# X-RAY SPECTROGRAPHIC ANALYSIS
# OF MINUTE MINERAL SAMPLES

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## ABSTRACT

X-ray spectral intensity ratios are used to determine directly atomic ratios in powdered mineral samples of one milligram size. Standardization and working curves for the determination of Cu/Fe, Pb/Sb and Ag/Sb are given. Effect of varying sample size is discussed.

In view of the quite small amounts of material normally available for mineral analyses, an investigation into the practicability of x-ray spectrographic analysis on small samples seemed desirable. For the purpose of this investigation it was decided to limit the size of sample to one milligram. Results of the investigation have shown, however, that satisfactory analyses may be obtained on samples of less than one milligram.

The elements chosen for this study were copper, iron, silver, lead and antimony which commonly occur in the sulphides and sulphosalts. These minerals, typified by complex intergrowths and assemblages, normally yield but little clean material for analysis and in this way illustrate the problem suggested above.

The x-ray equipment used for this study consisted of a Philips vacuum spectrograph with pulse height discriminator attachment. All analyses were done with a LiF analyzer crystal and scintillation counter. Primary radiation was supplied by a broad focus tungsten target x-ray tube. The discriminator was used solely for the purpose of minimizing counter noise.

### The problem

Quantitative x-ray spectrographic analysis would be a particularly simple matter if the intensities of the characteristic x-rays generated in an element depended only on the number of atoms of that element present in the sample. Unfortunately, a number of other factors influence the intensities of emitted spectra. The chief aim of a method of analysis is therefore to compensate for these factors, commonly referred to as matrix effects, so as to make intensities proportional to the number of atoms present.

The small amount of sample to be used in this study precludes application of the usual methods employed to control matrix effects such as

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dilution and addition of internal standards. However, since the final product of such analyses is a mineral formula deduced from atomic ratios, application of $x$-ray intensity data to provide atomic ratios directly would seem to be a direct route to this objective.

The method proposed here involves the derivation of the relation between intensity ratios and atomic ratios for pairs of elements in the sample being analyzed.[1] This use of intensity ratios is analogous to the use of intensity ratios in the internal standard method and may be expected to minimize interference effects and instrumental errors. Accordingly, standard working curves were prepared for various pairs of the elements under study showing the relation between intensity ratios of emitted $x$-ray spectra and their corresponding atomic ratios.

*Preparation of standards*

Analysed material was not available for use as standards, and therefore analysis of a suitable selection of minerals was a necessary first step. A list of minerals used in this study is given in Table 1, which includes the University of Toronto catalogue number, the chemical formula and the

TABLE 1. MINERAL SPECIES USED FOR ANALYSES OF ONE MILLIGRAM SAMPLES

| Mineral Species | | Formula | Symbol |
|---|---|---|---|
| Cubanite | UT-2-9-1 | $CuFe_2S_3$ | Cu |
| Chalcopyrite | UT-2-8-17 | $CuFeS_2$ | Ch |
| Stannite | UT-R-502 | $Cu_2FeSnS_4$ | St |
| Bornite | UT-R 586 | $Cu_5FeS_4$ | B |
| Andorite | UT-R 66 | $PbAgSb_3S_6$ | An |
| Zinckenite | UT-R 63, R 64 | $Pb_6Sb_{14}S_{27}$ | Zn |
| Jamesonite | UT-R 503 | $Pb_4FeSb_6S_{14}$ | Ja |
| Boulangerite | UT-R 347 | $Pb_5Sb_4S_{11}$ | Bo |
| Pyrargyrite | UT-R 499 | $Ag_3SbS_3$ | Py |
| Stephanite | ———— | $Ag_5SbS_4$ | S |
| Polybasite | UT-R 151 | $(Ag,Cu)_{16}Sb_2S_{11}$ | Po |

symbol used in this paper. Sufficient clean material representing each mineral was picked and finely ground to provide an ample stock supply both for analysis and for subsequent use as standards in preparation of the working curves. An effort was made to choose a sufficient variety of compositions in order to give reasonably spaced points on the analytical curves.

A one hundred milligram aliquot of the finely ground stock supply of each mineral was fused with four grams of potassium pyrosulfate to a homogeneous quiescent melt. The melt was poured into a porcelain mortar, covered, allowed to solidify, crushed and ground to a fine powder

[1]Intensity ratio data has been applied by Bertin (1964) to binary systems.

and placed in a labelled envelope. A similar set of synthetic samples was prepared in an identical fashion using carefully weighed amounts of artificial oxides and metals of the elements under study.

