

## ESTIMATION OF MASS ABSORPTION COEFFICIENTS BY COMPTON SCATTERING: IMPROVEMENTS AND EXTENSIONS OF THE METHOD

ROBERT C. REYNOLDS, JR., *Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire.*

### ABSTRACT

Methods are described which extend the usefulness of a previously published method for determining the mass absorption coefficient ( $\mu$ ) by means of Compton scattering. The original method was restricted to (1) rocks and minerals of intermediate atomic number, and (2) analysis of trace elements whose analytical line is of shorter wavelength than that of the absorption edge of the heaviest matrix element. Mass absorption coefficients can be determined for low atomic number matrices by the use of a long wavelength primary radiation, such as  $\text{CrK}\alpha$  (Ryland, 1964). Values of  $\mu$  for high atomic number matrices can be measured if a yttrium oxide filter is used to absorb interfering  $\text{MoK}\alpha$  radiation. The relation between  $\mu$  at  $0.9\text{A}$  and the reciprocal intensity of the Compton-scattered  $\text{MoK}\alpha$  indicates that  $\mu$  values can be measured, with an error of less than 3 percent, for materials whose mean atomic number is as high as  $\text{CuO}$ . Appropriate values for  $\mu$  can be computed for regions on the long wavelength sides of major element absorption edges by the use of a series of simultaneous equations in terms of (1) the mass absorption coefficient at  $0.9\text{A}$ , (2) the intensities of the  $\text{K}\alpha$  lines of the matrix elements, (3) published data on the rate of change of  $\mu$ , for each matrix element, with respect to wavelength, and (4) the major element analysis of a standard. Data are given for Fe, Mn, Ti, and V in several different matrices. Overall errors appear to be positive, and amount to 2 to 10 percent.

### INTRODUCTION

X-ray emission analysis of trace elements in rocks and minerals requires that some method be used to compensate for matrix differences between standard and unknown. Internal standard methods may be used (Hower, 1959), but direct numerical corrections can be applied if an appropriate, mass absorption coefficient ( $\mu$ ) is known for each of the specimens. Reynolds (1963) outlined a method that allows the determination of  $\mu$  based on the observation that  $\mu$  is inversely and closely related to the intensity of the Compton scattered portion of a primary x-ray beam of suitable wavelength: the theory need not be repeated.

The method has the following limitations:

1. Samples of very low  $\mu$  ( $\mu_{0.9} < 7$ )<sup>1</sup> cannot be dealt with easily because the requirements of infinite thickness become unreasonable in terms of sample-holder geometry.
2. Samples of very high  $\mu$  ( $\mu_{0.9} > 20$ ) are excluded. The weak Compton

<sup>1</sup> The symbol  $\mu_{0.9}$  refers to the mass absorption coefficient at  $0.9\text{A}$ . For the purposes of this paper,  $\mu$  values can be referred to any wavelength shorter than that of the iron absorption edge;  $0.9\text{A}$  was arbitrarily chosen.

scattering maxima from such materials cannot be resolved accurately from the much stronger  $\text{MoK}\alpha$  maxima.

3. Trace element analysis is restricted to elements whose x-ray emission line is of shorter wavelength ( $\lambda$ ) than that of the absorption edge of the heaviest matrix element.

Recent work indicates that all of these restrictions can be eliminated by suitable experimental procedures or by additional measurements on each sample, making the technique far more flexible and inclusive, without undue sacrifice of accuracy or brevity.

#### DETERMINATION OF $\mu$

*Analysis of low- $\mu$  samples.* While I was engaged in experimental work on the Compton method (Reynolds, 1963), independent and similar work was in progress elsewhere (Ryland, 1964). Ryland's method was developed for organic materials, which have much lower  $\mu$  values than rocks and minerals. The requirement of infinite thickness posed no problem because  $\text{CrK}\alpha$  primary radiation was used and this produced measurable Compton scattering from very light materials such as plastics and other organic compounds. Such long wavelength radiation is far less penetrating than  $\text{MoK}\alpha$ , but it produces little Compton scattering from rocks and minerals<sup>1</sup>. Ryland's method utilizes the ratio of Compton to coherent scattering, instead of the absolute intensity of Compton scattering; otherwise, her method is similar to mine.

