Clays and Clay Minerals, 1968, Vol. 16, pp. 325–336. Pergamon Press. Printed in Great Britain

QUANTITATIVE ANALYSIS OF NATURALLY OCCURRING MULTICOMPONENT MINERAL SYSTEMS BY X-RAY DIFFRACTION

CHARLES A. MOORE
Department of Materials Engineering, University of Illinois at Chicago Circle, Chicago, Illinois

(*Received* 29 *August* 1967)

Abstract—A theory for the quantitative analysis of multicomponent mineral systems by means of X-ray diffraction is presented. A linear interaction between mineral pairs is postulated. The theory is verified experimentally for bicomponent and tricomponent systems using a variety of sample preparation techniques including random powder mounts, suspensions sedimented onto glass slides, and pressed powder pellets. The minerals studied include quartz, fluorite, kaolinite, glauconite, illite, and montmorillonite.

The determination of the linear interaction factors for mineral pairs is treated theoretically and experimentally. Emphasis is placed upon techniques that are applicable to naturally occurring mineral systems. Four approaches are presented for determining linear interaction coefficients for various types of such mineral systems. These approaches are applied to the experimental data and the results are compared. Results accurate within 2 per cent are commonly obtained.

Experimental techniques are discussed and a qualitative and quantitative error analysis is presented. It is shown that the indicated quantities present may not be particularly sensitive to the value of the linear interaction coefficient.

INTRODUCTION

THE elements for the quantitative analysis of mixtures of several mineralogical components by X-ray diffraction were first expounded by Klug and Alexander (1954). Various schemes have since been devised to apply their principles [Moore (1965)]. Such approaches are based on the assumption that the intensity of any given diffraction maximum is linearly affected by the relative amounts of the other mineralogical components present. Mathematically speaking, a mineral suite composed of n different components may be described by an n dimensional linear manifold. The solution of such a system is facilitated by the principles of linear algebra, and statistical analysis may be applied through multiple linear regression. Practically speaking, the effect of the presence of any one mineralogical component on the intensity of a diffraction maximum of any other given component is expressed by a single constant. This paper discusses the evaluation of these constants and emphasizes the treatment of naturally occurring mineral systems.

NATURAL SYSTEMS

For purposes of this paper a naturally occurring mineral system is defined as a solid material composed of one or more recognizable crystalline structural configurations or units, each unit being associated with some standard configuration but not necessarily having a composition identical to that of the standard. The purpose of this definition is for the recognition of the fact that within a class of minerals designated by a common name, there may exist variable amounts of atomic substitution and/or degrees of crystallinity which might appreciably affect the intensity of the X-ray diffraction maximum for a given mineral sample. This results in complications in the application of the theoretical principles to such naturally occurring systems. For example, linear interaction factors derived using one mineral sample may or may not be applicable to the same mineral type occurring at a geologically different site. One would certainly not expect a 10 Å clay reflection to be caused by precisely the same structural configuration in all deposits. Moreover, within a single deposit a considerable variation in the diffraction characteristics of a given mineral may be encountered. In the following sections the theory of quantitative analysis of multicomponent mineral systems is developed and the special considerations for applications to naturally occurring systems are presented.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

THEORY

Notation:

Superscripts. A superscript serves two purposes:

1. To identify a particular sample, and
2. To relate the composition of that sample to other samples.

Subscripts. A subscript refers to a particular diffraction maximum for a particular mineral. This subscript will be a number in the theoretical development or a letter designating the mineral in the experimental sections; i.e., K for kaolinite, G for glauconite, etc. The choice of the *hkl* reflection to be used for a given mineral may be arbitrarily (or conveniently) chosen but must be consistently employed in the analysis. For this paper all reflections referred to are from the 001 planes of the clays.

Letters

- I net peak intensity; this may be defined either as total peak counts per second less background or as the integrated peak intensity less integrated background. For this paper the former definition is used.
- I° net peak intensity for a sample composed of only a single mineralogical component.
- c constant of the diffractometer geometry and of the mineralogical component.
- ρ density of the mineralogical component.
- μ linear absorption coefficient of the mineralogical component.
- $\bar{\mu}$ mass absorption coefficient of the mineralogical component as calculated from the chemical structural formula for the mineral, see Black (1963).
- x weight fraction of the component in a sample = weight of a given mineral present divided by the total weight of all minerals considered in the analysis.

Klug and Alexander (1948) have shown that the net diffracted intensity of the i^{th} component of an n component mixture may be written:

$$I_i^s = \frac{c_i x_i^s}{\rho_i \bar{\mu}^s} \tag{1}$$

where $\bar{\mu}^s$ is the mass absorption coefficient for the sample. Equation (1) may also be written

$$x_i^s = \frac{I_i^s \rho_i \bar{\mu}^s}{c_i}. \tag{2}$$

If the sum of the weight fractions of all of the mineralogical components considered in the analysis is taken to be unity we may write

$$\sum_{j=1}^{n} x_j^s = \frac{\sum_{j=1}^{n} \mu^s I_j^s \rho_j}{c_j} = 1. \tag{3}$$

Since $\bar{\mu}^s$ is a constant for a given sample it may be removed from the summation and Eq. (3) becomes

$$\bar{\mu}^s = \frac{1}{\sum_{i=1}^{n} I_j^s \rho_j / c_j}. \tag{4}$$

Substituting Eq. (4) into Eq. (2) yields

$$x_i^s = \frac{(\rho_i / c_i) I_i^s}{\sum_{j=1}^{n} I_j^s \rho_j / c_j} = \frac{R_i I_i^s}{\sum_{j=1}^{n} R_j I_j^s}. \tag{5}$$