Intensity measurements were made on the appropriate lines (Fe, Cu, Ag, Sb-$K\alpha_1$, Pb-$L\beta_1$) in the synthetic samples. Intensity ratios were calculated and plotted on linear graph paper against the corresponding atomic ratios. Similar readings made on the mineral samples provided intensity ratios which, when applied to the standard curves, rendered atomic ratios for the minerals.

The standard curves thus prepared are shown in Figs. 1-3. The atomic ratios have been plotted on the curves against the theoretical compositions of the minerals. The deviation from the standard curve is indicative of the purity of the samples selected. In Fig. 2 the atomic ratio for andorite deviates markedly from the Pb/Sb curve indicating an abnormally high lead content. Re-examination of the source material showed the presence of galena which would account for this condition. It did not seem practical to attempt to pick enough clean material for standardization; however, about 2 mg. of what appeared to be clean material was selected for analysis on the analytical working curves discussed below.

Table 2 compares the theoretical atomic ratios of the minerals with the ratios obtained from the standard curves.

TABLE 2. RESULTS OF X-RAY SPECTROGRAPHIC ANALYSIS

| Elements | Mineral | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Cu/Fe | Cubanite—Cu | 0.50 | 0.52 | 0.49 | 5.8 | 0.0 |
| | Chalcopyrite—Ch | 1.00 | 1.04 | 1.03 | 1.0 | 0.0 |
| | Stannite—St | 2.00 | 2.12 | 2.17 | 2.4 | 1.3 |
| | Bornite—B | 5.00 | 5.05 | 5.00 | 1.0 | 0.3 |
| Pb/Sb | Andorite—An | 0.33 | — | 0.35 | — | 1.5 |
| | Andorite*—An | — | 0.61 | 0.65 | 6.5 | — |
| | Zinckenite—Zn | 0.43 | 0.43 | 0.39 | 9.3 | 2.3 |
| | Jamesonite—Ja | 0.67 | 0.64 | 0.73 | 14.0 | 2.5 |
| | Boulangerite—Bo | 1.25 | 1.23 | 1.20 | 2.5 | 1.6 |
| Ag/Sb | Andorite—An | 0.33 | 0.30 | 0.29 | 3.3 | 0.0 |
| | Pyrargyrite—Py | 3.00 | 3.00 | 2.95 | 1.6 | 0.0 |
| | Stephanite—S | 5.00 | 4.87 | 5.04 | 3.5 | 3.4 |
| | Polybasite—Po | — | 8.15 | 8.30 | 1.8 | 1.2 |
| Average | | | | | 4.3% | 1.1% |

