

## QUANTITATIVE CLAY MINERAL ANALYSIS USING SIMULTANEOUS LINEAR EQUATIONS<sup>1</sup>

L. J. JOHNSON

Department of Agronomy, The Pennsylvania State University  
University Park, Pennsylvania 16802

C. H. CHU

A & L Eastern Agricultural Laboratory  
Richmond, Virginia 23234

G. A. HUSSEY

Agricultural Extension, The Pennsylvania State University  
University Park, Pennsylvania 16802

**Abstract**—A program of simultaneous linear equations has been developed to calculate component proportions and/or component property values for mineral mixtures in soil clays and sediments. The analysis is based on quantitatively measured chemical and physical properties of samples and involves (1) qualitative identification of the mineral components in the mixture by any appropriate means; (2) quantitative measure of the sample property values selected for use in the program; (3) estimation of the proportion of each component in the mixture by a technique such as X-ray powder diffraction; (4) assignment of limits to component property ranges; (5) selection of one of four available calculation options and application of the simultaneous linear-equations program; (6) examination of the residuals of the analysis and, if appropriate, adjustment of the initial estimates for component proportions or property ranges and then repeating step 5; and (7) verification of the final component proportions by comparison with information from step 1. Completeness and/or accuracy of the final results for component proportions may be checked by the closeness of approach to 1.0 for the sum of the component proportions. The method requires that, at minimum, the number of properties measured must equal the number of components in the samples being analyzed and that the minimum number of samples must equal the number of properties measured.

Using the clay fractions of 15 Pennsylvania soils containing kaolinite, illite, smectite, vermiculite, chlorite, interstratified vermiculite/chlorite, quartz, and noncrystalline material, and measuring methylene blue cation-exchange capacity, the amount of Ca displaced by Mg from a Ca-saturated clay, the amount of K displaced by  $\text{NH}_4$  from a K-saturated clay heated to 110°C, %  $\text{K}_2\text{O}$ , %  $\text{SiO}_2$ , % MgO, and weight loss at 110°–300°C and 300°–950°C, the adjustment of property values was found to have the lowest residual value and the most consistent results. The source of analytical errors was also located by examination of residual tables. Samples that were similar in composition gave more reliable component proportions.

**Key Words**—Cation-exchange capacity, Chemical analysis, Linear equations, Mineral analysis, Quantitative mineralogy, Weight loss.

### INTRODUCTION

The mineralogical composition of the clay fraction of a soil is one of the critical factors determining soil chemical and physical properties. The relation between qualitative clay-mineral composition and such soil properties as swelling potential, exchange capacity, and selective adsorption of ions is commonly discussed or implied. Precise assessments of these associations, however, are much less frequent, probably because of the difficulty in obtaining quantitative mineralogical

data for the sample under investigation. Qualitative information is commonly obtained by instrumental methods such as X-ray powder diffraction (Brindley, 1980; MacEwan, 1946) or differential thermal analysis (Barshad, 1965; MacKenzie, 1961); however the reliability of these methods can be severely limited when working with heterogeneous materials such as soil clay.

Attempts to obtain quantitative data have led to the development of methods that depend on the chemical and physical properties of clay (Alexiades and Jackson, 1966). In this approach, a chemical or physical property unique to or a dominant function of a single component is used as a quantitative measure. In general, each property is interpreted in terms of a single min-

<sup>1</sup> Authorized for publication as Paper No. 5651 in the Journal Series of the Pennsylvania Agricultural Experiment Station, University Park, Pennsylvania 16802.

eral. The reliability of the data is generally estimated by measuring how closely the component sum approaches 100%. McNeal and Sansoterra (1964), using methods similar to that of Alexiades and Jackson (1966), developed a set of simultaneous equations for the determination of montmorillonite, vermiculite, and chlorite. Pearson (1978) used total silicate-analysis data in simultaneous equations for the quantitative clay mineral analysis of fine-grained sedimentary rocks.

A logical extension of this procedure is to account for each chemical or physical property in terms of *all* components present in a clay sample rather than a single component. A simultaneous linear-equations program was developed by Hussey (1972) using rigorous evaluation of the chemical and physical properties for the quantitative determination of clay components. The program is similar to the analytical method of McNeal and Sansoterra (1964) except that the Hussey technique allocates sample properties to all components and provides for a range of component properties rather than assigning a single, fixed value. Four options are available with the program for calculating: (1) the component proportions with properties fixed, (2) the component property values with proportions fixed, (3) both the proportions and the property values adjusting proportions first, or (4) the same as (3) except that property values are adjusted first. Hussey (1972) applied the program to soil clay samples within a given profile, i.e., samples with similar component properties, and found that the results were considerably improved over the initial estimates produced by the common quantitative techniques.

The objectives of the present paper are (1) to evaluate Hussey's (1972) four computation options, (2) to illustrate the use of residuals in locating possible sources of error, and (3) to show the application of the program to soil clay samples which are derived from diverse parent materials.

### THEORY

In the quantitative clay analysis of Alexiades and Jackson (1966) each component in a sample is quantitatively evaluated on the basis of a single, measurable chemical or physical property. Chlorite and smectite contents, for example, are estimated from the following properties:

chlorite—from the weight loss between 300° and 950°C corrected for the weight losses of other components and weight gain for iron oxidation; and  
smectite—from the cation-exchange capacity determined by displacement of potassium by ammonium on a sample heated to 110°C (CEC K/NH<sub>4</sub>); corrections are made for other constituents.

For the technique described below no new analytical methods have been developed. The data collected by the methods of Alexiades and Jackson or any other

data that may be deemed appropriate can be used. The innovation exists in the manner of interpretation and calculation. It is assumed in the proposed technique that each component in a heterogeneous clay sample contributes to a measurable property of the sample in linear proportion to its content. The measured property of the sample is therefore the sum of the contributions of each of the sample's components as represented in the equation:

$$B_{pq} = \sum_r \alpha_{rp} \chi_{rq}, \quad (1)$$

where B represents the measured value of a property (number p) for a sample (number q),  $\alpha$  is the value of the property p for component r contained in sample q, and  $\chi$  is the proportion of component r in sample q.