Note that both the density and the constant of the geometry and component are accounted for by a single constant R. In Eq. (5) x_i^s is the unknown whose value is desired, the I values are the measured reflection intensities, and the R values represent coefficients, the determination of which constitutes the purpose of this paper. This objective is facilitated by inverting Eq. (5) to give

$$\frac{1}{x_i^s} = \frac{\sum_{j=1}^{n} R_j I_j^s}{R_i I_i^s}. \tag{6}$$

Since $R_i I_i^s$ is a constant in Eq. (6) we may divide each factor of the sum in the numerator by the term to yield

$$\frac{1}{x_i^s} = \sum_{j=1}^{n} \frac{R_j I_j^s}{R_i I_i^s}. \tag{7}$$

For convenience define

$$\beta_{ji} = \frac{R_j}{R_i} \tag{8}$$

so that Eq. (7) becomes

$$\frac{1}{x_i^s} = \sum_{j=1}^{n} \beta_{ji} \frac{I_j^s}{I_i^s}. \tag{9}$$

Note that $\beta_{ii} = R_i / R_i = 1$.

Equation (9) constitutes the fundamental statement of the linear effect of the presence of all other minerals on the net peak intensity of a given mineral. The β_{ij} values denote this linear interaction.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

VERIFICATION OF THE APPLICABILITY OF THE THEORY

The verification of the applicability of Eq. (9) to any given multi-component system under any given set of experimental conditions depends solely upon the existence of and the determinability of the linear interaction coefficients β_{ij}. The derivation of Eq. (9) presumed (after Klug and Alexander) a random orientation of the mineral grains composing the sample. In fact, the approach can be successfully applied to any system wherein the requisite linearity can be shown to exist. The following section will demonstrate the extent to which such linearity has been observed for commonly used experimental procedures. These procedures include random powder mounts, sedimented suspensions on glass slides, and pressed powder pellets.

In the particular case of a two component mixture Eq. (9) becomes

$$\frac{1}{x_1} = \beta_{11}\frac{I_1}{I_1} + \beta_{21}\frac{I_2}{I_1} = 1 + \beta_{21}\frac{I_2}{I_1} \qquad (10)$$

or, transposing the 1 to the left side of the equation

$$\frac{1}{x_1} - 1 = \beta_{21}\frac{I_2}{I_1}. \qquad (11)$$

In the bicomponent case a plot of $(1/x_1) - 1$ versus I_2/I_1 should be linear with slope equal to β_{21}.

Figure 1 presents the data of Williams (1959) for a bicomponent powder mount of sodium fluoride (fluorite) and silicon dioxide (quartz). Agreement with the linear hypothesis is seen to be good. Figures 2–4 show the data for bicomponent suspensions sedimented onto glass slides for mixtures of kaolinite (Huber Corporation, Huber, Georgia) and glauconite (Hornerstown Formation in Monmouth County, New Jersey); and of kaolinite (Huber) and montmorillonite (API H-23). The details used in obtaining these data may be found in the paper by Moore (1965). Again the requisite linearity is found to hold. Finally the criterion of linearity has been found to hold for pressed powder pellets of mixtures of quartz, muscovite and kaolinite by Doyle and Heron of Duke University (personal communication). Verification for a tricomponent sediment of kaolinite, montmorillonite and glauconite on glass slides as shown in Figs. 5 and 6 has been presented by Moore (1965). Thus it would appear that Eq. (9) holds for several commonly employed experimental techniques. This, of course, is not to say that it has general applicability. Indeed, for any proposed experimental procedure, Eq. (9) should be verified directly.

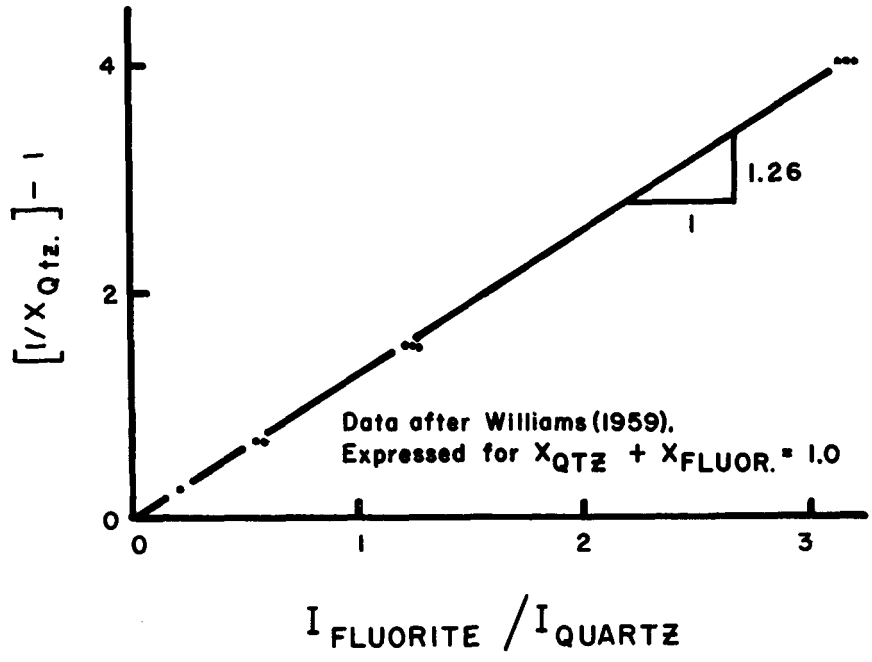


Fig. 1. Verification of Eq. (9) for random powder mounts.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