1. Theoretical atomic ratio, pure idealized mineral.
2. Atomic ratio derived from analysis—standardization curves.
3. Atomic ratio derived from one-milligram unfused samples—working curves.
4. Per cent deviation of atomic ratios (2) from working curves.
5. Per cent deviation from mean of two runs on one-milligram aliquots—reproducibility.
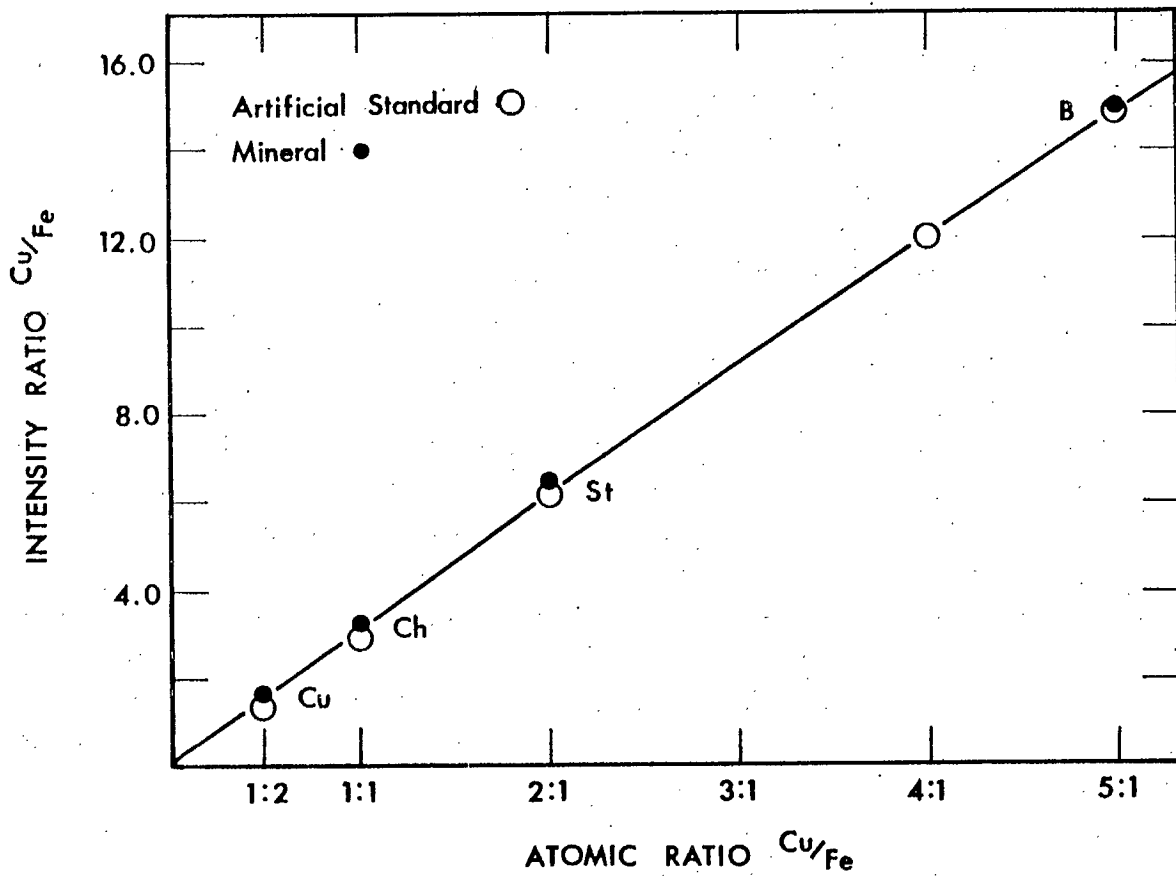
*Andorite contaminated with galena.
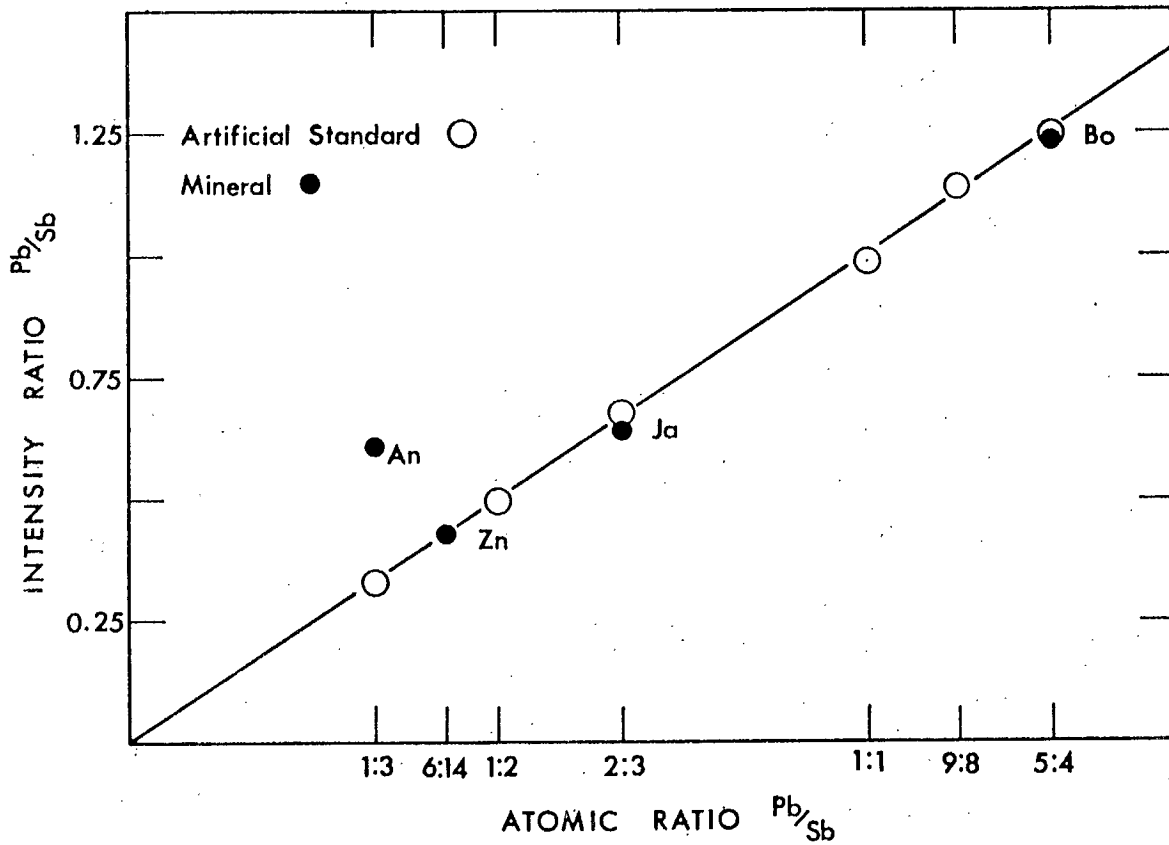
FIG. 1. Standardization Curve for Cu/Fe.