The minimum number of properties p to be measured must equal the number of components r in sample q. An equation is thus derived for each property resulting in a set of simultaneous linear equations, which, for a three-component sample would be:

$$\begin{aligned} B_{11} &= \alpha_{11}\chi_{11} + \alpha_{21}\chi_{21} + \alpha_{31}\chi_{31} \\ B_{21} &= \alpha_{12}\chi_{11} + \alpha_{22}\chi_{21} + \alpha_{32}\chi_{31} \\ B_{31} &= \alpha_{13}\chi_{11} + \alpha_{23}\chi_{21} + \alpha_{33}\chi_{31}. \end{aligned} \quad (2)$$

Each three-component sample would have a similar set of equations. If the property values are known for each component in a sample, then by measuring the sample properties B and substituting the values in Eq. (2) the unknowns, i.e., weight proportion of each component, can be calculated. Solutions are conveniently obtained by matrix algebra methods. Eq. (2) may be represented by the vector equation:

$$B = A \cdot \chi, \quad (3)$$

where:

$$\begin{aligned} B &= \begin{Bmatrix} B_{11} \\ B_{21} \\ B_{31} \end{Bmatrix} \text{ is the sample property vector,} \\ A &= \begin{bmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{bmatrix} \text{ is the component property} \\ &\quad \text{matrix, and} \\ \chi &= \begin{Bmatrix} \chi_{11} \\ \chi_{21} \\ \chi_{31} \end{Bmatrix} \text{ is the component} \\ &\quad \text{proportion vector.} \end{aligned}$$

When A and B are known,  $\chi$  may be calculated by:

$$\chi = A^{-1} \cdot B, \quad (4)$$

in which  $A^{-1}$  is the inverse of A. As an example, assume a clay mixture that contains three components—kaolinite, smectite, and vermiculite—and that the three properties to be used as quantitative measures are weight loss at 300°–950°C, CEC K/NH<sub>4</sub>, and CEC Ca/Mg.

Table 1. Property values of clay components and a clay mixture.

Property	Kaol	$\alpha^1$ Smec	Verm	B Clay mixture
Wt. loss 300°-900°C (%)	14	5	5	11.4
CEC Ca/Mg (meq/100 g)	10	100	160	49.0
CEC K/NH <sub>4</sub> (meq/100 g)	10	100	10	19.0

<sup>1</sup> Kaol = kaolinite; Smec = smectite; Verm = vermiculite.

The property values of the components,  $\alpha$ , and the clay mixture, B, are listed in Table 1. Substituting these values in Eq. (3) and solving according to Eq. (4) gives:

$$\chi = A^{-1} \cdot B$$

$$= \begin{pmatrix} 0.074 & -0.0022 & -0.0014 \\ -0.0074 & -0.00044 & 0.0108 \\ 0.0 & 0.0067 & -0.0066 \end{pmatrix} \cdot \begin{pmatrix} 11.4 \\ 49.0 \\ 19.0 \end{pmatrix} \quad \text{and}$$

$$\chi_{11} = \% \text{ kaol}/100 = 0.70$$

$$\chi_{21} = \% \text{ smec}/100 = 0.10$$

$$\chi_{31} = \% \text{ verm}/100 = 0.20$$

$$\Sigma = 1.00$$

Three assumptions underlie the above analysis: (1) All clay components in a sample are identified,

$$\sum_{i=1}^{i=r} \chi_i = 1.00;$$

(2) The measured sample property values are an accurate estimate of the true values; and (3) Property values,  $\alpha$ , of the clay components are known and, when more than one sample is included in the analysis, are similar for all samples.

Efforts to fulfill the requirement of assumption (1) necessitate a thorough qualitative analysis of the sample or samples. This information is needed before a final decision is made about the chemical and physical properties to be measured. Errors in measurement of the property values will result in deviation of the component proportions from the true values. This error is relatively greater the smaller the proportion of a component in a sample. With respect to assumption (3) there is often as much, if not more, uncertainty about the properties of the clay components in a sample than there is in the proportion contained. Characterization of the properties,  $\alpha$ , of a specific component in a mixture such as a soil clay can be a formidable task. Either the interference of associated material must be corrected for or the specific component of interest must be isolated, without alteration of its properties, before

characterization. In either case, difficulties abound leaving considerable uncertainty as to the appropriate property value to use. Complications arise because of variation in such factors as ionic substitution, crystallinity, and particle size. It would be desirable to calculate simultaneously both component property values and component proportions; this obviously is impossible for the method described above because there would be  $2n$  unknowns and only  $n$  equations.

An approximate solution to this dilemma was described by Booth (1966), and the calculations involved were programmed for the computer in FORTRAN by Hussey (1972). An abbreviated description of this procedure follows. Referring to Eq. (3), if the value for  $\chi$ , the component proportions, were known, the component properties could be calculated:

$$A = \chi^{-1} \cdot B. \quad (5)$$

This calculation requires that the number of samples analyzed must equal (or exceed) the number of properties in order to derive the required matrix for  $\chi$ . But if both A and  $\chi$  are unknown, how can the calculation of either commence? By the method of Booth (1966), estimated (or approximate) values of the unknowns can be used to initiate a calculation. When estimates are used, deviations from the true values are highly probable, and the equality in Eq. (3) no longer applies. The larger the deviation of the estimates from the true values the greater will be the magnitude of the inequality or error involved in using Eq. (3). To apply the Booth method to clay analysis, the best available values are assigned to A, the component properties, and estimated values E are used for  $\chi$ , the component proportions. Best available values are obtained from a search of the literature or from laboratory measurements. Estimates E for  $\chi$  may be derived by any appropriate technique such as X-ray powder diffraction, differential thermal analysis, and/or the procedures of Alexiades and Jackson (1966). The dot product  $A \cdot E$  does not equal B, but is an estimate of it. The differences between the two is called the residual,  $r$ , where:

