

## A METHOD FOR DETERMINING MINERAL COMPOSITIONS BY MEASUREMENT OF THE MASS ABSORPTION COEFFICIENT

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### ABSTRACT

A technique is described whereby measurement of the mass absorption coefficients of minerals can be used to give an estimation of the mineral composition. Direct measurements of  $\mu_{\text{SrK}\alpha}$  on chemically analyzed plagioclases demonstrates the applicability of the method. The straight line regression so derived from 41 plagioclase samples gives the following equation:  $\text{An } \% = 25.27 \mu_{\text{SrK}\alpha} - 164.66$ , with a standard deviation of 1.61 % An.

The method can be extended to other solid solution series, such as olivine, orthopyroxene and zinblend series, and calculated values of  $\mu_{\text{SrK}\alpha}$  for different members of these series are presented. By judicious selection of the wavelengths of the absorbed X-ray beam the effects of interfering elements can be reduced to a minimum.

Although the experimental work reported in this paper was done using an X-ray spectrograph, measurements of  $\mu$  can be made using a diffractometer.

The advantage of this method over other indirect methods for determining mineral compositions is that the measured values of  $\mu$  are directly related to the chemical compositions of the samples.

### INTRODUCTION

When X-rays are passed through matter they are both scattered and absorbed and, in general, absorption is the dominant process. If a beam of parallel, monochromatic X-rays of intensity  $I_0$  is passed through material of thickness  $t$  and density  $\rho$  then the intensity of the emergent radiation,  $I$ , can be related to  $I_0$  by the equation:

$$I = I_0 e^{-\mu \cdot \rho t} \dots \text{(Beer's Law)} \dots$$

where  $\mu$  is the mass absorption coefficient of the absorbing material. Both  $I$  and  $I_0$  are corrected for any counting losses.

Mass absorption coefficients (hereafter termed  $\mu$ ) have a fixed value for a given element for a particular wavelength of X rays. Furthermore, since  $\mu$  is an additive property it is directly related to the bulk chemical composition of the compound, or mixture.

In mineral groups displaying solid solution the progressive compositional change is matched by a change in  $\mu$ . Provided that there is sufficient contrast in  $\mu$  between the dominant cations making up the mineral (*e.g.* Ca and Na in plagioclases) the change in  $\mu$  of the total specimen can readily be detected. In this sense the application is restricted essentially to simple two component systems since the assumption is made that differences in  $\mu$  are directly related to changes in one of the cations. If more than two dominant cations are present (as in garnets) and these

contribute significantly to the total  $\mu$  then the method breaks down. However, in practice certain contributing cations can be ignored, either because they are present in such small amounts that their contribution to the total  $\mu$  is insignificant or because their  $\mu$  is low compared with that of the major cation. By measuring the total  $\mu$  at different wavelengths the influence of minor cations may, in some cases, be emphasised. Thus, by a combination of measurements, at different wavelengths, a better estimation of the mineral composition may be made.

#### METHOD

The method is dependent on the experimental determination of  $\mu$  and much of its usefulness depends on the rapidity with which  $\mu$  can be determined. The most rapid determinations are made by direct measurements of an attenuated and unattenuated X-ray beam passed through a finely-powdered sample of known mass per unit area. This technique has been described by Norrish and Taylor (1962), Sweatman *et al.* (1963), Sweatman *et al.* (1967) and by Norrish and Chappell (1967).

High intensity fluorescent SrK $\alpha$  radiation ( $I_0$ ) is obtained from a SrCO $_3$  pressed mount in the sample position of the spectrograph and excited using primary molybdenum radiation. A powdered sample is pressed into a perspex holder of known area (1.27 cm $^2$ ) using a piston-type die. The minimum weight which will be self-supporting in mounts of this type is about 200 mg. If only small amounts of sample are available, or if the radiation to be used is of a relatively long wavelength (*e.g.*, CoK $\alpha$ , 1.790 Å) then it is necessary to mix the sample with a known amount of some substance of low absorption, such as boracic acid or filter paper pulp (*e.g.* Whatman's ashless cellulose powder, Standard Grade). The measured  $\mu_{total}$  must then be corrected for the presence of the diluent:

$$\mu_{sample} = \frac{\mu_{total} - (1 - p)\mu_{diluent}}{p}$$

where  $p$  is the proportion of sample in the mixture. This pressed sample is placed in front of the scintillation counter and the intensity of the attenuated beam ( $I$ ) measured. In all measurements reported in this paper the ratio  $I_0/I$  ranged between 15 and 25, and count rates were corrected for dead time. Pulse height selection is used to eliminate possible higher order harmonics in the attenuated beam.

