ESTIMATE OF CLAY-MINERAL CONTENT: ADDITIONS OF PROPORTIONS OF SOIL CLAY TO CONSTANT STANDARD

ROBERT V. RUHE AND CAROLYN G. OLSON

Water Resources Research Center and Department of Geology
Indiana University, Bloomington, Indiana 47405

Abstract—The method of known additions for estimating clay-mineral content was reversed in that increasing proportions of soil clay were added to a standard composed of equal weights of kaolinite, illite, and montmorillonite. After glycolation, peak-area ratios were calculated from 7.2 (kaolinite), 10 (illite), 14 and 17 Å (vermiculite and montmorillonite) diffraction peaks of standard, mixes, and soil clay. Ratios were plotted against % soil clay from the standard (0%) through the mixes (14 to 77%). Curves of fit were calculated and projected to 100% soil clay giving theoretical values which agree with measured values. As weight proportions are known in the standard, the projections permit estimates of clay-mineral weight proportions in the soil clay.

Key Words—Constant standard, Quantitative analysis, Soil clay, X-ray powder diffraction.

INTRODUCTION

The clay mineralogy of sedimentary rocks, soils, and paleosols is routinely analyzed in this laboratory by X-ray powder diffraction techniques to determine whether the clay minerals may be used as stratigraphic (Frye *et al.*, 1968; Kleiss, 1973) or sedimentological indicators in the rocks or as weathering indicators in the soils and paleosols. Commonly, 20 to 30 stratigraphically aligned samples may be collected at a field site and are subsequently analyzed in the laboratory. Several hundred analyses may be involved in a single field project (Ruhe and Olson, 1978). The large amount of X-ray work, in addition to other analyses that must be performed, does not permit "in-depth" analysis of the clay mineralogy by known techniques of saturation with inorganic or organic compounds.

In translating the peaks of a diffraction pattern to an estimate of the quantities of the clay minerals in a sample, many problems may be encountered as have been discussed by Jackson (1956, 1975), Brindley (1961), and Dixon and Weed (1977). Regardless of these problems, the intensities of diffraction peaks, measured from peak heights or peak areas, do relate to the quantities of clay-mineral species present, and estimates of these quantities may be made by the method of known additions of an internal standard (Jackson, 1975; Brindley, 1961). In such methods, differing known weights of a standard are added to a soil containing the same component, and by measuring X-ray diffraction intensities before and after additions, the approximate weight proportion of that component can be estimated.

In the present work the procedure has been reversed. Increasing proportions of soil clay are added to a constant weight of a standard, and through a sequential change in X-ray diffraction intensities from 100% standard to 100% soil clay, estimates of the quantities of various components of the soil clay can be made.

LABORATORY METHODS

For X-ray powder diffraction analysis, oriented glass slides were prepared from the <2-μm fraction of the standard, the standard plus additions of soil clay, and the soil clay. The <2-μm fractions were separated by sedimentation following dispersion with sodium metaphosphate $(NaPO_3)_6$ buffered with sodium carbonate as employed for particle-size analysis by the pipet method (Soil Survey Staff, 1972). Duplicate slides were prepared. One slide was X-rayed before and after heating for 15 min at 450°C. The other slide was glycolated (ethylene-glycol vaporization in a desiccator for 48 hr) and then X-rayed. On selected samples a third slide was X-rayed following heating at 600°C. A Philips-Norelco XRG-2500 machine was used with Ni-filtered CuKα radiation with a scanning rate of 2° 2θ/min from 3° to 30° 2θ.

The clay-mineral standard is a 1:1:1 mix by weight of the <2-μm fractions of kaolinite KGa-1, montmorillonite TX-1 (The Clay Minerals Society standards), and illite (Blaylock, Oklahoma). The <2-μm fraction of soil clay was added to the standard mix in weight ratios of 0.5:3, 1:3, 2:3, 4:3, and 10:3. Thus, the 0.5:3 mix is half a part soil clay, one part kaolinite, one part illite, and one part montmorillonite or 14% weight percent soil clay, and the amount of soil clay in the mixes ranges from 0% (standard only) to 14, 25, 40, 57, and 77% in the mixes, to 100% (soil clay only). The sequence of seven samples was X-rayed before and after glycolation and after heating.

