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MATRIX CORRECTIONS IN TRACE ELEMENT ANALYSIS BY *X*-RAY FLUORESCENCE: ESTIMATION OF THE MASS ABSORPTION COEFFICIENT BY COMPTON SCATTERING

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ABSTRACT

An *x*-ray fluorescence method is described for the determination of trace elements of atomic number 28 (Ni) through 47 (Ag). Mass absorption coefficients for both reference standard and unknown material can be estimated by the use of measurements of the intensity of the Compton scattered portion of a $\mathrm{Mo}_{\mathrm{K}\alpha}$ primary beam. The precise (±2%) determination of mass absorption coefficients allows a single standard substance (G-1) to serve as a reference standard for the analysis of many trace elements in most common rocks and minerals. Overall errors in trace element analysis by the proposed method amount to approximately ±3%.

INTRODUCTION

Matrix correction in trace element analysis. The principal advantage of *x*-ray fluorescent methods of trace element analysis is that the relations governing inter-element and instrumental effects follow simple expressions; therefore it is often possible to make corrections mathematically rather than by the more time-consuming method of empirical calibration. The effects of enhancement may usually be disregarded in the analysis of trace elements (*i.e.*, elements present below the one per cent level). If the matrix is constant, a linear relation is found between the concentration of a given trace element (ppm Z) and the intensity of the radiation ($\mathrm{I}_{\mathrm{ZK}\alpha}$) from a member of the characteristic spectrum of that element. The relation, for very thick specimens, may be expressed as:

$$\mathrm{ppm\ Z} = \frac{\mu_\lambda}{\mathrm{k}} \mathrm{I}_{\mathrm{ZK}\alpha} \tag{1}$$

In the above equation the value of k is determined by (1) the efficiency and design of the *x*-ray spectrometer, and (2) the basic relations that govern the generation of the particular spectral line involved (ZK_α). The value of k is constant for all measurements made with a perfectly adjusted spectrometer. The other factor, μ_λ, the mass absorption coefficient, is a simple function of the composition of the sample and the radiation utilized in the analysis (ZK_α). The mass absorption coefficient times the density of a substance equals its linear absorption coefficient; this latter value is the one most commonly tabulated.

The value of k need never be determined in routine analysis if all measurements are referred to a standard substance. Data from the unknown are assembled in the form of Equation 1 and divided by data from the standard which is also assembled in the form of Equation 1. If the standard and unknown have the same matrix, $\mu_{\lambda/k}$ cancels out and the relation may be solved for ppm Z in the unknown. If the standard and unknown differ in μ_λ, k cancels out and the expression becomes:

$$\frac{\text{ppm } Z_x}{\text{ppm } Z_{std}} = \frac{\text{cps } ZK_{\alpha,x}}{\text{cps } ZK_{\alpha,std}} \times \frac{\mu_{\lambda,x}}{\mu_{\lambda,std}}$$

or

$$\text{ppm } Z_x = \frac{\text{cps } ZK_{\alpha,x}}{\text{cps } ZK_{\alpha,std}} \times \frac{\mu_{\lambda,x}}{\mu_{\lambda,std}} \times \text{ppm } Z_{std} \qquad (2)$$

where cps $ZK_{\alpha x}$ and cps $ZK_{\alpha,std}$ refer respectively to the intensities (in counts per second) of the background-corrected ZK_α peaks from the unknown and standard, $\mu_{\lambda,x}/\mu_{\lambda,std}$ refers to the mass absorption coefficients at wavelength λ of unknown and standard, and ppm Z refers to the concentration of element Z in the standard. There are limitations to the use of Equation 2 to be discussed below. However, for many types of analyses, the determination of μ_λ for both standard and unknown will allow exact matrix corrections to be made between unknowns and standards of differing bulk composition.

Equation 2 is valid only if the ZK_α radiation is of shorter wavelength than the wavelength of the absorption edge of the heaviest matrix element. Hower (1959) has pointed out that iron is the heaviest matrix element in common rocks and minerals. Therefore the equation is valid only for those elements whose atomic number is greater than 27, or for nickel and the heavier elements. Hower (1959) has defined as Region I the wavelength region shorter than the iron absorption edge. He noted that a ratio of mass absorption coefficients, calculated at any wavelength in Region I, remains constant for all other wavelengths in Region I. Therefore a measured value for $\mu_{\lambda,x}/\mu_{\lambda,std}$ allows a quantitative correction to be made for the difference in matrix between standard and unknown, provided, of course, that the K_α line of the analysis element lies in Region I.