This method of direct measurement of  $\mu$ , devised by Dr. K. Norrish, shows good reproducibility with respect to variations in the intensity of the incident beam (35,000 c.p.s. to 70,000 c.p.s.) and for different mounts and sample weights (Table 1).

An alternative procedure for determining  $\mu$  is the Compton scatter method which has been fully described by Reynolds (1963, 1967). He has shown that  $\mu$  "is inversely and closely related to the intensity of the Compton scattered portion of a primary X-ray beam," and has presented a method for measuring  $\mu$ , with an error of less than 3 percent, for materials of high mean atomic number. The mass absorption coefficient can then be computed for regions on the long wavelength series of major element absorption edges by the use of a series of simultaneous equations, Reynolds (1967). This method may be used for long wavelength radiation or for heavily absorbing samples if the operator wishes to avoid mixing the sample with a diluent.

#### EQUIPMENT

Measurements in this department have been made using a Phillips All-Vacuum Spectrograph. However, the method may readily be applied in laboratories where a diffractom-

TABLE 1. REPLICATE DETERMINATIONS OF THE MASS ABSORPTION COEFFICIENT USING DIFFERENT SAMPLE WEIGHTS AND DIFFERENT MOUNTS FOR  $\text{SrK}_\alpha$  RADIATION. DATA FROM VIRGO (1966)

| Sample              | $\mu_{\text{SrK}_\alpha}$ |      |      |
|---------------------|---------------------------|------|------|
|                     |                           |      |      |
| 221/35 plagioclase  | 7.66                      | 7.64 | 7.67 |
| 152/79 plagioclase  | 7.24                      | 7.25 | —    |
| OL/181 plagioclase  | 7.24                      | 7.28 | —    |
| 30829 plagioclase   | 7.69                      | 7.67 | 7.67 |
| 34611 plagioclase   | 6.96                      | 6.92 | 6.95 |
| S28 plagioclase     | 8.91                      | 8.88 | 8.90 |
| GI standard granite | 8.64                      | 8.67 | 8.65 |
| 30829 K-feldspar    | 9.27                      | 9.24 | —    |
| 34611 K-feldspar    | 9.48                      | 9.46 | —    |

eter is available, as shown by Norrish and Taylor (1962). Drawings of the necessary attachments for measuring  $\mu$  directly are available from Dr. K. Norrish.<sup>1</sup>

## RESULTS

*Plagioclase feldspar series.* The mass absorption coefficients of 41 plagioclase samples, analyzed for  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and, in some cases, for  $\text{SrO}$  and  $\text{BaO}$ , were measured directly for  $\text{SrK}_\alpha$  radiation using the pressed mount method. The data are presented in Figure 1, where  $\mu_{\text{SrK}_\alpha}$  is plotted against

$$\text{An}\% = \text{atomic ratio} \frac{\text{Ca}(+\text{Sr}) \times 100}{\text{Ca}(+\text{Sr}) + \text{Na} + \text{K}}$$

Although Sr is included in this equation its effect on the measured  $\mu$  is considered negligible since it is present in such small amounts.  $\text{K}_2\text{O}$ , because of the closeness of the mass absorption coefficients of  $\text{CaO}$  and  $\text{K}_2\text{O}$  (24.80 and 24.93 respectively), is potentially a more important source of error. However, most plagioclases have  $\text{K}_2\text{O}$  contents within approximately the same range. The 41 samples measured had  $\text{K}_2\text{O}$  contents ranging between 0.04 to 1.13 percent with an average of 0.36 percent. The 87 plagioclase analyses quoted in Deer, Howie and Zussman (1963) have an average  $\text{K}_2\text{O}$  content of 0.42 percent. Most of the scatter on the measured graph (Fig. 1) is probably due to the presence of  $\text{K}_2\text{O}$  and the standard deviation of the fitted line, giving a measure of the precision of the method, takes into account the presence of  $\text{K}_2\text{O}$ . However, significant amounts of  $\text{K}_2\text{O}$  in a plagioclase (*i.e.* > 1.0%  $\text{K}_2\text{O}$ ) would lead to greater errors in the determination. As a general approxi-