All mixtures of soil clay and standard were prepared in the wet state. A known volume of a stock suspension

of the 1:1:1 standard was corrected for the sodium metaphosphate dispersant and sodium carbonate buffer. Independently, the weight of <2-μm soil clay was determined by the standard pipet method of particle-size analysis (Soil Survey Staff, 1972). Aliquots of soil-clay suspensions of the desired weight ratios of 0.5:3 to 10:3 were added to the extractants from the standard stock. After thorough mixing by shaking, glass slides were prepared for X-ray work.

The change in X-ray powder diffraction patterns of the sequence (sample R-12) is evident in smoothed tracings following glycolation shown in Figure 1. The increasing intensity of the 14-Å peak of the soil clay is accompanied by the decreasing intensity of the 17-Å peak of the standard. The sequential change is illustrated more clearly by dismembering and reassembling the patterns as shown in Figure 2.

ANALYSIS OF X-RAY POWDER DIFFRACTION PATTERNS

Clay minerals are identified as follows: Kaolinite(K) has a 7.2-Å basal spacing which disappears on heating to 600°C leaving peaks only at 3.34, 4.98, and 10 Å. This indicates that little chlorite is present. Illite (I) has a 10-Å spacing before and after glycolation. Expandable clay minerals (X) (vermiculite and montmorillonite) have peaks at ~14 Å (air dry) and ~17 Å following glycolation that collapse to 10 Å on heating to 450°C.

The peak areas of the 7.2 (K), 10 (I), 14, and 17 Å reflections were measured after glycolation. See the 17-Å peak (Figure 2, X-3) for graphic definition of peak area where peaks are readily separable, or a plateau area (Figure 2, X-6) where 14- and 17-Å peaks merge in a composite pattern. The 14- and 17-Å peak areas were summed (X).

Peak-area ratios were calculated for K, I, and X of each diffraction pattern by dividing the sum of the peak areas for all three components into respective peak areas for each component:

$$\frac{K\ area}{K + I + X\ areas}, \quad \frac{I\ area}{K + I + X\ areas}, \quad and \quad \frac{X\ area}{K + I + X\ areas}.$$

These values may thus be expressed as relative ratio percentages (Figure 2).

