THE ANALYSIS OF ROCKS AND ORES BY X-RAY DIFFRACTOMETER[1]

W. PETRUK[2]
Mines Branch, Ottawa, Canada

ABSTRACT

This paper deals with the use of the *x*-ray diffractometer as a means of analysing a variety of rocks and ores. Three different methods were investigated; an internal standard method, a method requiring calculation of the mass absorption coefficients of the individual constituents of the sample, and a method which involves measuring the relative intensities of reflections from the sample holder. Tests on a variety of known samples indicate comparable accuracies, and that the mean deviation is 3–5 units. The major source of error is believed to be in sample preparation.

INTRODUCTION

During the course of mineralogical investigations of ores and mill products it is desirable, and frequently necessary, to determine the mineral content of samples. Semi-quantitative analysis of powders by means of the *x*-ray diffractometer is perhaps the easiest and often the only way of making such determinations. This analysis can be performed by using an internal standard or by methods based on the mass absorption coefficient of the sample. The former method involves mixing a known amount of carefully selected material into the sample; the latter does not require additional material, but involves either determining the mass absorption coefficient of the sample or measuring some factor which is dependent upon it. The present investigation was undertaken primarily to compare these methods.

APPARATUS AND EXPERIMENTAL PROCEDURES

The apparatus used in this investigation consisted of a Philips *x*-ray diffraction unit with a wide-angle goniometer, a scaling circuit, a Geiger counter, and a step recorder. Operating conditions were set at 45 kv and 10 ma using iron-filtered cobalt radiation. Cobalt radiation was selected instead of copper or iron radiation because it gives the strongest intensities of reflection from iron-bearing minerals.

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[2]Scientific Officer, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

The samples were prepared by grinding −65 mesh material in a mechanical mortar for 55 minutes. This grinding time was selected because tests with quartz, magnetite, and pyrite indicated that for the mortar used this time is adequate to achieve a uniform mixture of the components, at a suitable particle size.

The ground powders were mounted either in standard aluminium sample holders by the back mounting method, or in special sample holders described later in the text.

The samples were scanned at either 1° or ¼° per minute. Tests with pyrite show that a reflection scanned at ¼° per minute has a slightly better reproducibility than a reflection scanned at 1° per minute. Intensities were determined by measuring the peak heights and subtracting the background.

Analysis by the Internal Standard Method

Theoretical considerations

Analysis by the internal standard method is based on the relationship expressed by the equation:

$$x_a = KI_a/I_s \tag{1}$$

where x_a is the weight per cent of the unknown component (component a), I_a and I_s are the intensities of reflections from the unknown component and the internal standard respectively, and K is a constant. The value of K for a particular component-internal standard combination may be determined by measuring the intensities of reflections from a known mixture.

A mathematical expression for the value of K may also be derived from the basic principle of x-ray diffraction. This principle relates the intensity of a reflection to the mineral content of a sample and it is expressed by the equation (1):

$$I_a = Kf_a/\mu_A \tag{2}$$

where f_a is the fractional volume of component a and μ_A is the linear absorption coefficient of the sample.

For a pure sample of component a

$$I_{ao} = K/\mu_a \tag{3}$$

where I_{ao} is the intensity reflected by a pure sample of component a and μ_a is the linear absorption coefficient of component a. Dividing equation 2 by equation 3 we get:

$$\frac{I_a}{I_{ao}} = \frac{f_a\mu_a}{\mu_A} \tag{4}$$

Similarly, if an internal standard has been added to the sample, the intensity of its reflection would be related to its content in the sample by the equation:

$$\frac{I_s}{I_{so}} = \frac{f_s \mu_s}{\mu_A} \tag{5}$$

The subscript "s" refers to the internal standard.

$f = x\rho/\rho'$, where x is the weight fraction, ρ' the density of the mineral and ρ the density of the sample. The mass absorption coefficient μ' is defined by $\mu' = \mu/\rho'$.

By introducing x_s and μ' and rearranging the terms we get:

$$x = x_s \frac{I_a}{I_s}\left(\frac{\mu_s' I_{so}}{\mu_a' I_{ao}}\right) \tag{6}$$

A comparison of equation 6 with equation 1 shows that

$$K = x_s \frac{\mu_s' I_{so}}{\mu_a' I_{ao}}.$$

Its value can be calculated if μ_s', μ_a', I_{so} and I_{ao} have been previously established.

Experimental results

Six pyrite-pyrrhotite mixtures in known proportions were analysed by using pyrrhotite as an internal standard and six known quartz-magnetite mixtures were analysed by using magnetite as an internal standard. The value of K for each mineral-internal standard combination was determined experimentally by scanning in duplicate. The results are given in Table 1 and the difference between the determined and known mineral contents of each mixture was calculated as a mean deviation. The mean deviation for 12 analyses was 3.1.

A number of prepared mixtures containing two or more constituents were analysed for chalcopyrite, hematite, pyrrhotite, magnetite, magnesite and ilmenite by using a number of different internal standards. The value of K for each mineral-internal standard combination was calculated. The results are given in Table 2 and, as above, the difference between the determined and actual mineral content of each sample was calculated as a mean deviation. The mean deviation for 18 analyses was 4.4.