Ryland reports results on many elements in a wide variety of low atomic number matrices. Analytical results correlate very well with nominal values from known materials, and with data obtained by independent analytical methods. Her work demonstrates the high accuracy and precision that are obtainable with Compton scattering methods. In addition, she has shown that  $\mu$  can be measured on light matrices through the use of a suitable long wave-length primary radiation.

*Analysis of high- $\mu$  samples.* The accurate measurement of Compton scattering for high- $\mu$  samples requires that some method be employed to increase the resolution between  $\text{MoK}\alpha$  and  $\text{MoK}\alpha_C$  ( $\text{MoK}\alpha$ -Compton). This could be accomplished by refining the geometry of the spectrometer or by the development of a highly reflective analyzing crystal of smaller " $d$ " than lithium fluoride. A much simpler method is reported here, namely, the selective filtration of the  $\text{MoK}\alpha_C$  by means of a suitable filter. H. M. Dunn<sup>2</sup> suggested the utility of a technique, published by

<sup>1</sup> It seems that matrices in this  $\mu$  range require the use of primary radiation whose  $\lambda$  is at least as short as that of  $\text{MoK}\alpha$ . Tungsten L lines are unsuitable.

<sup>2</sup> I.B.M. Corp.; verbal communication.

Warren and Mavel (1964), on the selective filtration of Compton scattered radiation. The latter work dealt with diffractometer measurements of amorphous scattering; the elimination of Compton scattered radiation was required for the accurate measurement of the scattering profiles. The application is somewhat different from the requirements here, but the principle is easily applied to the present problem.

*Experimental.* The intensity ratio  $MoK_{\alpha c}/MoK_{\alpha}$  can be significantly increased by the use of a yttrium filter because these two wavelengths lie on opposite sides of the yttrium absorption edge. Yttrium oxide, mixed with Duco cement and acetone, was poured into a flat-bottomed dish and allowed to evaporate to dryness to give a film which contained 20 mg of

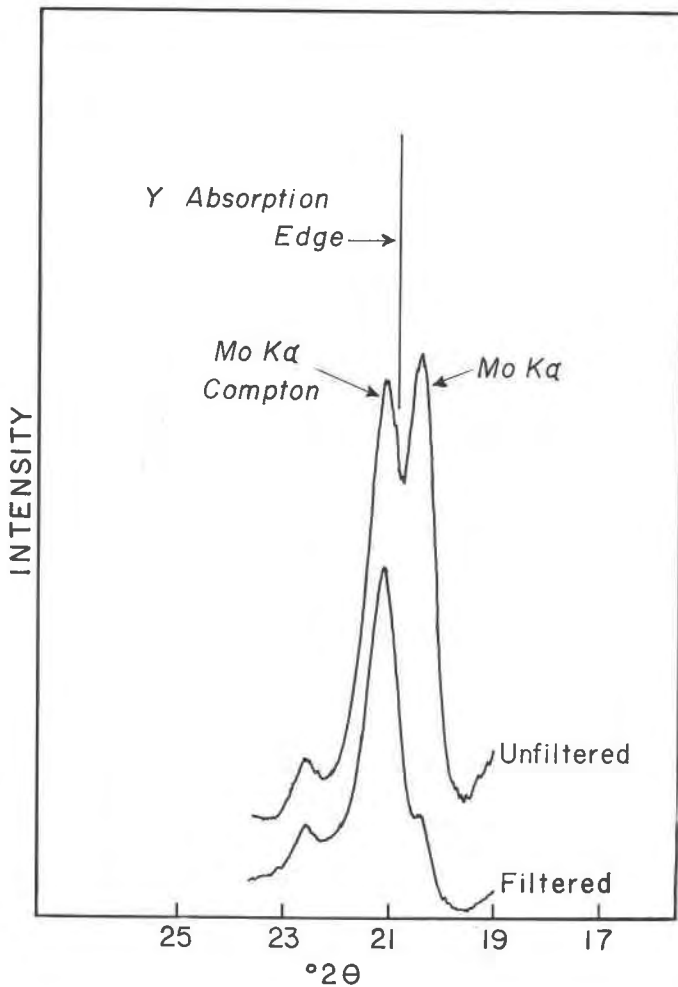


FIG. 1. The selective filtration of  $MoK_{\alpha c}$  by  $Y_2O_3$ .

