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THE DETERMINATION OF IRON IN SPHALERITE BY *X*-RAY FLUORESCENCE SPECTROMETRY*

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ABSTRACT

The mutual standards concept of *x*-ray fluorescence analysis furnishes a rapid, nondestructive method of determining the iron content of sphalerite within 2.5 to 5 per cent of the amount of iron present. Only 0.1 to 20 mg. of sample are needed. A set of independently determined standards is required. For best results, the thicknesses of the standards should be equal to those of the unknowns; samples should be run interspersed with standards; sample holders should be checked for reproducibility; and the amounts of cadmium, copper, and manganese should be analyzed for if their sum is suspected to be greater than 1 or 2 per cent.

INTRODUCTION

Temperature and fugacity of sulfur species are two of the variables in the formation of ore deposits. Kullerud (1953, 1959) showed that the iron content of sphalerite in equilibrium with FeS is a function of temperature. Barton and Kullerud (1958) demonstrated that the iron content of sphalerite in equilibrium with pyrite is a function of the fugacity of sulfur in the system as well as of temperature. Thus, under the proper circumstances, the iron content of sphalerite indicates the temperatures of formation of an ore body and/or the changes in fugacity of sulfur species during ore deposition. To facilitate such studies, an accurate quantitative measure of the iron content on a few milligrams or less of sample is desirable.

The present paper describes an analytical procedure capable of determining the content of iron to better than ±5 per cent of the amount of iron present, using as little as a milligram or less of sphalerite. The sample is not destroyed. No internal standardization or binders are required. The analysis takes about 15 minutes per sample. If care is taken, the reproducibility of the iron content may be determined to within about ±2.5 per cent of the amount present. The method of analysis has been briefly described in an abstract by Chodos, Rose, and Godijn (1957). Certain precautions that are necessary in order to obtain the best results were not stated in the abstract. Thus it seems advisable to describe the procedure at greater length. The method has been employed in the studies of sphalerite by Rose (1958) and Doe (1960).

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PROCEDURE

General

The method employs the "mutual standards technique" outlined by Coulliette (1943), where it is assumed that the sum of the metallic elements analyzed for equals 100 per cent. For sphalerite, this expression is:

$$X^{zn} + X^{fe} + \Sigma X^{a} = 100 \text{ per cent} \tag{1}$$

where X^{zn} and X^{fe} are the concentrations of ZnS and FeS in weight per cent, and ΣX^{a} is the sum of all the other metallic elements, expressed as sulfides, in the sphalerite. If a sample of sphalerite is bombarded with tungsten *x*-rays, the elements in the specimen will give off their characteristic *x*-rays. The intensity ratio of the Zn to Fe radiation emitted by the sample will be proportional to the ZnS to FeS weight ratio. The relationship between the intensity ratio and weight ratio can be determined from analyzing a set of standards in which the weight ratio is known (Fig. 1). The iron content in weight per cent may be obtained from the weight ratio by rearranging equation 1:

$$X^{fe} = (100 - \Sigma X^{a})/(1 + X^{zn}/X^{fe}) \tag{2}$$

The ΣX^{a} term (mostly manganese, cadmium, and copper) is less than 1 per cent for most specimens of sphalerite. If ΣX^{a} is 1 weight per cent, the assumption that ΣX^{a} is 0 would give an answer for the FeS content only 1 per cent of the FeS content greater than the true value. As most samples of sphalerite contain about 1 to 15 per cent FeS by weight, the error in assuming that the ΣX^{a} term is 0 will be less than 0.1 per cent FeS by weight for most samples. In addition, 0.1 per cent FeS is smaller than the uncertainty in the solvus of the FeS-ZnS system as determined by Kullerud (1953).

In this procedure, 0.1 to 20 mg. of ground sphalerite are weighed into a flat-bottomed circular cavity (1/32-inch deep × $\frac{1}{4}$-inch diameter) drilled into a lucite holder. The holder is inserted into the spectrometer, which is equipped with a high-purity tungsten *x*-ray tube (Phillips FA-60). The tube is operated at 45 kv and 25 ma. The fluorescent radiation is diffracted from a lithium fluoride crystal in conjunction with a 0.020-inch ×3-inch parallel plate collimator. The fluorescent intensity at the iron and zinc peak maxima is measured with a flow proportional counter, using argon-methane gas. The positions of the peak maxima are determined from time to time by counting over the peaks in steps of 0.02° 2θ. The positions of the peaks are quite stable and showed no change over a period of 9 months. For each peak, 25,600 counts are taken to obtain good counting statistics. In addition, 6400 counts for background are taken at about 1.5° 2θ on either side of the peak maxima.