Equation 2 will give erroneous results if it is applied to the analysis of an element such as manganese or iron, whose K_α line is of longer wavelength than the iron absorption edge. For iron-containing matrices, values of μ_x and μ_{std} both decrease abruptly at wavelengths just longer than that of the iron absorption edge. The magnitude of the absorption discontinuity depends in part on the amount of iron present in each. The value μ_x/μ_{std} therefore becomes indeterminate unless other data are available on the amounts of iron in standard and unknown.

Equation 2 fails for an additional reason if the K_α line of the analysis element falls outside of Region I. The equation assumes that radiation from one trace element is not likely to be enhanced by the radiation from another trace element. However, radiation from a trace element may be enhanced by radiation from a matrix element. Enhancement occurs when the K_α radiation of a matrix element has a wavelength equal to or shorter than the wavelength of the absorption edge of the trace element. This situation will not arise for trace elements whose K_α line lies in Region I. The absorption edges of all such elements will lie at wavelengths shorter than that of the K_α radiation from the heaviest matrix element (iron). Under these conditions, enhancement from $\text{Fe}K_\alpha$ cannot occur and Equation 2 remains valid.

Internal standardization is the most widely used method of matrix compensation or correction. A properly chosen spectral line from a properly selected internal standard element will be absorbed to the same extent as the analysis line from the analysis element. Taking the ratio of the intensities of these two lines causes the cancellation of the μ coefficients of Equation 2. Hower (1959) has given a discussion of the extended use of internal standardization for the analysis of trace elements in rocks and minerals. The main disadvantage of the internal standard method is that it adds greatly to analysis time. A suitable element must be weighed accurately and mixed thoroughly into each analytical specimen. The method is capable, however, of giving very high precision and accuracy.

Another approach to matrix corrections is given by Andermann and Kemp (1958). They point out that, for a given concentration of a trace element, the ratio of the intensity of the analysis line to the intensity of the adjacent background remains relatively constant in samples of different μ_λ. They use the background intensity as a built-in internal standard. This method is very rapid and simple, but the results are in general only semi-quantitative.

A method is described here that combines the accuracy of the internal standard method with the speed and simplicity of the method of Andermann and Kemp. Accurate values for μ_λ from standards and unknowns are determined by measuring the intensity of the Compton scattered portion of the K_α line from a molybdenum *x*-ray tube.

Compton scattering. Monochromatic *x*-rays, impinging on a sample, are both scattered and absorbed. The scattered radiation is of two types, Compton (or incoherent) and Rayleigh (or coherent). Rayleigh scattering occurs with no change in wavelength. It is this type of scattering that produces diffraction phenomena. The other type of scattering, Compton scattering, produces radiation of longer wavelength than that of the primary radiation. Furthermore, the wavelength (λ) depends on the angle between the scattering direction and the incident beam. Compton scattering may be visualized as an elastic collision between a photon and an electron, whereby the photon loses some of its energy as a result of the collision and emerges at some angle ϕ from the incident beam with a wavelength of $\lambda+\Delta\lambda$. The exact relation, developed by Compton (Compton and Allison, 1935, p. 48) is:

$$\Delta\lambda = \frac{h}{mc}(1 - \cos\phi)$$

where h is Planck's Constant, m is the rest mass of an electron, and c is the velocity of light. Johnson and Stout (1958) have made a study of Compton scattering using commercially available analytical equipment.

Some generalizations concerning Compton radiation are of interest in considering its applicability in trace element analysis. The energy of an *x*-ray photon is given by $e_\lambda = hc/\lambda$. The energy with which an electron in a given energy level is bound (e_b) increases with increasing atomic number. When short wavelength *x*-rays ($\lambda \cong 0.1$ Å) are scattered from an element of low atomic number, *e.g.*, carbon, most of the scattering is incoherent. Incoherent scattering predominates, therefore, when $e_\lambda \gg e_b$. In the heavier elements, e_b approaches or may exceed e_λ. When e_b approaches or exceeds e_λ, the scattering is largely coherent, *i.e.* there is no change in wavelength. This situation occurs when wavelengths such as MoK_α or CuK_α are scattered from the heavier elements. The scattered radiation from a series of elements irradiated with a suitable incident beam, shows a progressive increase in the ratio of Rayleigh/Compton scattering with increasing atomic number. This relation is well displayed by curves in Compton and Allison (1935, p. 205).