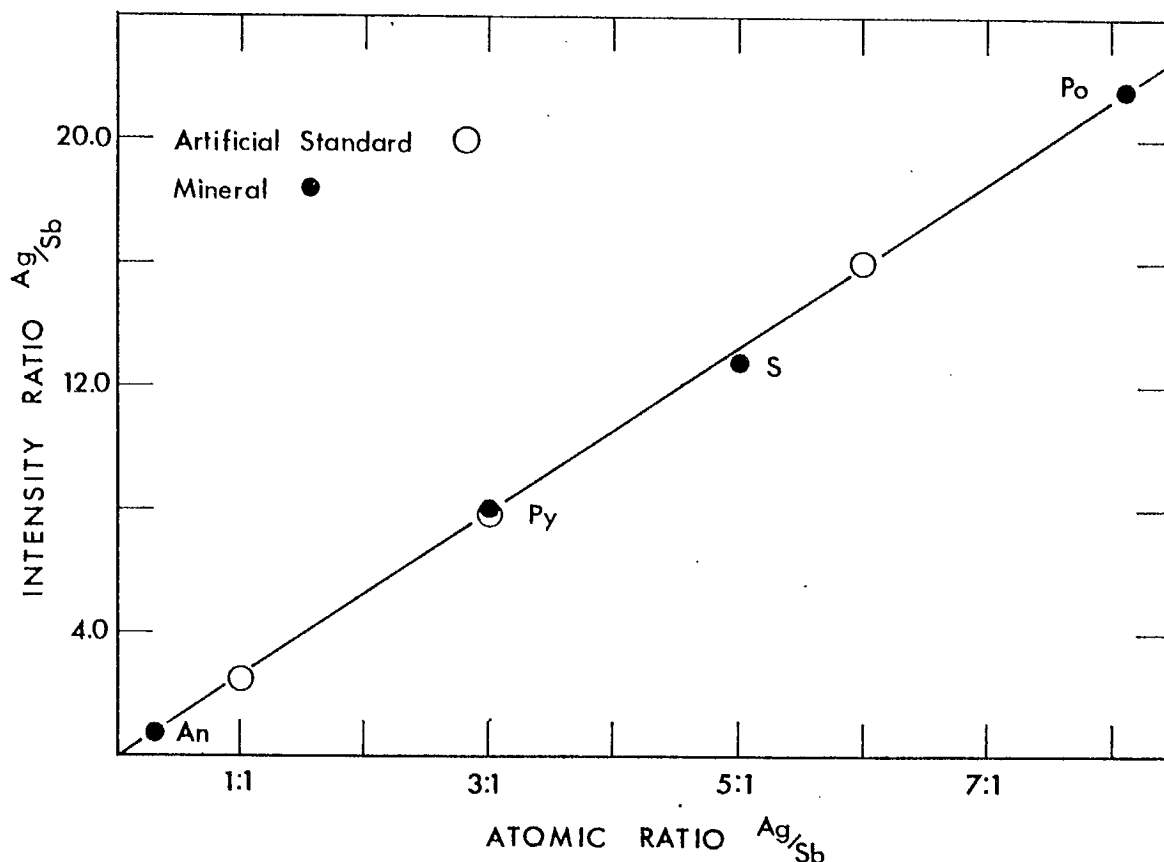FIG. 2. Standardization Curve for Pb/Sb.

FIG. 3.   Standardization Curve for Ag/Sb.

## Preparation of working curves

A finely ground 1 mg. aliquot of each analysed mineral sample was placed on the centre of the mylar in the inverted sample tray, spread out somewhat with a drop of alcohol, and allowed to dry. Ratios calculated from intensity measurements made on the samples prepared in this way were plotted as before on linear graph paper against the established atomic ratios. Each mineral was run at least twice to test reproducibility. All values obtained were plotted as shown on the working curves with the mean obtained by straight arithmetic averaging.

