THE AMERICAN MINERALOGIST, VOL. 44, JANUARY–FEBRUARY, 1959

MATRIX CORRECTIONS IN THE *X*-RAY SPECTROGRAPHIC TRACE ELEMENT ANALYSIS OF ROCKS AND MINERALS

JOHN HOWER, *Montana State University, Missoula, Montana.*

ABSTRACT

Three matrix effects must be accounted for in *x*-ray spectrographic analysis. They are: (1) attenuation of the incoming beam, (2) mutual excitation of the elements, and (3) absorption of the outgoing fluorescent radiation. Only effects (1) and (3) are appreciable for most trace elements in the *x*-ray spectrographic analysis of common rocks and minerals. The effects are determined by the mass absorption coefficient of the rock or mineral. Curves are plotted of the mass absorption coefficient versus wave length for elements that are commonly major constituents in rocks and minerals. These plots show that the relative absorptions of the elements are virtually constant at all wave lengths. Curves are presented of the absorption of various rocks relative to an aluminum oxide standard. The relative absorptions are virtually constant between absorption edges. A complete matrix correction can be made for nickel and heavier elements by determining the absorption of a rock relative to aluminum oxide at one wave length. The relative absorption can be determined by two methods: (1) by calculation if the major constituent analysis is known; the necessary data are presented, (2) by use of an internal standard if it is not. Partial matrix corrections can be made for the lighter elements Co, Mn, Cr, V, and Sc. Both methods are illustrated.

INTRODUCTION

As in other instrumental methods of chemical analysis, the primary problem in *x*-ray spectrography is to adjust intensity measurements on an unknown sample to the basis of a standard. The intensity measurements in *x*-ray spectrography are counting rates of the characteristic radiation of the analysis elements. The purpose of this paper is to outline methods of matrix correction in the quantitative *x*-ray spectrographic trace element analysis of rocks and minerals. The specific method outlined assumes that the rock or mineral contains as major constituents only the following elements: C, O, Na, Mg, Al, Si, K, Ca, Ti, and Fe. The presence of other elements as major constituents will alter the specific method suggested, but not the principles on which it is based.

Emission spectroscopists have developed the internal standard method to correct for the effects of a changing matrix on the intensities of the optical emission lines of the elements. The selection of an internal standard in emission spectroscopy is dictated by the average gross composition of the samples, the chemical compounds present, the relative volatility of the elements, and the excitation potentials of the analysis elements. In trace element analysis of rocks and minerals by *x*-ray spectrography, the matrix correction for most elements is wholly one of correcting the gross *x*-ray absorption coefficient of the analysis sample to the basis of a standard. The gross absorption coefficient of the sample is dependent only on bulk chemical composition. Matrix corrections for major constituent analysis are more complex and have been worked out for simple systems only (Beattie and Brissey, 1954, Burnham et al., 1957). Partial matrix corrections have been used by the addition of an internal standard (e.g. Norton, 1957, Stevenson, 1954).

The following effects have to be taken into account in making a matrix correction in any spectrographic analysis (Sherman, 1955): (1) The attenuation of the incoming exciting beam, (2) mutal excitation of the elements, and (3) absorption of the outgoing fluorescent characteristic radiation of the analysis elements. Methods of correcting for these effects in the trace element analysis of rocks and minerals will be discussed in the main body of this paper.

USE OF ABSORPTION COEFFICIENTS FOR MATRIX CORRECTION

The equation for the absorption of x-rays takes the form:

$$I_x = I_o e^{-\mu x}$$

where

I_o is the intensity of the primary beam
I_x is the intensity of the beam after passing a distance x through a given material
μ is the linear absorption coefficient of the material

The linear absorption coefficient is dependent on the wavelength of the beam and the density of the material. A more useful form of the absorption coefficient is μ/ρ, where ρ is the density of the material. This is called the mass absorption coefficient and is independent of the physical state of the sample.