TABLE 1. DETERMINATION OF MINERAL CONTENTS OF PREPARED MIXTURES
(by internal standard method and experimental determination of the value of K)

	Internal standard			Mineral analysed for						
Mixture	mineral	"d" of reflection	known (wt. %)	mineral	"d" of reflection	known (wt. %)	determined mineral content (wt. %)	Diff. between determined and known mineral contents (wt. %)	I/I_s (observed)	K_{exp}
Pyrite-pyrrhotite	pyrrhotite	2.64 Å	50%	pyrite	2.70 Å	50%	standard	—	2.37	0.422
"	"	2.64	95	"	2.70	5	7.5%	+2.5%	0.19	0.422
"	"	2.64	85	"	2.70	15	15.1	+0.1	0.42	0.422
"	"	2.64	75	"	2.70	25	29.5	+4.5	0.93	0.422
"	"	2.64	60	"	2.70	40	34.0	−6.0	1.34	0.422
"	"	2.64	40	"	2.70	60	59.0	−1.0	3.49	0.422
"	"	2.64	15	"	2.70	85	80.0	−5.0	12.60	0.422
Magnetite-quartz	magnetite	2.52	50	quartz	3.34	50	standard	—	2.73	0.366
"	"	2.52	95	"	3.34	5	3.6	−1.4	0.10	0.366
"	"	2.52	85	"	3.34	15	9.4	−5.6	0.30	0.366
"	"	2.52	75	"	3.34	25	19.6	−5.4	0.72	0.366
"	"	2.52	60	"	3.34	40	37.0	−3.0	1.68	0.366
"	"	2.52	40	"	2.34	60	62.5	+2.5	4.26	0.366
"	"	2.52	15	"	3.34	85	84.5	Mean deviation ± 3.1	15.40	0.366

TABLE 2. DETERMINATION OF MINERAL CONTENTS OF PREPARED MIXTURES
(by internal standard method and calculation of the value of K)

Mixture	Internal Standard: mineral	Internal Standard: "d" of reflection	Internal Standard: known (wt. %)	Mineral Analysed for: mineral	Mineral Analysed for: "d" of reflection	Mineral Analysed for: known (wt. %)	determined mineral content (wt. %)	Difference between Determined and Known Mineral Contents (wt. %)	I/I_s (observed)	K_{calc}
Pyrite-chalcopyrite-pyrrhotite	pyrite	2.42 Å	50	chalcopyrite	3.03 Å	25	19.5	−5.5	1.30	0.30
	"	2.42	50	pyrrhotite	2.06	25	21.2	−3.8	0.48	0.88
Pyrite-chalcopyrite-pyrrhotite-magnetite	"	2.70	20	chalcopyrite	3.03	20	14.1	−5.9	1.26	0.56
	"	2.70	20	pyrrhotite	2.64	20	14.9	−5.1	0.31	2.45
	"	2.70	20	magnetite	2.54	40	46.2	+6.2	1.85	1.25
Pyrite-chalcopyrite-pyrrhotite-magnetitie-ilmenite	"	2.70 + 2.42 + 2.20 + 1.91	20	chalcopyrite	3.03 + 1.85	20	17.7	−2.3	0.93	0.95
	"	"	20	pyrrhotite	2.64 + 2.06	20	19.0	−1.0	0.44	2.14
	"	"	20	magnetite	2.99 + 2.54 + 2.10 + 1.71	20	29.0	+9.0	1.11	1.32
	"	"	20	ilmenite	2.74 + 1.72	20	13.4	−6.6	0.38	1.77
Pyrite-magnesite	"	"	50	magnesite	2.74	50	48.5	−1.5	1.21	0.80
Pyrite-hematite	"	2.42 + 2.20	30	hematite	3.68	70	78	+8.0	0.58	4.45
Hematite-chalcopyrite	hematite	2.69	70	chalcopyrite	3.03	30	24.3	−5.8	0.55	0.62
Hematite-magnesite	"	2.69	70	magnesite	2.74	30	27.9	−2.1	1.05	0.38
Magnetite-ilmenite-hematite	magnetite	2.54	50	ilmenite	2.74	42	40.5	−1.5	0.98	0.83
	"	2.10	50	hematite	2.69	8	10.4	+2.4	0.70	0.29
Magnetite-hematite	hematite	2.69	85	magnetite	2.10	15	21	+6.0	0.07	3.50
Pyrrhotite-ilmenite	pyrrhotite	2.06	80	ilmenite	2.74	20	17.1	−2.9	0.34	0.63
Pyrrhotite-pyrite	"	2.06	50	pyrite	2.70	50	53.0	+3.0	1.74	0.61
								Mean deviation ± 4.4		

Analysis by Calculating the Mass Absorption Coefficients

Theoretical considerations

The theory for analysing binary mixtures was developed by Klug & Alexander (1954) and is expressed by the equation:

$$I/I_0 = \frac{x\mu_1'}{x(\mu_1' - \mu_2') + 1} \tag{7}$$

where I is the intensity of a reflection due to component 1; I_0 the intensity diffracted by a unit weight of component 1; x is the weight fraction of component 1; μ_1' and μ_2' are the mass absorption coefficients of components 1 and 2 respectively. For the purpose of analysing multicomponent mixtures, equation 7 can be extended by considering μ_2' as the mass absorption coefficient of the matrix.

The relationship expressed by equation 7 can be simplified to:

$$I/I_0 = \frac{xY}{x(Y - 1) + 1} \tag{8}$$

by combining the values of μ_1' and μ_2' so that $Y = \mu_1'/\mu_2'$.