$Y_2O_3$  per  $cm^2$ . The dried film was mounted over the spectrometer detector slit. The weight of  $Y_2O_3$  per  $cm^2$  was selected to provide the largest absorption of  $MoK\alpha$  consistent with minimum absorption of  $MoK\alpha_C$ .

A General Electric XRD-5 spectrometer, equipped with a molybdenum-target tube and a LiF analyzing crystal, was operated at 50KVP and 40MA. Scattering profiles were obtained from a glass slide, with and without the filter (Fig. 1). In addition, the absolute intensity of filtered  $MoK\alpha_C$  was obtained from a variety of materials whose absorption coefficients cover the range from  $\mu_{0.9} \approx 10$  to  $\mu_{0.9} \approx 80$  (Table 1, Fig. 2).

*Results.* Figure 1 shows the profile of scattered  $MoK\alpha$ - $MoK\alpha_C$  radiation from a glass slide. The position of the yttrium absorption edge is indicated. Table 1 lists and Figure 2 shows a

TABLE 1. RELATION BETWEEN  $\mu_{0.9}$  AND RECIPROCAL INTENSITY OF FILTERED  $MoK\alpha_C$

Material	$\mu_{0.9}$	Sec/100K counts
G-1	9.91	136.5
W-1	15.20	197.0
CaF <sub>2</sub>	20.12	281.2
KCl	26.84	340.7
TiO <sub>2</sub>	29.14	363.8
K <sub>2</sub> CrO <sub>4</sub>	29.32	385.7
V <sub>2</sub> O <sub>5</sub>	31.30	390.8
KMnO <sub>4</sub>	31.73	402.5
Zn(Ac) <sub>2</sub> ·2H <sub>2</sub> O	32.29	378.3
CrO <sub>3</sub>	32.51	425.8
CuSO <sub>4</sub>	42.85	491.5
MnO <sub>2</sub>	42.97	509.8
Fe <sub>2</sub> O <sub>3</sub>	52.55	602.6
Mn	66.60	722.4
NiO	69.29	753.9
CuO	76.78	820.1

series of materials, their calculated values for  $\mu_{0.9}$  (based on data from Liebafsky *et al.*, 1960), and the number of seconds required to accumulate 100,000 counts on the filtered  $MoK\alpha_C$ .

*Discussion.* The use of an yttria filter<sup>1</sup> efficiently removes interference by  $MoK\alpha$  (see Figure 1); a good correlation, between  $\mu_{0.9}$  and  $MoK\alpha_C$ , extends to matrices as heavy as CuO (Figure 2). There is some scatter about the curve, but the more deviant points (e.g. Zn Ac<sub>2</sub>·2H<sub>2</sub>O) involve errors of only about 3% in estimated  $\mu_{0.9}$ . These deviations may reflect uncertainties in published data on mass absorption coefficients of these elements. In any event, this error is still tolerable for most trace element studies. It is concluded that matrix corrections, utilizing the  $MoK\alpha_C$ , are feasible for materials whose mean atomic number is as high as CuO, provided that  $MoK\alpha$  interference is removed by some means such as selective filtration by yttrium oxide.

<sup>1</sup> It appears that the use of such filters has received little attention, at least in geological studies. Another example of selective filtration, presently under study, is the efficiency of a LiBr filter in removing  $SrK\alpha$  interference from the  $RbK\alpha$  in materials of very high Sr/Rb ratio.

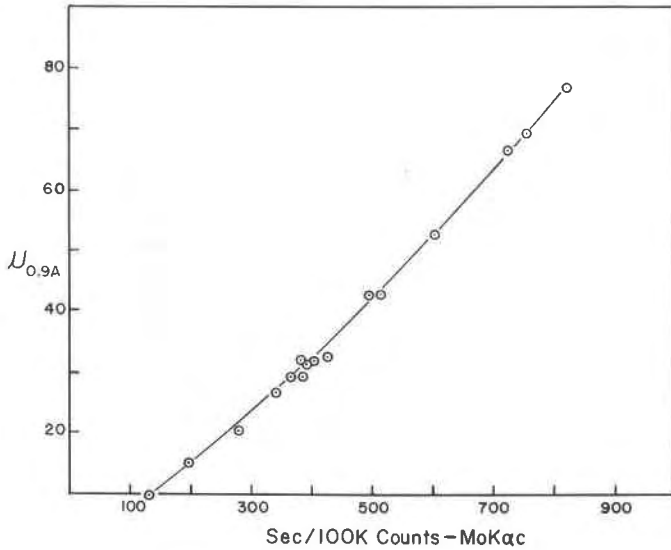


FIG. 2. Relation between Compton scattering and the mass absorption coefficient.