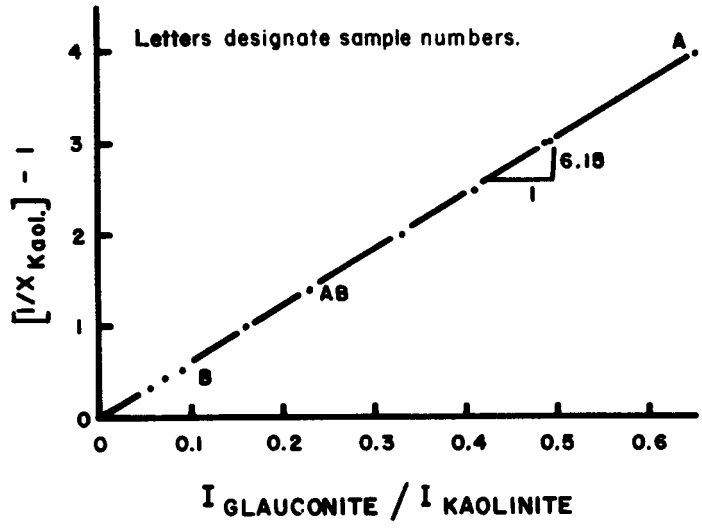


Fig. 2. Verification of Eq. (9) for sedimented glass slides.

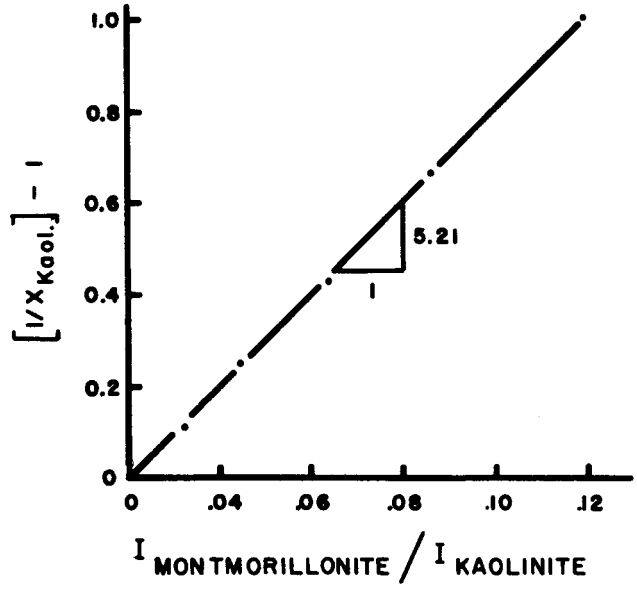


Fig. 3. Verification of Eq. (9) for sedimented glass slides.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

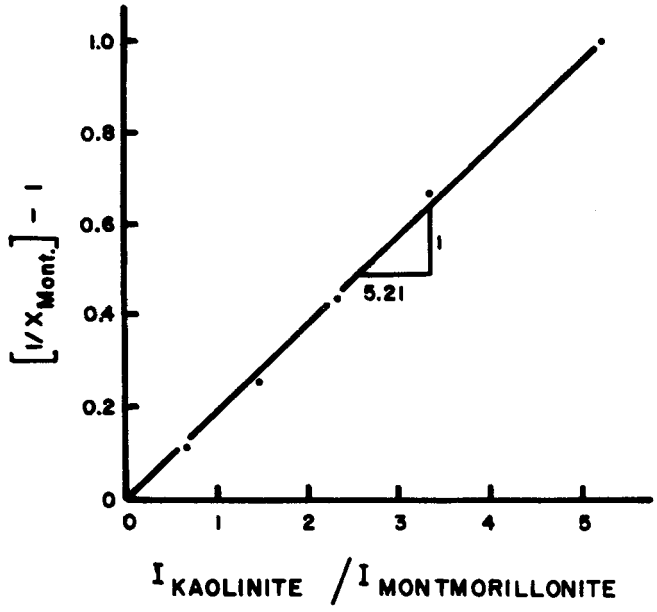


Fig. 4. Verification of Eq. (9) for sedimented glass slides.

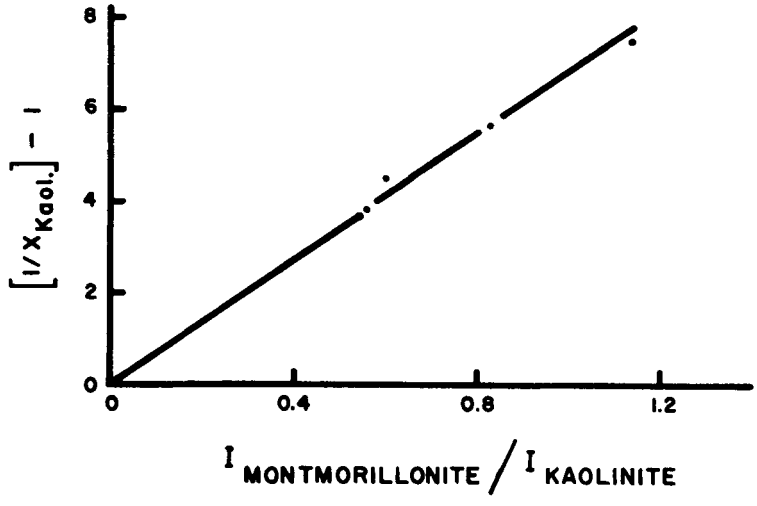


Fig. 5. Verification of Eq. (9) for tricomponent mixtures.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