Results of ±5 per cent of the amount of iron present or better can be

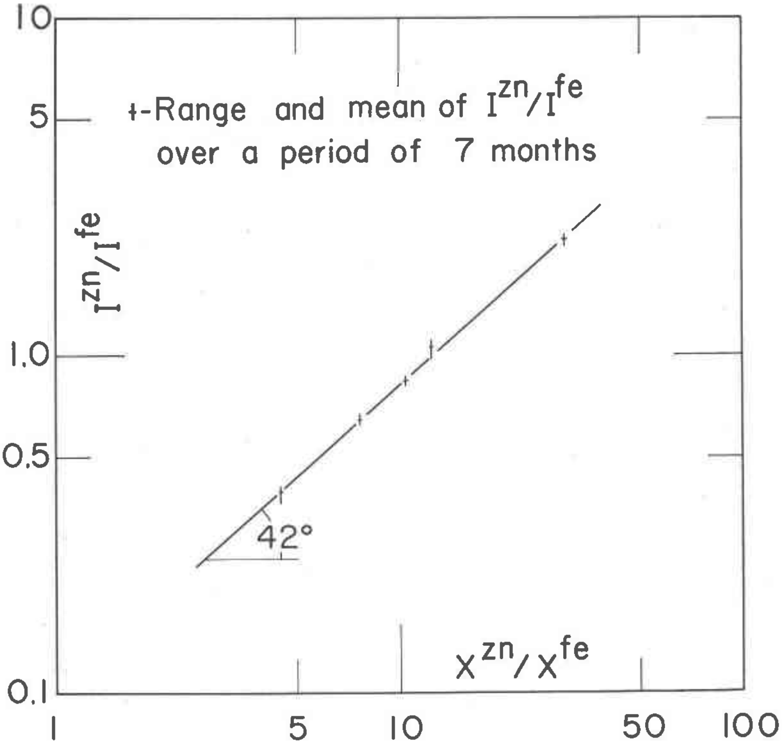

FIG. 1. The Zn to Fe fluorescent intensity ratio (I^{zn}/I^{fe}) versus the ZnS to FeS weight ratio (X^{zn}/X^{fe}) of five chemically determined sphalerites.

obtained provided the following variables are taken into account: the standards, background, sample thickness effect, sample holder effect, and absorption and enhancement effects of metallic elements other than iron or zinc. Short discussions of these topics and of the reproducibility of the method are given below.

Standards

To begin with, synthetic mixtures of ZnS, pyrite, and iron powder were used for standards. The results of samples analyzed chemically by B. Doe at the Missouri School of Mines and by L. Shapiro of the U. S. Geological Survey indicated a small systematic difference between the results of the chemical analyses and the synthetic standards. The reasons for the discrepancy are related to the "matrix" effect (Claisse, 1956). This effect has been found repeatedly in our work and is further illustrated by working curves for the analysis of sulfide nodules from meteorites (Chodos and Nichiporuk, 1958). The present standards consist of nine specimens of sphalerite calibrated by E. Godijn and A. Rose for iron and zinc content by "wet" chemical procedures. Iron in the standards was determined by reduction in a silver reductor followed by titration with ammonium sulfate. Zinc in the standards was determined by precipitation as zinc ammonium phosphate, ignition at 900° C., and weighing as zinc pyrophosphate. In addition, these specimens were analyzed for Mn and Cd by arc-excitation optical spectrography.

Background

The $\frac{1}{4}$-inch diameter of the sample well used is small compared with the area of the beam from the *x*-ray tube. Thus the background measured is from the sample holder as well as the sample. The background counting rates are found to be independent of the iron content of the sphalerite. However, some experiments showed background to vary with time, probably due to fluctuations in the electronics. Thus it is necessary to subtract this background from the zinc and iron radiation to achieve the best results.

Sample Thickness Effect

For a sample evenly spread in the well of the sample holder described above, Doe (1960) calculated that a 10-mg. sample of sphalerite should act as an "infinitely" thick sample. In practice, it was found that a sample of 15 mg. or greater acts "infinitely" thick (Fig. 2). If the standards are "infinitely" thick and the unknowns are very thin (for example, a sample size of 1 mg. spread over the $\frac{1}{4}$-inch well), the results for the unknowns may be in error by as much as 20 per cent, or even more (see Fig. 2). This is in accord with the theory of absorption of *x*-rays. For best results, the standards and unknowns should be measured at the same thicknesses.