ANALYSIS OF LOW ATOMIC NUMBER ELEMENTS

Hower (1959) has pointed out that iron is the heaviest element in most rocks and common silicates. He has also shown that for such materials, the ratio  $\mu$ -unknown/ $\mu$ -standard is constant for all wavelengths shorter than that of the iron absorption edge; a different ratio obtains for the region between the iron absorption edge and the absorption edge of the next major constituent (usually calcium). These two ratios differ by an amount that is related to the difference between the iron content of the sample and that of the unknown. It is shown in the next section that a group of simultaneous equations, in terms of known or measurable parameters, can be solved to give % Fe and  $\mu$  for the long wavelength region. Once  $\mu$  is known for this region, comparison with a suitable standard allows the analytical determination of Mn, Cr, V, Ti, and Sc.

*Derivation.* Let  $Fe$  denote the weight fraction of iron in a sample, and let  $R$  denote the sum of the weight fractions of all other elements.  $Fe + R = 1$ . Similarly, let  $\mu_{\lambda}^{Fe}$  and  $\mu_{\lambda}^R$  signify the mass absorption coefficients, respectively, of iron and the sum of the other elements at wavelength  $\lambda$ . If  $\mu_{\lambda}$  is the mass absorption coefficient of an unknown matrix, then

$$\mu_{0.9} = Fe \cdot \mu_{0.9}^{Fe} + R \cdot \mu_{0.9}^R, \quad \text{and} \quad (1)$$

$$\mu_{1.94} = Fe \cdot \mu_{1.94}^{Fe} + R \cdot \mu_{1.94}^R. \quad (2)$$

The value 1.94A denotes a wavelength longer than that of the iron absorption edge. The variation of mass absorption coefficients, with respect to wavelength, is such that

$$\mu_{1.94} \approx b \cdot \mu_{0.9} \quad (3)$$

where  $b$  is nearly constant for all elements that have no absorption edges within the wavelength range of interest.

Equation 1 may be rearranged to give:

$$\mu_{0.9} - Fe \cdot \mu_{0.9}^{Fe} = R \cdot \mu_{0.9}^R, \quad (4)$$

and Equation 3 can be substituted into a rearranged form of Equation 2 with the result:

$$\frac{\mu_{1.94} - Fe \cdot \mu_{1.94}^{Fe}}{b} = R \cdot \mu_{0.9}^R. \quad (5)$$

The right-hand sides of Equation 4 and 5 are identical, therefore

$$\mu_{1.94} - Fe \cdot \mu_{1.94}^{Fe} = b(\mu_{0.9} - Fe \cdot \mu_{0.9}^{Fe})$$

and the variables  $R$  and  $\mu_{0.9}^R$  disappear. The latter result can be solved for  $\mu_{1.94}$  to give:

$$\mu_{1.94} = b(\mu_{0.9} - Fe \cdot \mu_{0.9}^{Fe}) + Fe \cdot \mu_{1.94}^{Fe}. \quad (6)$$

Further progress here requires that data be introduced from a standard of known  $Fe$  and  $\mu_{1.94}$ . The general relation between fluorescent intensity and concentration may be written:

$$Fe^u = \frac{I(Fe)^u}{I(Fe)^s} \cdot \frac{\mu_{1.94}^u}{\mu_{1.94}^s} \cdot Fe^s \quad (7)$$

where superscripts  $u$  and  $s$  denote unknown and standard respectively, and  $I(Fe)$  refers to the intensity of the  $FeK\alpha$ . The right-hand side of Equation 7 can be substituted into Equation 6 wherever  $Fe$  appears, and the result solved for  $\mu_{1.94}^u$ , giving:

$$\mu_{1.94}^u = \frac{b \cdot \mu_{0.9}^u \cdot \mu_{1.94}^s \cdot I(Fe)^s}{(\mu_{1.94}^s \cdot I(Fe)^s) - (Fe^s \cdot I(Fe)^u \cdot (\mu_{1.94}^{Fe} - b \cdot \mu_{0.9}^{Fe}))}. \quad (8)$$

The values for  $\mu_{1.94}^{Fe}$  and  $\mu_{0.9}^{Fe}$  can be obtained from published tables (e.g. Liebhafsky *et al.*, 1960), and  $b$  can be calculated.  $Fe^s$  and  $\mu_{1.94}^s$  can be computed if major element data are available for the standard (e.g. W-1, G-1). Finally,  $\mu_{0.9}^u$  can be determined by the Compton scattering method (Reynolds, 1963), and  $I(Fe)^s$  and  $I(Fe)^u$  can be measured. There-

fore, Equation 8 can be solved to provide a mass absorption coefficient for the unknown that applies to the region on the long wavelength side of the iron absorption edge.