Next, the ratio percentages for K, I, and X were plotted for the standard (0% soil clay), through increasing percentages of soil mix (14 to 77%) to the 100% soil clay (Figure 3). Curves were fitted mathematically for K, I, and X from the standard through the soil mix of 77% (10:3) and were then projected to the 100% soil clay. Peak-area ratios were *predicted* for the soil clay (Kp, Ip, and Xp) and compared to measured values obtained from the diffraction patterns. Note the reasonable agreement between predicted and measured values for sample Or-9g (Figure 3). Note further that, the curve for K is a parabolic function, while for I and X, the curves are linear. Among the 19 experimental sets, the
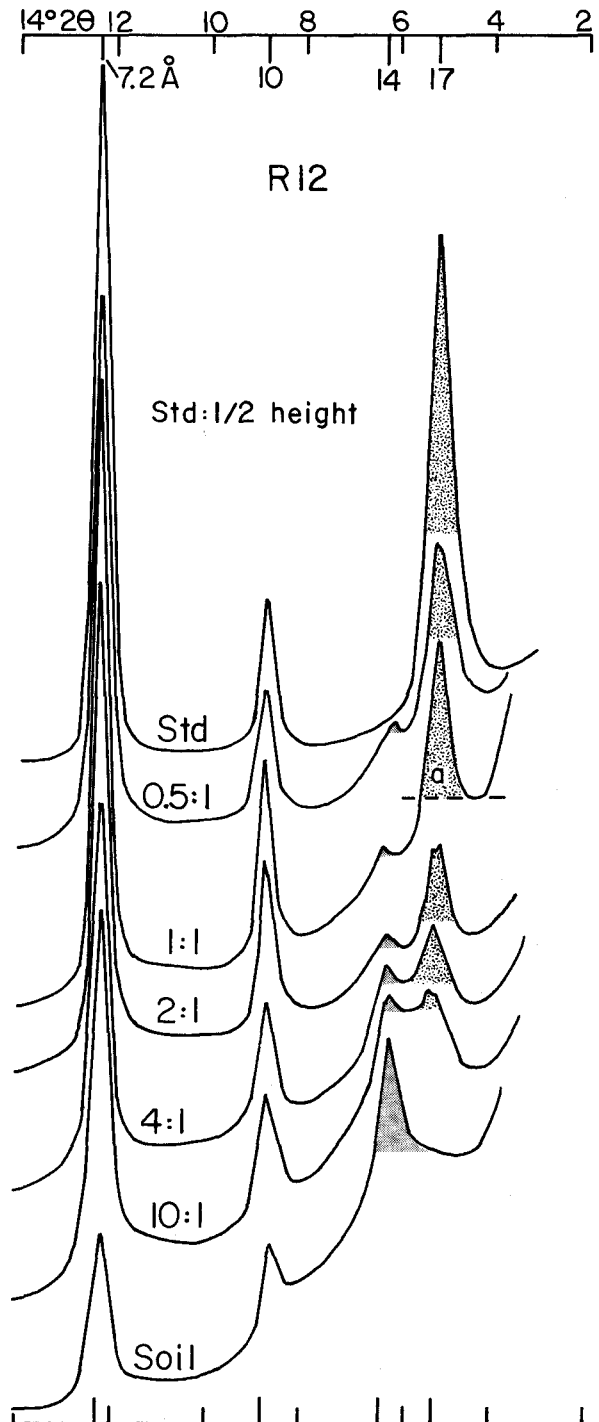

Figure 1.   Smoothed X-ray powder diffraction patterns following glycolation of sample R-12 showing progressive changes from the standard, through a sequence of increasing additions of soil clay to the standard, and the soil clay. Mixes are 0.5 part soil clay to 3 parts by weight of standard, etc. Standard scale is half the peak heights of other patterns.
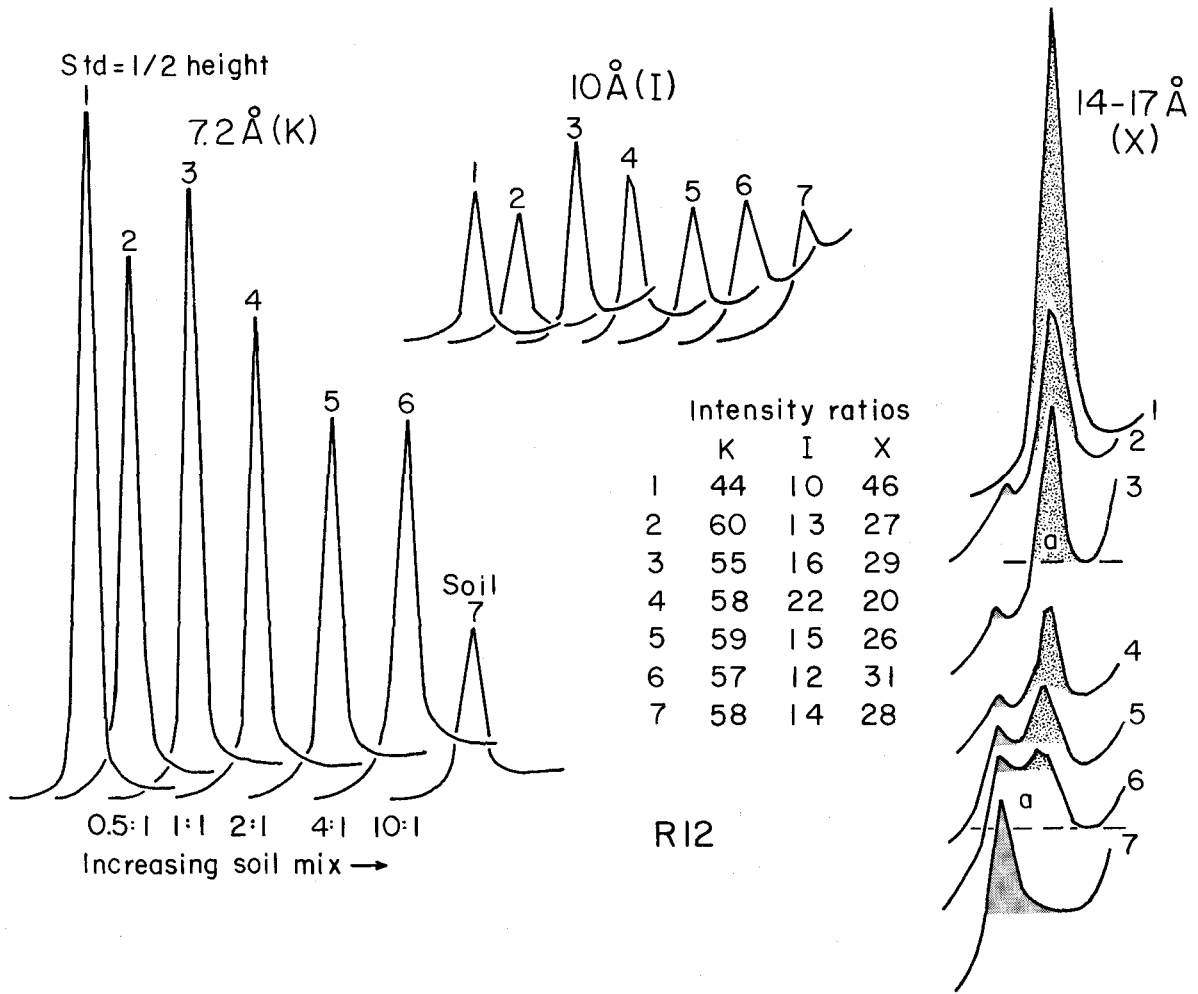
Intensity ratios