$$r = (A \cdot E) - B, \quad (6)$$

and is a measure of the error involved in using the assigned and estimated values for A and  $\chi$ . A residual,  $r$ , results from each sample analyzed or property measured and can be positive or negative. To arrive at a single overall measure of the error a grand residual,  $R^2$ , is calculated by summing  $r^2$ :

$$R^2 = \sum_{i=1}^{i=q} r_i^2.$$

The objective is to reduce the error, measured by  $R^2$ , to a minimum. Booth's technique derives new estimates, E, so as to decrease  $R^2$  toward zero. These new estimates are arrived at by applying a correction to the

previous estimate that is a function of the current value of  $r$  and the assigned values for  $A$ :

$$E_{n+1} = E_n - \left[ \left( \frac{r \cdot AA'r}{AA'r \cdot AA'r} \right) \cdot A'r \right],$$

where  $E_n$  is the present estimate of the component proportion,  $E_{n+1}$  is the new estimate,  $r$  is the current value of the residual,  $A$  is the component property matrix, and  $A'$  is the transpose of  $A$ . New estimates serve to calculate new, reduced residuals which in turn are used to derive new estimates. This cycle or iterative process is continued until  $R^2$  reaches a minimum. The criterion for minimization is four hundred iterations unless a minimum is attained at an earlier stage as indicated by an increase following a continuous series of reductions in  $R^2$ .

A similar iterative process can now be applied to adjust values of component property values, with the newly adjusted component proportions remaining fixed, in an attempt to reduce  $R^2$  further. The process of component-property adjustment has a constraint not present in the process for component proportions. Rather than permit the properties to adjust to whatever values a minimization of  $R^2$  would require, fixed ranges are established for each component property within which the adjustments are confined. This recognizes the fact that the specific property of a given component type may differ for samples of different origin. The difference will not assume any arbitrary value but will be within some finite range. The CEC Ca/Mg of kaolinite, for example, will not equal, e.g., 30 meq/100 g, but will very likely fall within the range 5–10 meq/100 g. Upper and lower limits are thus assigned to each component property. These limits are derived from a search of the literature. Information of this kind, however, is of limited availability, and for some materials personal laboratory experience must be used to arrive at reasonable values. Because in the calculating process, single values of the component properties are used, to commence calculation the midpoint of the range is assigned as the initial value. In an ideal situation, where the true component property values are known, only adjustments to proportions are necessary. Accuracy of the calculated proportions is then a function only of the sample properties.

The technique for adjusting component property values does, none the less, offer a promising opportunity. It provides a method for calculating the property or properties of a component within a mixture when the proportions and properties of the other components are known. The calculation becomes increasingly possible when more reliable data on component properties within mixtures are accumulated. The program then can alternately adjust component properties (proportions remaining fixed) and component proportions (properties remaining fixed) to attain a minimi-

zation of the total grand residual which is the sum of the grand residuals over samples or over properties. When the last value of the total grand residual does not differ by more than 3.0% from the penultimate one, minimization is assumed.

The output of the program is the finally adjusted sets of component property values and proportions. In addition, the residual for each property within each sample can be printed out and examined to determine the property within each sample contributing most to the grand residuals. This technique provides a means of isolating the input data that may be least reliable.

## EXPERIMENTAL

### Materials

Fifteen soils from Pennsylvania (Table 2) were selected, using available mineralogical data, to provide a wide spectrum of clay mineral types and content. The soils were treated with sodium hypochlorite to remove organic matter (Anderson, 1963). After ultrasonic dispersion (Edwards and Bremner, 1967), the clay fraction ( $<2 \mu\text{m}$ ) was separated by sieving and centrifugation. Free iron oxides were removed by the citrate-bicarbonate-dithionite method (Mehra and Jackson, 1960), and the samples were washed free of excess salts ( $\text{AgNO}_3$  test) by deionized water, ethanol and acetone and dried at  $110^\circ\text{C}$ .

### Initial estimate of the component proportions

Two methods were used to give an initial estimate of the component proportions: (1) the X-ray powder diffraction (XRD) technique of Mossman *et al.* (1967), which uses an internal standard, and (2) the quantitative methods of Alexiades and Jackson (1966). The internal standard used was a pyrophyllite obtained from Ward's Natural Science Establishment, Rochester, New York, which was ground and ultrasonically treated in suspension to decrease the particle size to  $<2 \mu\text{m}$ . Fifteen milligrams of the suspended clay-size pyrophyllite was mixed with 150 mg of soil clay. The mixture was mounted on a ceramic slide by suction (Rich, 1969), and powder XRD patterns were obtained for samples after: (1) Mg-saturation and drying at room temperature, (2) Mg-saturation and glycerol treatment, (3) K-saturation and drying at room temperature, (4) K-saturation and heating to  $300^\circ$  and  $500^\circ\text{C}$ , and (5) boiling in 6 N HCl and K-saturation.

The component proportions arrived at by these methods are shown in Table 3. All values, except for quartz and noncrystalline material, were rounded to the nearest 5%.

### Program constraints and sample property selection

A requirement of the simultaneous linear-equations program is that the number of samples, the number of properties, and the number of clay components used

Table 2. Identification number, soil series, horizon, and the parent material of the Pennsylvania soil clays.