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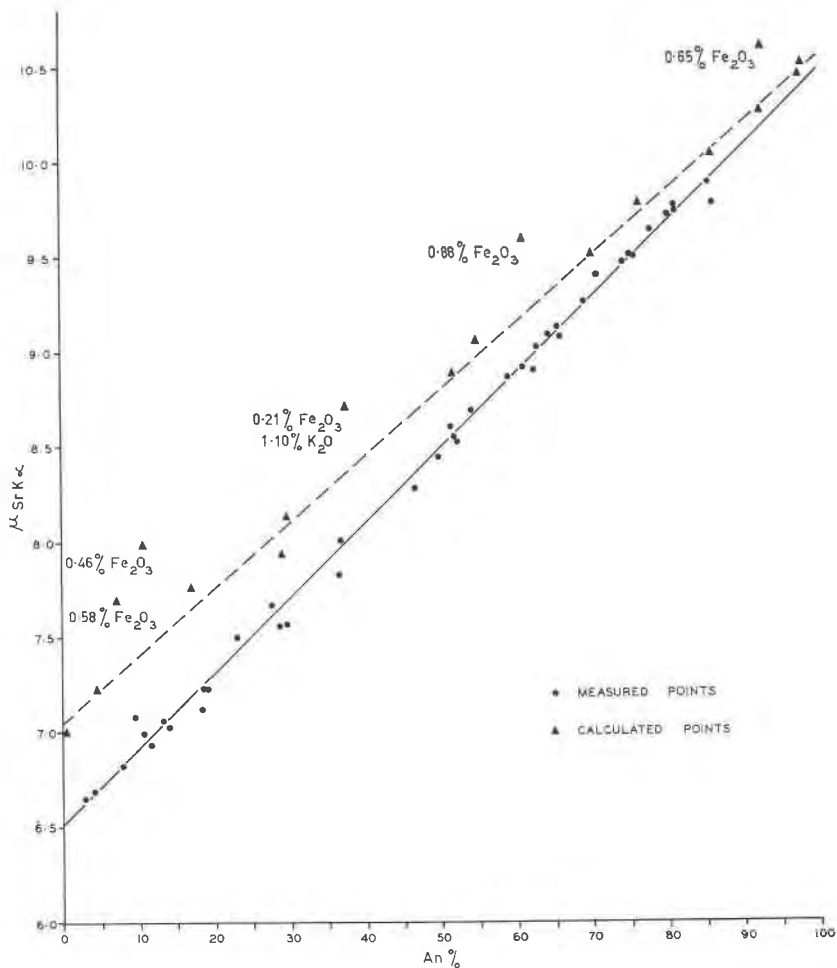


FIG. 1. Plot of

$$\text{An}\% \left( = \frac{\text{Ca}(+\text{Sr}) \times 100}{\text{Ca}(+\text{Sr}) + \text{Na} + \text{K}} \right), \text{ against } \mu_{\text{SrK}\alpha},$$

which is calculated and measured directly. Plagioclase compositions determined from chemical analyses. Measured values of  $\text{SrK}_\alpha$  (41 samples) from Kleeman (1965), Virgo (1966), Oliver (unpublished) and Moore (unpublished). Calculated values of  $\mu_{\text{SrK}\alpha}$  from published analyses, Deer, Howie and Zussman (1963).

mation, for every 0.5 percent  $\text{K}_2\text{O}$  present in plagioclase sample the measured anorthite content increases by about 2 percent anorthite.

A least squares fit of the measured data in Figure 1 gave a straight line fit with an equation:

$$\text{An}\% = 25.27\mu_{\text{SrK}\alpha} - 164.66 \quad (s = 1.61\% \text{ An}).$$

No improvement resulted from a second order curve.