	K	I	X
1	44	10	46
2	60	13	27
3	55	16	29
4	58	22	20
5	59	15	26
6	57	12	31
7	58	14	28

R12

Figure 2.   Dismembered X-ray powder diffraction patterns following glycolation of sample R-12. Cf. Figure 1. Peak area is graphically defined by area a above broken line in X-3 and X-6. Peak-area ratios (times 100) for components are given for sequential changes in peaks from standard (1) to soil clay (7).
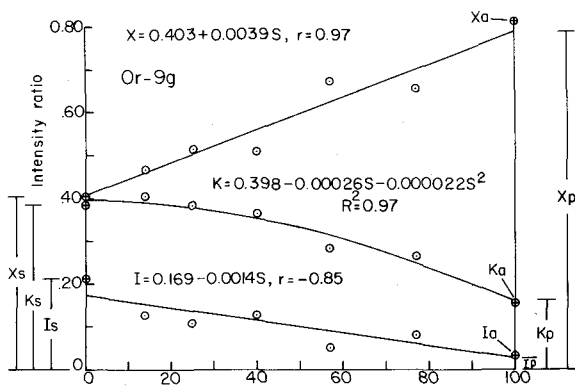

Figure 3.   Mathematical fit of regression lines showing sequential changes in peak-area ratios from standard through mix of 10:3. Projections to 100% soil clay theoretically predict peak-area ratios Kp, Ip, and Xp. Measured actual values are Ka, Ia, and Xa. Peak-area ratios for the standard are Ks, Is, and Xs. Regression equations and coefficients of correlation and determination are given. Sample is Or-9g.

mathematical variations from standard to soil clay for any component may be linear, logarithmic, exponential, hyperbolic, or polynomial. Any one set may have three different mathematical expressions. For the 19 experimental sets, close agreement was obtained between predicted and observed peak area ratios for the unmixed soil clays (Figure 4).