Sample	Soil identification number	Soil series	Horizon	Parent material
1	S64Pa 14-15-2	Berks	B22	shale
2	S61Pa 32-53-3	Library	B22gt	shale and limestone
3	S64Pa 22-02-5	Tioga	B23	alluvium
4	S59Pa 19-16-3	Chenango	B3	glacial outwash
5	S64Pa 14-01-1	Edom	Ap	limestone and shale
6	S64Pa 52-08-9	Tioga	C7	alluvium
7	S59Pa 19-19-7	Wellsboro	B3	glacial till
8	S64Pa 26-11-5	Purdy	B23gt	lacustrine deposit
9	S65Pa 20-06-4	Titusville	Bx1g	glacial till
10	S65Pa 28-12-2	Duffield	B1	limestone
11	S62Pa 06-05-7	Edgemont	C1	quartzite
12	S65Pa 28-11-1	Duffield	Ap	limestone
13	S64Pa 14-17-1	Wiltshire	Ap	limestone
14	S61Pa 01-17-3	Mt. Lucas	B22t	diabase
15	S64Pa 14-11-4	Gatesburg	B21	calcareous sandstone

in the computation procedure be equal. Although the program was written to accommodate a maximum of nine samples, the main limiting factor was the number of properties suitable for distinguishing among clay species within a mixture. An ideal property should have a distinct value or range for each clay mineral type. Properties of this kind may not be available for all soil clay components. From the chemical and physical properties determined in this study, eight were selected for use in the computer program, including cation-exchange capacities determined by the methylene blue adsorption (CEC MB) method of Pham Thi Hang and Brindley (1970), by the amount of Ca displaced by Mg from a Ca-saturated clay (CEC Ca/Mg), and by the amount of K displaced by NH<sub>4</sub> from a K-saturated clay heated to 110°C; % weight loss between 100° and 300°C and between 300° and 950°C; and % K<sub>2</sub>O, % SiO<sub>2</sub>, and % MgO by the method of Medlin *et al.* (1969). The measured values of these

properties for the samples are listed in Table 4. Feldspar was not included in the computer analysis in order to limit the number of components to eight. The values for % K<sub>2</sub>O and % SiO<sub>2</sub> in Table 4 were corrected accordingly.

#### Component property ranges

An upper and lower limit for each component property was assigned based on data available in the literature or from unpublished laboratory measurements. The ranges used are given in Table 5. The midpoint of the range was used as the initial value for the component property in the computer program.

#### Sample grouping

Inasmuch as eight properties were selected to be used in the computer program, the 15 samples had to be divided into groups of 8 samples each. Four groups (I-IV) were formed emphasizing either within group sim-

Table 3. Initial estimate (%) of the component proportions.<sup>1</sup>

Sample	Kaol	Verm	Smec	Illi	Ch	Verm-ch	Qtz	Nonc	Total
1	5	5	0	25	10	35	13	5	98
2	5	5	20	60	5	0	3	2	100
3	15	10	5	40	10	10	3	6	99
4	5	15	0	30	15	20	10	5	100
5	5	10	5	15	10	20	27	6	98
6	5	15	5	35	10	20	3	4	97
7	5	5	0	60	15	5	5	4	99
8	50	5	5	30	0	0	3	5	98
9	15	10	30	15	5	10	7	10	102
10	10	5	30	10	25	5	6	9	100
11	65	0	10	15	0	0	1	9	100
12	10	5	10	10	40	10	9	9	103
13	25	5	10	15	10	10	16	10	101
14	45	30	10	0	0	0	1	15	101
15	75	0	5	10	0	0	6	4	100

<sup>1</sup> Kaol = kaolinite; Verm = vermiculite; Smec = smectite; Illi = illite; Ch = chlorite; Verm-ch = interstratified vermiculite/chlorite; Qtz = quartz; Nonc = noncrystalline.

Table 4. Measured sample properties.<sup>1</sup>

Sample	Cation-exchange capacity (meq/100 g)			Weight loss (%)		Chemical composition (wt. %)		
	Ca/Mg	K/NH <sub>4</sub>	MB <sup>2</sup>	100°–300°C	300°–950°C	K <sub>2</sub> O	SiO <sub>2</sub>	MgO
1	14.7	10.9	9.0	1.4	6.7	3.5	55.1	2.0
2	32.2	22.2	23.0	0.6	5.7	6.0	53.5	1.6
3	25.2	19.3	16.0	1.4	7.5	4.6	47.9	1.9
4	16.9	13.1	10.0	1.4	7.3	3.4	50.0	2.2
5	25.5	18.5	16.0	0.8	6.3	2.6	65.5	2.2
6	25.6	16.9	13.0	1.3	6.5	4.7	47.0	2.3
7	16.6	12.2	10.0	0.5	7.0	6.1	49.3	2.4
8	19.3	15.9	16.0	1.4	8.5	3.5	49.3	1.2
9	52.2	36.9	39.0	1.5	7.7	2.6	55.1	1.6
10	40.2	33.0	34.0	2.5	8.3	1.6	50.7	6.6
11	13.9	11.2	11.0	1.3	11.5	1.9	51.9	0.9
12	26.8	19.4	18.0	2.0	8.3	1.8	49.1	8.6
13	24.2	20.2	17.0	1.2	8.1	2.5	53.6	2.4
14	36.0	27.3	26.0	3.1	10.2	0.5	50.9	2.4
15	15.0	10.0	7.0	0.5	10.8	1.2	51.4	0.9

<sup>1</sup> All properties are based on 110°C dried sample weight except % SiO<sub>2</sub>, which is based on 950°C dried sample weight.

<sup>2</sup> Methylene blue.

ilarity (I, II) or diversity (III, IV) of clay mineral types. Illite is the dominant clay in Group I, samples 1 to 8, and kaolinite or montmorillonite is the dominant clay in Group II, samples 8 to 15. Group III consists of samples 5 to 12; Group IV of samples 1 to 4, 8, and 13 to 15. Sample 8 was made common to all four groups to provide a reference point for evaluating the influence of within-group clay composition on the calculated component proportions.