Sample Holder Effect

The sample holder and the position of the sample holder in the *x*-ray beam are found to influence the Zn/Fe intensity ratio from a sample. The position of the holder in the *x*-ray beam may affect the Zn to Fe intensity ratio by about 4 or 5 per cent. Thus holders should be constructed with the samples located in the same positions in the *x*-ray beam. Certain lucite holders were found to give consistently different answers, up to 5 per cent of the amount of iron present, from others for the same sample. If more than one sample holder is to be used, the holders should be checked for reproducibility between holders. The reason for the holder effect is not clear but may be related to radiation damage of the lucite holders.

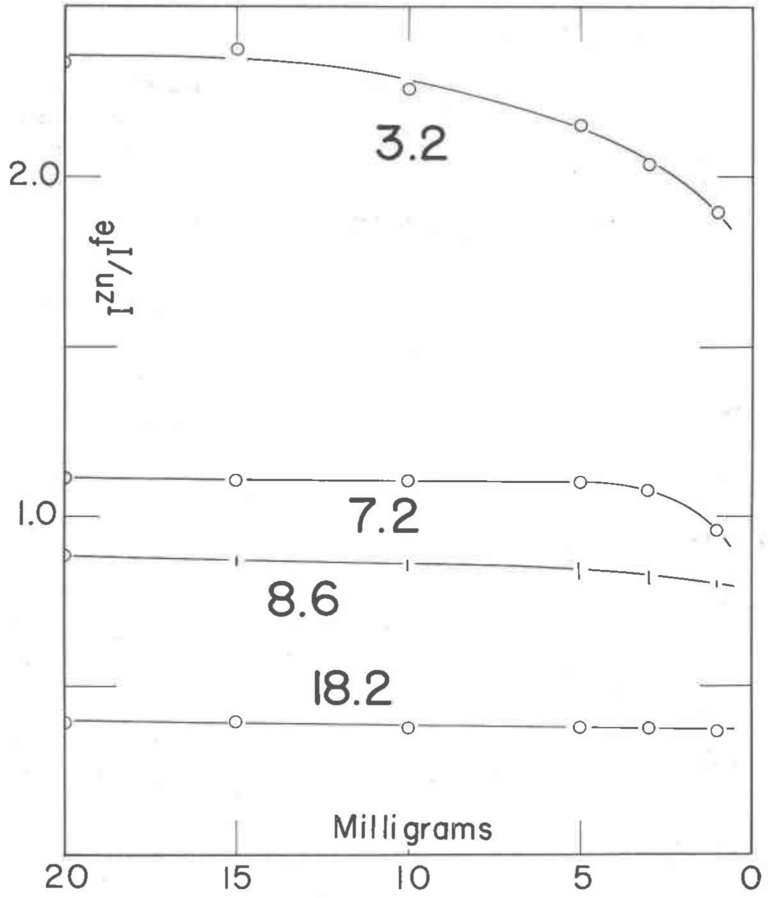

FIG. 2. The effect of sample thickness (in milligram equivalents) on the Zn to Fe fluorescent intensity ratio (I^{zn}/I^{fe}) for sphalerite. (Numbers near curves give the concentration of FeS in weight per cent for the sample represented by the curve. The thickness is represented by the number of milligrams of sample spread over the $\frac{1}{4}$-inch well of the sample holder.)

Absorption and Enhancement Effects

Sphalerite in nature commonly contains small amounts of Mn and Cu in addition to Fe. The presence of Mn and Cu could influence the Zn/Fe intensity ratio. Manganese may absorb zinc radiation. Fluorescent radiation from any copper present will fluoresce iron. To determine the possible effects of copper and manganese on the intensities of zinc and iron radiation, the following tests were performed. Ten per cent Mn_3O_4 produced a decrease in the Zn/Fe ratio equivalent to about 12 per cent of the amount of iron present. One per cent of Mn_3O_4 mixed with a sample produced no definite change in the per cent FeS found. Ten per cent CuO produced a slightly smaller change than the equivalent amount of manganese. Most samples of sphalerite analyzed by Rose (1958) and Doe (1960) contained less than 1 per cent manganese and 0.2 per cent copper. Thus, in general, the absorption and enhancement effects are believed to be equivalent to less than 2 per cent of the amount of iron reported.

Reproducibility

A set of five standards was analyzed a total of 18 times over the period of analysis in 1958 (7 months). These data enable an estimate of the reproducibility of the curve for intensity ratio versus concentration ratio. The standards were run interspersed with the unknowns on each day of analysis. The best straight-line curve is fitted through the average values for each standard in Fig. 1. Figure 1 also shows the total range of intensity ratios encountered over the period of analysis, as well as the average values. The range of a ratio over the 7 month period was about ±5 per cent of the average value.