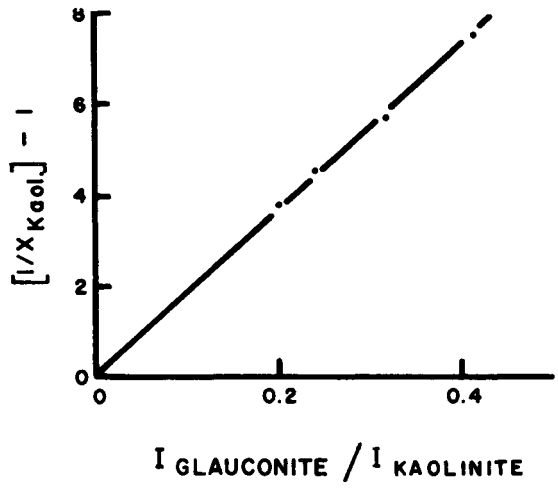


Fig. 6. Verification of Eq. (9) for tricomponent mixtures.

EVALUATION OF THE CONSTANTS OF LINEARITY

Having verified the applicability of Eq. (9) it is necessary to obtain values for the constants of linearity, β_{ij}. The following section will demonstrate several methods that have been developed to obtain these constants in naturally occurring mineral systems. The four approaches to be described for various types of bicomponent systems will be termed the *pure component approach*, the *direct calibration approach*, the *intercept approach*, and the *blend approach*.

The *pure component approach* as described by Black (1963) gives the R_i values of Eq. (5) as

$$R_i = \frac{1}{\bar{\mu} I_i^0}. \tag{12}$$

From Eq. (8) it is seen that

$$\beta_{ij} = \frac{R_i}{R_j}. \tag{13}$$

Thus the β value between any two components may be calculated directly if their R values are known. A knowledge of the R value presupposes a knowledge of the chemical structural formula for each mineral and the existence of a pure sample of each of the mineral components that is exactly like the analogous mineral in the sample.

In order to verify the pure component approach a bicomponent series of kaolinite (Huber) and glauconite (Hornerstown) was prepared as described by Moore (1965). Based on a formula for kaolinite of $Al_4Si_4O_{10}(OH)_8$ and the use of CuKα radiation, the mass absorption coefficient is calculated as 30·38. Unfortunately, the chemical composition of glauconite is not definite. A formula is:

$$(OH)_4\,(K, Ca_{0.5}, Na)_{1.68}\,(Si_{7.30}Al_{0.70}) \cdot (Al_{0.94}Fe_{1.94}Fe_{0.38}Mg_{0.80})O_{20}.$$

The relative proportions of K, Ca, and Na in the Hornerstown glauconite are unknown. For all K and no Ca or Na, the mass absorption coefficient is 83·66; for all Na and no Ca or K the mass absorption coefficient is 76·71. X-ray diffractograms of pure kaolinite gave a net intensity of 502 counts/sec, and for pure glauconite a net intensity of 33·4 counts/sec was obtained. The value of R for kaolinite, R_K, then is $6{\cdot}58 \times 10^{-5}$; and the value of R for glauconite, R_G, ranges from $3{\cdot}92 \times 10^{-4}$ for all Na to $3{\cdot}59 \times 10^{-4}$ for all K. Based on these values, the value of β_{GK} ranges from 5·44 for kaolinite and K-glauconite to 5·96 for kaolinite and Na-glauconite.

The *calibration approach* is the simplest and most direct approach. It is based upon the fundamental linear statement of Eq. (9) and determines the β value from the slope of a plot of $(1/x_1)-1$ versus I_2/I_1. This approach may be applied to Williams' (1959) data of Fig. 1 for fluorite and quartz to yield a value for β_{FQ} of 1·26. Similarly, Fig. 2 for kaolinite and glauconite yields a value for β_{GK} of 6·15. This value may be directly compared with the pure component approach value of from 5·44 to 5·96. Figures 3 and 4 for kaolinite and montmorillonite (Moore 1965) give a value of 5·21 for β_{MK}.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

The *intercept approach* is derived by considering a bicomponent system composed of an unknown percentage of component i and an unknown percentage of component j. Suppose that one of these components, say component i, is obtainable in the pure form. For the present it will be assumed that the pure mineral i is exactly like component i present in the unknown sample with respect to mineralogy, degree of crystallinity, and all other properties that affect the diffraction of X-rays. It will be shown subsequently that nonidentical pure components may be easily and directly used. The second unknown component may be of any known or unknown mineralogy. A typical example of such a bicomponent system that might occur naturally would be a mixture of kaolinite and some interstratified or mixed layer mineral. The kaolinite would be easily identifiable and obtainable in a pure form, whereas the interstratified mineral might be difficult to identify.

From Eq. (11) we may write

$$\frac{1}{x_i^u} - 1 = \beta_{ji} I_j^u / I_i^u \qquad (14)$$

where the superscript u implies the original unknown sample. To a known weight (in solution or in powder form) of the unknown sample having a weight of dry material, w^u, add a known weight of the pure form of component i having a weight of dry material, w_i^y. To define the amount of pure component i added let $y = w_i^y / w^u$ = ratio of weight of material added to weight of original sample (Eq. (15)). For this new sample we may write by analogy to Eq. (14)

$$\frac{1}{x_i^u + y} - 1 = \beta_{ji} \frac{I_j^u + y}{I_i^u + y}, \qquad (16)$$

where the superscript $u+y$ implies a new sample formed by adding a known weight of pure component i to the original unknown sample.