This relationship is shown graphically in Fig. 1 for a wide range of values of Y and all possible values of x and I/I_0. The mineral content of a mixture can be determined by measuring the value of I/I_0 and calculating the value of Y from the mass absorption coefficients of μ_1' and μ_2'. The mass absorption coefficient of any material can be calculated from its composition. As an illustration a calculation for the specific case of pyrite (FeS_2) is given below. For a wavelength $\lambda = 1.790$ Å (Co$K\alpha$), μ_{Fe}' and μ_S' are 59.5 and 139 respectively (Peiser *et al.*, 1955). Since pyrite contains 46.55 per cent Fe and 53.45 per cent S, the mass absorption coefficient of pyrite is $(59.5 \times 0.4655) + (139 \times 0.5345) = 102$. The mass absorption coefficients of a number of minerals and rock types irradiated with Co$K\alpha$ were calculated and their values are listed in Appendix 1.

When the composition of the matrix is known, the mass absorption coefficient (μ_2') can be readily calculated. If on the other hand it is not known, then it is necessary to estimate the approximate mass absorption coefficient of the matrix by identifying the minerals in the matrix and by estimating the approximate amount that each contributes towards the value of μ_2'. The following example of an analysis for chalcopyrite is given to illustrate this approach. The matrix was estimated to contain about 20 per cent pyrite, 30 per cent quartz and 50 per cent calcite. From Appendix 1 μ_1' for chalcopyrite is 95.3; μ_2' for the matrix is $(102 \times 0.20) + (54.7 \times 0.30) + (113.6 \times 0.50) = 93.6$; hence $Y = 95.3/93.6 = 1.02$.

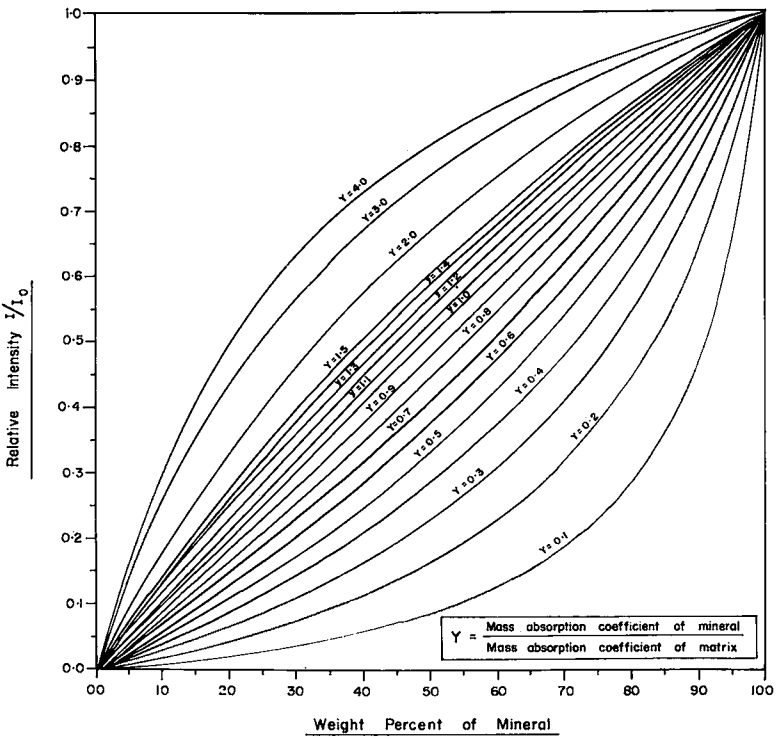

FIG. 1. Relationship between the relative intensity of a diffracted x-ray beam and the mineral content in a sample.

Experimental results

In order to show that the relation expressed by equation 8 is valid, six mounts containing 50 per cent pyrite and seven mounts containing 70 per cent hematite were analysed. The matrices of these mixtures consisted of a number of different materials, so that the Y values ranged between 2.75 and 0.42 for pyrite samples and 1.30 and 0.20 for hematite samples. The results, plotted in Fig. 2, show that the points fall close to the theoretical curves established by equation 8.

Lum (1960) analysed a number of known two-mineral mixtures with Y values near 1. He prepared two mounts of each mixture and scanned the strong reflection of each mineral at $\frac{1}{4}°$ per minute. The average value of I/I_0 and the appropriate theoretical curves are plotted in Figs. 3, 4 and 5. They show that there is very little scatter about the theoretical curve.

Dr. E. H. Nickel of the Mines Branch analysed a number of quartz-pollucite mixtures of known composition by scanning one mount of each

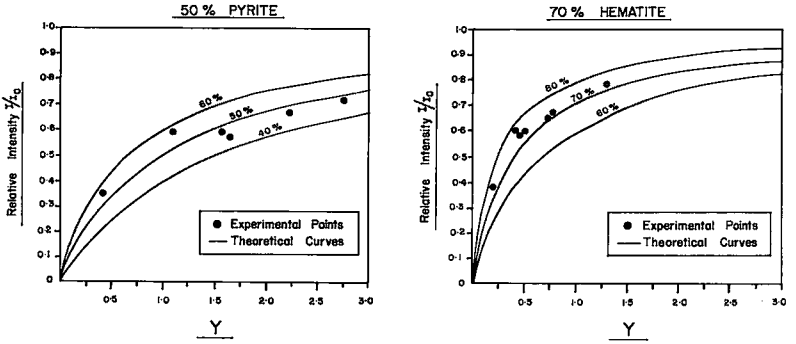

FIG. 2. Relationship between the relative intensity and Y for mixtures containing 50 per cent pyrite and 70 per cent hematite.