A simple example of how mass absorption coefficients can be used in x-ray spectrography is as follows. A sample of iron and a sample of aluminum contain equal amounts of nickel in the part-per-million range. The difference between the measured intensity of the NiKα radiation from the two samples can be determined simply on the basis of the mass absorption coefficients of the matrices. The mass absorption coefficient of iron at 1.659 Å (NiKα radiation) is 410; that of aluminum is 60.7. That is, iron absorbs NiKα radiation 410/60.7 (6.75) times as efficiently as aluminum. As will be shown later, the incoming radiation that excites NiKα radiation is absorbed the same relative amount. Nickel is not excited by either Fe or Al characteristic radiation. The NiKα radiation from the aluminum sample would thus be 6.75 times as intense as that from the iron. Note that only relative absorption is important. If the samples have the same effective volume, the *absolute* amount of nickel in the iron sample is greater by the ratio of the density of iron to the density of aluminum. However, this increase is exactly compensated for by the increase in *absolute* absorption of the iron sample, providing both samples have the same surface area and their thickness is in excess of significant penetration. In the analysis of unknown samples the process would be worked in reverse; i.e., equal intensities from both samples would mean 6.75 times as much nickel in the iron sample than in the aluminum.

For compounds, the mass absorption coefficients of the constituent elements are additive. A generalized equation for calculating the mass absorption coefficient of a compound (Cullity, 1956) is:

$$\mu/\rho \text{ compound} = w_1(\mu/\rho)_1 + w_2(\mu/\rho)_2 + \cdots w_n(\mu/\rho)_n$$

where, $w_1, w_2, \cdots, w_n$ are the weight fractions of each element in the compound and $(\mu/\rho)_1, (\mu/\rho)_2, \cdots (\mu/\rho)_n$ are the mass absorption coefficients of each element at a given wavelength. As an example, μ/ρ for Al_2O_3 can be calculated for NiKα radiation. Aluminum oxide is 52.9% Al and 47.1% O; μ/ρ of Al at NiKα is 60.7 and μ/ρ of O is 14.0. Therefore, the mass absorption coefficient of Al_2O_3 at NiKα is

$$\begin{aligned}\mu/\rho(Al_2O_\epsilon) &= 0.529 \times 60.7 + 0.471 \times 14.0 \\ &= 38.7\end{aligned}$$

EFFICIENT RANGE OF THE *X*-RAY SPECTROGRAPH FOR TRACE ELEMENT ANALYSIS

The lightest element that can be detected with present commercially available *x*-ray spectrographic equipment is Mg (atomic number 12). The sensitivity of *x*-ray spectrographs drops off with decreasing atomic number from somewhere around Z=28 (Ni). For the analysis of trace elements in rocks the sensitivity is generally sufficient only for those elements higher than Ca (Z=20). Therefore, the discussion of trace element analysis will be restricted to elements from Z=21 and higher. When desirable, however, the principles can be applied to the other elements.

CALCULATION OF THE MASS ABSORPTION COEFFICIENT OF A ROCK

It is possible, by using data present in the literature (Handbook of Chem. and Phys., 1949, pp. 2031–2036) to calculate the mass absorption coefficient of any rock in the range of wavelengths used for *x*-ray spectrographic trace element analysis (approximately 0.4 to 3.0 Å). Figures 1*a* and 1*b* are plots of the available data of the mass absorption coefficient (μ/ρ) versus wave length (λ) for the elements that are commonly major constituents (>1 per cent) in rocks and minerals. The elements included are Fe, Ca, Mg, Na, Al, O and C. Iron is plotted separately because of its absorption discontinuity (the K absorption edge) in the wave-length