It is useful to retain the amounts of analysed samples as reference standards. However, the procedure of mounting the samples directly on the mylar in the inverted sample holders is not practical as it is almost impossible to recover the material from the mylar or to remount the mylar once it is removed from the sample holder. Thus a method for retaining standards on permanent mounts was devised.

The method consists of making sample holders from the bottom section of one-inch cardboard pillboxes which can be placed inside the inverted sample trays. The holders are made by first removing the flat bottom cover with a razor blade, after which the outer ring is removed. The

bottom then is covered with mylar. It was found necessary, however, to put a narrow strip of drafting tape around the pillbox, so that the mylar is held firmly in place by the outer ring. The holder and its component parts are shown in Fig. 4.

The holders are easily and cheaply made, and can be used for retaining standards permanently. In this manner, one is able to accumulate complete sets of reference standards ready for immediate use.
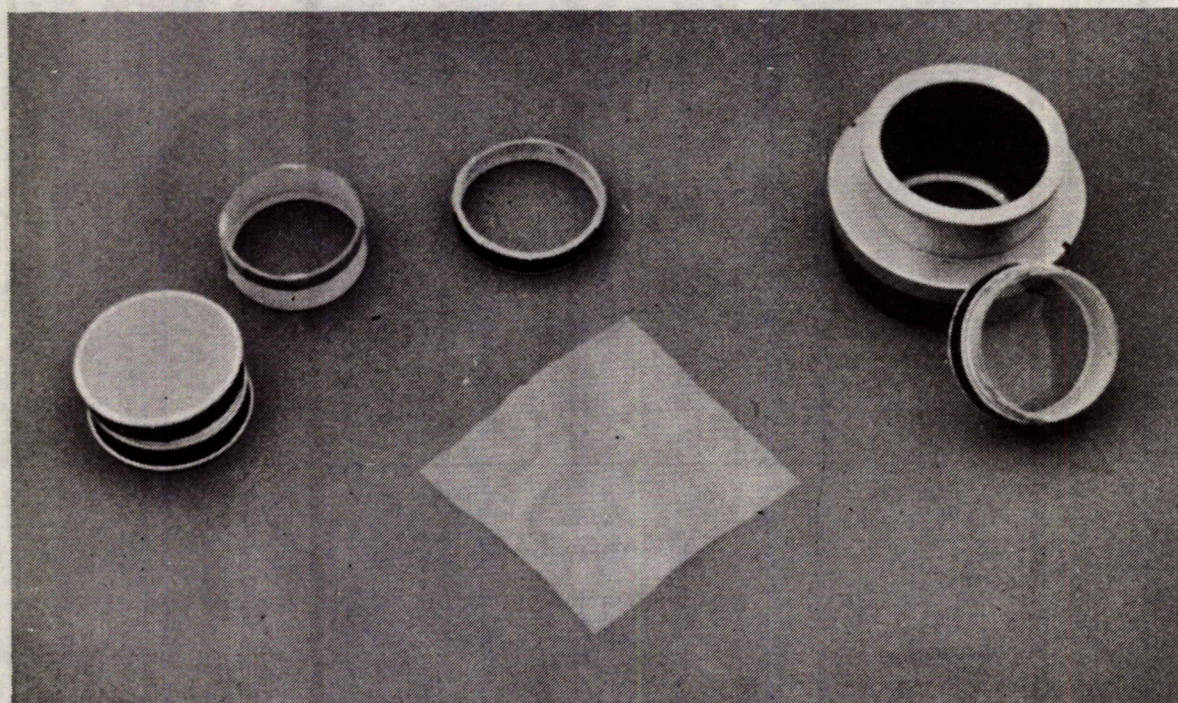


FIG. 4.   Sample holder and components.

## Discussion of the working curves

The analytical working curves are shown in Figs. 5–7. The results for each mineral were plotted on the working curves at the compositions determined from the standardization curves. Each mineral was run twice using separate one-milligram aliquots, the values obtained being plotted separately. The spread of these duplicate determinations indicates the reproducibility that may be expected.