On the same graph (Fig. 1) are plotted 16 points for which  $\mu_{\text{SrK}\alpha}$  values were calculated (using tables published by Heinrich, 1966) from analyses published in Deer, Howie and Zussman (1963). The degree of scatter for the calculated points is much greater than for the measured points, and the line not only has a different slope but is displaced upwards, particularly at the albite end. The reason for the difference in slope and position of the two lines is not known, although it may be due to uncertainties in the published mass absorption coefficients of the elements. Similar discrepancies may be found between measured and calculated mass absorption coefficients at longer wavelengths. The high degree of scatter is in large part due to the fact that those analyses displaced significantly upwards from the line are unusually rich in iron, an element which contributes strongly to the total  $\mu_{\text{SrK}\alpha}$ . It appears then that the plagioclases for which  $\mu_{\text{SrK}\alpha}$  was measured are essentially free of iron. If an operator suspects high iron ( $>0.1\%$   $\text{Fe}_2\text{O}_3$ ) in plagioclase it would be better to use a radiation for which the mass absorption contribution by iron is low. For example, at the  $\text{SrK}\alpha$  wavelength the mass absorption contributions by  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  are 24.80, 5.34, 52.55 and 47.54 respectively while at  $\text{CoK}\alpha$  wavelength they are 176, 39.1, 49.2 and 46.2 respectively. Figure 2 shows 25 plagioclase analyses (from Deer, Howie and Zussman, 1963) plotted against their calculated mass absorption coefficients for  $\text{CoK}\alpha$  radiation (Heinrich, 1966). A least squares regression analysis gave the following result, with only slight improvement for the second order fit:

$$\text{An}\% = 4.07\mu_{\text{CoK}\alpha} - 211.85 \quad (s = 2.34\% \text{ An})$$

The advantages of this indirect method for determining the composition of plagioclases over other indirect methods is that it is independent of the structural state of the plagioclase. The most promising X-ray method has been the determination of  $\Gamma = \text{angular separation } 2\theta (131) + 2\theta (220) - 4\theta (1\bar{3}1)$  of Smith and Gay (1958). However, this parameter is dependent on (1) the  $\text{K}_2\text{O}$  content and (2) on the structural state of the plagioclase (Kleeman and Nesbitt, 1967; Bambauer *et al.*, 1967; Smith and Gay, 1958).  $\Gamma$  cannot readily be used to determine the compositions of plagioclases from different environments. The mass absorption method is applicable to all plagioclases, irrespective of their history. There are two disadvantages. The first, which applies to all mineral groups, is the necessity to have a pure specimen. The second, peculiar to the plagioclases, is that  $\text{SrK}\alpha$  radiation cannot be used for iron-bearing

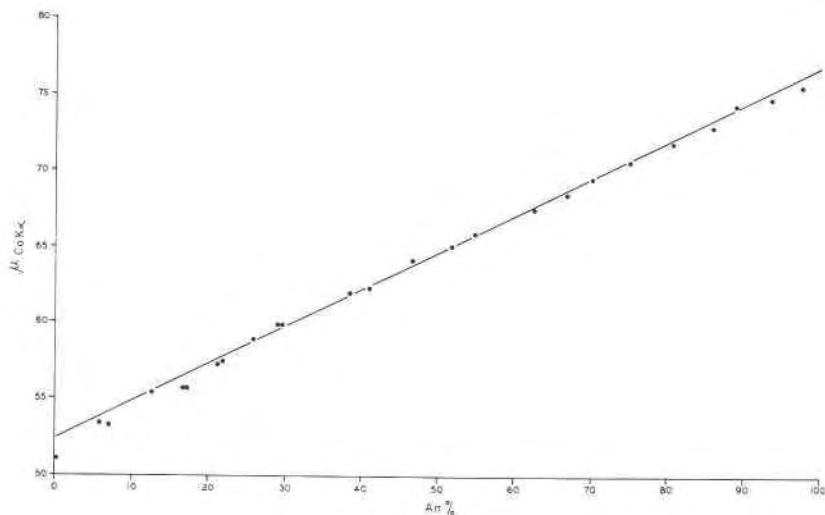


FIG. 2. Plot of plagioclase composition as

$$\text{An}\% \left( = \frac{\text{Ca} + \text{Sr}}{\text{Ca} + \text{Sr} + \text{Na} + \text{K}} \times 100 \right), \text{ against } \mu_{\text{CoK}\alpha},$$

which is calculated from published analyses, Deer, Howie and Zussman (1963).

samples and it is necessary to use  $\text{CoK}\alpha$  radiation. This increases the time needed for making measurements since the samples must either be mixed with some substance of low absorption or else the mass absorption coefficients must be measured by the Compton scatter method.