By induction, this procedure can be used to compute absorption coefficients across the absorption edge of any major constituent; reiterations of these calculations, with appropriate changes in relevant parameters, provide absorption data across a series of absorption edges. It should be noted that substitution of the proper  $\mu_{1.94}^u$  into Equation 7 allows the determination of the iron content of the unknown.

If the methods described above appear to be tedious, it should be re-

TABLE 2. VALUES OF  $b$  ( $\mu_{1.94}/\mu_{0.9}$ ) FOR COMMON MINERALS

Mineral	$\mu_{1.94}$	$\mu_{0.9}$	$b$ ( $\mu_{1.94}/\mu_{0.9}$ )	Mean for silicates
Silica	60.53	7.92	7.64	7.60 ± 0.15
Orthoclase	85.15	10.86	7.84	
Albite	56.70	7.54	7.52	
Anorthite	89.92	11.45	7.85	
Muscovite	73.66	9.57	7.70	
Montmorillonite	56.03	7.48	7.49	
Mg-Chlorite	48.51	6.54	7.42	
Kaolinite	48.13	6.33	7.60	
Enstatite	54.91	7.32	7.50	
Forsterite	52.51	7.07	7.43	
Alumina	51.93	7.37	7.05	
Calcite	132.30	15.69	8.43	
Dolomite	86.28	10.41	8.29	
Gypsum	111.17	13.32	8.35	
Anhydrite	135.52	16.27	8.33	
Halite	131.70	16.35	8.05	

membered that Equation 8 has been left in a general form to facilitate its use in a variety of analytical situations. Suppose a specific application is involved, for example, analyses that are referred to W-1 as a standard. The weight fraction of iron in W-1 is 0.0778 (Fleischer and Stevens, 1962), and  $\mu_{1.94}$  for W-1 is 78.36. The value 7.6 is selected for  $b$  (Table 2), and according to data in Liebhafsky *et al.* (1960),  $\mu_{0.9}^{Fe} = \mu_{1.94}^{Fe} = 74$ . These values may be substituted into Equation 8 to give an example of a typical "working form" of this equation, *viz.*,

$$\mu_{1.94}^u = \frac{15.67 \cdot \mu_{0.9}^u \cdot I(Fe)^s}{2.062 \cdot I(Fe)^s + I(Fe)^u} \tag{9}$$

The solution of Equation 9 requires that  $I(\text{Fe})^s$  be measured once for the standard and that  $\mu_{0.9}^u$  and  $I(\text{Fe})^u$  be measured for each sample.

Values for  $\mu_{1.94}^u$  can be utilized in trace element analysis by recourse to a generalized form of Equation 7. For example, if the application is to chromium analysis:

$$\text{ppm Cr}^u = \frac{I(\text{CrK}\alpha)^u}{I(\text{CrK}\alpha)^s} \cdot \frac{\mu_{1.94}^u}{\mu_{1.94}^s} \cdot \text{ppm Cr}^s.$$

*Assumptions.* The derivation given above assumes (1) that enhancement of the analytical spectra, by the  $\text{FeK}\alpha$ , is negligible, and (2) that the

TABLE 3. ANALYTICAL DATA ON MATERIALS OF KNOWN COMPOSITION.  
THE UPPER MEMBER OF EACH PAIR IS THE MEASURED VALUE;  
THE LOWER (IN BRACKETS) IS THE ACCEPTED VALUE