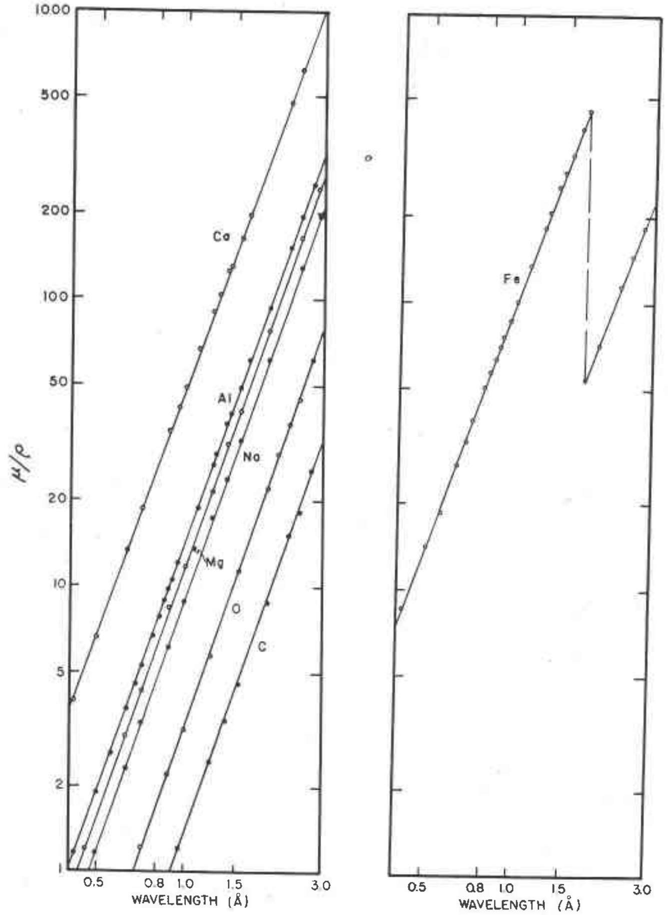

FIG. 1. Plots of the available data of mass absorption coefficient (μ/ρ) versus wave length (λ) for elements that are commonly major constituents in rocks and minerals.

range of interest. The slopes of these curves are tabulated in Table 1. Note that there is only a small change in slope (increasing with decreasing atomic number) between the lightest and heaviest element. This means that the relative absorptions of the elements are virtually independent of wave length.

No mass absorption coefficient data are available for the elements Si, K, and Ti, but it is possible to obtain the data empirically. If several points of the μ/ρ versus λ curve for an element can be found, the full curve can be drawn by using an average slope obtained from two bracketing elements. The points to define the position of the curve can be ob-

TABLE 1. SLOPES OF THE MASS ABSORPTION COEFFICIENT VERSUS WAVE-LENGTH CURVES

Element	Slope of μ/ρ vs. λ curve
Fe	2.81
Ca	2.81
Al	2.84
Mg	2.89
Na	2.89
O	2.93
C	2.94

tained from a relationship between the absorption coefficient at a given wave length and the wave length of the K absorption edge. A plot of this kind is shown in Fig. 2; the mass absorption coefficients at 1.000 Å are plotted against the K absorption edges for the elements bracketing K, Si, and Ti. Since the K absorption edges of K, Si, and Ti are known, their mass absorption coefficients at 1.000 Å can be obtained empirically from the curve. By finding several points in this manner and using slope averages of bracketing elements, accurate curves can be plotted for K, Si, and Ti.

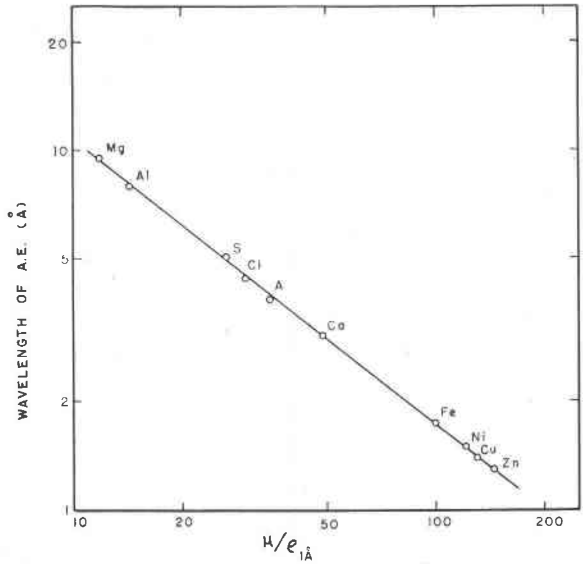

FIG. 2. Relation between the mass absorption coefficient at a given wave length and the wave length of the K absorption edge.