*Olivine and orthopyroxene series.* The mass absorption method is applicable to both the olivine and orthopyroxene series. Figure 3 shows a plot of olivine compositions against their calculated  $\mu_{\text{SrK}\alpha}$  values (analyses from Deer, Howie and Zussman, 1963). In this case the relationship is non-linear. For the olivine series the method has little application because X-ray diffraction methods (*e.g.* Yoder and Sahama [1957]) have been shown to be very suitable and have the added advantage that the olivines need not be completely separated from associated minerals.

In the case of the orthopyroxenes this method has decided advantages over other indirect methods, such as optics and cell size variation, in that it is independent of changes in cell size and the presence of minor elements (*e.g.* Al and Cr), which have negligible effect on the total  $\mu_{\text{SrK}\alpha}$ . Figure 4 presents the data for orthopyroxenes (analyses from Deer, Howie and Zussman, 1963 and  $\mu_{\text{SrK}\alpha}$  calculated from Heinrich, 1966).

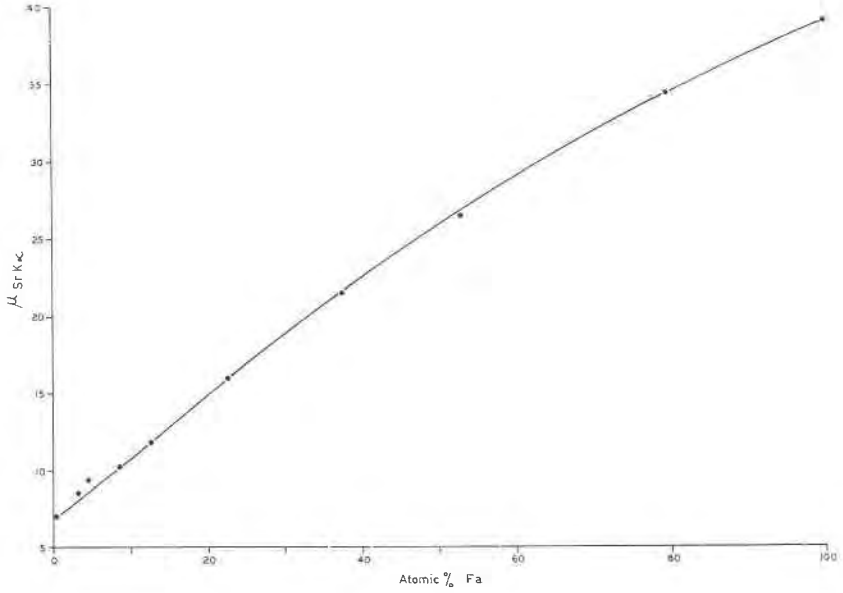


FIG. 3. Plot of olivine composition, as atomic percentage fayalite, against  $\mu_{Sr:K\alpha}$ , which is calculated from published analyses, Deer, Howie and Zussman (1963).

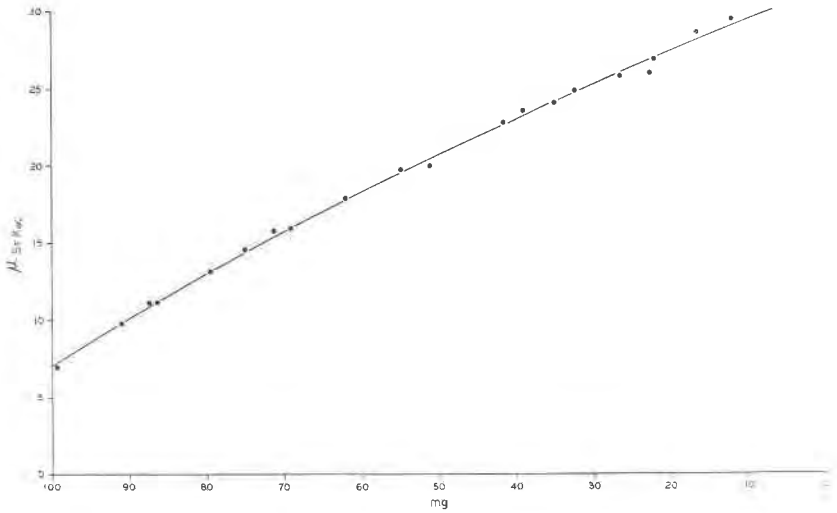


FIG. 4. Plot of orthopyroxene composition, as

$$\text{mg} \left( = \frac{100 \text{ Mg}}{\text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}} \right), \text{ against } \mu_{Sr:K\alpha},$$

which is calculated from published analyses, Deer, Howie and Zussman (1963).

