neighbours does not affect appreciably the intensities of the primary and the fluorescent radiation associated with it. Since the element to be analysed is in high concentration in these grains, its sensitivity defined as the ratio of the measured intensity to the concen-

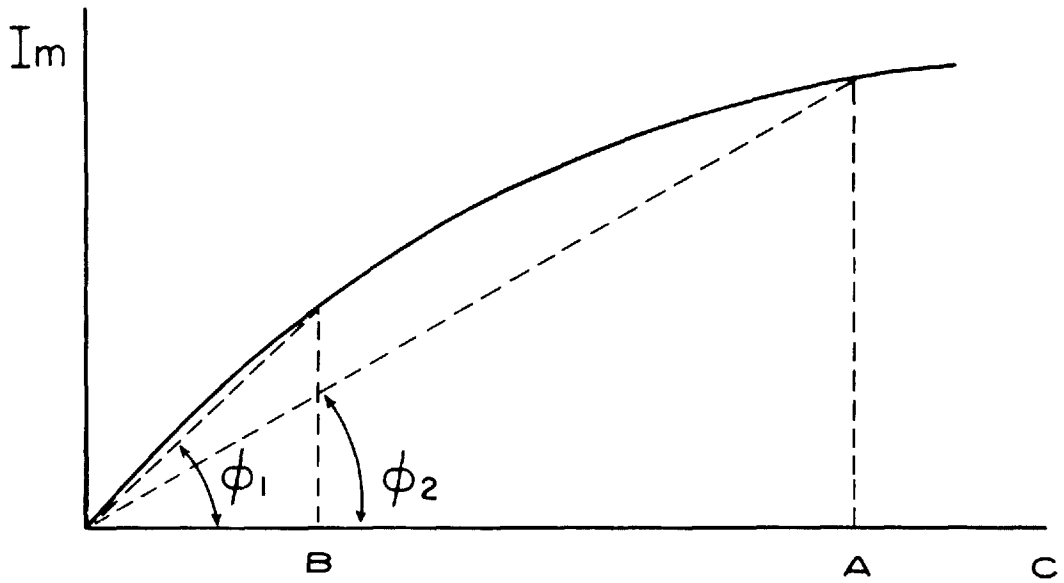

FIG. 3 TYPICAL INTENSITY Im CURVE OF AN X-RAY FLUORESCENCE LINE AS A FUNCTION OF THE CONCENTRATION C OF THE CORRESPONDING ELEMENT.

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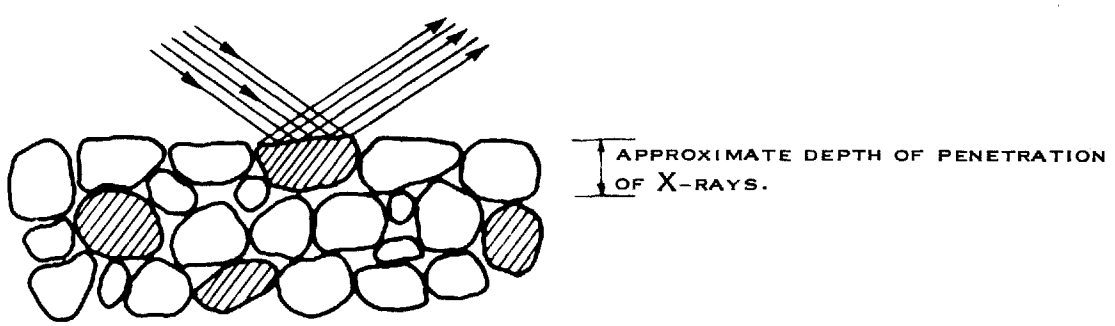

FIG. 4 EXPANDED SECTION THROUGH A HETEROGENOUS SAMPLE SHOWING THE PATH OF THE X-RAYS.

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tration will be equal to $\tan \phi_2$ (Figure 3). If the same element were in a perfectly homogeneous sample, its sensitivity would be given by $\tan \phi_1$ which is larger than $\tan \phi_2$.

If the diameters of the grains are less than the depth of penetration of the X-rays, those deeper under the surface will now participate in the total measured intensity. The primary as well as the fluorescent rays associated with those grains will have to traverse a length of sample and are thus affected to a certain extent by the matrix as a whole. The intensity coming from such grains corresponds to an angle ϕ closer to ϕ_1.

It can be concluded that, as particle sizes decrease, the angle ϕ_2 moves towards ϕ_1. Generally the intensities of fluorescent radiations from heterogeneous samples are observed to increase by grinding the samples, until they approach the limit corresponding to perfectly homogeneous samples.

Since 90% of the total radiation of most rocks comes from a sample thickness of only 100 microns or less, grain size effects are of utmost importance in their analysis.

In order to illustrate the extent to which the grain size may affect the X-ray intensities, mixtures of 10% CuO of uniform particle sizes, and 90% calcite were prepared. The CuK_β line intensities were measured, and plotted as a function of grain size (Figure 5). Note the decrease in intensity with particle size as predicted. The same effect has been observed on other mixtures.

One might conclude that if provisions are made to keep the grain sizes constant, sufficiently accurate analyses can be made. This might be true for certain types of ores,but not for all, because the underlying reason for the preceding observations is not the grain size itself, but the proximity of atoms of the same kind. That also changes with the chemical combination of the element analyzed. The chemical bonding between atoms has practically no measurable effect on the intensities of the K or L lines of most elements, but the crystal structure of the compound results in definite distances between atoms of the same kind, and these distances vary with the nature of the compound. This is effectively a dilution of the element in the grain. If the element belongs to a larger or a smaller molecule, the dilution factor will vary. Point A (Figure 3), which represents the concentration of the element in the grains,will change its position.. The sensitivity, given by $\tan \phi_2$ is seen to increase towards $\tan \phi_1$, the limiting value, as the size of the molecule increases.

To check this theory a number of synthetic samples containing 1% Cr in calcite were prepared.

Reagent grade Cr samples in the form of oxide, chromate, etc. were used. All these salts were screened to $-250 + 325$ mesh, and very carefully mixed by hand, with the calcite, in order to reduce the possibility of change in grain size. The CrK_α intensities were then measured and plotted as a function of the mean Cr-Cr interatomic distances in the salts. (Figure 6, curve A.)

The results agree with those predicted by the theory, namely, that the intensity increases with separation of the Cr atoms. The deviations of the points from the curve are due to a number of causes, as: unknown purity of the products used, change in grain size