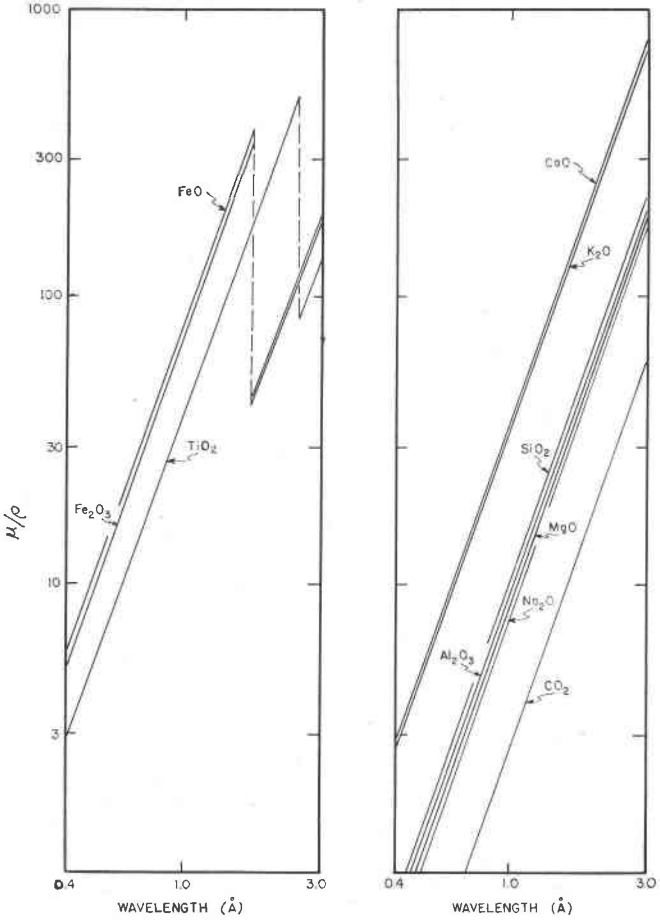

FIG. 3. Plots of the mass absorption coefficients of the oxides of all elements that are commonly major constituents in rocks and minerals.

Since chemical analyses are reported as oxides of the elements, it is more convenient to work with the mass absorption coefficients of the oxides. Mass absorption coefficient versus wave-length curves for the oxides of all the common major elements are plotted in Fig. 3. Points for the curves were calculated by use of equation (2). Now, by further use of equation (2) it is possible to calculate the mass absorption coefficient of a rock or mineral at any wave length. The solid curve in Fig. 4 is a plot of μ/ρ versus λ for the standard diabase W-1. The chemical analysis was taken from Goldich and Oslund (1956). The curve shows discontinuities at 1.744 Å (K absorption edge of Fe) and at 2.497 Å (K absorption edge of

Ti). For use in trace element analysis it is more informative to plot the absorption of W-1 relative to the absorption of some standard matrix. Aluminum oxide has been chosen as a standard matrix because of its practical convenience in the preparation of trace element standards. The dashed curve in Fig. 4 is a plot of the ratio $\mu/\rho_{W-1}/\mu/\rho_{Al_2O_3}$ versus λ. The discontinuities are still present at the absorption edges, but between absorption edges the relative absorptions of the diabase and Al_2O_3 remain virtually constant. For example, there is a change of only 3 per cent between the relative absorptions at 0.4 Å and 1.744 Å.

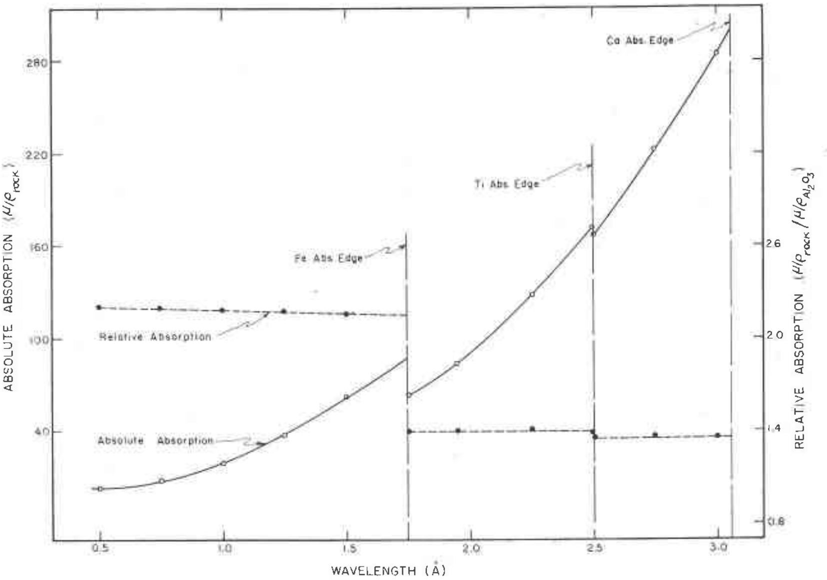

FIG. 4. Plots of the mass absorption coefficient of the standard diabase W-1 (solid curve) and the absorption of the diabase relative to Al_2O_3 versus wave length.