The effect of sample size was investigated. In addition to the one-milligram samples, five-milligram samples were run for several minerals as indicated by the open circles on the working curves for Cu/Fe and Pb/Sb (Figs. 4 & 5). Intensity ratios remained unchanged except in the case of bornite which showed a marked deviation from the curve. This effect may be expected if the enhancement-absorption effects between $CuK\alpha_1$ and $FeK\alpha_1$ are considered. In the five-milligram sample the added depth of sample will increase these effects. The result will be a decrease in the Cu/Fe intensity ratio as observed.
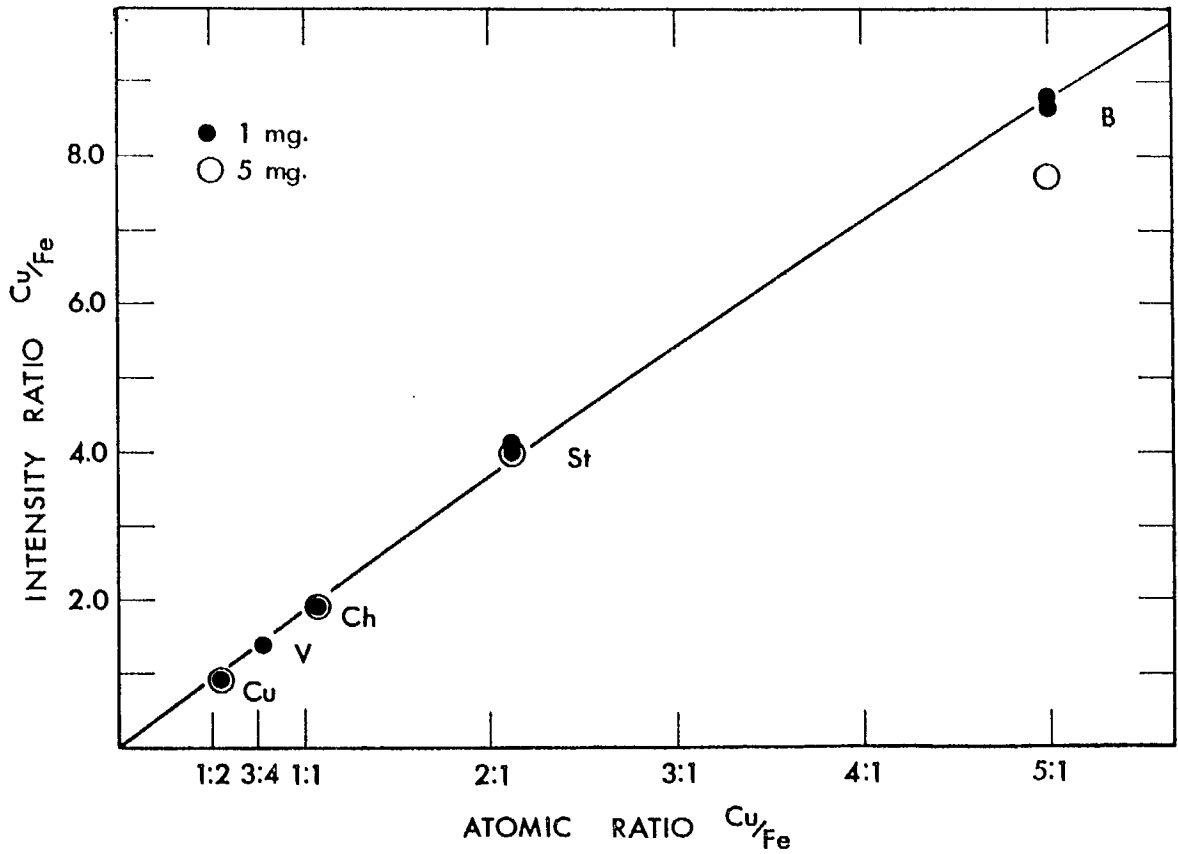
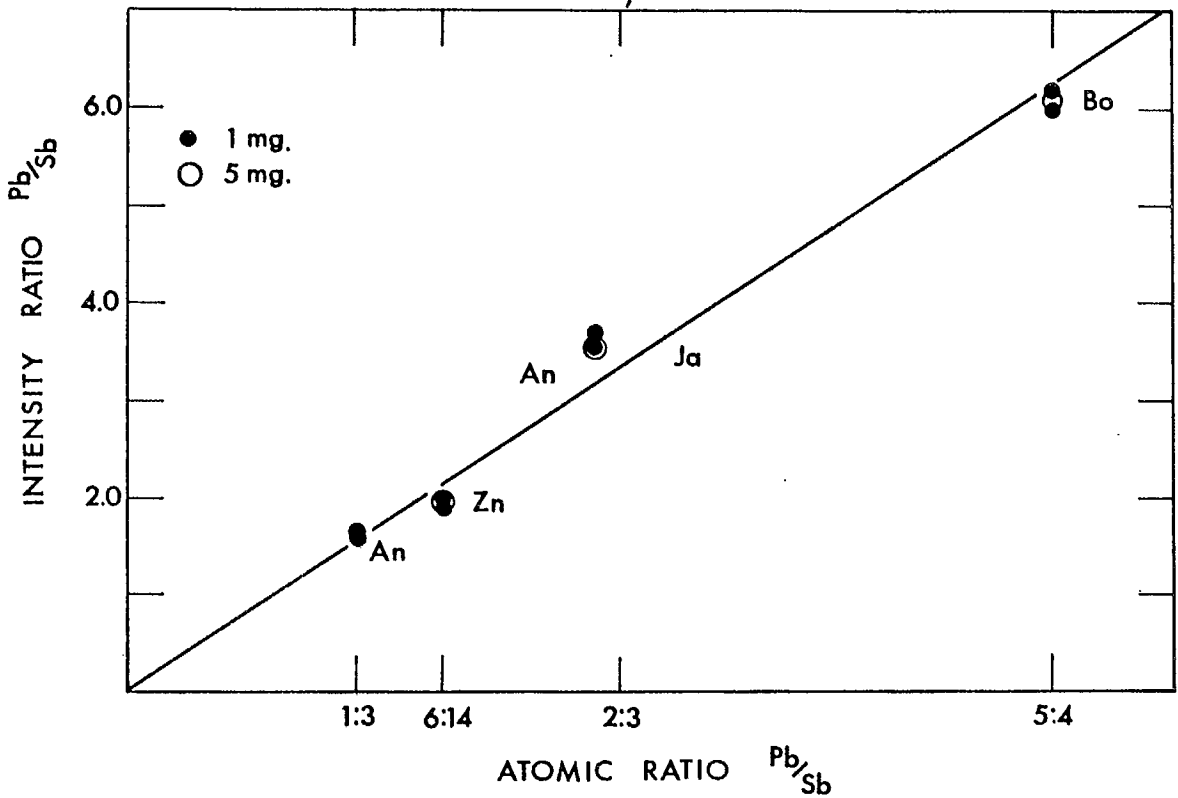FIG. 5. Working Curve for Cu/Fe.
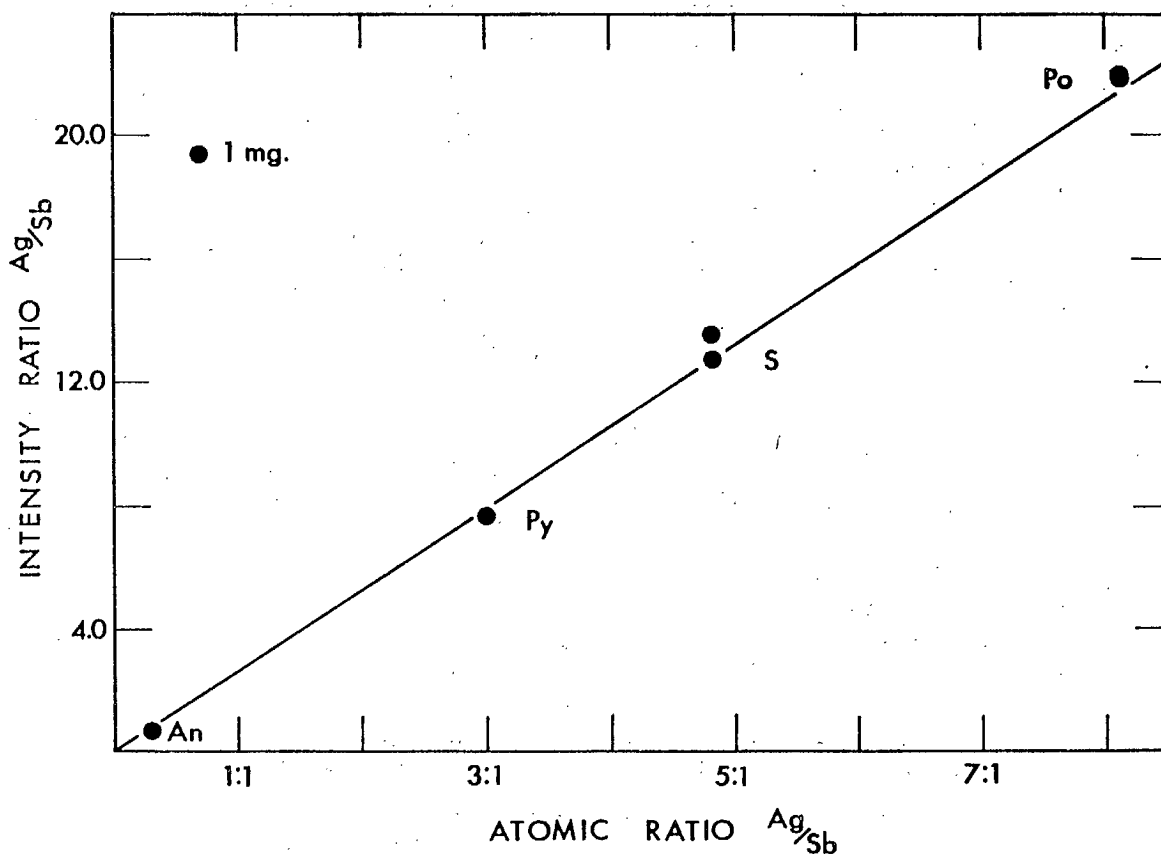