It may be shown algebraically that

$$\beta_{ij} = \left[y + \frac{1+y}{\dfrac{I_j^u}{\beta_{ij} I_i^u}} \right] \cdot \left[\frac{I_j^{u+y}}{I_i^{u+y}} \right]. \qquad (17)$$

For critical work or when there is doubt as to the likeness of the pure component i added and of component i in the original sample, it is best to select several values of y and plot β_{ij} versus y as in Fig. 7. If a relationship of the form of curve (a) is found, this implies that the pure component added is indeed like the mineral in the original sample. Conversely, if a relationship of the form of curve (b) is obtained, this implies that the pure component added is different from the mineral in the original sample. In this case the value of β to use is that obtained by extrapolating the curve to $y = 0$. This approach is essentially the same as that described by Brindley and Udagawa (1961).

In order to verify the intercept approach, two test series were performed. In the first series a bicomponent kaolinite (Huber) and glauconite (Hornerstown) mixture was studied using the kaolinite as the pure component added. Since the unknown sample was laboratory mixed, the kaolinite added was in fact identical to that in the original sample. Nevertheless, several values of y ranging from 0·5 to 2·69 were used. Figure 8 shows that the β values were essentially constant at $\beta_{KG} = 0{\cdot}165$ or $\beta_{GK} = 6{\cdot}06$. In the second series it was desired to determine the amount of kaolinite in the -2μ fraction of a commercial illite (grundite) from Illinois. Since no pure kaolinite from the site at which the illite was obtained was available, a

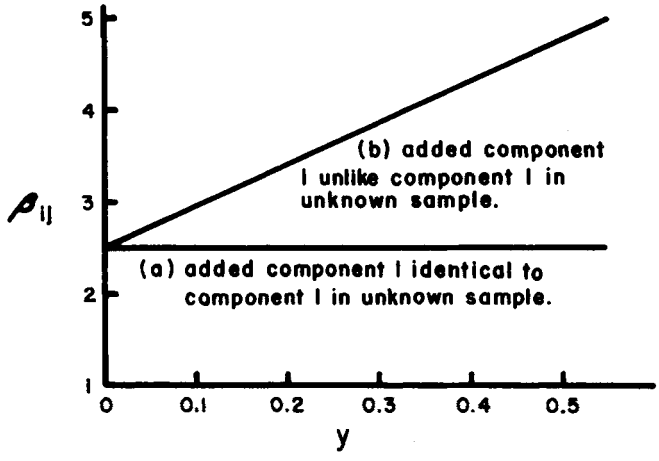


Fig. 7. Example of modified intercept approach.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

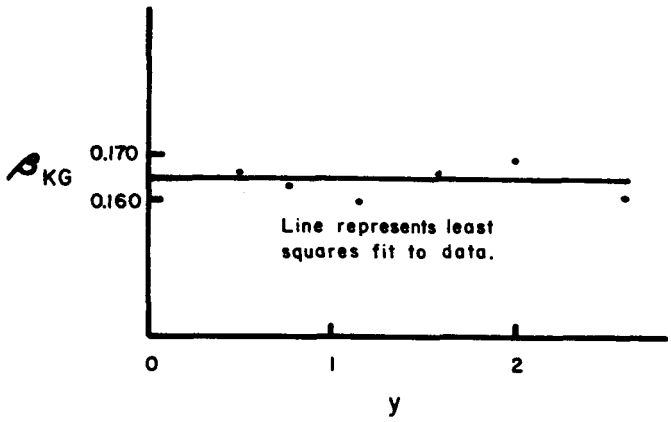


Fig. 8. Modified intercept approach applied to kaolinite–glauconite series.

Georgia kaolinite (Hydrite-UF) was chosen. It was anticipated that the two kaolinites would differ, therefore several values of y ranging from 0·177 to 1·0 were chosen. The results are shown in Fig. 9. The relationship is of the form of curve (b) of Fig. 7 indicating that the two kaolinites were indeed different. The intercept for $y = 0$ gives a value of 0·135 for β_{KI} or 7·41 for β_{IK}.

The *blend approach* as applied to bicomponent systems allows for the evaluation of the β_{ij} values when pure samples of neither component are available. The basis of the approach is that if two samples with differing relative proportions of the two components are blended or mixed in a known ratio, the β values may be obtained by X-raying these three samples. Consider samples A and B from a bicomponent system and let sample A have relative proportions of components 1 and 2 different from the relative proportions of components 1 and 2 in sample B. It is assumed that components 1 and 2 in both samples A and B are identical with respect to their properties affecting the diffraction of X-rays. Considering component 1 in sample A we may write

$$\frac{1}{x_1^A} - 1 = \beta_{21}\frac{I_2^A}{I_1^A}, \tag{18}$$

and for sample B,

$$\frac{1}{x_1^B} - 1 = \beta_{21}\frac{I_2^B}{I_1^B}. \tag{19}$$

Now if we blend M parts (by weight) of sample A with 1 part (by weight) of sample B we may write