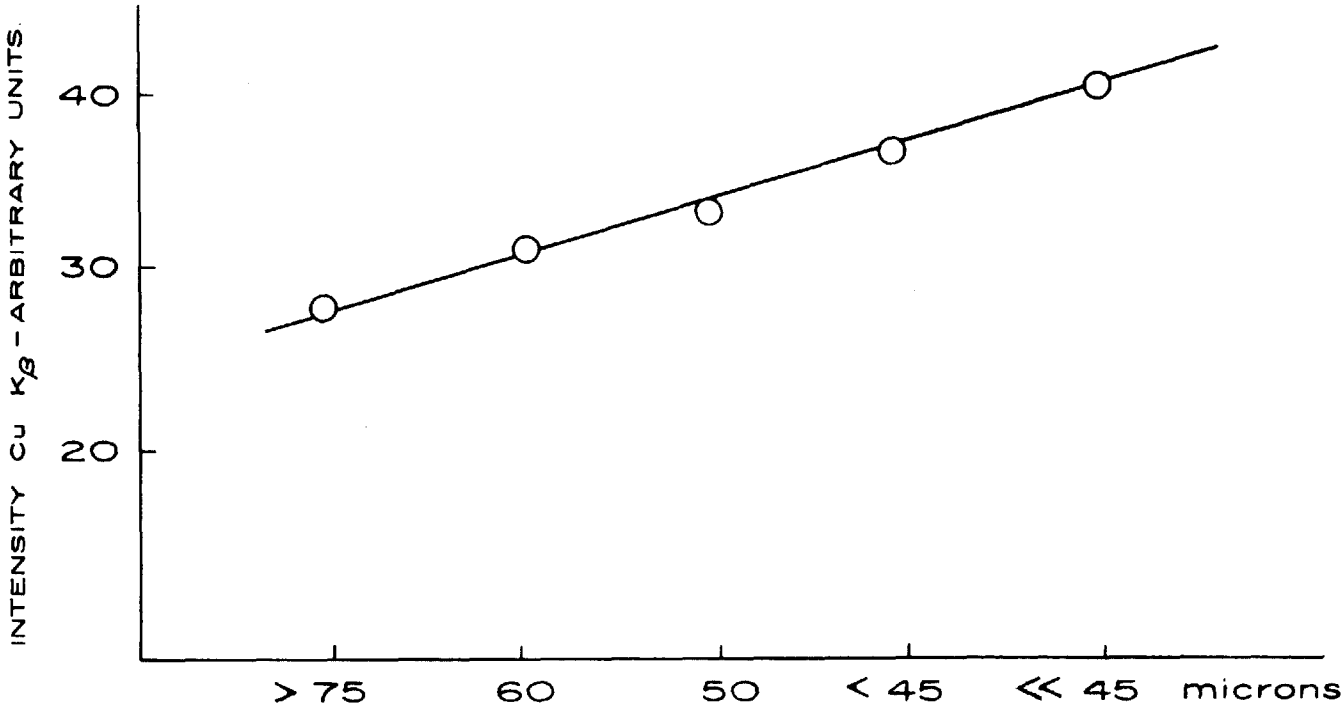

FIG. 5 INTENSITY OF Cu Kβ LINE IN SAMPLES CONTAINING 10% CuO, AS A FUNCTION OF GRAIN SIZE OF THE CuO

during mixing, segregation during sample packing, statistical variations on recorder readings, matrix effects, etc.

After these measurements were done, the samples were mixed with five times their weight of borax, fused over a Mecker gas burner, and finally crushed to about -200 mesh. This method of sample preparation eliminated the chemical combinations of the former compounds and should now result in the equalization of the intensities of the Cr fluorescent lines. The results are shown in Figure 6, curve B. Apart from the small variations due to the causes mentioned above, we note that the intensities are now all equal. Many mixtures with elements other than chromium have shown essentially a similar relation.

These experiments were done during the initial period of this research project and have not been effected under the best experimental conditions. They serve however to illustrate the exactitude of the theory.

General application of the theory

The above theoretical study shows that,if accurate analyses are to be made, it is not advisable to work on powders.

In certain cases where the grain size and the chemical composition of the matrix is fairly constant, it might be possible to obtain satisfactory results. However, if unforeseen changes happen in the sample, the results of the analysis will be erroneous.

In order to control some of these accidental effects the sample should be crushed and powdered extremely fine in order to make it almost homogeneous; but this is unpractical with the present available equipment. Fortunately, the ideal homogeneous

dispersion can be obtained much more easily by means of a liquid or solid solution of the sample.

In this case, the equation 7, generalized for a multi-component system,

$$I_m = \frac{k\,C}{\sum a_n(\mu_1+\mu_2)_n} \quad \ldots\ldots\ldots (10)$$

can now be applied and employed with great advantage. Here, I_m is the measured intensity, k is an unknown proportionality constant, C is the concentration, in the solution, of the element analyzed, a is the weight percentage of each element, μ_1 and μ_2, their mass absorption coefficients for the excitation and emission wavelengths respectively. The sum Σ is extended over all the elements present in the solution.

For an easier understanding, we will separate in equation 10, the factors that belong to the element under consideration (1), those which belong to the sample matrix (m), and those from the diluent (d);

$$I_m = \frac{k a_1}{a_1(\mu_1+\mu_2)_1 + \sum a_m(\mu_1+\mu_2)_m + \sum a_d(\mu_1+\mu_2)_d} \quad \ldots (11)$$

where obviously:

$$a_1 + \sum a_m + \sum a_d = 1 \ldots\ldots\ldots (12)$$

For a given sample, $(\mu_1+\mu_2)_1$ and $(\mu_1+\mu_2)_m$ are fixed and the ratio of a_1 to $\sum a_m$ is a constant. By virtue of equation 12, we see that the only factors that can be changed in equation 11 are the a_d and $(\mu_1+\mu_2)_d$. If the term $\sum a_d(\mu_1+\mu_2)_d$, which is a constant of the solvent, could be increased considerably, relative to the first two terms of the denominator, we would obtain the following advantages:

1° a decrease in matrix effect due to a relative decrease of the term $\sum a_m(\mu_1+\mu_2)_m$;

2° a wider linearity relationship between intensity (I_m) and concentration (a_1), through a decrease of the term $a_1(\mu_1+\mu_2)_1$.

If the ratio of $\sum a_d(\mu_1+\mu_2)_d$ to $a_1(\mu_1+\mu_2)_1 + \sum a_m(\mu_1+\mu_2)_m$ could be made sufficiently high, these advantages can be of such a degree that a single determination of the absolute intensity of any emission line would be sufficient for a determination of the percentage of the corresponding element.

This desirable condition can be obtained by a proper choice of the solvent material.

The absorption coefficients of the liquid solutions are so low, that only by a very high dilution of the sample it is possible to mask the first two terms of the denominator in equation 11. With such samples, appreciable intensity which would normally be obtained from atoms deep under the sample surface will be lost due to the geometry of the instruments.

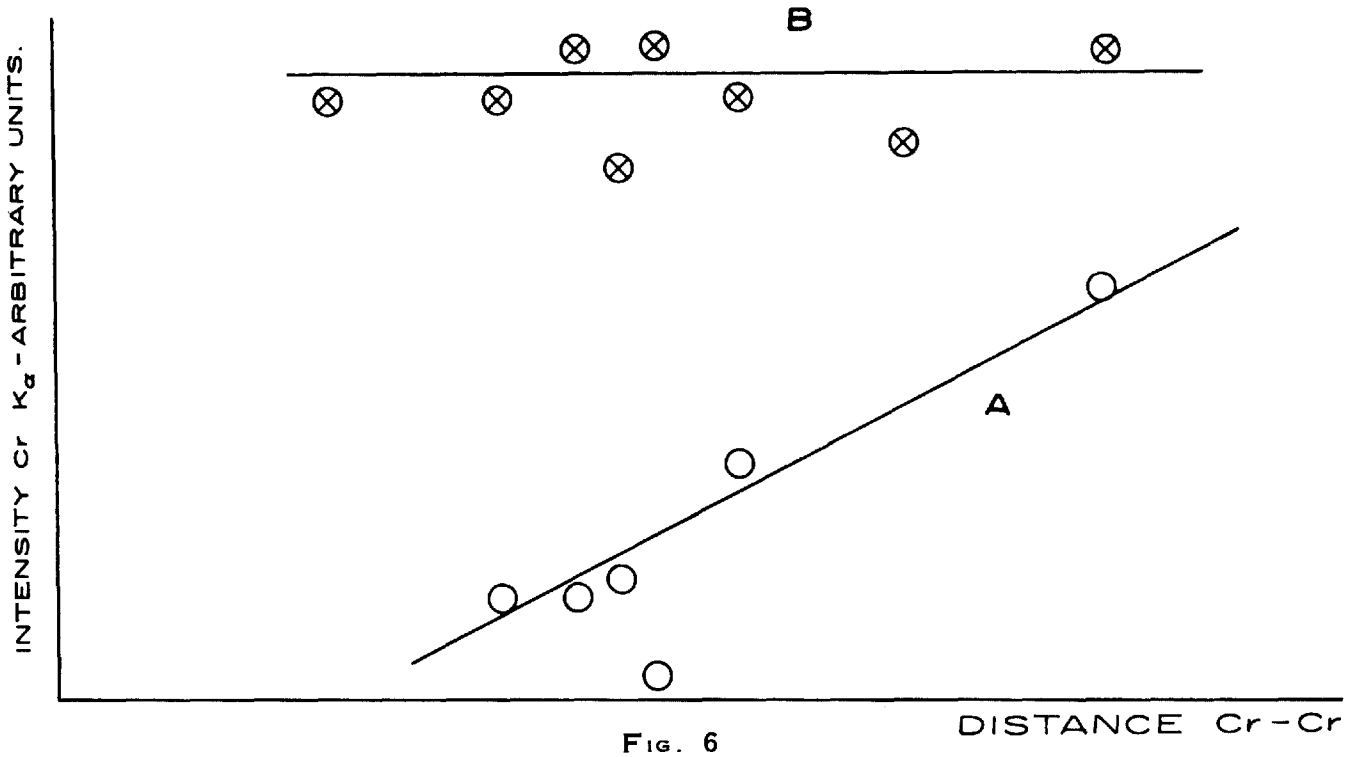

FIG. 6

INTENSITY OF CR $K\alpha$ LINE IN SAMPLES CONTAINING A CONSTANT PERCENTAGE (1%) OF THAT ELEMENT, AS A FUNCTION OF THE CR-CR INTERATOMIC DISTANCES IN THE MOLECULES THAT CONTAIN THESE ATOMS,

A - ON MIXED POWDERS,

B - AFTER FUSION (SEE TEXT).