Because the peak-area ratios Ks, Is, and Xs in the standard (Figure 3) correspond to a weight proportion of 33.3% each, the predicted intensity ratios for 100% soil clay, Kp, Ip, and Xp should do likewise. In sample Or-9g (Figure 3) the prediction equations for Kp, Ip, and Xp in general form are:

$$Kp = a - bS - cS^2$$

$$Ip = a - bS$$

$$Xp = a + bS$$

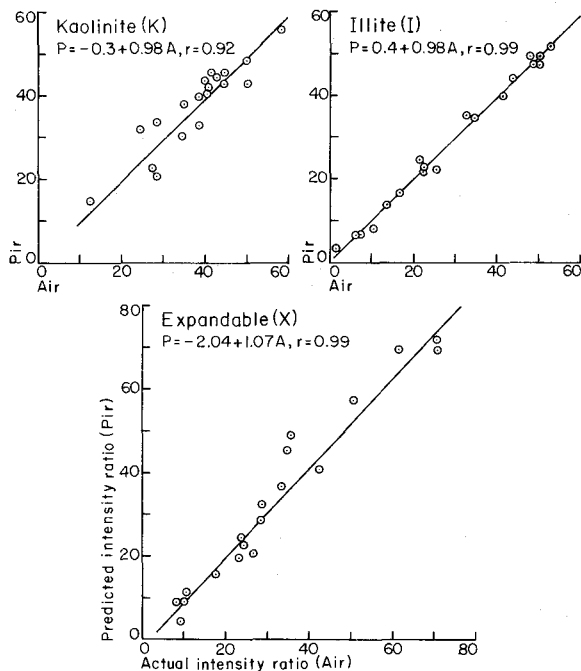where S is the soil clay %, and a is a constant corre-

Figure 4. Comparisons of theoretically predicted peak-area ratios (Pir) and measured, actual peak-area ratios (Air) for K, I, and X at 100% soil mix in 19 experimental sets. Note that the relations are almost 1:1 for all components.
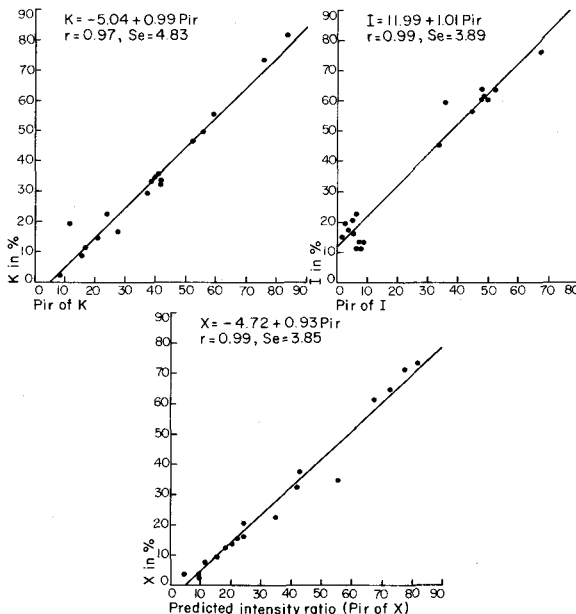

Figure 5. Relations of calculated amounts (%) of K, I, and X and their predicted peak-area ratios. The equations are predictive models for estimating the amount of each component.

sponding to the peak-area ratio for the standard clay. It therefore follows that a is equal to 33.3% for each equation (weight proportion of standard) and that this value can be substituted for a. Each equation can then be solved for 100% soil clay ($S = 100$). In sample Or-9g:

$$K = 0.333 - 0.00026(100) - 0.000022(100^2)$$
$$= 0.087 \quad \text{or} \quad 9\%$$
$$I = 0.333 - 0.0014(100)$$
$$= 0.193 \quad \text{or} \quad 19\%$$
$$X = 0.333 + 0.0039(100)$$
$$= 0.723 \quad \text{or} \quad 72\%$$

A similar procedure can be carried out for the 18 other experimental sets. The weight proportions, then, can be related to predicted peak-area ratios (Figure 5), and general prediction equations can be calculated for components as:

$$K\ (\%) = -5.04 + 0.99 Pir_K$$
$$I\ (\%) = 11.99 + 1.01 Pir_I$$
$$X\ (\%) = 4.72 + 0.93 Pir_X$$

These predictions have coefficients of correlation of 0.97 to 0.99 and standard errors of estimate of 4 to 5%. Because predicted and actual peak-area ratios are in

close agreement (Figure 4), the actual peak-area ratios of unknown samples of a larger array, from which the experimental sets were selected, now can be substituted for the predicted peak-area ratios of K, I, and X, allowing weight proportions to be estimated.