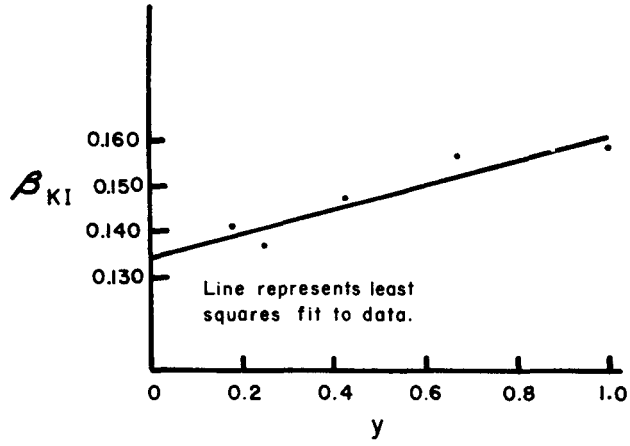


Fig. 9. Modified intercept approach applied to kaolinite–illite series.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

$$\frac{1}{x_1^{MAB}} - 1 = \beta_{21} \frac{I_2^{MAB}}{I_1^{MAB}}. \quad (20)$$

However, since the blend ratio is known it follows that

$$x_1^{MAB} = \frac{M(x_1^A) + x_1^B}{M+1}. \quad (21)$$

Once a value of M is chosen it is possible to combine Eqs. (18), (19), (20), and (21) to yield a single equation in the unknown β_{21} and the knowns I_2^A/I_1^A, I_2^B/I_1^B, and I_2^{MAB}/I_1^{MAB}. For convenience we will choose $M = 1$, and the combined equation becomes

$$\beta_{21} = \frac{2(I_2^{AB}) - I_2^A - I_2^B}{2\left(\frac{I_2^A I_2^B}{I_1^A I_1^B}\right) - \frac{I_2^{AB} I_2^A}{I_1^{AB} I_1^A} - \frac{I_2^{AB} I_2^B}{I_1^{AB} I_1^B}}, \quad (22)$$

where AB denotes a 1 to 1 blend (by weight) of samples A and B.

In order to verify the blend approach, two samples designated A and B on Fig. 2 were blended in a 1 to 1 ratio to yield sample AB of the same figure. Inserting the peak height ratios from these three kaolinite–glauconite samples into Eq. (22) yielded a value of 5·97 for β_{GK}. It should be pointed out that the success with which the blend approach may be applied depends strongly upon samples A and B having large differences in their relative proportions of components 1 and 2. As the relative proportions in the two samples approach the same value, Eq. (22) becomes rapidly unstable due to its dependency on the quotient of the differences between two large but nearly equal numbers.

In the preceding paragraphs the application of four approaches for the evaluation of the linear coefficients of interaction between mineral pairs has been described in detail for bicomponent systems. These same principles may be extended for use individually or in combination in the analysis of multicomponent systems.

To conclude this section the experimental data presented will be summarized and the results of the several approaches for the bicomponent glauconite–kaolinite series will be compared. Table 1 summarizes the β values for mineral pairs obtained by the various approaches.

It may be seen from Table 1 that the values for β_{GK} obtained by the several approaches vary from 5·44 to 6·15. In order to show graphically the effect of such a variation, Fig. 10 plots calculated percentage kaolinite (using the two β values and experimental peak height ratios) versus the actual percentage kaolinite. The 45° line represents the line of perfect agreement. In both of these extreme cases good agreement is found, the calibration slope method yielding the more accurate values. Of course, the intermediate β values obtained by the other methods would give results intermediate between those of the extreme β values shown. In the following section the dependency of the calculated percentage present upon the β values will be investigated qualitatively and quantitatively.

DISCUSSION

This section will be devoted to a discussion of the factors to be considered in the application of the analytical procedures described. As with any analytical procedure, the accuracy obtainable depends upon the experimental technique employed. While the procedure was formulated specifically to reduce the sensitivity of the results to experimental technique, there are certain considerations that will enhance accuracy. A general warning is in order concerning sampling techniques. X-ray diffraction exposes only a small portion of the material to examination. If the results of this examination are to reflect the properties of the parent population, the sample must be representative. Once a representative sample has been obtained it must be prepared to be subjected to irradiation. While the mathematical derivation of the analytical procedure presupposed a sample in which the mineral grains were randomly oriented, the experimental phase of this work has shown that

Table 1. Summary of β values

Approach	Minerals	β value
Pure component	Glauconite–Kaolinite	$\beta_{GK} = 5{\cdot}44$–$5{\cdot}96$
Calibration slope	Fluorite–Quartz	$\beta_{FQ} = 1{\cdot}26$
Calibration slope	Glauconite–Kaolinite	$\beta_{GK} = 6{\cdot}15$
Calibration slope	Montmorillonite–Kaolinite	$\beta_{MK} = 5{\cdot}21$
Intercept	Glauconite–Kaolinite	$\beta_{GK} = 6{\cdot}06$
Modified intercept	Illite–Kaolinite	$\beta_{IK} = 7{\cdot}41$
Blend	Galuconite–Kaolinite	$\beta_{GK} = 5{\cdot}97$

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

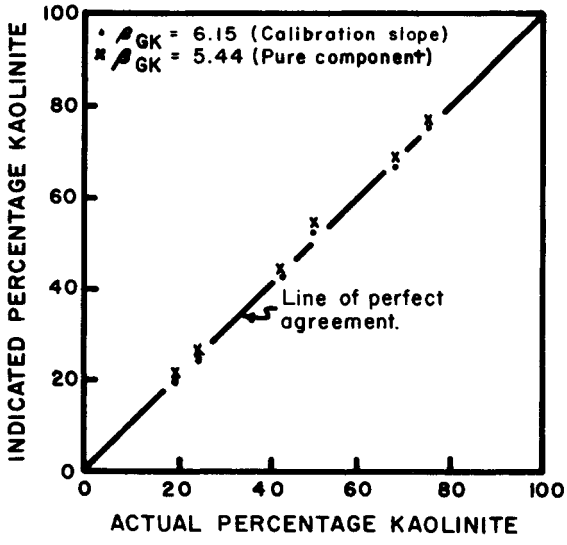


Fig. 10. Effect of variation in β on agreement in kaolinite–glauconite series.