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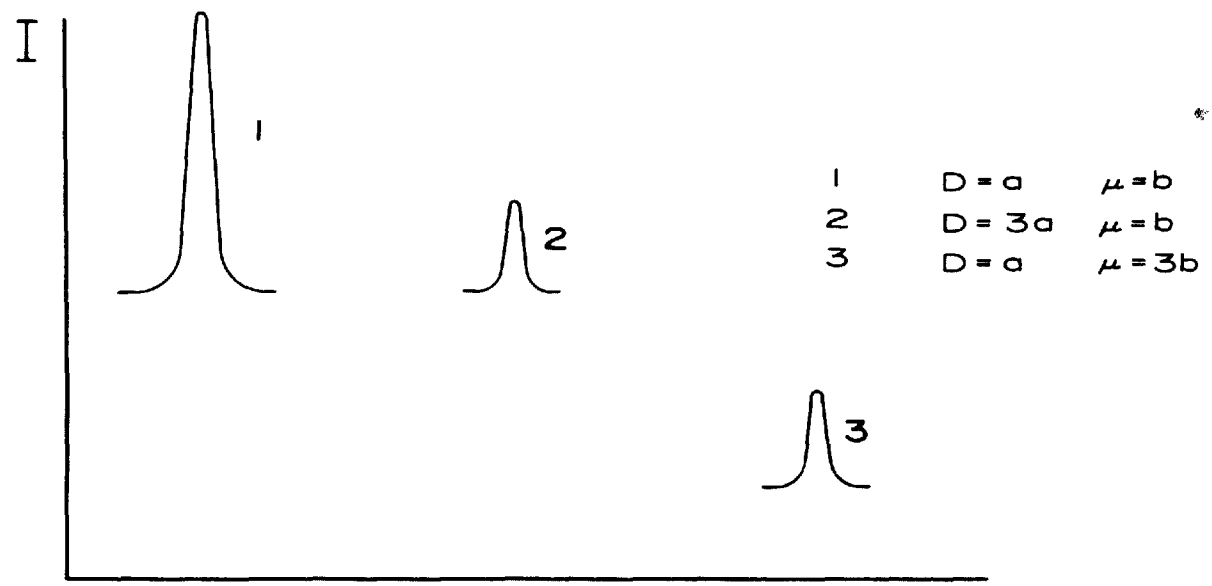

FIG. 7 EFFECT OF DILUTION (D) AND ABSORPTION (μ) OF THE FLUX ON THE INTENSITY OF THE X-RAY FLUORESCENCE LINES AND ON THE BACKGROUND.

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Many other difficulties and annoyances do not favour this method of sample preparation. It is a necessity that the solvent always be the same, if percentage determinations from absolute intensities without the use of an internal standard are desired. It is difficult to find a solvent that will dissolve most of the minerals in a short time and without too much difficulty. There is also the problem of corrosion of the sample holder by acid solutions and danger of spilling when liquid samples are used with the sample holders.

The author prefers to use solid solvents such as borax, and to prepare his samples as glass disks for the following reasons:

1° possibility of dissolving in an easy and rapid manner almost all minerals in the same flux;

2° availability of fluxes with different degrees of absorption for X-rays;

3° ease of manipulation;

4° prepared samples can be kept indefinitely without special containers, and without any danger of contamination. This is especially important for standards.

With the above method of sample preparation, it is possible to eliminate the matrix effect, either by great dilution of the sample ($1-\sum a_m$ very small) or by using a highly absorbing flux $(\mu_1+\mu_2)_d$ large). These two methods of preparation are not equivalent. This can be shown in the following way: let us start with a prepared sample where there is still some matrix effect. In these conditions, and for rough calculations, equation 11 can be simplified and rewritten:

$$I_m \cong \frac{k\, a_1}{\sum a_d\,(\mu_1+\mu_2)_d} \quad \ldots\ldots\ldots\ldots (12)$$

As shown previously, the matrix effect depends on the ratio

$$M.E. \;\propto\; \frac{a_1\,(\mu_1+\mu_2)_1 + \sum a_m\,(\mu_1+\mu_2)_m}{\sum a_d\,(\mu_1+\mu_2)_d} \quad \ldots\ldots (13)$$

These two equations, 13 and 14, show that both the intensity (I_m) and the matrix effect $(M.E.)$ will each be changed by a factor p , either by decreasing the concentration (a_1) by the factor p or by increasing the absorption $(\mu_1+\mu_2)_d$ of the flux by the same factor. At first sight there does not seem to be any advantage one way or the other. However, by increasing the dilution, the line intensity is decreased without change in the background (Figure 7), while, by increasing the absorption of the flux, the background intensity decreases almost linearly with the line intensity.

When a fusion method is used, the background intensity is usually quite constant. However, when the line intensities are low compared to it and background corrections are not made, a small variation in its intensity will be reflected on the concentration by the factor $\frac{\text{background intensity}}{\text{net line intensity}}$. Obviously, the background must be kept as low as possible for these samples. This can be accomplished by increasing the absorption of the flux in preference to an increase in dilution.

THE FUSION METHOD*

The fusion method we are to describe can be used with almost all minerals with the exception of sulfides. For these, supplementary manipulations are required, and will be explained at the end of this section.

Materials:

The materials are as follows: platinum crucible, Mecker gas burner, forceps, hot plate with controlled temperature, "transite" (thermal insulator) plate, metallic ring and the flux.

Depending on one's preference, the "transite" plate may have any shape or thickness. Its use will be described in the later section. The metallic ring can be made by rolling over a 1 1/4 in. O.D. pipe a bare No.10 electrical wire. A chromel A wire is to be preferred to a copper wire.

Fused borax was used as the base material for the flux since it dissolves most of the minerals and because transparent glass discs are easily made from it. Barium peroxide, BaO_2, barium sulfate, $BaSO_4$, potassium pyrosulfate, $K_2S_2O_7$, etc. are added to the borax when a more absorbing glass is desired or when dealing with sulfides.

Weighing

A constant quantity of sample of the order of 100 mg. is weighed accurately. A Roller-Smith torsion balance has been found to be convenient for this work. The weighed sample is then transferred into a platinum crucible. If a small quantity of sample is used, a zero balance reading is made, to correct for part of the sample that may have remained in the pan. Ten grams of fused borax are added. Mixing is not necessary; however it is recommended because a homogeneous melt is obtained sooner.

Fusion

The crucible is now placed over a very hot flame from a Mecker gas burner, and the sample melted. The crucible is heated a little longer with occasional agitation to ensure homogeneity in the melt. This requires a total of 5 to 15 minutes, depending on the rapidity of the sample to react with borax.

Casting the glass discs

The melt is now ready for the casting of the glass. At this time, the hot plate, with the "transite" plate on it, should have reached a temperature of about 450°C.

The procedure is as follows:

1. Place on the hot plate a ring which has been kept at room temperature.

2. Immediately pour into it the hot melt.

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*A fusion method has been described in ARL Spectrographer's News Letters (Vol. VII, No.3, 1954). Our method differs from that one, being simpler, more general and more accurate.

3. Let it cool for about one or two minutes.

4. Turn over the transite plate and push the disc on it with the aid of a transite stick.

5. Let stand on a table until cool enough for handling.

6. Remove the disc from the ring.

The sample should be transparent and of a uniform colour. It should have a flat surface on one side and a smooth convex surface on the other side. It is now ready for use on the X-ray spectrograph.

This procedure is simple but very critical. If the ring is left on the hot plate too long before pouring the melt, it will stick to the disc. If the hot plate is too warm, the disc will stick to it; if not warm enough the surface of the disc will be irregular. We have been using a hot plate with an aluminum top and have not had any trouble. A steel top may oxidize to such an extent that the disc may stick to it; there is also a danger of contamination when iron is analyzed. If the hot disc comes in contact with a cold metallic object, it will crack; if chilled too rapidly, it may explode when handled.