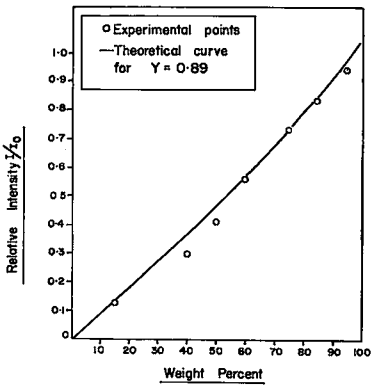

FIG. 3. Relationship between relative intensity and percentage of magnetite in quartz-magnetite mixtures.

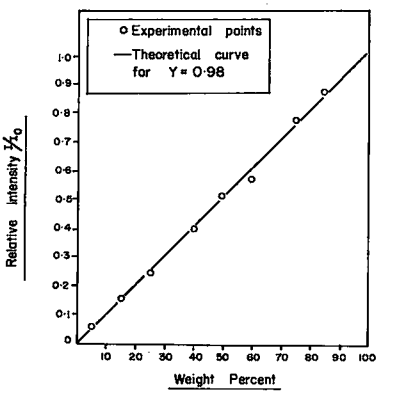

FIG. 4. Relationship between relative intensity and percentage of hematite in magnetite-hematite mixtures.

mixture across the strong pollucite reflection at $\frac{1}{4}°$ per minute. The Y value of these mixtures was 3.66. The results, plotted in Fig. 6, also show that there is little scatter about the theoretical curve.

The writer prepared and analysed a number of polycomponent mixtures with $Y = 0.5$. Each mixture was scanned across a number of reflections of the mineral being analysed at 1° per minute and the average value of I/I_0 was determined. The results are plotted in Fig. 7. This method was further tested by analysing two unknown samples of titaniferous magnetite from Papineau Township in Ontario, and five chemically analysed rock samples. The mineral contents of the titaniferous magnetite samples were then determined by concentrating the minerals and weighing the

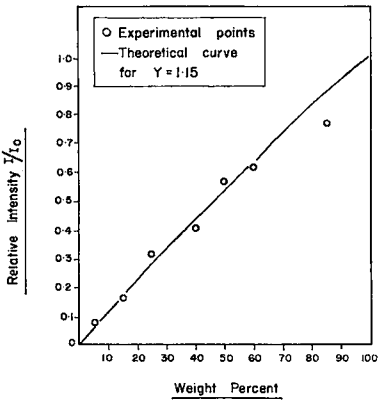

FIG. 5. Relationship between relative intensity and percentage of pyrite in pyrite-pyrrhotite mixtures.

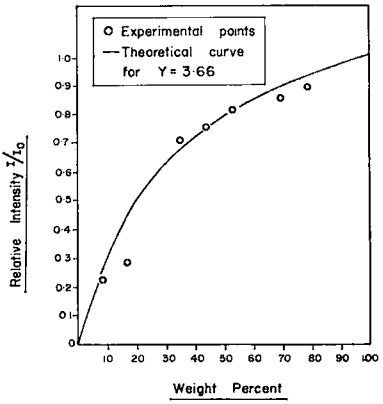

FIG. 6. Relationship between relative intensity and percentage of pollucite in pollucite-quartz mixtures.

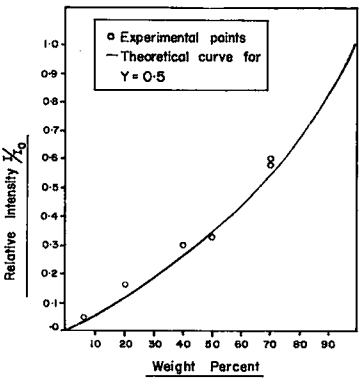

FIG. 7. Relationship between relative intensity and percentage of different minerals in a variety of mixtures all with Y = 0.5.

concentrates, and the normative mineral contents of the rock samples, given in Table 3, were calculated from the chemical analyses. The results of x-ray diffraction analyses are summarized in Table 3a.

In order to evaluate the results obtained when analysing binary mixtures by this method, 56 determinations were made from prepared pyrite-pyrrhotite, pyrite-quartz, and quartz-magnetite mixtures (see

Table 4). The chemical content of each pyrite-pyrrhotite and quartz-magnetite mixture was determined from one run, but the mineral content of the pyrite-quartz mixture was determined from a number of runs (see Tables 4 and 4a). The differences between the determined and actual mineral contents of the first two suites of mixtures, calculated as a mean deviation, are ±3.1. The difference between the determined and actual mineral content of the quartz-pyrite mixture, determined from 12 and 16 runs, is ±1.7 and ±1.0 respectively. No tests were made to evaluate the results obtained when analysing polycomponent mixtures.