## RESULTS AND DISCUSSION

### Comparison of computational options

Four options were available for the computational analysis of the data. In options 1 and 2, component proportions and component properties are calculated, respectively, with the other parameter remaining fixed at a single preassigned value. Options 3 and 4 adjust both the component proportions and properties in an alternate stepwise manner. In the first step, one param-

eter remains fixed while the other is adjusted to minimize the residuals. The parameter roles are reversed in the second step, with the new values of the parameter adjusted in step one being the fixed value in step two. The alternate adjustment of the two parameters is continued until the total grand residual ( $\Sigma R^2$ ) reaches a minimum, which is defined as the point where the last value of the total grand residual does not differ by more than 3% from the penultimate value. The two options differ in that option 3 adjusts component proportions, whereas option 4 adjusts component properties in the first step.

The minimization of the total grand residual for the four options is shown in Figure 1 for sample Group I. Comparable results were found for sample Group II. With options 1 and 2 the total grand residual attained a minimum after only 2 to 4 adjustments. This was to be expected because the initial values for component proportions and properties were not true values and the fixed parameter limited the minimization. The ex-

Table 5. Range of property values for clay components.

Component	Cation-exchange capacity (meq/100 g)			Weight loss (%)		Chemical composition (wt. %)		
	Ca/Mg	K/NH <sub>4</sub>	MB <sup>1</sup>	100°–300°C	300°–950°C	K <sub>2</sub> O	SiO <sub>2</sub>	MgO
Kaolinite	5–10	5–10	5–10	0–0	12–14	0–0	52–54	0–0
Vermiculite	120–180	15–25	10–20	0–2	4–6	0–0	40–50	0–6
Smectite	80–120	70–100	80–120	0–2	4–7	0–0	55–65	1–6
Illite	15–30	15–30	15–30	0–2	3–5	9–11	53–58	0–4
Chlorite	15–30	15–30	15–30	0–1	9–14	0–0	30–40	10–40
Vermiculite/chlorite	20–40	15–20	15–25	0–1	4–6	0–0	40–50	0–15
Quartz	0–0	0–0	0–0	0–0	0–0	0–0	100–100	0–0
Noncrystalline	50–100	50–100	10–30	0–1	5–12	0–0	45–55	0–0

<sup>1</sup> Methylene blue.

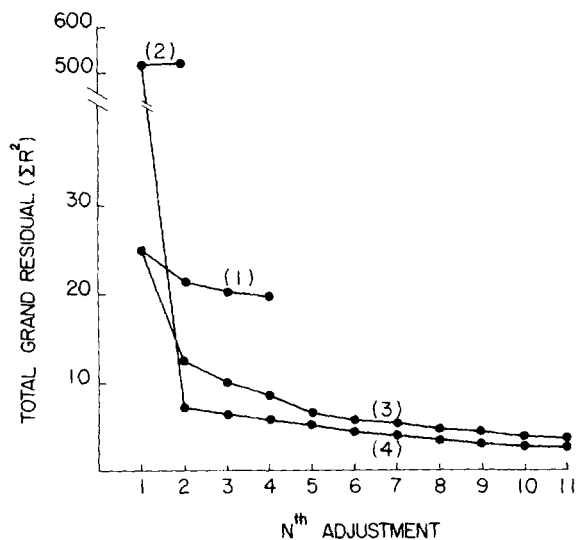


Figure 1. Minimization of the total grand residuals ( $\Sigma R^2$ ) in four options: (1) component proportions adjusted only; (2) component properties adjusted only; (3) component proportions adjusted first; and (4) component properties adjusted first.

ceptionally high residual for option 2 was a consequence of an additional limitation. The property value adjustments were confined to a preassigned range whereas no restriction was imposed on the adjustment of component proportions in option 1. If the true value for one of the parameters were known, an exact solution of the simultaneous linear equations would be possible using options 1 or 2. With the available data, these options were not applicable.

When both parameters were adjusted, option 3 or 4, the total grand residual was decreased to a much lower value than was obtained with option 1 or 2 (Figure 1). The basis used for choosing between option 3 or 4 was the consistency of the program output with the experimental data available. It can be seen (Figure 2) that the largest change of a parameter occurred in the first adjustment. With option 3, which adjusts component proportions first, no restriction on the magnitude of the adjustment other than the reduction of the grand residual ( $R^2$ ) were apparent. Thus, in some samples, a final value for a clay type proportion resulted that was inconsistent with the experimental data. Option 4, which adjusts component properties in the first step, led to no apparent contradictions, probably a consequence of the additional restriction within option 4 where property value adjustments were confirmed to a preassigned range. For this reason option 4 was preferred.

#### Sources of residual

The objective of the computer program was to reduce the total grand residual to a minimum. Reduction

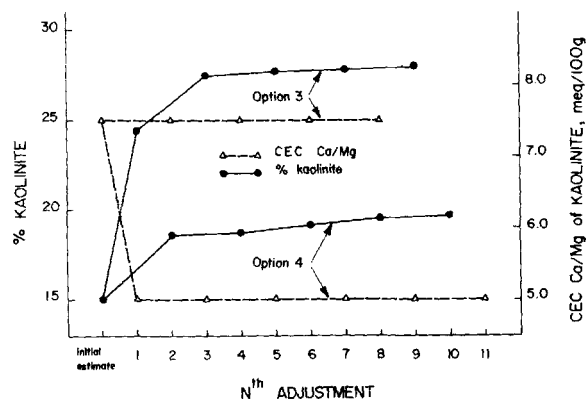


Figure 2. Adjustment of percentage of kaolinite and CEC Ca/Mg for sample 9 using options 3 and 4.

of the total grand residual value for soil clay samples to zero was not possible, mainly because of: (1) the experimental error in determining sample properties, and (2) the diversity of the properties for a given component from sample to sample. The value of the minimized total grand residual was affected by the magnitude of these two factors. From experience, the reasonable value for a minimum total grand residual is below five for a comparable group of samples.