X-Ray Measurements

The glass disc is placed in the sample holder so as to expose its flat surface to the X-ray beam. The sample holder should be equipped with a mask in order that the exposed surface of the disc is always of the same dimension. As absolute intensities are measured, the position of the sample holder should be reproducible.

Readings are taken as usual.

The case of the sulfide ores and those which contain graphite

Since borax does not dissolve sulfide minerals directly, some preliminary transformation must be made. Various methods have been tried to accomplish this transformation but they were found to be long and difficult.

Two simple and rapid methods are proposed.

The first method consists in adding to the weighed sample a constant amount of about ten times its weight of potassium pyrosulfate and gently heating the mixture over a small flame until the sample is completely dissolved. This takes about one to two minutes. The borax is then added, and the fusion is carried on in the usual manner.

The second alternative method is to add to the weighed sample, 1 1/2 to 2 grams of barium peroxide BaO_2; mix roughly; add the borax over this and then fuse in the manner described previously. The great absorption of the barium for the X-rays results in a still greater reduction of the matrix effect.

In ores where graphite is found it is recommended that half of the barium peroxide be replaced by barium sulfate. This helps to oxidize the graphite, which otherwise would reduce part of the sulphides, into metals which then do not react with borax.

Suggested procedures

Depending of the nature of the samples, the composition of the disc can be varied in a number of ways. Some suggestions will now be made for a few general cases.

1.- For any percentage in matrices of relatively constant composition.
Mix one part of sample with 100 parts of borax. It is not necessary to use barium oxide or sulfate unless sulfides or graphite are present.

2.- For high percentages in variable matrices.
Same procedure as in 1.

3.- For medium percentages in variable matrices.
The use of an absorber such as the barium salts is recommended.

4.- For low percentages in variable matrices.
A background correction might be required when the net line intensity is of the order of, or smaller than, the the background intensity.

5.- Use of an internal standard.
When the line intensities are very low, the desired accuracy might not be obtained by the above procedures. The internal standard method can then be used in conjunction with the fusion method. In this case, the quantity of sample in the disc may be increased up to 10 or 30% of the total weight. This can be done because the matrix effect is now corrected by the internal standard. This procedure still eliminates the grain size and the chemical combination effects.

RESULTS

A few examples of analyses will be given below to show how this fusion method can be varied depending on the kind of samples and of the accuracy desired.

Iron Ores

The ores were previously analyzed chemically; the composition varied from 40 to 65% Fe, 0.2 to 23% Mn, with varying amounts of SiO_2 and Al_2O_3.

The samples were prepared by mixing 35 mgs. of the ore, 18 mgs. Co_2O_3 as the internal standard, and 8 gms. of fused borax as the flux.

The K_α lines of Fe, Co and Mn were measured with a statistical accuracy of 0.2% (102400 counts) for Fe and Co, and 0.4% (25600 counts) for Mn. A LiF analyzing crystal and a Geiger counter were used. No correction was made for background.

In Figure 8, the FeK_α intensities are plotted as a function of percentage. In order to show how the use of the internal standard may improve the accuracy, the intensity ratios of FeK_α / CoK_α are plotted as a function of percentage in Figure 9. With the exception of one reading, the accuracy is practically the same in the two cases. One advantage in not using the internal standard is that the time required for the analyses is much shorter than when the internal standard is used.

The absolute intensities of MnK_α lines are plotted as a function of percentage in Figure 10. The deviations average only 0.05%.

The data for the curves of Figures 8 to 10 are given in Table 1.

Table 1

Comparison of Assay Results for Iron Ores

% given (chemical)		% found (X-rays)					
		With internal standard		Without internal standard			
Fe	Mn	Fe	dev.	Fe	dev.	Mn	dev.
37.56	23.00	37.6	.0	37.6	.0	Not significant (x)	
42.12	3.26	42.1	.0	41.1	1.0	3.47	.21
47.84	12.05	48.0	.2	48.0	.2	12.00	.05
51.31	1.80	51.1	.2	51.3	.0	1.74	.06
52.21	8.94	52.3	.1	52.4	.2	8.97	.03
58.19	1.43	58.0	.2	57.8	.4	1.50	.07
59.55	0.99	59.5	.0	59.8	.2	0.96	.03
60.21	0.42	60.5	.3	60.2	.0	0.44	.02
64.09	0.21	64.0	.1	64.0	.1	0.17	.04

(x) Insufficient number of samples in this range.

Sulfide minerals

Analyses of Fe, Zn, Pb and Cu have been done on ores containing the sulphides of these elements. Some graphite was also found in them.

The direct fusion method was used; 55 mgm. of sample were mixed with 1 gm. BaO_2 and 1 gm. $BaSO_4$; 10 gm. of borax were added, and the whole fused in the flame.

The FeK_α, ZnK_α, PbL_β and CuK_α line plus background intensities were measured with 0.4% accuracy (25600 counts) and plotted as a function of concentration in Figures 11 to 15. Some of the deviations might be due to the inaccuracy of the chemical analyses and to the impossibility with the sample holder used, to keep absolutely constant the position of the sample in the X-ray beam. Note the large range of concentrations for Pb, and the almost perfect linearity of all the curves.

The results of these analyses are given in Table 2.

Table 2

Comparison of Assay Results for Sulfide Ores

% Fe			% Zn			% Pb			% Cu		
given	found	dev.	given	found	dev.	given	found	dev.	given	found	dev.
11.8	11.6	.2	(x)	(x)		.89	.80	.1	.26	.22	.04
11.8	12.0	.2	11.7	11.7	.0	49.1	49.0	.1	.07	.27	.20
17.6	17.6	.0	13.0	13.3	.3	35.6	35.8	.2	.07	.08	.01
24.8	24.8	.0	14.0	13.9	.1	17.4	18.2	.8	.08	.24	.16
27.7	27.7	.0	5.5	5.7	.2	26.1	26.0	.1	.12	.24	.12
29.8	29.8	.0	8.8	8.7	.1	5.74	5.75	.0	.45	.45	.00
34.2	34.7	.5	2.6	2.6	.0	1.05	1.05	.0	.16	.00	.16
36.5	36.5	.0	3.3	3.9	.6	1.30	1.60	.3	(x)	(x)	
36.9	36.8	.1	6.9	6.9	.0	3.44	3.55	.1	(x)	(x)	
40.2	40.2	.0	4.7	4.7	.1	1.40	1.35	.05	1.40	1.40	.00
38.6	38.9	.3	4.5	4.3	.1	.78	.90	.1	.91	.95	.04
mean deviation:		.1	mean deviation:		.15	mean deviation:		.2	mean deviation:		.1

(x) Concentration too high to be determined from available calibration curve.

Niobium and tantalum analyses

Two samples of chemically separated niobium and tantalum oxides were analyzed for niobium and tantalum using the fusion method, with Sr as an internal standard. The composition of the melt was as follows: 100 mgs. of sample, 50 mgs. of $SrCO_3$ and 8 gms. of fused borax.

The same accuracy was obtained whether the absolute intensities for Nb and Ta or relative intensities of Nb/Sr and Ta/Sr were used. The sum of the two oxides in one case gave 98.0% and in the other case 101.5% compared to 100.0% as it should be.

Effect of matrix on Fe analyses

In order to investigate the effect of matrix on absolute intensities, and to what extent this interference can be eliminated by making a fusion in borax or in a more absorbing glass, samples containing 20% Fe_2O_3 in various mixtures were prepared.

Alumina and silica were used as typical low absorbing matrices and Ta, Cr and Sn as high absorbing ones. These represent the extreme cases.

Measurements of the FeK_α line intensities were made 1° on the powder mixtures; 2° on the samples fused in borax with a dilution ratio of 1:100; 3° same as 2°, but with the addition of 10% potassium pyrosulfate.

For comparison purposes, the intensities in the alumina matrix have been taken to correspond to exactly 20.0% Fe_2O_3. When the intensities in the other matrices are compared to them on a linear scale, the percentages reported in Table 3 are obtained.

Matrix effect on the analysis of a sample containing 20% Fe_2O_3.

20% Fe_2O_3 in	% Fe_2O_3 found		
	Non-diluted powders	Sample fused in borax	Sample fused in borax and $K_2S_2O_7$
Al_2O_3	20.0	20.0	20.0
SiO_2	19.0	19.7	20.1
Ta_2O_5	7.4	19.2	19.8
Cr_2O_3	5.1	19.4	19.7
SnO_2	5.6	18.3	19.2

The fusion in borax alone eliminates the greatest part of the matrix effect. The addition of a small quantity of potassium pyrosulfate reduces it further by a factor of two. It is probable that the addition of a barium salt would reduce it to practically nothing.