TABLE 3. NORMATIVE MINERAL CONTENTS OF ROCK SAMPLES

Mineral	Normative Mineral Content (Wt. Per cent)				
	Sample A	Sample B	Sample C	Sample D	Sample E
Quartz	8.3	9.7	44.0	46.4	53.0
Albite	3.7	3.7	37.9	0.9	0.8
Anorthite	19.2	20.0	0.6	8.8	9.6
Mafics (pyroxene, chlorite and garnet)	47.9	50.3	10.8	28.1	22.8
Calcite	15.3	7.3	4.9	11.0	8.6
Apatite	0.3	0.2	—	0.2	0.2
Chalcopyrite	2.4	4.9	0.4	1.4	1.9
Pyrrhotite	0.1	0.2	1.2	0.3	0.1
Chromite	0.3	0.3	0.2	0.3	0.3
	97.5	96.6	100.0	97.4	97.3

TABLE 3*a*. MINERAL CONTENTS OF UNKNOWN SAMPLES AS DETERMINED BY CONCENTRATING THE MINERALS, BY CHEMICAL ANALYSIS, AND *x*-RAY DIFFRACTOMETER ANALYSIS

Sample	Magnetite		Ilmenite		Hematite		Quartz	
	Weight per cent, as determined by		Weight per cent, as determined by		Weight per cent, as determined by		Weight per cent, as determined by	
	Concentrating minerals	*x*-ray	Concentrating minerals	*x*-ray	Concentrating minerals	*x*-ray	Calc. of Chem. analyses	*x*-ray
No. 180 (Tit. Mag.)	32	36	14.5	16	2.5	4		
No. 181 (Tit. Mag.)	47	51	25	24	4.0	5		
A (rock)							8.3	9.0
B (rock)							9.7	16.5
C (rock)							44.0	48
D (rock)							46.4	49
E (rock)							53.0	65

TABLE 4. DETERMINATION OF MINERAL CONTENTS OF PREPARED MIXTURES (BY METHOD OF CALCULATING MASS ABSORPTION COEFFICIENTS)

Mixture	Mineral Involved	I/I_0 (observed)	Y	Known Mineral Content (wt. %)	Analysed Mineral Content (wt. %)	Difference between Analysed and Known Mineral Contents (wt. %)
Pyrite-pyrrhotite	pyrite	0.087	1.15	5	7.9	+2.9
"	"	0.168	1.15	15	15.2	+0.2
"	"	0.322	1.15	25	29.2	+4.2
"	"	0.410	1.15	40	38.0	−2.0
"	"	0.575	1.15	50	54.0	+4.0
"	"	0.620	1.15	60	58.7	−1.3
"	"	0.770	1.15	85	74.5	−10.5
"	pyrrhotite	0.075	0.87	15	9.0	−6.0
"	"	0.363	0.87	40	40.0	0.0
"	"	0.494	0.87	50	53.0	+3.0
"	"	0.620	0.87	60	65.8	+5.8
"	"	0.740	0.87	75	73.5	−1.5
"	"	0.810	0.87	85	83.5	−1.5
"	"	0.945	0.87	95	95.2	+0.2
Quartz-magnetite	quartz	0.042	1.12	5	4.0	−1.0
"	"	0.110	1.12	15	10.0	−5.0
"	"	0.230	1.12	25	21.0	−4.0
"	"	0.415	1.12	40	38.5	−1.5
"	"	0.490	1.12	50	46.0	−4.0
"	"	0.560	1.12	60	53.0	−7.0
"	"	0.850	1.12	85	83.3	−1.7
"	magnetite	0.125	0.89	15	14.0	−1.0
"	"	0.30	0.89	40	33.0	−7.0
"	"	0.41	0.89	50	45.0	−5.0
"	"	0.56	0.89	60	59.2	−0.8
"	"	0.73	0.89	75	75.5	+0.5
"	"	0.83	0.89	85	85.0	0.0
"	"	0.94	0.89	95	95.0	0.0
Pyrite-quartz	pyrite	0.666	1.86	50	51.7	+1.7 (av of 12)
"	quartz	0.357	0.54	50	51.0	+1.0 (av of 16)

ANALYSIS BY MEASURING THE RELATIVE INTENSITIES OF REFLECTIONS FROM THE SAMPLE HOLDER

Theoretical considerations

Williams (1959) has described a method of analysis which involves measuring the intensities of x-rays diffracted from the sample holder with and without a finite thickness of sample. He developed the following equation to relate the concentration of the unknown component in the sample to the intensity of the analytical peak:

$$xP = -(I/W)\log(I'_s/I'_0)\sin\theta_h\left[\frac{1}{1-(I'_s/I'_0)\,r}\right] \qquad (9)$$

where $P = I_0A/B$, and $r = \sin\theta_h/\sin\theta$.