The scattering of the characteristic wavelengths produced by commercially available tubes changes from predominantly the Compton type to the Rayleigh type over the range in atomic number that characterizes the common matrix elements of rocks and minerals. Both the mass absorption coefficient, at a given wavelength (μ_λ), and the relative intensity of Compton scattering are related to atomic number.[1] Therefore the ratio of Compton/Rayleigh scattering should be related to μ_λ over the range in atomic number covered by the rock-forming elements.

Initial tests of the above concepts showed only a fair correlation between the ratio of Compton/Rayleigh scattering and calculated values of μ_λ. However, a much better relation was obtained by neglecting the Rayleigh scattering and plotting μ_λ against the reciprocal of the intensity

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[1] The intensity of Compton scattering is also proportional to Z/M, where Z is the atomic number and M is the atomic weight. This term has a value of very nearly $\frac{1}{2}$ for all of the common matrix elements in rocks. However, variations in the value of Z/M cause variations of one to two per cent in the relation between μ_λ and the intensity of Compton scattering. Some of the deviations shown in Fig. 1 are probably due to this factor.

of the Compton scattered radiation. Diffraction phenomena probably account for the poorer results obtained in the initial studies. The intensity of Rayleigh scattering depends, in part, on the preferred orientation of lattice planes of the proper d-spacing to cause diffraction at the scattering angle. Compton scattered radiation is incoherent, *i.e.*, there is no fixed phase relationship, among the scattering centers, between the incident and the scattered radiation. Therefore the possibility does not exist for in and out of phase relationships that produce diffraction maxima and minima. For these reasons, intensity measurements of Compton scattered radiation are free from the systematic errors that affect the measurement of Rayleigh scattering.

The principles discussed above suggest that a good approximation of the mass absorption coefficient of a given matrix may be obtained by studying the relation between μ_λ and the Compton scattered portion of an incident beam of suitable wavelength. The intensity of the Compton scattered radiation should decrease with increasing μ_λ because (1) less Compton scattering is generated in matrices of higher μ_λ and (2) matrices of high μ_λ cause a greater portion of the outgoing scattered beam to be absorbed in the sample.

PROCEDURE

Instrumentation. All measurements were carried out with a General Electric XRD-5 spectrometer. A molybdenum tube, operated at 48 KV and 40 MA, provided the primary radiation source; the spectra were dispersed by a lithium fluoride analyzing crystal: the angular divergence of the dispersed beam was limited by a 0.010 inch Soller Slit. A G.E. no. 6 proportional counter (no pulse height analysis) was used as the detector. The geometry of the XRD-5 goniometer provides a 90° angle between the primary and scattered beams. Substitution of the value of 90° into the Compton equation yields $\Delta\lambda = 0.0243$ Å. The wavelength of the Compton scattered portion of the primary beam is 0.0243 Å longer than that of the MoK_α primary. Therefore the wavelength of the Compton scattered maximum is 0.711 plus 0.024 or 0.735 Å. A lithium fluoride analyzing crystal was used despite the fact that it provides poor resolution of the Compton and Rayleigh scattered peaks. However a crystal of smaller d-spacing (and hence better resolution) such as quartz or topaz causes a prohibitive diminution of intensities.

The sample holder set at 30° to the incident beam consists of an aluminum block into which has been cut a rectangular depression 1.9 cm × 1.3 cm × 0.35 cm. A minimum depth of 0.35 cm is required if low-μ_λ materials, such as aluminum oxide, are to act as infinite thicknesses when radiated by wave-lengths in the vicinity of MoK_α. If the sample is not infinitely thick, the Compton scattered maximum will contain a component from the sample holder.

Analysis of μ standards. A study was made of the Compton scattering from a series of materials of known μ_λ. The standards were selected so that they covered a range in μ_λ similar to that of common rocks and minerals. The group contains examples of pure compounds, mixtures of compounds, rocks, and pure elements. All were analyzed as powders except for aluminum, which is in the form of a metal plate. The variation of form was selected to elucidate any departures from the theory due to effects of mixing, chemical bonding, number of components, and grain size.