FIG. 6. Working Curve for Pb/Sb.

FIG. 7.   Working Curve for Ag/Sb.

The carefully selected two milligrams of andorite referred to above gave the correct atomic ratio for Pb/Sb when analysed on the Pb/Sb working curve. A one-milligram sample taken from the impure finely ground stock material gave almost the same ratio as that obtained by analysis on the standardization curve. This is shown as the small open circle on the Pb/Sb working curve.

The mineral jamesonite deviated from the working curve by 14.0 per cent (Table 2), which was more than three times the average for the twelve analyses. This mineral is highly sectile and the sample used was a mat of fine needle-like crystals. Such material tends to pack and smear rather than grind, even under very light grinding pressures. The light grinding used here did not eliminate the needle-like characteristic. It is possible that these properties have something to do with the observed deviation inasmuch as preferred orientation would be a notable feature of the sample as presented to the x-ray beam.

## ANALYSIS OF VALLERIITE

Valleriite is a copper iron sulphide, for which a number of formulae have been proposed. It is a massive mineral resembling pyrrhotite in

colour and graphite in physical properties. The cleavage is perfect, hardness is quoted as very soft, and the powder photograph of the mineral has been indexed as rhombohedral, Evans *et al.* (1964). It is a mineral of limited occurrence, but found in a number of high temperature copper deposits, of which the original discovery was at the Aurora Mine, Sweden.

For the analysis, two milligrams of the mineral were carefully selected from a Royal Ontario Museum specimen (M 17023) of the locality, Kaveltorp, Sweden. Very little material was available, hence the fusion analysis had to be omitted. Since the physical properties are similar to graphite, the mineral would not grind well, but was easily crushed to a fine powder.

The analysis gave a Cu/Fe ratio of 0.80. Various Cu/Fe ratios are indicated by analyses which appear in the literature. Hiller (1939) gives 0.50 and 0.75, Evans *et al.*, (1964) gives values of 0.71 and 0.87. A ratio of 1.0 was determined by Morimoto of the Geophysical Laboratory, Washington, (priv. comm.). Apparently some substitution between Cu and Fe is possible although it is also possible that some of the iron is associated with the Mg-Al second phase proposed by Evans to explain the presence of a second weaker lattice appearing in single crystal patterns of valleriite.

## SUMMARY

The above described method offers a simple rapid means of establishing atomic ratios in very small ore-mineral samples. A few of the more noteworthy aspects of the method may be summarized as follows:

1. It is apparent from the level of intensities obtained on these tests that quite useful data may be derived from samples weighing less than one milligram.

2. Based on the observed deviation of intensity ratios from the working curves drawn for one-milligram samples, the accuracy with which atomic ratios may be determined is on the average about ±4 per cent.

3. Reproducibility of intensity ratios as determined by two and three runs on separate one-milligram aliquots of sample is about ±1 per cent.

4. The accuracy with which atomic ratios may be established is equal to that obtained with other procedures and methods using larger samples.

5. One milligram of pure material is easier to obtain than the amount required for other methods.

6. The time required for analysis, once standards are established, is but a few minutes.

7. Analyses may be repeated as often as is desirable.

8. Sample size need be known only approximately.

9. Physical properties of minerals such as sectility and ductility may render sample preparation difficult and have adverse effects on results.

## REFERENCES

BERTIN, E. P. (1964): Intensity ratio technique for $x$-ray spectrometric analysis of binary samples, *Anal. Chem.*, **36**, No. 4, 826–832.

EVANS, H. T. JR., MILTON, C., CHAO, E. C. T., ADLER, I., MEAD, C., INGRAM, B., & BERNER, R. A. (1964): Valleriite and the new iron sulfide, mackinawite, *U.S. Geol. Surv. Prof. Paper*, **475-D**, D64-69.

HILLER, J. E. (1939): Zur Kristallstruktur des Valleriits, *Zeits. Krist.*, **101**, 425–434.

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