In equation 9 x, I, and I_0 are the same as in equation 7, with I and I_0 being reflected at the glancing angle θ; A is the cross-sectional area of the

TABLE 4*a*. DETERMINATIONS OF MINERAL CONTENT OF A SAMPLE OF FIXED COMPOSITON (BY METHOD OF CALCULATING MASS ABSORPTION COEFFICIENTS)

Mixture	Mineral Involved	I/I_0 (observed)	Y	Known Mineral Content (wt. %)	Analysed Mineral Content (wt. %)	Difference between Analysed and Known Mineral Contents (wt. %)
Pyrite-quartz	pyrite	0.650	1.86	50	50.0	0.0
"	"	0.650	1.86	50	50.0	0.0
"	"	0.650	1.86	50	50.0	0.0
"	"	0.725	1.86	50	58.0	+8.0
"	"	0.725	1.86	50	58.0	+8.0
"	"	0.650	1.86	50	50.0	0.0
"	"	0.650	1.86	50	50.0	0.0
"	"	0.804	1.86	50	68.5	+18.5
"	"	0.690	1.86	50	54.0	+4.0
"	"	0.554	1.86	50	40.0	−10.0
"	"	0.687	1.86	50	53.5	+3.5
"	"	0.535	1.86	50	38.0	−12.0
mean	"	0.666	1.84	50	51.7	+1.7
Pyrite-quartz	quartz	0.40	0.54	50	56.0	+6.0
"	"	0.393	0.54	50	55.0	+5.0
"	"	0.273	0.54	50	41.5	−8.5
"	"	0.295	0.54	50	44.0	−6.0
"	"	0.35	0.54	50	50.0	0.0
"	"	0.388	0.54	50	54.7	+4.7
"	"	0.322	0.54	50	47.5	−2.5
"	"	0.475	0.54	50	63.0	+13.0
"	"	0.317	0.54	50	47.0	−3.0
"	"	0.40	0.54	50	56.0	+6.0
"	"	0.36	0.54	50	51.5	+1.5
"	"	0.40	0.54	50	56.0	+6.0
"	"	0.320	0.54	50	47.0	−3.0
"	"	0.295	0.54	50	44.0	−5.0
"	"	0.390	0.54	50	55.0	+5.0
"	"	0.330	0.54	50	48.0	−2.0
mean	"	0.357	0.54	50	51.0	+1

incident beam; B is the surface area of the powder and W is the weight of the powder; I'_s and I'_0 are the intensities of a reflection from the sample holder at a glancing angle θ_h with and without the sample respectively. P is a constant for a particular mineral if A, B and the incident radiation are constant. The value of P is determined by running a standard sample containing a known concentration of the mineral involved.

Experimental results

The author tested this method by analysing known mixtures mounted in two different copper sample holders which were recessed 0.01 inch and 0.005 inch respectively. It was found that the copper reflections from the sample holder were completely absorbed by samples with mass absorption coefficients above 55 and 75 respectively. The values of the mass absorption coefficients of 18 samples were reduced by diluting the samples with

material that has a low mass absorption coefficient. Two-thirds gum arabic by weight was added to each sample. These samples were mounted in the more deeply recessed sample holders and scanned at $\frac{1}{4}°$ per minute. This enabled the method to be extended to include samples with mass absorption coefficients up to 100.

In order to determine whether the method could be further extended to analysing samples with higher mass absorption coefficients, tests were made with a variety of mounts. Single-layered mounts were prepared by dusting the samples on cellulose tape. The intensities of reflections diffracted from a sample so mounted were too low to be considered useful. Thicker mounts were prepared by dusting a powder on several pieces of cellulose tape and fixing them together. These mounts, however, did not have a uniform thickness and the results were not reproducible.

Cold-setting mounts were prepared in 0.001 inch deep and 0.003 inch deep recesses in a copper sample holder from a mixture containing $33\frac{1}{3}$ per cent mounting medium by weight. Glycol phthalate, produced by General Electric, was found to be a suitable mounting medium because it melts at a relatively low temperature, solidifies upon cooling, and can be powdered and mixed with a sample at room temperature. The mounts were prepared by dusting the mixture of sample and glycol phthalate into the copper sample holder and melting to a paste over a hot plate. When the mixture had cooled and solidified, the surface was flattened to the level of the sample holder by hand grinding on a glass plate with 600 alundum. Using mounts that were prepared in this manner, it was possible to analyse successfully samples with mass absorption coefficients at least as high as 200.

The accuracy of this method was evaluated as in the previous instance by calculating the difference between the determined and actual mineral contents of prepared mixtures as a mean deviation (see Table 5). The mean deviation determined for 8 mounts prepared in a cold-setting medium was 4.4.

Comparison of the Three Methods of Analysis

In order to provide a comparison of the three methods described, the pyrite contents of seven known pyrite-pyrrhotite mixtures and the quartz contents of five rock samples of known composition were determined by each method. The results are given in Tables 6 and 7. Table 6 indicates that the pyrite content in a known matrix (pyrrhotite) can be determined by each method with comparable accuracy. Columns 3 and 4 of Table 7 show that the quartz content in an unknown matrix (rock sample) can also be determined with comparable accuracy by the internal standard

TABLE 5. DETERMINATION OF MINERAL CONTENTS OF PREPARED MIXTURES
(by the method which involves measuring the relative intensities of x-rays reflected from the sample holder)