Sample	Iron	Manganese	Titanium	Vanadium
G-1	1.36 (1.37)	214 (230)	1540 (1500)	
Al-Fe Oxides	10.6 (10.5)			
Al-Fe Oxides	7.7 (7.2)	615 (575)	1283 (1209)	
0.77 Al-Fe Oxides +0.13 $\text{CaCO}_3$	6.1 (5.7)	530 (505)	1103 (1063)	
$\text{Al}_2\text{O}_3$		662 (641)	1334 (1348)	
Al-Fe Oxides	11.8 (11.8)			549 (507)
0.77 Al-Fe Oxides +0.13 $\text{CaCO}_3$	10.2 (10.3)			481 (443)

value for the constant  $b$  is, to a good approximation, constant for major constituent elements. Measurements of enhancement coefficients for  $\text{FeK}\alpha$  on Mn-, Cr-, V-, Ti-, and  $\text{ScK}\alpha$  should not be difficult to obtain, but at the present time such determinations have not been made. Nevertheless, data presented below (Table 3) indicate that serious errors cannot be ascribed to this source.

The variability of  $b$  can be evaluated by the examination of computed values for various minerals. Table 2 shows values for  $\mu_{1.94}$ ,  $\mu_{0.9}$ , and  $b$  for



a series of common minerals. Computed mass absorption coefficients are based on tables published by Liebhafsky *et al.* (1960). It can be seen that the variability is small ( $\sim \pm 2\%$ ) among the silicate minerals. Alumina, carbonates, and sulfates show larger deviations. The information in Table 2 suggests that some judgement is required in the selection of an appropriate  $b$  value if matrix corrections involve rocks that contain appreciable amounts of non-silicate material. The range of choice is small, however, and for most materials only a crude appraisal of lithology is necessary.

*Experimental work.* The theory described above was checked by analytical determinations of Fe, Mn, Ti, and V in standard materials of widely divergent matrix characteristics. The standard W-1 was used as a reference material for all analyses.

X-ray data were obtained with a General Electric XRD-5 spectrometer. A molybdenum-target tube, operated at 50KVP and 40MA, served as the primary radiation source for the measurements of  $\mu_{0.9}$  and  $I(\text{FeK}\alpha)$ . A tungsten-target tube and a helium atmosphere were used for the determinations of Mn, V, and Ti. All spectra were resolved with a LiF crystal.

Artificial standards were prepared by blending weighed amounts of matrix materials ( $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$ ) in a Wiggle-Bug. Standard solutions of soluble V and Mn salts were added, by pipetting, to matrix preparations in evaporating dishes. The resulting mixtures were evaporated to dryness and ground, first by hand in an agate mortar, and then mechanically in a Wiggle-Bug. Titanium standards were prepared by direct mixing of  $\text{TiO}_2$  with matrix preparations.

*Results and discussion.* Table 3 shows a comparison between measured values and actual or accepted values for a series of standard materials. The data suggest the presence of non-random errors. Insofar as the limited number of data permit conclusions, V seems to give the poorest results, and all significant errors are positive, *i.e.*, the method gives somewhat high results. The largest discrepancies are  $\sim +8\%$ , and the overall errors are in the vicinity of  $+4\%$ . There appears to be no correlation between positive errors and iron content, therefore enhancement effects cannot be the sole cause of these discrepancies. Other possible causes include (1) uncertainties in published values for mass absorption coefficients (cf. Liebhafsky *et al.*, 1960, p. 313), (2) variations in  $b$  (Equation 3), and (3) incomplete homogenization of the artificial standards. Regardless of the cause, the magnitude of the errors probably does not prohibit the use of these methods for many trace element studies.

## REFERENCES

- 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. *Amer. Mineral.* **44**, 19.
- LIEBHAFSKY, H. A., H. G. PFEIFFER, E. H. WINSLOW AND P. D. ZEMANY (1960) *X-ray Absorption and Emission in Analytical Chemistry*. John Wiley and Sons, Inc., N. Y.
- REYNOLDS, R. C. (1963) Matrix corrections in trace element analysis by x-ray fluorescence. Estimation of the mass absorption coefficient by Compton scattering. *Amer. Mineral.* **48**, 1133.
- RYLAND, A. L. (1964) A general approach to the x-ray spectroscopic analysis of samples of low atomic number. (*Abstr.*) *Amer. Chem. Soc. Ann. Meet.*
- WARREN, B. E. AND G. MAVEL (1964) Elimination of the Compton component in amorphous scattering. (*Abstr.*) *Amer. Crystallogr. Ass. Ann. Meet.*

*Manuscript received November 22, 1966; accepted for publication March 27, 1967.*