Least-squares regression analysis of the data shows the second order fit is better with the following equation:

$$\text{mg} = 119.90 - 2.54\mu_{\text{SrK}\alpha} - 0.041\mu_{\text{SrK}\alpha}^2 \quad (s = 1.38\% \text{ mg})$$

where

$$\text{mg} = \left( \frac{\text{Mg} \times 100}{\text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}} \right).$$

A straight line fit of the same gives a standard deviation of 2.11 percent mg.

*Zinblende series.* The composition of opaque minerals is particularly difficult to determine indirectly because of the limitations imposed on optical methods. X-ray diffraction techniques are also difficult because such small changes are caused in cell size by relatively large differences in composition. The method of mass absorption coefficient measurement appears to be well suited, although there are problems caused by the increased degree of absorption for most opaque minerals. The ZnS-(Fe, Mn)S system has been chosen to show the applicability of the technique described in this paper. The data, shown in Figure 5, are taken from Skinner (1961). The relationship between  $\mu_{\text{SrK}\alpha}$  and the weight percent ZnS-(Fe, Mn)S is linear. In this case the system has three components and the mass absorption coefficients for FeS and MnS, at the SrK $\alpha$  wavelength, are very close (49.1 and 45.1 respectively). Thus, the minerals can be treated as a simple binary mixture. A line drawn for a theoretical, pure ZnS-FeS mixture has almost the same position and slope as that shown in Figure 5, showing the effect of MnS is negligible. By using a different radiation (e.g. CoK $\alpha$ ) the effect of MnS on the total  $\mu$

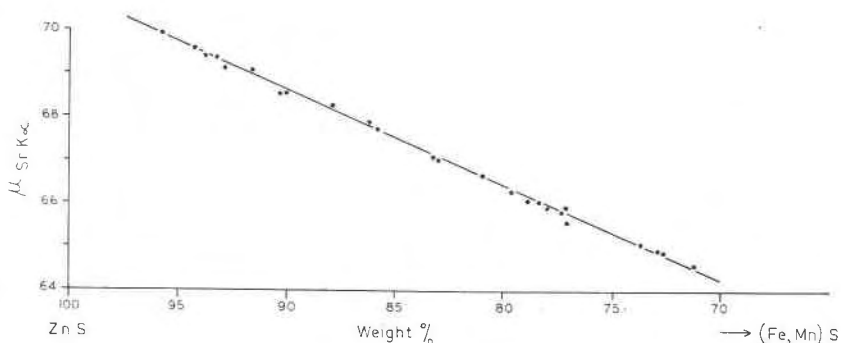


FIG. 5. Plot of zinblende composition, as wt % ZnS-(Fe, Mn)S, against  $\mu_{\text{SrK}\alpha}$ , which is calculated from published analyses, Skinner (1961).



can be made appreciable and the method may thus be extended to give information about the amount of MnS in the zincblendes.

### CONCLUSIONS

A method of indirectly determining the composition of minerals by measuring their mass absorption coefficients has been described. The method seems to have much potential with a wide field of applicability. By judicious selection of the wavelength of the absorbed X-ray beam the effects of interfering elements (*e.g.* iron in plagioclase) can be reduced to a minimum. Direct measurements on the plagioclase series demonstrates the applicability of the method. Calculations based on published analyses of olivines, orthopyroxenes and zincblendes indicate that the method may be applied to other solid solution series. It should be noted, however, that values of  $\mu$  measured directly will probably not be the same as those calculated from published tables (such as Heinrich, 1966), as has been shown for the plagioclase series for SrK $\alpha$  radiation.

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*Note added in proof.* Since the completion of this work it has been pointed out to the author that Overkott (1958) had proposed a similar method for the determination of plagioclase compositions after noting the linear dependence of the calculated  $\mu$  values of plagioclases and their An contents. He further pointed out that the method has a possible application in determining the proportions of different mineral phases in a mixture.

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