There is a suggestion that the standardization curve shifts position slightly for different days, as shown on Fig. 3. If the standards as analyzed on 6-12-58 are considered as unknowns and their iron concentrations are determined from the standard curve for 10-7-58, all the standards are indicated to have higher concentrations (by roughly 5 per cent) than the known values. Treatment of the data indicated that the standard deviation of the ZnS/FeS weight ratio is about 1.6 per cent of the ratio, using the curve for Fig. 1. If new working curves are constructed each day, the standard deviation is reduced to about 1.2 per cent.

Results from this procedure agree well with the results obtained from completely independent methods. Splits of five samples of sphalerite from the Balmat No. 2 mine, New York, analyzed at the Missouri School of Mines (Doe, 1956) were reanalyzed by the present method. At the Missouri School of Mines, iron was determined by a permanganate titration and zinc by a potassium ferrocyanide titration using a diphenylamine internal indicator (Kolthoff and Sandell, 1952). The comparison is:

FeS* (wt. %) Volumetric	FeS† (wt. %) Fluorescent
13.2	13.9
7.4	7.0, 7.2, 7.8
8.8	8.8
7.6	7.4
10.6	10.6, 10.8

* Missouri School of Mines (B. R. Doe, analyst).

† California Institute of Technology (B. R. Doe, analyst).

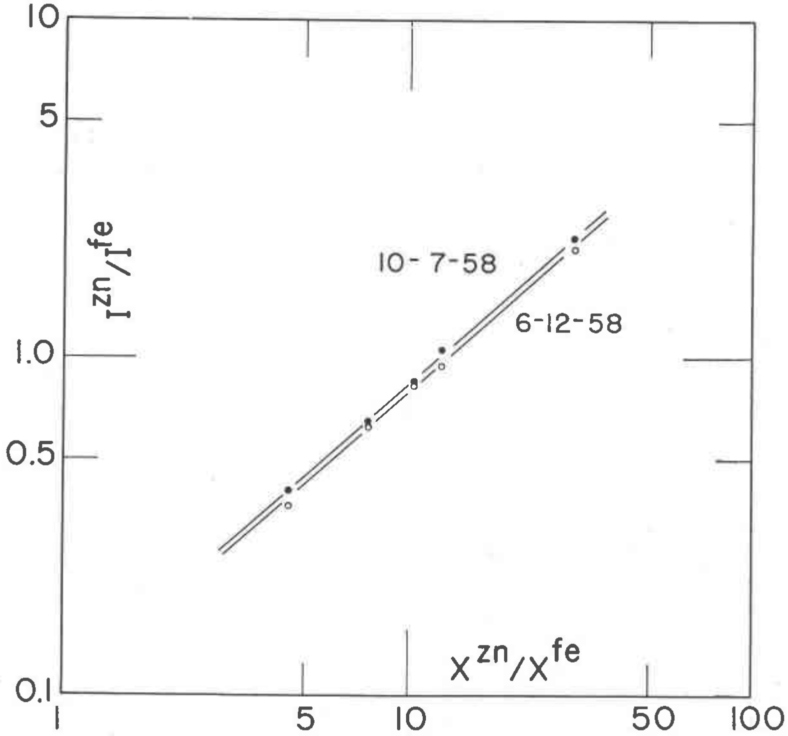

FIG. 3. Shift with time in the position of the standard curve for the Zn to Fe fluorescent intensity ratio (I^{zn}/I^{fe}) versus the ZnS to FeS weight ratio (X^{zn}/X^{fe}) for sphalerite.

Thus, the results obtained by the *x*-ray fluorescence technique are in good agreement with those of standard chemical techniques.

CONCLUSIONS

X-ray fluorescence provides a rapid, nondestructive means of accurately determining the amount of iron in sphalerite. Only a few milligrams or less of sample are needed. The reproducibility of the method is better than 5 per cent of the iron present if standards and unknowns have approximately the same thickness. A set of independently determined standards is required in the procedure. Samples analyzed by this method agree within 5 per cent of the amount present with iron determined by other generally reliable methods.

The amount of iron in sphalerite may be determined to within 2 or 2.5 per cent of the amount present: (1) if sample holders are carefully chosen so that there is no sample holder effect, (2) if the amounts of manganese and copper are small or known, (3) if a set of standards is analyzed interspersed with unknowns on the day of analysis, and (4) if the thicknesses of standards and unknowns are approximately the same.

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