The 19 soil samples examined in this study were selected to represent the range of X-ray powder diffraction patterns found in 145 analyses from a field study of loesses and associated paleosols in southwest Indiana (Ruhe and Olson, 1978). For the remaining 126 samples, the prediction equations slightly overestimate the sums of components. The mean sum was 101.2% with a standard deviation of 2.9% and a range of 95.7 to 104.8%. Perhaps wider discrepancies than the range of a 10% error would result if the method were seriously in fault.

No claim is made for universal use of the general prediction equations. They apply only to the cited study. For example, this method of additions of proportions of soil clay has been used in an ongoing study of the origin of terra rossa on limestone and other soils associated with sandstone, siltstone, and shale in southern Indiana. The general prediction equations for K, I, and X in these soils differ from those formulated for the study of loess and associated paleosols. Consequently, if this method of additions is used, it should be tested for each new situation.

ACKNOWLEDGMENTS

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Резюме—Метод известных добавок для оценки содержания глинистых минералов был изменен таким образом, что почвенная глина добавлялась в увеличивающейся пропорции к эталону, составленному из равных весов каолинита, иллита, и монтмориллонита. После гликоляции были вычислены отношения пиковых зон от дифракционных пиков 7,2 (каолинит), 10 (иллит), 14 и 17 Å (вермикулит и монтмориллонит) для эталона, смесей, и почвенной глины. Строились графики зависимостей отношений и % почвенной глины, начиная от эталоиа (0%) до смесей (14 до 77%). Вычисленные интерполяционные кривые экстраполированы до 100% почвенной глины, что определило теоретические значения, соответствующие измеренным значениям. Поскольку пропорции веса известны в эталоне, экстраполяции позволяют высчитать приблизительные пропорции веса глинистых минералов в почвенной глине.

Resümee—Die Methode für die Bestimmung von Tonerden, in der bekannte Additionen zugemischt werden, wurde herumgedreht, indem zunehmende Mengen von Tonerden zu einem Standart gegeben wurden, der aus gleichen Gewichtsteilen von Kaolinit, Illit, und Montmorillonit bestand. Nach Glykolierung wurden die Verhältnisse der Signalflächen für Standart, Mischung, und Tonerden von den 7,2 (Kaolinit), 10 (Illit), 14 und 17 Å (Vermiculit und Montmorillonit) Diffraktionssignalen berechnet. Die Verhältnisse wurden gegen Prozent Erden vom Standart (0%) bis Mischungen (14 bis 77%) graphisch dargestellt. Anpassungskurven wurden berechnet und auf 100% Tonerde projektiert, was theoretische Werte ergibt, die mit den gemessenen Werten übereinstimmen. Da die Gewichtsproportionen im Standart bekannt sind, erlauben diese Projektionen die Bestimmungen der Verhältnisse von Ton zu Mineralien in den Tonerden.

Résumé—La méthode d'additions connues pour estimer le contenu minéralogique d'argile a été inversée de sorte que des proportions croissantes de sol argilique ont été ajoutées à une norme composée de poids équivalents de kaolinite, d'illite, et de montmorillonite. Après la glycolation, des rapports de régions de sommet ont été calculés de 7,2 (kaolinite), 10 (illite), 14 à 17 Å (vermiculite et montmorillonite) des sommets de diffraction de la norme, des mélanges, et du sol argilique. Ces rapports ont été comparés graphiquement au % du sol argilique de la norme (0%) jusqu'à celui des mélanges (14 à 77%). Des courbes ont été calculées et projetées à 100% du sol argilique fournissant des valeurs théoriques qui s'accordent avec les valeurs mesurées. Comme les proportions de poids sont connues dans la norme, les projections permettent des estimations de proportions de poids d'argile dans le sol argilique.