CONCLUSION

It should be noted that this fusion method is still in its infancy and that this report is a preliminary one. However, the results obtained so far have been very encouraging, and the work is being continued in the laboratories of the Quebec Department of Mines to improve the method. The main effort is made towards the analysis in the low percentage levels with an accuracy of ± 0.02% absolute. This order of accuracy seems reasonable to attain.

New improvements in the instrumentation, such as higher energy X-ray excitation tubes, scintillation and proportional counters, sensitive detectors for the low energy radiations, energy discriminators, etc, will greatly increase the accuracy of the analyses, especially at the low percentage level.

It is certain that the method can be applied already to the analyses of all elements above atomic number 22 and whose concentration is above a few tenths of one percent. The analyses of the lighter elements can probably be made at higher concentration levels. The accuracy will be comparable to that obtained in routine chemical analyses and the results will be obtained more rapidly, especially when the sample composition does not vary over too wide a limit.

ACKNOWLEDGMENTS

The writer wishes to express his sincere thanks to Dr. A.-O. Dufresne, Deputy Minister of Mines who made this paper possible, to Dr. Maurice Archambault, Director of the Research Laboratories Branch, for his kind cooperation and practical suggestions, to Mr. D. Lamontagne, chemist, for help in carrying out the work, and to Mr. F. East, physicist, for criticism of the manuscript.

May 1956.

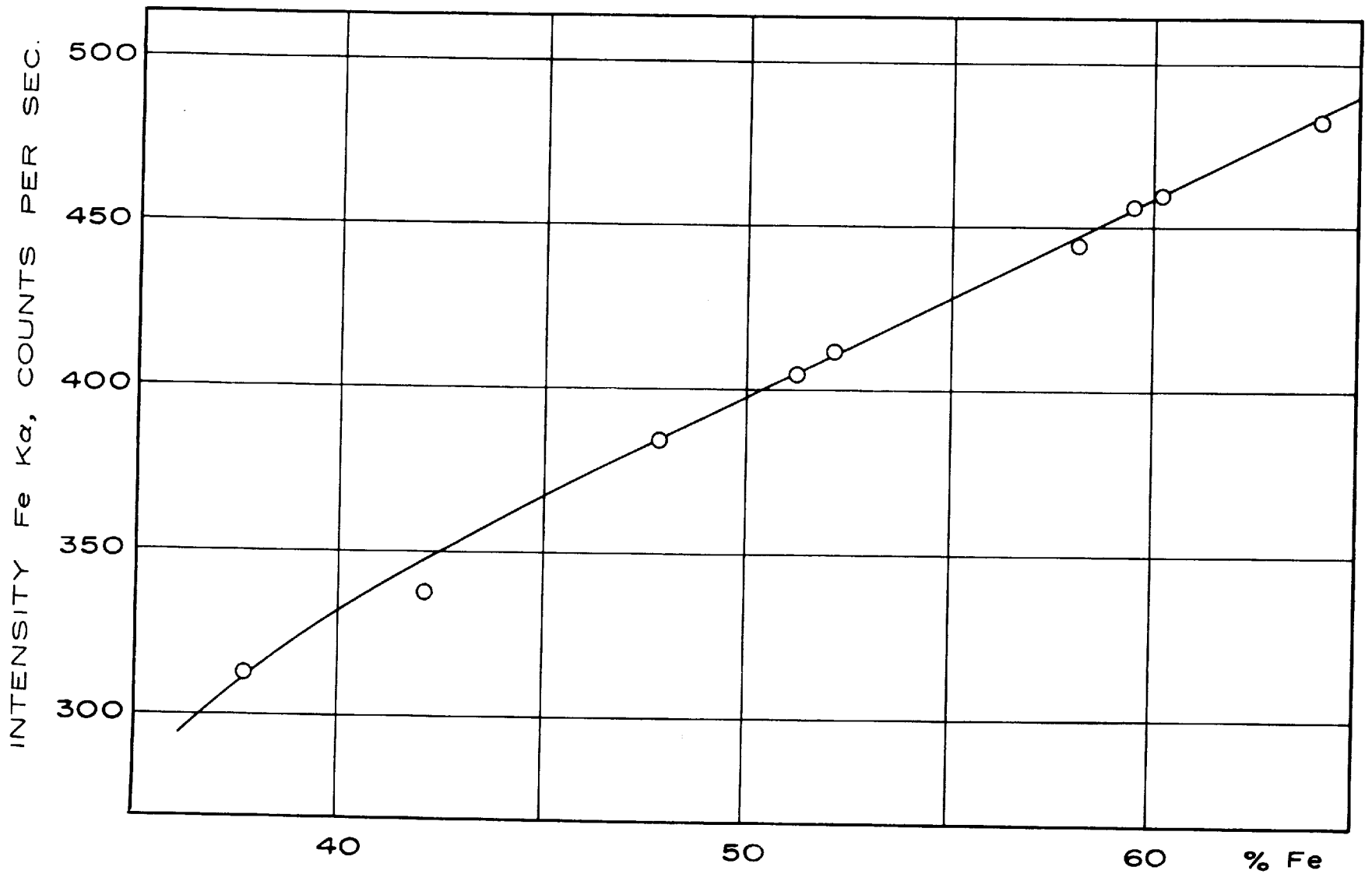

FIG. 8 ANALYSIS OF FE IN IRON ORES.

D.M.Q. 1956 No. 1138

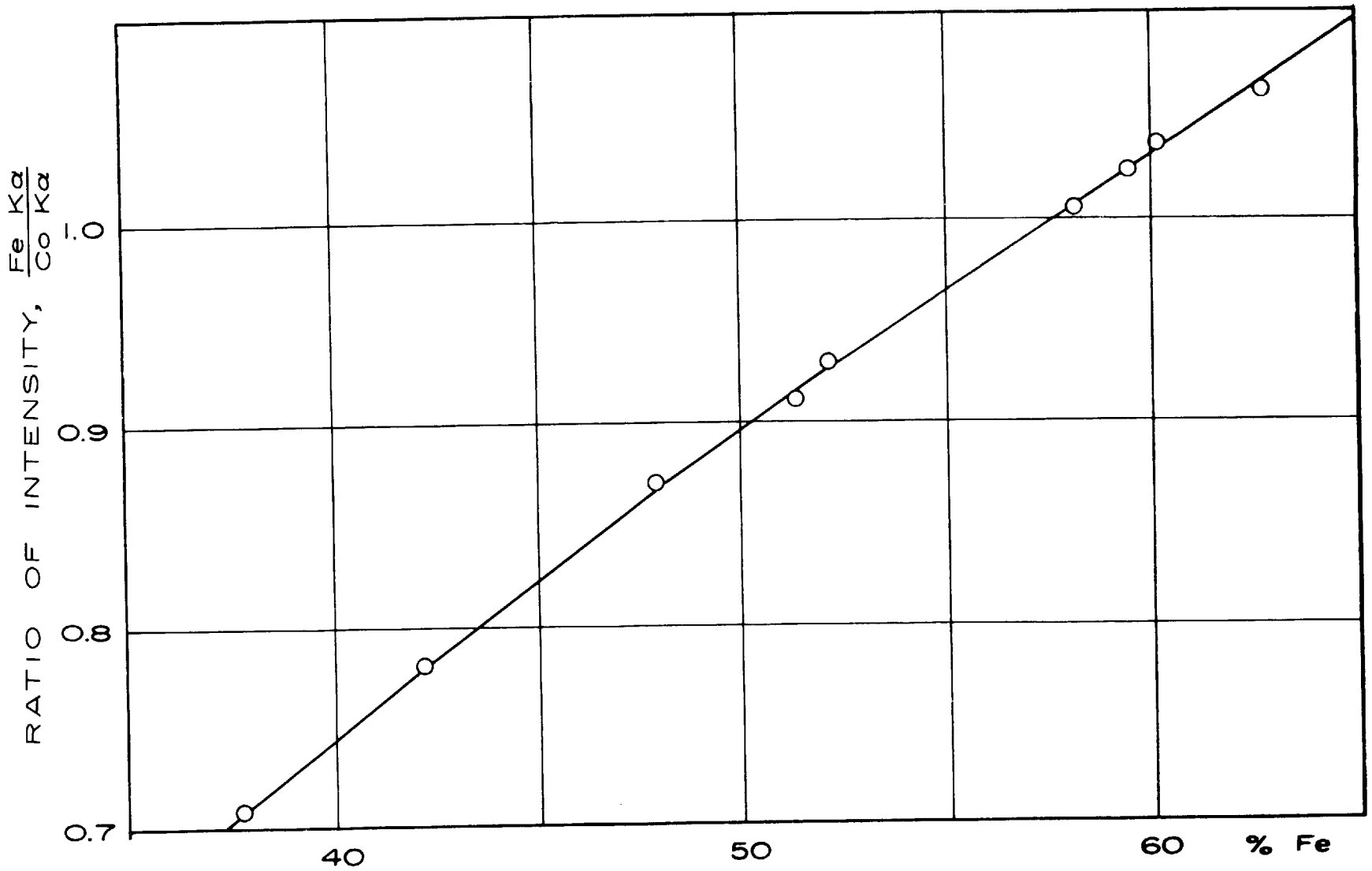

FIG. 9 ANALYSIS OF FE IN IRON ORES.