#### Use of residual values to locate sources of experimental error

One of the outputs of the computer program was a table in which the squared residual ( $r^2$ ) for each property within each sample is printed out. By use of this table possible major sources of experimental error that led to a relatively large total grand residual (greater than five) could be isolated. During the initial run of the program, the total grand residual for sample Group II was relatively high, 9.97 (Table 6). Percent weight loss from 110° to 300°C for sample 15 was the major contributor. On review of the experimental data it was found that this sample had the highest percentage of weight loss (110° to 300°C) among the 15 samples (4.03%) and the lowest  $\text{SiO}_2:\text{Al}_2\text{O}_3$  molar ratio (0.4) for material dissolved by 0.5 N NaOH. These data suggested the possibility of gibbsite in this sample. The X-ray powder diffraction pattern was re-examined and a diffraction peak at 4.83 Å, which disappeared on heating the sample to 300°C, was noted. Because of the dehydroxylation of the gibbsite, the observed weight-loss value from 110° to 300°C could not be accounted for by the eight components used. After correcting for the estimated gibbsite content, the contribution to the residual of this property for sample 15 and the total grand residual were reduced (Table 6). The weight loss from 110° to 300°C over all samples, however, was still the major contributor (77%) to the total grand residual (Table 6), suggesting that the ranges assigned to this

Table 6. Residual squares ( $r^2$ ) for 110°–300°C weight loss<sup>1</sup> before and after correction for gibbsite in sample 15 and the grand residuals ( $R^2$ )<sup>2</sup> of Group II.

		Sample number								
		8	9	10	11	12	13	14	15	$R^2$
Before	$r^2$	0.00	0.55	0.08	0.14	0.15	0.33	0.81	7.35	9.41
	$R^2$	0.01	0.61	0.10	0.18	0.16	0.36	0.86	7.69	9.97 <sup>3</sup>
After	$r^2$	0.04	0.22	0.00	0.22	0.10	0.12	0.41	0.09	1.20
	$R^2$	0.05	0.23	0.00	0.30	0.10	0.13	0.45	0.28	1.56 <sup>3</sup>

<sup>1</sup> The small  $r^2$  values for properties other than 110°–300°C weight loss are not included.

<sup>2</sup>  $R^2 = \Sigma r^2$ ; the summation is over properties or over samples.

<sup>3</sup> The total grand residuals ( $\Sigma R^2$ ).

Table 7. Component proportions for sample 8 and total grand residuals ( $\Sigma R^2$ ) for different sample groups.

Sample group <sup>1</sup>	Component proportion (%) <sup>2</sup>								Total	Final $R^2$
	Kaol	Verm	Smec	Illi	Ch	Verm-Ch	Qtz	Nonc		
I	39	3	9	32	4	0	3	3	93	3
II	46	3	8	31	0	0	0	5	93	2
III	42	3	9	31	3	0	2	4	94	3
IV	46	3	9	31	2	0	1	3	95	5

<sup>1</sup> Group I: Samples 1–8; Group II: Samples 8–15; Group III: Samples 5–12; Group IV: Samples 1–4, 8, 13–15.

<sup>2</sup> Abbreviations are the same as in Table 3.

Table 8. Final adjusted component properties for Group I.

Component	Cation-exchange capacity (meq/100 g)			Weight loss (g)		Chemical composition (wt. %)		
	Ca/Mg	K/ $\text{NH}_4$	MB <sup>1</sup>	100°–300°C	300°–950°C	$\text{K}_2\text{O}$	$\text{SiO}_2$	MgO
Kaolinite	5.0	5.7	6.2	0.0	14.0	0.0	52.0	0.0
Vermiculite	120.0	15.2	10.0	1.7	6.0	0.0	40.2	0.1
Smectite	80.0	70.7	85.0	0.9	4.0	0.0	57.9	2.9
Illite	15.0	15.6	15.0	1.0	5.0	11.0	53.0	1.0
Chlorite	15.0	15.0	15.0	0.5	14.0	0.0	30.7	14.8
Vermiculite/chlorite	20.0	15.0	10.0	1.0	5.5	0.0	50.0	0.0
Quartz	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0
Noncrystalline	50.0	50.1	10.0	8.6	12.0	0.0	45.1	0.0

<sup>1</sup> Methylene blue.

property for the clay components are more questionable than those for the other properties.

#### Effects of sample diversity

Inasmuch as sample 8 was made common to all four sample groups, it was used as a reference for the effect of sample diversity. The component proportions for sample 8 and the total grand residual differed when the associated samples were changed (Table 7). If the analytical errors are considered to be similar for all the samples, the magnitude of the total grand residual likely represented the degree of sample diversity in a given group. This diversity is consistent with the smaller total grand residuals for Groups I and II, where an attempt was made to increase compositional uniformity, than for Groups III and IV (Table 7). The results for other groups also showed that the total grand residual was

<1.0 for samples from the same profile and >50 for a group with highly diverse composition. Thus, if a low residual is associated with more reliable values, samples which are similar in composition will yield more dependable component proportions from this type of computation.

#### Adjusted component properties and proportions

The final adjusted properties for Group I are given in Table 8 (the values for Group II are very similar). Most adjusted property values reached a limit of the assigned property range because, in option 4, component properties were adjusted first. Inasmuch as the magnitude of this adjustment was the largest of the series, it more readily forced the component property values to a limit.