Compton scattered intensities were measured from each of the standards according to the following procedure. The standards were tightly packed into the aluminum sample holder. Care was taken to ensure that the surface of the sample was flush with the surface of the sample holder. The instrument was allowed to stabilize for 45 minutes at operating voltage and tube current. The intensity of the Compton scattered portion of the MoK_α primary (hereafter referred to as $MoK_{\alpha c}$) was measured by recording the time required to accumulate 100,000 counts. No background correction was required. The large number of counts used provides a negligible counting error (0.3 per cent standard deviation).

The values of μ at $\lambda = 0.9$ Å were calculated for each of the standards (Hower, 1959, p. 21); absorption data from Liebhafsky *et al.* (1960, p. 314) were used in the calculations. The values were computed for a wavelength of 0.9 Å because 0.9 Å is a convenient intermediate point in the range of wavelengths that are of interest here.

RESULTS

Table 1 shows the materials studied, their physical form, and measured values of the reciprocal of the intensity of the $MoK_{\alpha c}$, expressed in seconds per 100,000 counts (sec/100K). With the present equipment, it is not feasible to extend the study very far beyond the values of μ_λ given for these materials. The low μ_λ region is limited by the requirement of very large sample thicknesses; the high μ_λ region is limited by the difficulty of accurately measuring a weak peak ($MoK_{\alpha c}$) that is imperfectly resolved from a strong one (MoK_α). However, the range in μ_λ represented by the materials of Table 1 covers the μ_λ range of most geological materials except for organic materials and metallic ores.

Figure 1 shows a plot of the data of Table 1. The straight line was fitted by regression analysis; its equation is:

$$\mu_{0.9\text{Å}} = 0.0934 \times \frac{\text{sec}}{100\text{K}} - 0.530$$

The distribution of the points about the line provides a standard deviation of 0.22 in the value of $\mu_{0.9\text{A}}$. It is concluded that the method outlined above provides a good measure of μ_λ over the range of $\mu_{0.9}=7.3$ to $\mu_{0.9}=20.0$.

A curve similar to that of Fig. 1 can be constructed and used in other laboratories for the routine estimation of μ_λ. The curve should be checked against a standard each time that the geometry of the spectrometer is disturbed. If necessary, the curve can be relocated by remeasuring two standards. G-1 and W-1 will serve as suitable standards for recalibration.

TRACE ELEMENT ANALYSIS

Method. The accurate estimation of μ_λ allows the analysis of trace elements to be carried out without recourse to the construction of working curves, the compounding of standards, or the mixing of internal standards with the analytical specimens. One standard is required in which the concentration of the analysis element is known. The value μ_λ for the matrix of the standard can be estimated by the use of Fig. 1; μ_λ can be computed if the major element composition of the standard is known. The concentration of some element Z in an unknown X is determined by Equation 2 (*q.v.*).

TABLE 1. COMPTON SCATTERING FROM MATERIALS OF KNOWN $\mu_{0.9\text{Å}}$

Material	Form	$\text{MoK}_{\alpha c}$ Sec/100 K	$\mu_{0.9\text{Å}}$
Al_2O_3	fine powd.	85.4	7.37
G-1	coarse powd.	112.8	9.91
W-1	fine powd.	169.0	15.20
Al Plate	coarse crystalline	130.9	11.80
Quartz	coarse powd.	91.2	8.19
S	fine powd.	207.8	19.30
CaF_2	fine powd.	221.4	20.12
$CaCO_3$	fine powd.	175.8	15.68
KNO_3	fine powd.	150.9	13.26
NaCl	fine powd.	184.5	16.35
$CaSO_4$	fine powd.	179.3	16.26
85% Al_2O_3+15% Fe_2O_3	fine powd.	155.3	14.16

$$\text{ppm } Z_x = \frac{\text{cps } ZK_{\alpha,x}}{\text{cps } ZK_{\alpha,\text{std}}} \times \frac{\mu_{0.9\text{Å},x}}{\mu_{0.9\text{Å},\text{std}}} \times \text{ppm } Z_{\text{std}}$$

where cps $ZK_{\alpha,x}$ and cps $ZK_{\alpha,\text{std}}$ refer respectively to the intensities (in counts per second) of the background corrected ZK_α peaks in the un-