D.M.Q. 1956 No. 1139

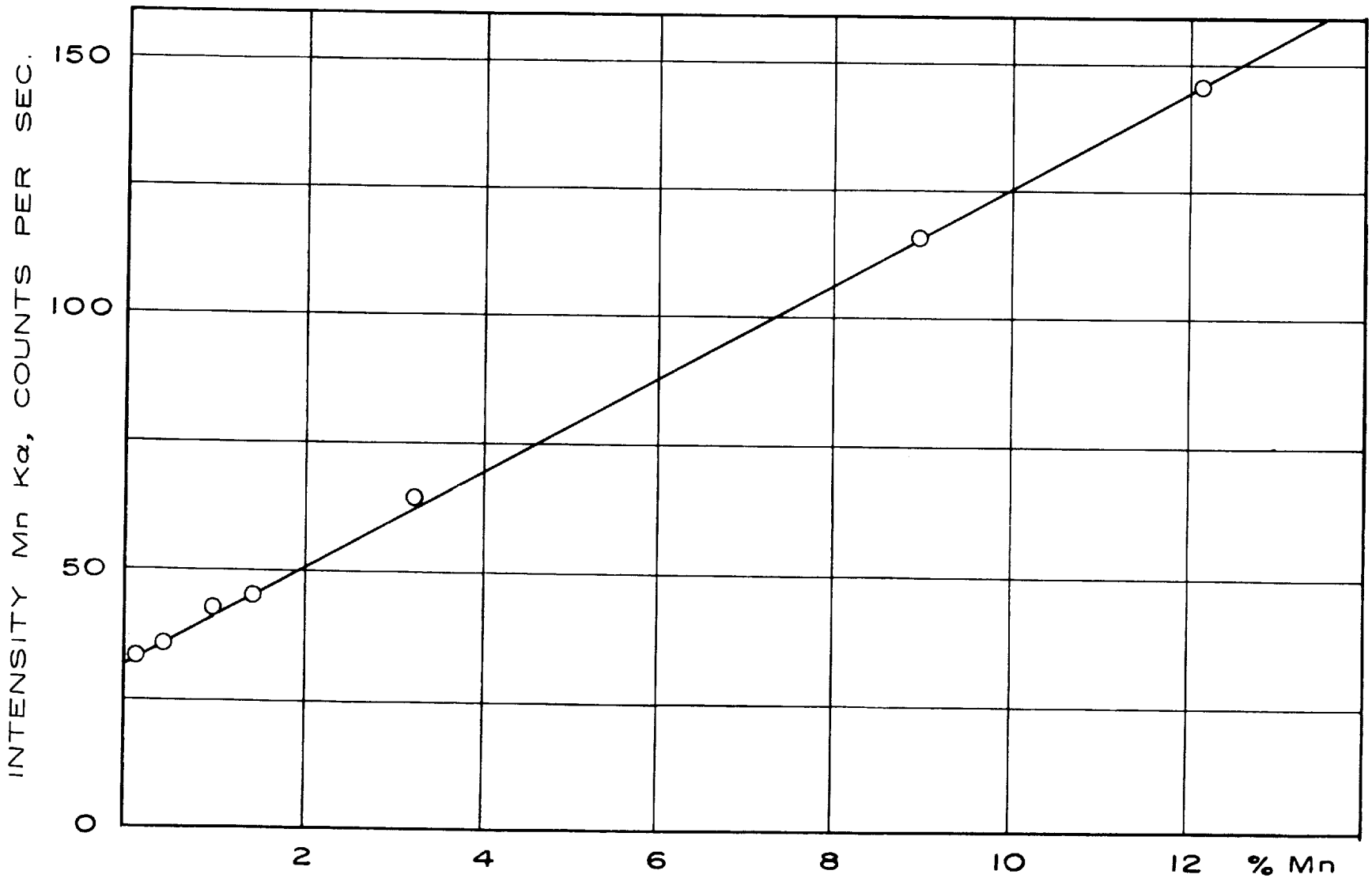

FIG. 10 ANALYSIS OF MN IN IRON ORES

D.M.Q. 1956 No. 1140

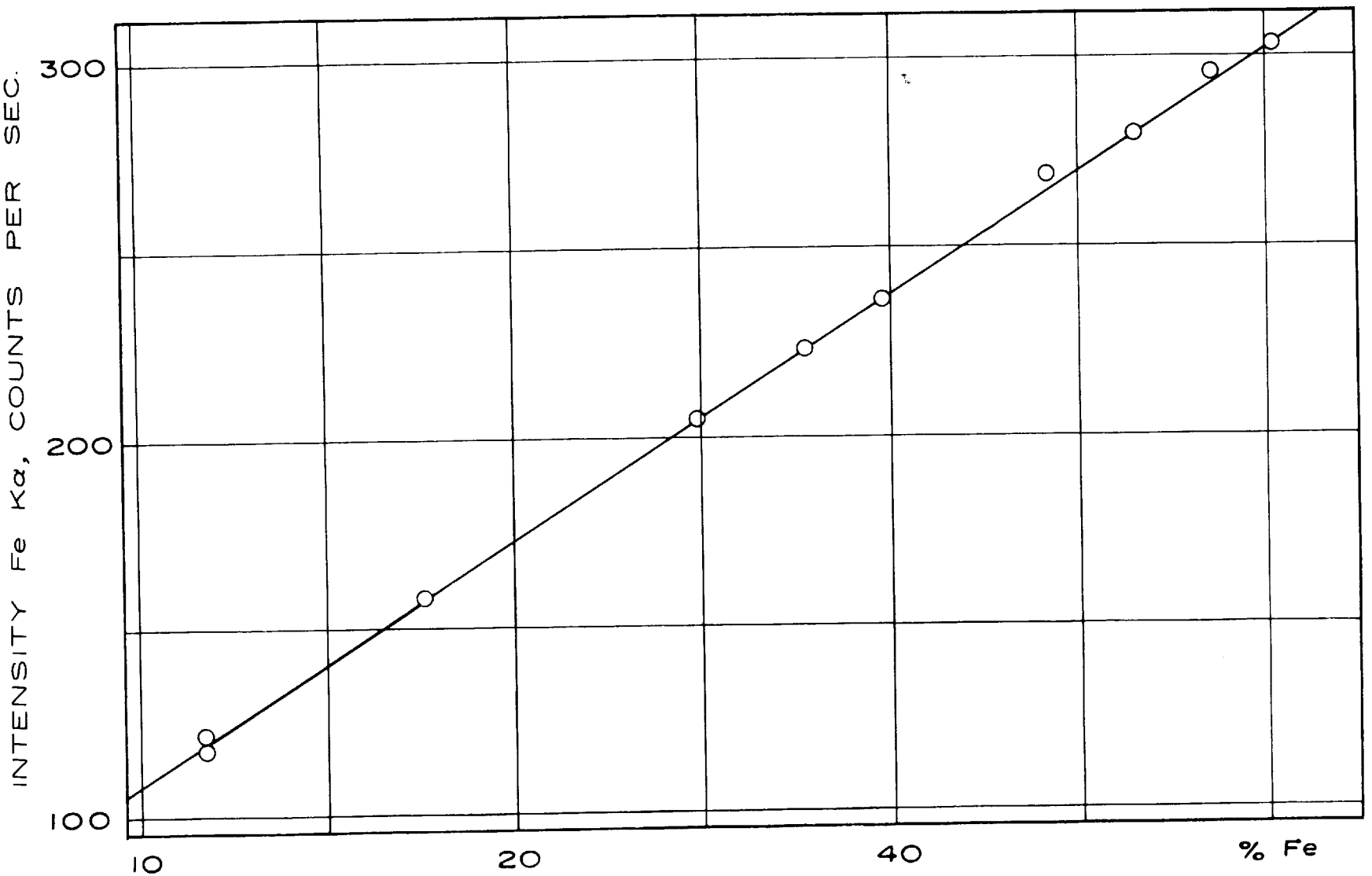

FIG. II ANALYSIS OF FE IN SULPHIDE ORES.