The same relation holds for all varieties of silicate rocks. Figure 5 shows relative absorption curves calculated for a diabase (W-1), a granite (G-1), a shale, and a dunite.

MATRIX CORRECTIONS

For convenience the x-ray spectrum is broken up into three regions: region (1), wave lengths shorter than the K absorption edge of iron, region (2), wave lengths between the K absorption edges of iron and titanium, and region (3), wave lengths between the K absorption edges of titanium and calcium. For the characteristic K radiation, region (1) includes all elements from nickel on up in atomic number; region (2)

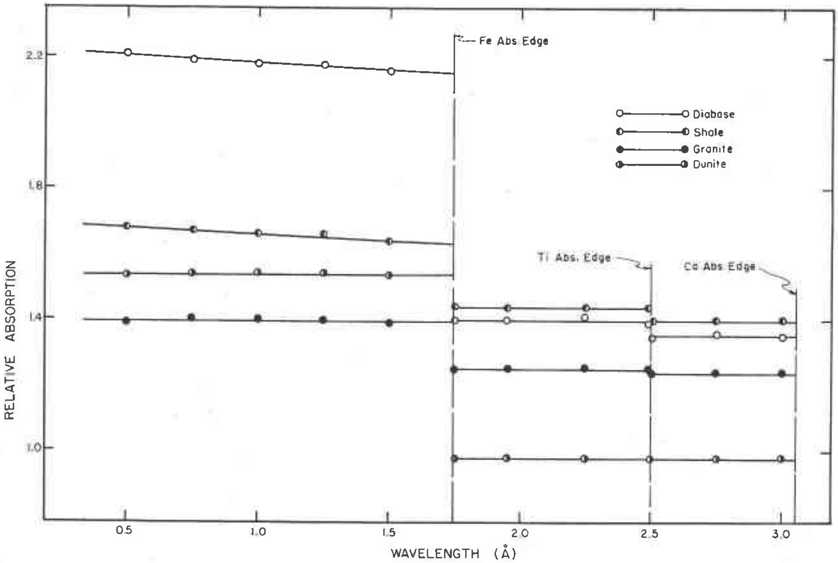

FIG. 5. Plots of the relative absorption versus wave length for a granite[1], a diabase[2], a shale[3], and a dunite[4].

1. The standard granite G-1 from Goldich and Oslund (1956).
2. The standard diabase W-1 from Goldich and Oslund (1956).
3. Analysis from Murray (1954), shale sample M52204.
4. Analysis from Clarke (1924), pg. 468, sample F.

includes cobalt, manganese, chromium, and vanadium; region (3) only scandium. Therefore, region (1) is quantitatively the most important.

The complete and partial corrections of matrix effects can now be discussed.

Attenuation of the Incoming Beam

The characteristic radiation of an element is generated by incoming *x*-rays of wave length shorter than the absorption edge (K or L) of the element. The excitation efficiency is greatest near the absorption edge. The curves in Fig. 5 show that the exciting radiation is absorbed (attenuated) a constant relative amount in a given rock for all elements with absorption edges in region (1). Therefore, the absorption of the analysis sample relative to a standard need be determined at only one point in order to make a quantitative correction for all elements in this region. The situation for elements with absorption edges at longer wave lengths is more complicated. For elements in region (2) a portion of the exciting radiation is absorbed strongly by iron, as it is for elements in region (1), and the rest only weakly absorbed. Unless the relative contributions from each region to the excitation of the elements in regions (2) and (3) can be determined precisely, a quantitative correction cannot be made. No attempt will be made here to determine precisely this effect in these regions. Therefore, analysis of Co, Mn, Cr, V, and Sc must be considered only semi-quantitative. An approximate correction is suggested below.