Table 9 shows the adjusted values for component



Table 9. Final results (%) for component proportions.<sup>1,2</sup>

Sample	Kaol	Verm	Smec	Illl	Ch	Verm-ch	Qtz	None	Total
1	17	3	0	30	11	10	19	3	93
2	7	8	15	55	4	3	6	1	99
3	15	5	6	42	9	9	1	8	95
4	15	3	0	30	14	15	10	6	93
5	8	5	9	24	12	21	26	5	110
6	2	8	2	42	13	19	3	6	95
7	15	5	0	49	11	0	9	3	92
8	46	3	8	31	0	0	0	5	93
9	20	12	34	23	0	14	0	5	109
10	9	5	25	14	28	3	6	14	104
11	72	2	4	16	2	0	0	4	100
12	11	7	6	16	38	0	11	10	99
13	28	3	7	23	8	21	6	10	106
14	45	7	19	4	8	0	2	18	103
15	68	5	0	10	1	4	4	6	98

$\bar{x} \pm s = 99.3 \pm 6.0$

<sup>1</sup> Results obtained for samples 1–7 are from Group I; samples 8–15 are from Group II.

<sup>2</sup> Abbreviations are the same as in Table 3.

Table 10. The linear correlation coefficient (r) between initial and adjusted component proportions.<sup>1</sup>

	Kaol	Verm	Smec	Illl	Ch	Verm-ch	Qtz	None
r	.97**	.31	.91**	.97**	.95**	.65**	.77**	.80**

\*\* Significant at the .01 level.

<sup>1</sup> Abbreviations are the same as in Table 3.

proportions for Groups I and II. The sum of component proportions averages  $99.3 \pm 6.0\%$ . All values correlated significantly with initial estimates except those for vermiculite (Table 10). The adjusted component proportions are for vermiculite (Table 10). The adjusted component proportions are probably more reliable than the initial ones because of their consistency with the observed chemical and physical properties, a requirement of the method of computation. The accuracy of the adjusted values, however, is dependent on that of the assigned property range. Improvement of the component proportions derived from this program awaits the procurement of more reliable values for soil clay properties.

#### REFERENCES

- Alexiades, C. A. and Jackson, M. L. (1966) Quantitative mineralogical analysis of soils and sediments: in *Clays and Clay Minerals, Proc. 14th Natl. Conf., Berkeley, California, 1966*, S. W. Bailey, ed., Pergamon Press, New York, 35–52.
- Anderson, J. U. (1963) An improved pretreatment for mineralogical analysis of samples containing organic matter: in *Clays and Clay Minerals, Proc. 10th Natl. Conf., Austin, Texas, 1961*, Ada Swineford and P. C. Franks, eds., Pergamon Press, New York, 380–388.
- Barshad, I. (1965) Thermal analysis techniques for mineral identification and mineralogical composition: in *Methods of Soil Analysis*, C. A. Black, ed., Amer. Soc. Agronomy, Madison, Wisconsin, 699–742.
- Booth, A. D. (1966) *Numerical Methods*: Butterworth, London, 76–123.
- Brindley, G. W. (1980) Quantitative X-ray mineral analysis of clays: in *Crystal Structures of Clay Minerals and their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 411–438.
- Edwards, A. P. and Bremner, J. M. (1967) Dispersion of soil particles by sonic vibration: *J. Soil Sci.* **18**, 47–63.
- Hussey, G. A., Jr. (1972) Use of a simultaneous linear equations program for quantitative clay analysis and the study of mineral alteration during weathering: Ph.D. thesis, The Pennsylvania State University, University Park, Pennsylvania, 1–62 (Diss. Abstr. 33:5619, Microfilm No. 73-13994).
- MacEwan, D. M. C. (1946) The identification and estimation of the montmorillonite group of minerals, with special reference to soil clays: *J. Soc. Chem. Ind.* **65**, 298–305.
- MacKenzie, R. C. (1961) The quantitative determination of minerals in clays: *Acta Univ. Carol. Geol. Suppl.* **1**, 11–21.
- McNeal, B. L. and Sansoterra, T. (1964) Mineralogical examination of arid-land soils: *Soil Sci.* **97**, 367–375.
- Medlin, J. H., Suhr, N. H., and Bodkin, J. H. (1969) Analysis of silicate employing LiBO<sub>2</sub> fusion: *At. Absorpt. Newsl.* **8**, 25–29.
- Mehra, O. P. and Jackson, M. L. (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate: in *Clays and Clay Minerals, Proc. 7th Natl. Conf., Washington, D.C., 1958*, Ada Swineford, ed., Pergamon Press, New York, 317–327.
- Mossman, M. H., Freas, D. H., and Bailey, S. W. (1967) Orienting internal standard method for clay mineral X-ray analysis: in *Clays and Clay Minerals, Proc. 15th Natl. Conf., Pittsburgh, Pennsylvania, 1967*, S. W. Bailey, ed., Pergamon Press, New York, 441–453.

- Pearson, M. J. (1978) Quantitative clay mineral analyses from the bulk chemistry of sedimentary rocks: *Clays & Clay Minerals* **26**, 423–433.
- Pham Thi Hang and Brindley, G. W. (1970) Methylene blue absorption by clay minerals, determination of surface area and cation exchange capacities: *Clays & Clay Minerals* **18**, 203–212.
- Rich, C. I. (1969) Suction apparatus for mounting clay specimens on ceramic tile for X-ray diffraction: *Soil Sci. Soc. Amer. Proc.* **33**, 815–816.

(Received 8 April 1983; accepted 2 July 1984)

**Резюме**—Разработана программа для системы линейных уравнений для расчета пропорций компонентов и/или величин свойств компонентов смесей минералов в почвенных глинах и отложениях. Анализ основан на измеренных количественно химических и физических свойствах образцов и включает (1) качественную идентификацию минеральных компонентов в смеси любым соответствующим методом; (2) количественное измерение свойств образцов, предназначенных для использования в программе; (3) определение пропорции каждого компонента в смеси при помощи такого метода, как рентгеновская порошковая дифракция; (4) приписание пределов диапазоном свойств компонента; (5) выбор одной из четырех имеющихся расчетных возможностей и применение программы системы линейных уравнений; (6) проверка разности анализа и, если необходимо, корректировка исходных пропорций компонентов или диапазонов свойств и затем повторение стадии (5); и (7) проверка окончательных величин пропорций компонентов путем сравнения с информацией, полученной в стадии (1). Полнота и точность окончательных результатов по пропорциям компонентов может быть проверена по тому насколько сумма пропорций компонентов близка к 1,0. Метод требует, чтобы число измеряемых свойств равнялось, как минимум, числу компонентов в образцах и чтобы минимальное число образцов равнялось числу измеряемых свойств.