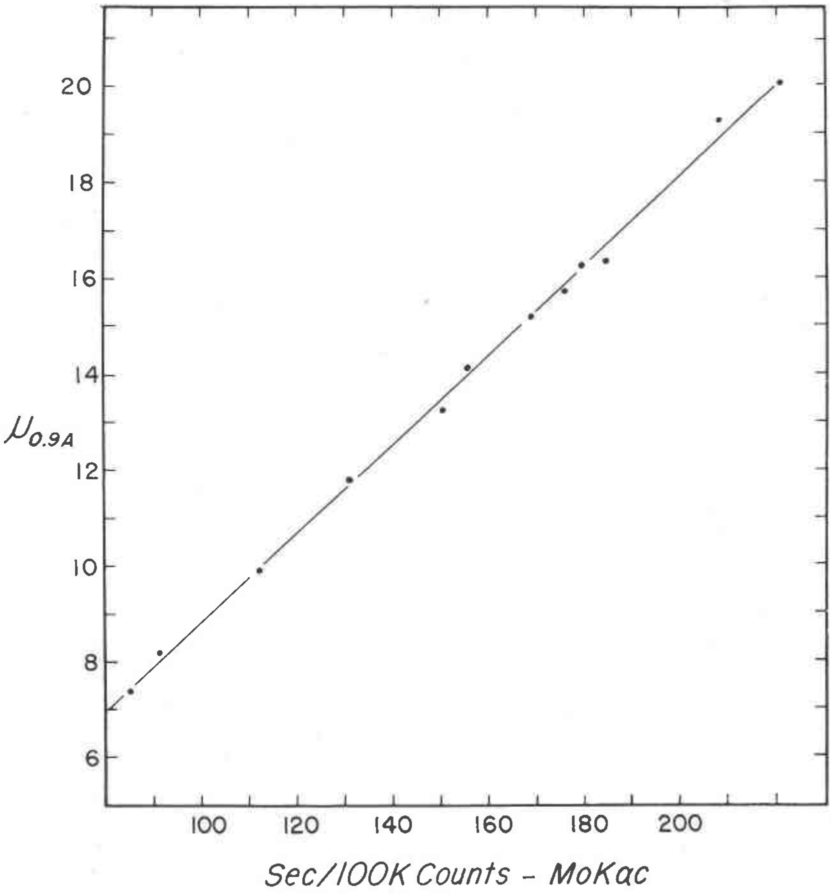

FIG. 1. Relation between Compton scattering and the mass absorption coefficient from materials of known composition.

known and the standard, $\mu_{0.9\text{Å}x}/\mu_{0.9\text{Å},std}$ refers to the mass absorption coefficients at 0.9 Å of unknown and standard, and ppm Z_{std} refers to the concentration of element Z in the standard.

Test of the method. A series of analyses were performed in order to test the overall accuracy of the measurements of μ_λ and the validity of Equation 2. The samples were selected to represent the following conditions: (1) The standard and unknown differ greatly in μ_λ (all cases), (2) The standard contains a high concentration of the analysis element compared to the unknown (Rb in G-1, W-1), (3) The wavelength of the K_α line of the analysis element lies close to the iron absorption edge (Ni), and (4) The wavelength of the K_α line of the analysis element is much shorter than that of the iron absorption edge (Zr). Values of $\mu_{0.9\text{Å}}$ were estimated for each of the materials that were treated as unknowns; the $\mu_{0.9\text{Å}}$ values were determined by measuring the reciprocal intensity of the $\mathrm{MoK}_{\alpha c}$ radiation from each unknown and reading the appropriate value for $\mu_{0.9\text{Å}}$ from Fig. 1. Two standards were used in the trace element determinations, G-1 and a synthetic standard of aluminum oxide to which had been added 195 ppm Ni. Values of $\mu_{0.9\text{Å}}$ were calculated for each of the two standards using data from Leibhafsky *et al.* (1960, p. 314).

The analyses were performed using the same equipment that is described above except that a tungsten tube was used as a radiation source for the analysis of nickel and zirconium. The source was operated at 48 KV and 40 MA; a lithium fluoride analyzing crystal was used throughout. Appropriate K_α peak intensities were measured from standards and unknowns. The intensities were obtained by accumulating 10,000 counts on both the peaks and their adjacent backgrounds and making the usual background correction. The corrected peak intensities and values for $\mu_{0.9\text{Å}}$ were assembled in the form of Equation 2 and the final concentrations of the analysis elements were computed.