Mutual Excitation of the Elements

This effect is negligible for the bulk of the trace elements—all those in region (1). Mutual excitation at the trace element level is not appreciable. Therefore, no correction is necessary when analyzing for Ni and heavier elements by using their K characteristic radiation. The effect should be appreciable for Mn, Cr, V, and Sc since they absorb iron characteristic radiation strongly. If the other matrix effects could be determined quantitatively, this effect could be determined empirically for these lighter elements. An approximate correction is suggested below

Absorption of the Outgoing Fluorescent Characteristic Radiation

The curves in Fig. 5 show that the absorption of the analysis sample relative to the standard need be known at only one point in each region to make a quantitative correction. Trace elements do not contribute appreciably to the absorption. For example (Fig. 5), TiO_2 as a major constituent at 1.1 per cent in W-1 introduces an absorption difference of only four per cent.

SUGGESTED ANALYTICAL METHOD

Standards for silicate rocks and minerals can be prepared by mixing any desired analysis elements and the internal standards suggested below with aluminum oxide. The specific method of matrix correction is best treated by regions:

Region (1)

This region contains the bulk of the trace elements. A quantitative matrix correction can be made simply by determining the absorption of the analysis sample relative to aluminum oxide at some point in the region. The relative absorption can be determined by calculation if the major constituent analysis is known or by use of an internal standard if it is not. For the calculation method working curves would be drawn on the basis of absolute intensities. The necessary mass absorption coefficient data are presented in Table 2. Any element in region (1) can serve as an internal standard for samples with unknown major constituent analysis. Arsenic (Table 3) is suggested because of its geological rarity.

TABLE 2. MASS ABSORPTION COEFFICIENTS OF THE OXIDES OF THE MAJOR ELEMENTS AT 1.000, 1.930, AND 2.505 Å

Oxide	1.000 Å (Region 1)	1.930 Å (Region 2)	2.505 Å (Region 3)
SiO_2	10.1	65.8	135
Al_2O_3	9.13	59.8	129
Na_2O	7.56	51.1	106
MgO	8.36	55.1	115
CaO	36.7	228	462
K_2O	34.9	225	450
Fe_2O_3	70.8	56.3	116
FeO	78.5	60.3	124
TiO_2	38.7	248	85.0
CO_2	2.65	18.2	37.2
H_2O	3.13	21.7	44.5

Regions (2) and (3)

Only a semi-quantitative matrix correction can be made for Co, Mn, Cr, V, and Sc. The absorption of the fluorescent radiation can be adjusted quantitatively either by calculation or by use of one of the elements as an internal standard. However, the mutual excitation and the relative absorption of the incoming beam cannot be determined quantitatively. An approximate matrix correction for both of these effects can be made by using one of the elements as internal standard. The correction is only approximate because each element is affected somewhat differently by the matrix. Scandium is suggested as the internal standard when titanium is low, cobalt when titanium is high. A less accurate, but simpler, correction can be made when the major constituent analysis is known by making only an absorption correction by calculation. The necessary data are presented in Table 2.

Carbonate rocks can be analyzed in the same manner, but the standards should be prepared in a calcium carbonate matrix. Calcium is the dominant absorber in carbonate rocks and the slope of the μ/ρ versus λ curve is enough different from aluminum oxide to bring about a ten per

TABLE 3. SUGGESTED INTERNAL STANDARDS

	Region (1) 1.744 Å	Regions (2) and (3) 1.744–3.070 Å
Low Ti	Arsenic	Scandium
High Ti	Arsenic	Cobalt

cent change from 0.4 to 3.0 Å. A single internal standard would suffice for most carbonate rocks. The data in Table 2 permit calculation if the major constituent analysis is known.

SEMI-QUANTITATIVE APPLICATIONS

The gross mass absorption coefficient of rocks is not greatly variable. The absorption usually varies between one and two times that of aluminum oxide. Even when the major constituent analysis is not known and no internal standard is used, a fairly good analysis could be made by guessing at the absorption of the rock relative to aluminum oxide. Igneous rocks lend themselves well to such estimates. Figure 6 is a plot of the absorption relative to aluminum oxide, for the three regions, of the average igneous rocks ranging from basalt to rhyolite. The compositions used to calculate the points were taken from Daly (1933). By knowing approximately the rock type, the relative absorption can be estimated from the curves.