several techniques known to induce preferred orientation of anisotropically shaped mineral grains also obey the requisite linearity implicit in Eq. (9). For instance, mixtures sedimented on glass slides as used in the glauconite–kaolinite, montmorillonite–kaolinite, and illite–kaolinite series are specifically employed in clay mineral analysis to accentuate the basal reflections. The results of Heron and Doyle for pellets of mixtures of orienting (kaolinite) and non-orienting (quartz) minerals pressed under anisotropic stress conditions probably induced partial preferential orientation in one phase (kaolinite) of the sample. Even though these procedures have been shown empirically to be valid there are two points worthy of consideration. First, since X-rays are most strongly diffracted from the uppermost grains of the sample, preparation techniques that induce a poorly controlled preferential orientation of the sample surface should be avoided. Especially undesirable is the leveling of the surface of a random powder sample by pressing with a glass plate. Secondly, any technique that induces preferred orientation must be reproduced exactly if the original β values are to apply. Thus β values that are obtained using such techniques may be difficult to transfer from laboratory to laboratory or even from operator to operator. Therefore it is recommended that random mounts as described by McCreery (1949) be used whenever possible. For minerals with anisotropic shape or with anisotropic cleavage it may be desirable to disperse the mineral grains in a synthetic resin such as epoxy and regrind in order to eliminate preferred orientation.

Techniques employed in obtaining the actual diffractograms are becoming less critical as improvements are introduced in X-ray diffraction apparatus. A good measure of both sample preparation technique and X-ray equipment operation technique is *reproducibility*. If successive and repeated runs on two identically prepared samples give good agreement for the peak intensity ratios, then the techniques employed may, with reasonable certainty, be expected to yield acceptable results. In analyzing diffractograms it must be decided whether net peak heights or net peak areas are to be used. An integrated intensity (peak area) is a more valid quantity from a theoretical point of view. Moreover, since the peak width at half height (which is usually used to compute area) is less sensitive to scanning techniques than is peak height, this value has a stabilizing influence on indicated intensity. Nevertheless, the writer finds that oscillating over the peaks several times at a low scan speed (say 1/4° 2θ/min) and using net peak height alone yields quite adequate values. The writer has been specifically unsuccessful in obtaining consistent fixed time counts by setting the goniometer "on the peak" for a single determination.

Since the determination of the β values depends upon experimentally obtained values, it is useful to examine the effect of an error in the calculation of β on the indicated percentage of the mineral components present when the erroneous value is applied. As an example consider the case of $\beta_{21} = 5{\cdot}0$. Figure 11 plots actual percentage of

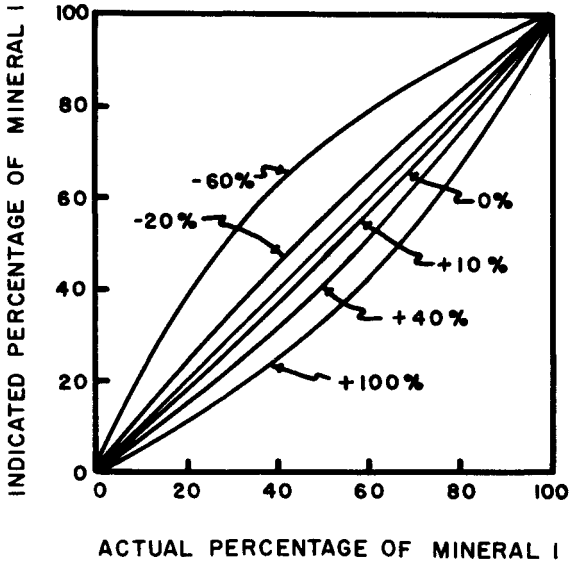


Fig. 11. Effect of errors in β on agreement of indicated and actual percentages.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

mineral 1 present, x_1 (actual), versus indicated percentage of mineral 1 present, x_1 (indicated), for several positive and negative errors in β_{21}. The error in β is calculated as $100[x_{(\text{erroneous})} - x_{(\text{actual})}]/[x_{(\text{actual})}]$. The 45° line labeled 0 per cent corresponds with the perfect agreement line of Fig. 10. It is seen that positive errors in β_{21} underestimate the percentage of component 1 present, and conversely for negative errors. The error in indicated percentage of component 2 will have an equal and opposite value to the error in indicated percentage of component 1 since Eq. (3) requires that the sum of the percentages present be 100 per cent. It may also be seen that the absolute percentage error defined as $[x_{1(\text{indicated})} - x_{1(\text{actual})}] \times 100$ is largest when the percentages of the two components are nearly equal. The error tends to zero as the proportions approach either single pure component end point. In every case the maximum percentage error is substantially less than the percentage error in β. Typically it is less by a factor of 1/4. Thus for $\beta_{21} = 5$ a 10 per cent error in β always results in an absolute percentage error in x_1 of less than 2·5 per cent.

Acknowledgments – The author is indebted to S. Duncan Heron, Jr., William J. Furbish, Charles E. Weaver, and James K. Mitchell for their advice and support during the execution of this work. Appreciation is expressed to Duke University, the Georgia Institute of Technology, and the University of California, Berkeley for making available the X-ray diffraction equipment and laboratory space.