TABLE 2. RESULTS OF TRACE ELEMENT ANALYSES

Element	Unknown	$\mu_{0.9\text{Å}}$ Unknown (Measured)	ppm Measured	ppm Recommended	Reference Standard	$\mu_{0.9\text{Å}}$ Standard (Calculated)
Sr	W-1	15.2	210	220	G-1	9.91
Rb	W-1	15.2	20	22	G-1	9.91
Zr	W-1	15.2	101	100	G-1	9.91
Ni	W-1	15.2	75	80	Al_2O_3+195 ppm Ni	7.37
Sr	Sr in calcite	16.5	127	125	G-1	9.91
Sr	Sr in calcite	16.3	513	500	G-1	9.91
Ni	Ni in $Al_2O_3+Fe_2O_3$	14.0	191	187	Al_2O_3+195 ppm Ni	7.37

Table 2 shows the results of the analyses. Materials of known composition were prepared by adding specific amounts of nickel and strontium to an aluminum oxide-ferric oxide matrix and a calcite matrix respectively. The nickel and strontium concentrations added are listed in Table 2 as recommended values. Recommended values for strontium, rubidium, zirconium, and nickel in G-1 and W-1 are taken from Fleischer and Stevens (1962). These authors list two recommended values for strontium in G-1 and W-1. These are 280 or 250 ppm strontium in G-1 and 220 or

175 ppm strontium in W-1. The values of 280 ppm strontium in G-1 and 220 ppm strontium in W-1 have been used here because they show the closest agreement with the data. However, if the lower recommended strontium values are correct, an unexplained error exists in the measured values for strontium.

The measured values for the trace elements show good agreement with the recommended values. The rubidium content of W-1 shows the largest percentage difference; the poor agreement is doubtless due to the low level of rubidium in W-1. The peak to background ratio is so low that the standard counting error (based on 10,000 counts) of the background corrected peak accounts for an error of 10%. If the value for rubidium in W-1 is excluded, the per cent average deviation of the other measured values from their respective recommended values is 3.2%. This deviation compares favorably with the errors normally associated with standard methods of *x*-ray fluorescence analysis of trace elements.

CONCLUSIONS

The estimation of mass absorption coefficients by Compton scattering provides the basis for a rapid method of quantitative trace element analysis. The method seems capable of dealing with most geological materials; organic materials and metallic ores are common exceptions. The method can be used for many rocks, carbonates, sulfates, oxides and silicates. The range of elements that can be studied is limited in the long wave-length direction by the absorption edge of iron. The short wavelength limit is controlled by the capability of existing equipment to excite and measure the K_α spectra of the heavier elements. The practical range with present equipment extends from nickel to silver ($Z=28$ to $Z=47$).

A pair of standards, such as G-1 and W-1, can serve as calibration standards for many of the trace elements within the useful range of the method. Other standards can be prepared to include elements which are below practical analytical limits in G-1 and W-1.

The accuracy of the method appears to compare favorably with other methods of quantitative trace element analysis. However, because absolute intensities are used throughout, attention must be paid to details that might not be important in methods that utilize the measurement of peak ratios. The instrument must be allowed to stabilize at operating voltage and current for at least one-half hour; the sample surface must be flush with the surface of the sample holder and reproducibly positioned; and the sample must exceed the requirements of infinite thickness for all measurements.

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REFERENCES

ANDERMANN, G. AND J. W. KEMP (1958) Scattered *x*-rays as internal standards in *x*-ray emission spectroscopy. *Anal Chem.* **30,** 1306.

COMPTON, A. H. AND S. K. ALLISON, (1935) *X-rays in Theory and Experiment.* D. van Nostrand Co., Inc., Princeton, N. J.

FLEISCHER, M. AND R. E. STEVENS (1962) Summary of new data on rock samples G-1 and W-1. *Geochim. Cosmochim. Acta* **26,** 525.

HOWER, J. (1959) Matrix corrections in *x*-ray spectrographic trace element analysis of rocks and minerals. *Am. Mineral.* **44,** 19.

JOHNSON, C. M. AND P. R. STOUT (1958) Fluorescent *x*-ray spectrometry, interferences from Compton scattering from matrices of low atomic number. *Anal Chem.* **30,** 1921.

LIEBHAFSKY, H. A., H. G. PFEIFFER, E. H. WINSLOW AND P. D. ZEMANY, (1960) *X-ray Absorption and Emission in Analytical Chemistry.* John Wiley & Sons, Inc., N. Y.

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