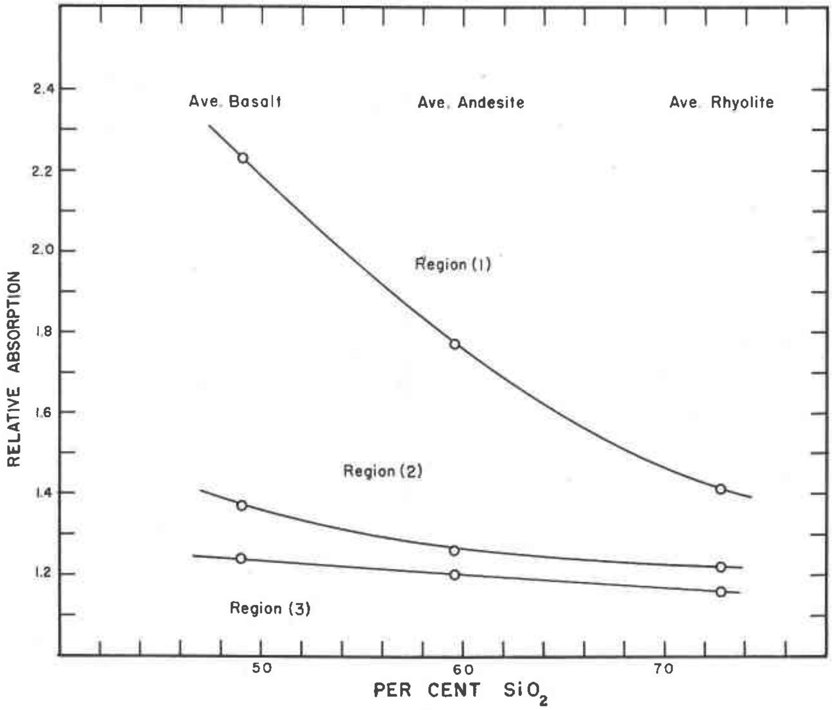

FIG. 6. Relative absorptions, in the three wave-length regions, of average igneous rocks ranging from basalt to rhyolite.

Quite good corrections can be made by calculation in the trace element analysis of a suite of samples of a mineral with relatively constant and fairly well known major constituent composition. Calcite, dolomite, and many of the simpler ore minerals such as galena and pyrite could be treated in this manner.

MATRIX CORRECTIONS IN G-1 AND W-1

The author does not have an *x*-ray spectograph available with which to present successful analyses following exactly the line of this technique. However, a trace element analysis of the standard granite, G-1, and the standard diabase, W-1, reported by Hower and Fancher (1957) is susceptible to this treatment. Internal standards were used for matrix corrections. The major constituent analyses are also known, so both methods of matrix correction can be illustrated.

The trace elements determined in G-1 and W-1 are Mn, Ni, Cu, Zn, Rb, Sr, and Zr. The Kα radiation of Mn lies above the K absorption edge of Fe (region 2); the K radiation of all the other elements lies below the K absorption edge of Fe. Selenium was used as the internal standard for elements in region (1); the titanium already present in G-1 and W-1 was used as the internal standard for manganese. Standards were prepared by mixing oxides of the trace elements in aluminum oxide.

Tables 4*a* and 4*b* show the absorption corrections in regions (1) and

TABLE 4*a*. CALCULATED ABSORPTION OF G-1 RELATIVE TO Al_2O_3 IN REGIONS (1) AND (2)

Oxide	Weight* Fraction	Region (1)		Region (2)	
		$\mu/\rho_{1.0\,\mathring{A}}$	Wt. Frac. $\times\mu/\rho_{1.0\,\mathring{A}}$	$\mu/\rho_{1.93\,\mathring{A}}$	Wt. Frac. $\times\mu/\rho_{1.93\,\mathring{A}}$
SiO_2	0.7248	10.1	7.31	65.8	47.6
Al_2O_3	0.1420	9.13	1.30	59.8	8.5
Na_2O	0.0329	7.56	0.25	51.1	1.7
MgO	0.0037	8.36	0.03	55.1	0.2
CaO	0.0135	36.7	0.50	228	3.1
K_2O	0.0552	34.9	1.93	225	12.3
Fe_2O_3	0.0078	70.8	0.55	56.3	0.4
FeO	0.0097	78.5	0.76	60.3	0.6
TiO_2	0.0026	38.7	0.10	248	0.6
Total			12.74		75.0
Absorption relative to Al_2O_3			1.40		1.25

TABLE 4b. CALCULATED ABSORPTION OF W-1 RELATIVE TO Al_2O_3 IN REGIONS (1) AND (2)