D.M.Q. 1956 No. 1141

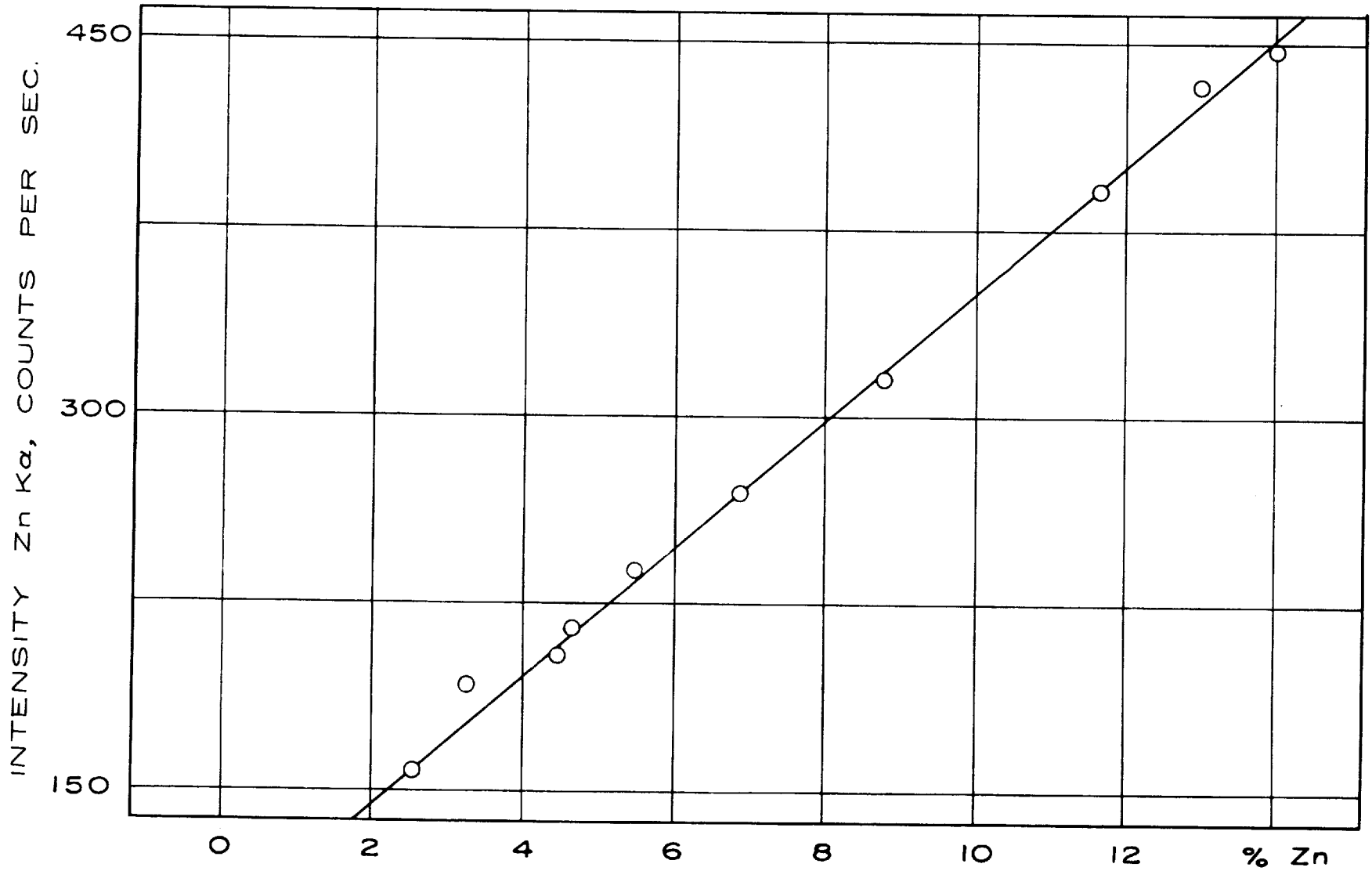

FIG. 12 ANALYSIS OF ZN IN SULPHIDE ORES.

D.M.Q. 1956 No. 1142

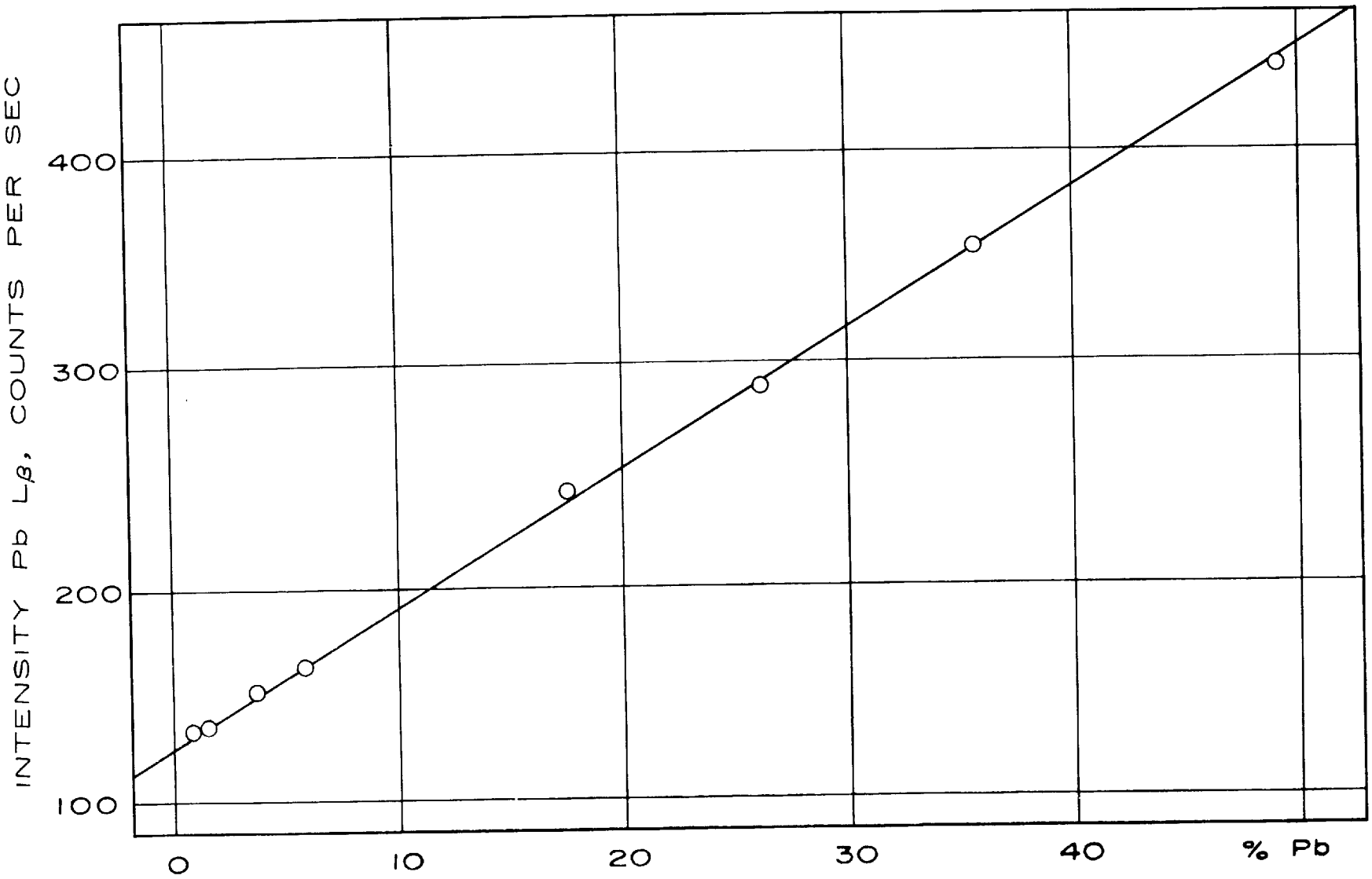

FIG. 13 ANALYSIS OF PB IN SULPHIDE ORES.