Mixture	Mineral Analysed for		Experimental Results					Analysed (wt. %)	Known (wt. %)	Difference between Analysed and Known Mineral Content
	mineral	"d" of reflection	P	I_s'/I_0'	"d" of reflection from sample holder	I	W (grams)			
Pyrite-pyrrhotite	pyrite	2.70Å	1285	0.077	2.09Å	44	0.023	standard	85	
"	"	2.70	1285	0.083	2.09	44.5	0.023	83.4	95	−11.6
"	"	2.70	1285	0.074	2.09	33	0.028	55.0	60	−5.0
"	"	2.70	1285	0.050	2.09	26	0.031	43.1	50	−6.9
"	"	2.70	1285	0.074	2.09	28	0.027	46	40	+6.0
"	"	2.70	1285	0.133	2.09	21	0.024	31.8	25	+6.8
"	"	2.70	1285	0.120	2.09	8	0.021	14.3	15	−0.7
"	"	2.70	1285	0.100	2.09	2	0.023	3.4	5	−1.6
Pyrite-diorite	"	2.70	1285	0.149	2.09	33.5	0.023	52.0	50	+2.0
Pyrite-pyrrhotite	pyrrhotite	2.65	624	0.074	2.09	12	0.028	standard	40	
"	"	2.65	624	0.100	2.09	28	0.023	98.0	95	+3.0
"	"	2.65	624	0.120	2.09	24	0.021	87.6	85	+2.6
"	"	2.65	624	0.133	2.09	21	0.024	63.6	75	−6.4
"	"	2.65	624	0.074	2.09	18	0.027	59.7	60	−0.3
"	"	2.65	624	0.077	2.09	5	0.023	19.6	15	+4.6

Mean deviation ±4.4

TABLE 6. PYRITE CONTENT OF THE ARTIFICIAL PYRITE-PYRRHOTITE MIXTURES

Known weight per cent pyrite	Weight per cent pyrite, as determined with the x-ray diffractometer: by calculating mass absorption coefficients	by measuring relative intensities	by internal standard method. (internal standard = pyrrhotite)
5	8	3.4	7.5
15	15	14.3	15.1
25	29.3	31.8	29.5
40	37.5	50.0	34.0
50	53.5	43.1	standard
60	58.5	58.2	59.0
85	75.0	85.0	80.0
mean deviation	3.5	3.9	3.2

TABLE 7. QUARTZ CONTENT OF FIVE CHEMICALLY ANALYSED ROCK SAMPLES

Weight per cent quartz as calculated from chemical analyses	Weight per cent quartz, as determined with the x-ray diffractometer: by calculating mass absorption coefficients	by measuring relative intensities	by internal standard method. (internal standard = 50% MgO)
8.3	9.0	11.6	5.7
9.7	16.5	10.3	7.2
44.0	48.0	40.0	41.7
46.4	49.0	43.0	41.3
53.0	65.0	56.8	59.5
mean deviation	5.2	3.0	3.8

method and by the method which involves measuring the relative intensities of reflections from the sample holder. On the other hand, column 2 of Table 7 shows that quartz in an unknown matrix cannot be determined as accurately by the method which involves calculating the mass absorption coefficient.

EVALUATION OF THE ERROR OF ANALYSIS

From the tables presented in the previous section it is clear that the deviation or difference between the known mineral content of a sample and that derived from x-ray determinations is constant and independent of the absolute magnitude of the mineral content. This means that for each mineral there may be a minimum amount that can be determined with certainty. For the minerals tested these limits appear to be between 3 per cent and 5 per cent of the sample.

Several tests were designed to locate the principal sources of error. The instrumental error was established by scanning reflections from one mount a number of times at $\frac{1}{4}°$ per minute and repeating this test intermittently for six months. It was found that the instrumental error is approximately equal to background fluctuations. This is negligible when the intensity of a reflection is high, but is of some significance when the intensity to be measured is comparatively low.

The errors due to sampling were evaluated by scanning 25 separately prepared mounts of the same pyrite-quartz mixture. The values of I/I_0 of the strong reflections were measured from each scan and a mean deviation was determined from these measurements. It is 4.6, which is approximately of the same order as the deviations observed in Tables 1, 2, 3, 5, 6 and 7. This suggests that the major source of error is in sample preparation, although there are other possible sources of error, such as x-ray counting statistics, beam and target variations, etc.

An attempt was made to reduce the errors due to sample preparation by preparing mounts in which the grains were allowed to settle in a viscous cold-setting medium. Five mounts containing 50 per cent quartz and 50 per cent pyrite were prepared in this manner and the surface of each mount was ground smooth. The mounts were scanned across the strong quartz reflections at $\frac{1}{4}°$ per minute and the quartz content was determined by the method of calculating the mass absorption coefficients of the constituents and by the internal standard method. The results of this limited investigation suggest that the error of analysis is not reduced significantly by preparing mounts in a cold-setting medium. It is possible that a rotary sample holder would eliminate a number of the errors due to sample preparation and this is being investigated.

Conclusions

This investigation of three different methods of analysing mineral mixtures by means of the x-ray diffractometer shows that the methods are approximately of equal accuracy. The simplest method should, therefore, be selected for use in routine analyses. The method of calculating the mass absorption coefficients of the constituents of a sample requires very little sample preparation but it may involve some calculation of results; the internal standard method requires little interpretation of results, but it involves mixing a known amount of internal standard into the sample; the method of measuring the mass absorption coefficient of a sample, however, involves an elaborate technique of sample preparation as well as extensive calculations. It is suggested, therefore, that the method of calculating the mass absorption coefficients of the constituents of a

sample is preferable for routine analysis when the composition of the matrix is known or can be estimated with reasonable accuracy. If the composition of the matrix cannot be satisfactorily estimated the results will be subject to large errors; under these conditions the internal standard method should be used.

Tests on the error of analysis show that the error is independent of the mineral content of the sample and most of it may be due to sample preparation.