Oxide	Weight* Fraction	Region (1)		Region (2)	
		$\mu/\rho_{1.0\,\text{Å}}$	Wt. Frac. $\times\mu/\rho_{1.0\,\text{Å}}$	$\mu/\rho_{1.93\,\text{Å}}$	Wt. Frac. $\times\mu/\rho_{1.93\,\text{Å}}$
SiO_2	0.5255	10.1	5.31	65.8	34.6
Al_2O_3	0.1498	9.13	1.35	59.8	9.0
Na_2O	0.0214	7.56	0.16	51.1	1.1
MgO	0.0659	8.36	0.55	55.1	3.6
CaO	0.1098	36.7	4.03	228	25.0
K_2O	0.0062	34.9	0.22	225	1.4
Fe_2O_3	0.0141	70.8	1.00	56.3	0.8
FeO	0.0871	78.5	6.84	60.3	5.3
TiO_2	0.0108	38.7	0.41	248	2.7
Total			19.89		83.5
Absorption relative to Al_2O_3			2.18		1.40

* Analyses taken from Goldich and Oslund (1956).

(2) on the basis of calculation from the known major constituent analysis.

Table 5 shows the absorption corrections in these regions as determined by Se and Ti internal standards. Counting rates are given for the internal standards in Al_2O_3 and in G-1 and W-1. The counting rates given for Ti in G-1 and W-1 are adjusted to a basis of 4000 ppm. The calculated matrix corrections are shown for comparison. The comparison shows that the analyses reported would be substantially the same for either technique. The largest discrepancy is in W-1, which has a high iron content, in region (2), where mutual excitation effects are significant.

TABLE 5. ABSORPTION OF G-1 AND W-1 RELATIVE TO Al_2O_3 IN REGIONS (1) AND (2) BY THE INTERNAL STANDARD METHOD

Counting Rate (counts/second) 500 ppm Se			Counting Rate (counts/second) 4000 ppm Ti			Relative absorption region (1)		Relative absorption region (2)	
Al_2O_3	G-1	W-1	Al_2O_3	G-1	W-1	G-1	W-1	G-1	W-1
720	503	336	237	194	178	1.43	2.14	1.22	1.33
Calculated relative absorption						1.40	2.18	1.25	1.40

ACKNOWLEDGMENTS

The writer is particularily indebted to Dr. Hugh D. Burnham of the Shell Research Laboratory, Wood River, Illinois, for introducing him to the quantitative aspects of x-ray spectrography.

REFERENCES

BEATTIE, H. J., AND BRISSEY, R. M. (1954) Calibration method for x-ray fluorescence spectrometry: *Anal. Chem.*, **26,** 980–983.

BURNHAM, H. D., HOWER, J., AND JONES, L. C. (1957) Generalized x-ray emission spectrographic calibration applicable to varying compositions and sample forms: *Anal. Chem.*, **29,** 1827–1834.

CLARKE, F. W. (1924) The data of geochemistry: *U.S.G.S. Bull.* **770,** 468.

CULLITY, B. D. (1956) Elements of x-ray diffraction: Addison-Wesley Pub. Co., 11–12.

DALY, R. A. (1933) Igneous rocks and the depths of the earth: McGraw-Hill, 9–28.

GOLDICH, S. S., AND OSLUND, E. H. (1956) Composition of Westerly granite G-1 and Centerville diabase W-1: *Bull. Geol. Soc. Am.*, **67,** 811–815.

HOWER, J., AND FANCHER, T. W. (1957) Analysis of standard granite and standard diabase for trace elements: *Science*, **125,** 498.

MURRAY, H. H. (1954) Genesis of clay minerals in some Pennsylvanian shales of Indiana and Illinois: Clays and Clay Minerals, Second Nat. Conf. on Clay Min., 47–67.

NORTON, D. A. (1957), Fluorescence as applied to cyrtolite: *Am. Mineral.*, **42,** 492–505.

SHERMAN, J. (1955) The theoretical derivation of fluorescent x-rays from mixtures: Pitts. Conf. on Anal. Chem., 1955.

STEVENSON, J. S. (1954) Determination of columbian in ores by x-ray fluorescence: *Am. Mineral.*, **39,** 436–443.

Manuscript received April 26, 1958