D.M.Q. 1956 No. 1143

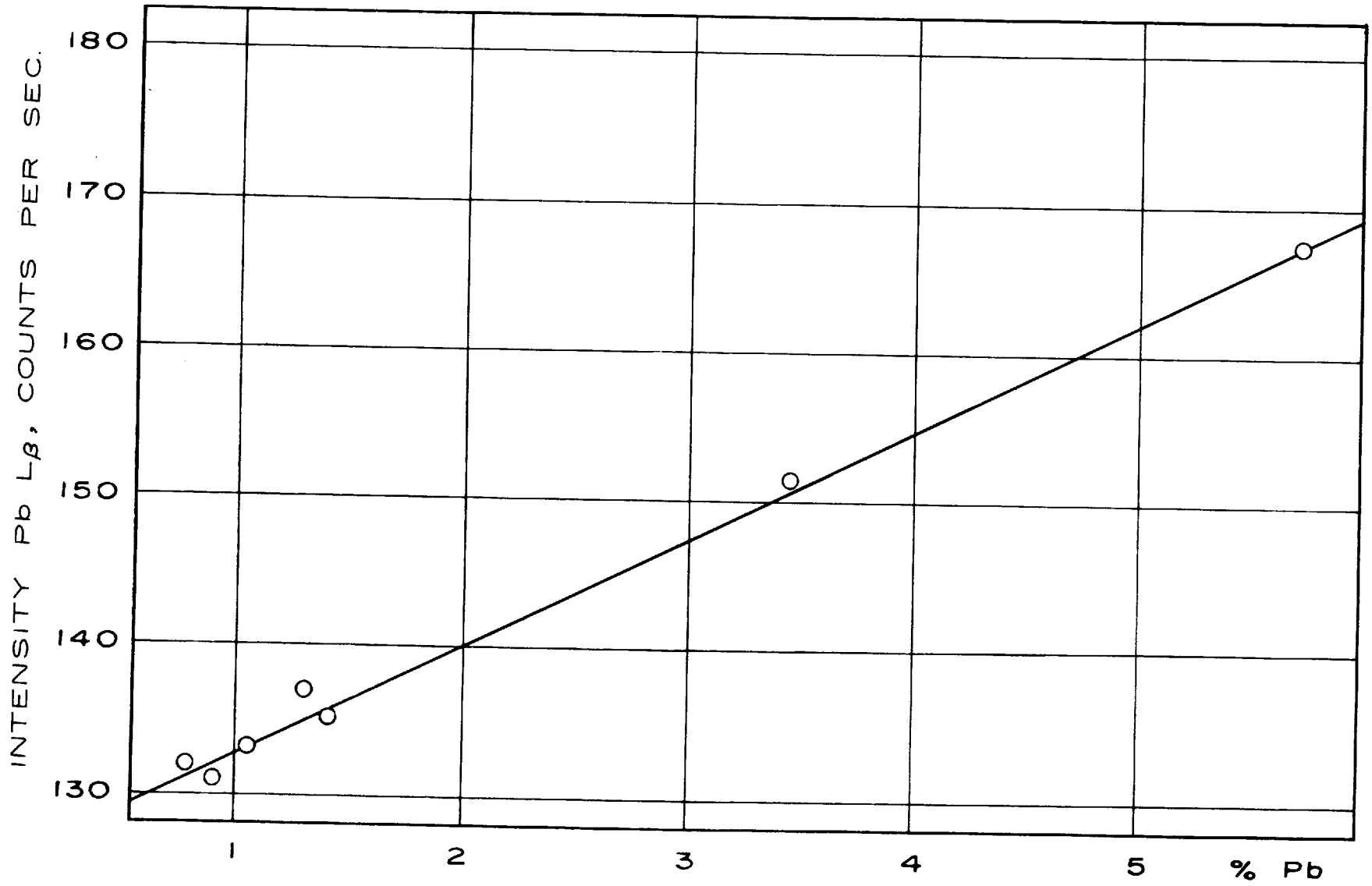

FIG. 14 ANALYSIS OF PB IN SULPHIDE ORES.

D.M.Q. 1956 No 1144

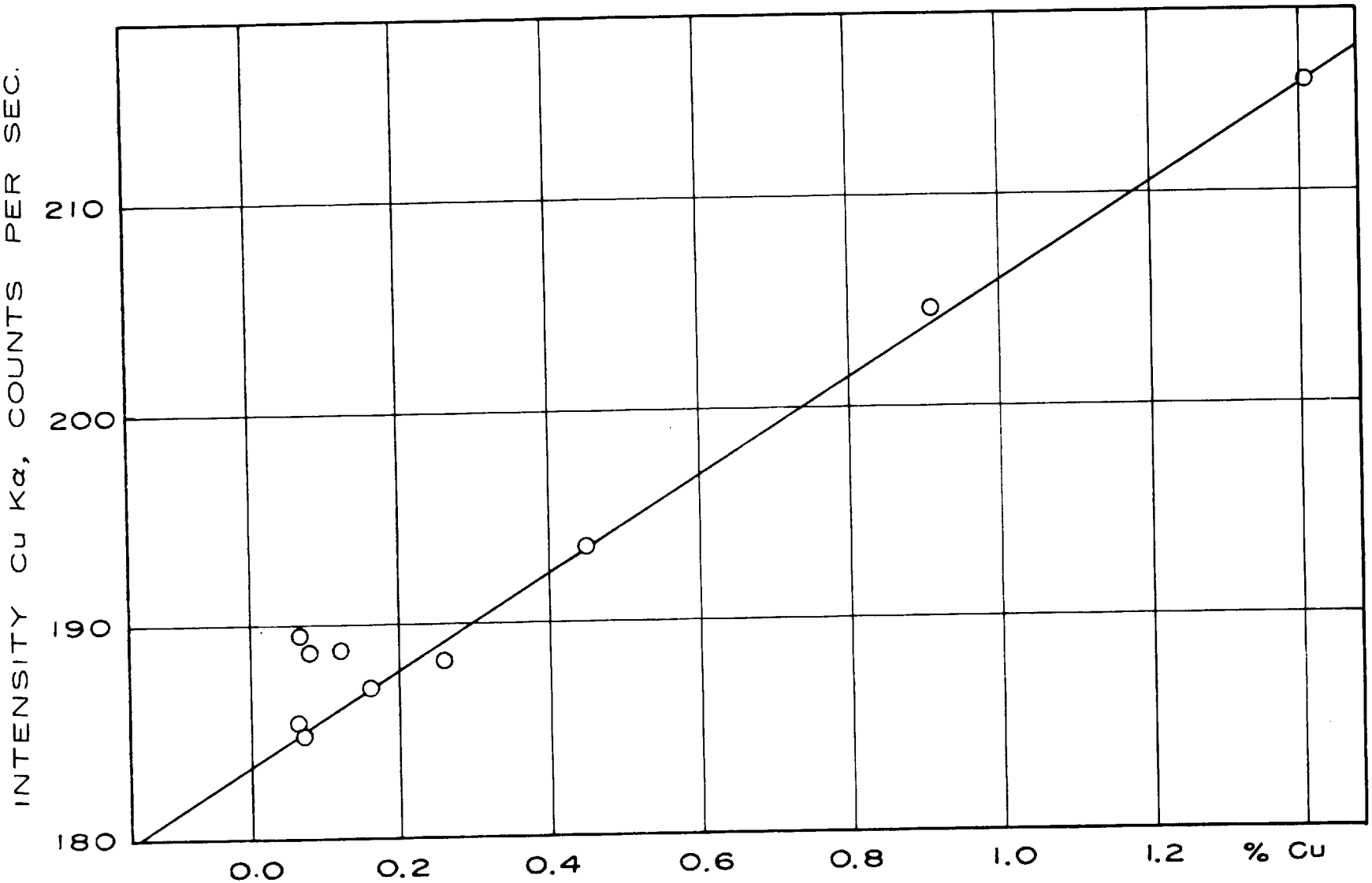

FIG. 15 ANALYSIS OF Cu IN SULPHIDE ORES.

D.M.Q. 1956 No. 1145