REFERENCES

Black, R. H. (1963) Quantitative diffractometric powder analysis of multicomponent mixtures: *Norelco Reporter* Vol. **X**, No. 1, 14–15.

Brindley, G. W., and Kurtossy, S. S. (1961) Quantitative determination of kaolinite by X-ray diffraction: *Am. Mineralogist* **46**, 1205–1215. See also discussion by Van der Marel in Vol. **47**, 1209–1213, and reply by Brindley and Kurtossy in the same issue.

Brindley, G. W., and Udagawa (1961) Chap. 14 *in X-ray Identification and Crystal Structures of Clay Minerals:* London Mineralogical Society (Clay Minerals Group), 2nd Ed., 495–496.

Klug, H. P., and Alexander, L. E. (1964) *X-ray Diffraction Procedures:* Wiley, New York.

McCreery, G. L. (1949) Improved mount for powdered specimens used on the Geiger counter X-ray Spectrometer: *J. Am. Ceram. Soc.* **32**, 141–146.

Moore, Charles A. (1965) The use of X-ray diffraction for the quantitative analysis of naturally occurring multicomponent mineral systems: *Southeastern Geology* **6**, 139.

Williams, P. P. (1959) Direct quantitative diffractrometric analysis: *Anal. Chem.* **31**, 1842–44.

Résumé – Il s'agit d'une théorie pour l'analyse quantitative des systèmes minéraux à constituants multiples par diffraction de rayons X. On postule une inter-réaction linéaire entre les paires minérales. On vérifie la théorie de manière expérimentale pour les systèmes à deux et à trois constituants en utilisant un certain nombre de techniques de préparation d'échantillons, y-compris des montages de poudre faits au hasard, des suspensions en sédiments sur plaques de verre, et des pastilles de poudre comprimée. Les minéraux étudiés comprennent le quartz, la fluorite, la kaolinite, la glauconite, l'illite, et la montmorillonite.

La fixation des facteurs d'inter-réaction linéaire pour les paires minérales est traitée sur le double plan théorique et expérimental. Les techniques qui s'appliquent à des systèmes minéraux naturels sont particulièrement accentuées. Quatre modes d'approche sont donnés pour fixer les coefficients d'inter-réaction linéaire pour différents types de systèmes minéraux. Ils sont employés pour des données expérimentales et les résultats comparés. Ceux-ci sont souvent corrects à 2% près.

Il y a une discussion des techniques expérimentales et une analyse de la marge d'erreur sur le double plan quantitatif et qualitatif. Il est démontré que les quantités indiquées présentes ne sont pas nécessairement particulièrement sensibles à la valeur du coefficient d'inter-réaction linéaire.

Kurzreferat – Es wird eine Theorie für die Analyse mineralogischer Vielkomponentensystem mittels Röntgenbeugung dargelegt. Eine lineare Wechselwirkung zwischen Mineralpaaren wird postuliert. Die Theorie wird versuchsmässig für Zwei- und Driekomponentensysteme überprüft wobei eine Anzahl verschiedener Arten der Probenvorbereitung, wie unter anderem das Fixieren gepulverter Proben, die Sedimentierung von Suspensionen auf Objektträgern und die Komprimierung zu Tabletten, zur Anwendung gelangt. Die untersuchten Minerale umfassen Quarz, Fluorit, Kaolinit, Glaukonit, Illit und Montmorillonit.

Die Bestimmung der linearen Wechselwirkungsfaktoren für Mineralpaare wird theoretisch und experimentell behandelt, wobei besondere Bedeutung auf Methoden gelegt wird, die sich auf natürlich vorkommende Mineralsysteme anwenden lassen. Es werden vier Wege beschrieben für die Bestimmung der linearen Wechselwirkungskoeffizienten verschiedener Arten solcher Mineralsysteme. Ein Vergleich der vermittels dieser Wege erhaltenen Resultate mit Versuchsdaten ergab, dass die Resultate im allgemeinen eine Genauigkeit von etwa 2 Prozent aufwiesen.

Experimentelle Methoden werden erörtert und es wird eine qualitative und quantitative Versuchsfehleranalyse dargelegt. Es wird gezeigt, dass die gefundenen Mengen möglicherweise nicht besonders empfindlich gegenüber dem Wert des linearen Wechselwirkungskoeffizienten sind.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press

Резюме—Доклад содержит сообщение о теории количественного анализа многокомпонентных минеральных систем, пользуясь дифракцией рентгеновских лучей. Линейное взаимодействие между парами минералов принимается за очевидное. Теорию проверяют экспериментальнo для двухкомпонентных и трехкомпонентных систем, применяя разные способы набора образцов, включая беспорядочные порошкограммы, суспензии осажденные на предметные стекла и гранулы прессованного порошка. Исследуемые минералы включают кварц, флюорит, каолинит, глауконит, иллит и монтмориллонит.

Определение факторов линейного взаимодействия для пар минералов рассматривается как теоретически, так и экспериментальнo. Особое внимание уделяется методам, применимым для природных минеральных систем. Представлены четыре подхода для определения коэффициентов линейного взаимодействия различных типов таких минеральных систем. Подходы эти применяются с экспериментальными данными, а результаты сравниваются. Обычно получают результаты с точностью до 2%.

Обсуждаются экспериментальные методы и приводится качественный и количественный анализ погрешности. Доказывается, что указанные имеющиеся количества могут быть не особо чувствительными на значение коэффициента линейного взаимодействия.

https://doi.org/10.1346/CCMN.1968.0160502 Published online by Cambridge University Press