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Appendix 1. Mass Absorption Coefficients of Rocks and Minerals irradiated with Co$K\alpha$ X-rays

Rocks			
Alkali granite	60.5	Quartz gabbro	66.6
Average granite	61.9	Gabbro	69.4
Average granodiorite	62.3	Anorthosite	69.7
Quartz diorite	64.1	Peridotite	58.2
Diorite	65.2		

APPENDIX 1—(*continued*)

Minerals	
Aegirite $NaFeSi_2O_6$	50.3
Albandite MnS	323.4
Albite $NaAlSi_3O_8$	51.7
Almandine $Fe_3Al_2(SiO_4)_3$	51.7
Andalusite, kyanite and sillimanite Al_2OSiO_4	50.6
Anglesite $PbSO_4$	260.5
Anhydrite $CaSO_4$	117.9
Anorthite $CaAl_2Si_2O_8$	79.6
Antigorite $Mg_6Si_4O_{10}(OH)_8$	45.7
Apatite $Ca_5F(PO_4)_3$	132.0
Argentite Ag_2S	307.0
Arsenopyrite FeAsS	100.7
Augite $Ca(Mg,Fe,Al)(Al,Si)_2O_6$	61.2
Azurite $Cu_3(OH)_2(CO_3)$	55.4
Biotite $K(MgFe)_3(OH)_2AlSi_2O_{10}$	63.6
Barite $BaSO_4$	320.0
Beryl $Be_3Al_2Si_6O_{18}$	47.7
Bornite Cu_5FeS_4	92.6
Brucite $Mg(OH)_2$	41.8
Calcite and aragonite $CaCO_3$	113.6
Cassiterite SnO_2	305.2
Cerussite $PbCO_3$	279.5
Chalcocite Cu_2S	91.7
Chalcopyrite $CuFeS_2$	95.3
Chlorite $(Mg_5Al)(AlSi_3)O_{10}(OH)_8$	45.3
Chlorite $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$	48.3
Chromite $FeCr_2O_4$	145.9
Chrysoberyl $BeAl_2O_4$	41.5
Cinnabar HgS	303.7
Cobaltite CoAsS	102.2
Corundum Al_2O_3	48.3
Diopside $CaMgSi_2O_6$	87.7
Dolomite $(Ca,Mg)CO_3$	75.0
Enargite Cu_2O	73.2
Enstatite $Mg_2Si_2O_6$	52.4
Epidote $Ca_2Al_2Fe(OH)(SiO_4)_3$	82.8
Ferberite $FeWO_4$	171.4
Fluorite CaF_2	182.9
Franklinite $ZnFe_2O_4$	57.0
Galena PbS	325.2
Goethite–Limonite $Fe_2O_3.H_2O$	44.9
Gypsum $CaSO_4.2H_2O$	97.5
Halite NaCl	114.0
Hastingsite $NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	68.3
Ferrohastingsite $NaCa_2Fe_4Al_3Si_6O_{22}(OH)_2$	67.1
Hausmanite Mn_3O_4	316.1
Hematite Fe_2O_3	47.7
Huebnerite $MnWO_4$	239.2
Hypersthene $Fe_2Si_2O_6$	54.6
Ilmenite $FeTiO_3$	124.2
Malachite $Cu_2(OH)_2(CO_3)$	53.9
Magnetite Fe_3O_4	48.6
Manganite MnOOH	276.8
Magnesite $MgCO_3$	30.1
Molybdenite MoS_2	200.8
Muscovite $KAl_2AlSi_3O_{10}(OH)_2$	65.9
Nepheline $NaAlSiO_4$	49.1
Niccolite NiAs	97.5
Olivine $(Fe,Mg)_2SiO_4$	48.8
Orthoclase $KAlSi_3O_8$	75.5
Pentlandite $Fe_{4.5}Ni_{4.5}S_8$	91.3
Periclase MgO	44.2
Perovskite $CaTiO_3$	190.0
Psilomelane $(Ba,H_2O)_2Mn_5O_{10}$	348.8
Pyrite FeS_2	102
Pyrochlore $Ca_{2.2}Na_{0.3}Fe_{0.2}Ce_{0.4}Nb_{1.3}Ti_{0.7}(OH)O_6$	200.5
Pyrrhotite FeS	88.5
Pollucite $Cs_4Al_4Si_9O_{26}.H_2O$	234.9
Pyrolusite MnO_2	279.7
Pyrope $Mg_3Al_2(SiO_4)_3$	50.0
Quartz SiO_2	54.7
Ramsdellite MnO_2	278.0
Realgar AsS	122.2
Rhodochrosite $MnCO_3$	215.3
Rutile TiO_2	266.5
Scheelite $CaWO_4$	205.1
Siderite $FeCO_3$	37.9
Smithsonite $ZnCO_3$	54.6
Sphalerite ZnS	105.1
Sphalerite $0.6ZnS \cdot 0.4FeS$	98.5
Spinel $MgAl_2O_4$	47.2
Stibnite Sb_2S_3	329.0
Strontianite $SrCO_3$	111.8
Tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$	69.9
Wüstite FeO	50.0
Witherite $BaCO_3$	354.1
Wolframite $(Fe,Mn)WO_4$	205.2
Wollastonite $Ca_3Si_3O_9$	119.8
Wulfenite $PbMoO_4$	266.5
Zincite ZnO	75.1
Zircon $ZrSiO_4$	126.0