Используя частицы глины 15 почв из Пенсильвании, содержащих каолинит, иллит, смектит, вермикулит, хлорит, слоистый вермикулит/хлорит, кварц и некристаллический материал, и измеряя катионообменную способность метиленовой сини, количество Ca, вытесненное Mg из глины, насыщенной Ca, количество K, вытесненное NH<sub>4</sub> из глины, насыщенной K, подогретой до 110°C, % K<sub>2</sub>O, % SiO<sub>2</sub>, % MgO и потерю веса при 110°–300°C и 300°–950°C, было установлено, что корректировка величин свойств имела наименьшую величину разности и наиболее согласующиеся результаты. Источник аналитических погрешностей был установлен путем проверки таблиц разностей. Образцы, сходные по составу, давали более надежные пропорции компонентов. [E.G.]

**Resümee**—Es wurde ein Programm zur Auflösung simultaner linearer Gleichungen entwickelt, um die Komponentenanteile und/oder Komponenteneigenschaftswerte für Mineralgemenge in Bodentonen und Sedimenten zu berechnen. Die Analyse beruht auf quantitativ gemessenen chemischen und physikalischen Eigenschaften der Proben und beinhaltet (1) die qualitative Identifikation der Mineralkomponenten im Gemenge mittels jeder geeigneten Methode; (2) die quantitative Messung der Probeneigenschaftswerte, die für dieses Programm ausgewählt wurden; (3) die Abschätzung des Anteils jeder Komponente im Gemenge z.B. mittels Röntgenpulverdiffraktion; (4) die Festlegung der Grenzen für die Komponenteneigenschaftsbereiche; (5) die Auswahl von einer der vier zur Verfügung stehenden Berechnungsoptionen und die Anwendung des Programms simultaner linearer Gleichungen; (6) die Prüfung der Residuen der Analyse und, wenn möglich, die Angleichung der ursprünglichen Schätzungen für die Komponenteneigenschaften oder Komponenteneigenschaftsbereiche und dann die Wiederholung des Schrittes 5; (7) Überprüfung der endgültigen Komponenteneigenschaften durch Vergleich mit den Ergebnissen aus Schritt 1. Die Vollständigkeit und/oder die Richtigkeit der Endergebnisse für die Komponenteneigenschaften können dadurch überprüft werden, indem die Summe der Komponenteneigenschaften möglichst nahe an den Wert 1,0 herankommen soll. Die Methode fordert, daß die Zahl der gemessenen Eigenschaften mindestens gleich der Zahl der Komponenten in den zu analysierenden Proben sein muß, und daß die Mindestzahl der Proben gleich der Zahl der gemessenen Eigenschaften sein muß.

Unter Verwendung der Tonfraktionen von 15 Bodenproben von Pennsylvania, die Kaolinit, Illit, Smektit, Vermiculit, Chlorit, Vermiculit/Chlorit-Wechselagerung, Quarz, und schlecht kristallisiertes Material enthielten, und bei denen die Methylenblau-Kationenaustauschkapazität gemessen wurde, sowie die durch Mg ersetzte Ca-Menge bei Ca-gesättigtem Ton, die durch NH<sub>4</sub> ersetzte K-Menge bei einem K-gesättigten Ton, der auf 110°C erhitzt wurde, sowie bei Bestimmung von % K<sub>2</sub>O, % SiO<sub>2</sub>, % MgO, und von dem Gewichtsverlust bei 110°–300°C und 300°–950°C, zeigt sich, daß die Anpassung der Eigenschaftswerte die niedrigsten Restwerte ergeben und die am besten übereinstimmenden Ergebnisse. Die Ursachen der analytischen Fehler wurden durch die Überprüfung der Residuentabellen ebenfalls lokalisiert. Proben mit ähnlicher Zusammensetzung ergaben verlässlichere Komponentenverteilungen. [U.W.]

**Résumé**—Un programme d'équations linéaires simultanées a été développé pour calculer les proportions de composés et/ou les valeurs des propriétés de composés pour des mélanges minéraux dans des argiles et des sédiments de sol. L'analyse est basée sur les propriétés chimiques mesurées quantitativement et les propriétés physiques des échantillons et implique (1) l'identification qualitative des composés minéraux dans le mélange par n'importe quel moyen approprié; (2) la mesure quantitative des valeurs des propriétés des échantillons sélectionnées pour être utilisées dans le programme; (3) l'estimation de la proportion de chaque composé dans le mélange par une technique telle que la diffraction des rayons-X; (4) l'assignation de limites aux gammes de propriétés des composés; (5) la sélection de l'une de quatre options de calculs disponibles et l'application du programme d'équations linéaires simultanées; (6) l'examen des résiduels

de l'analyse, et si c'est approprié, l'ajustement des estimations initiales pour les proportions des composés ou pour les gammes des propriétés et puis la répétition de l'étape 5; et (7) la vérification des proportions de composés finales en comparant avec l'information de l'étape 1. L'entièreté et/ou l'exactitude des résultats finaux pour les proportions des composés peut être vérifiées par la proximité de l'approche de 1,0 pour la somme des proportions des composés. La méthode exige qu'au minimum, le nombre des propriétés mesurées soit égal au nombre des composés dans les échantillons analysés, et que le nombre minimum d'échantillons soit égal au nombre de propriétés mesurées.

En utilisant les fractions d'argile de 15 sols de Pennsylvanie contenant de la vermiculite, de la chlorite, de la vermiculite/chlorite interstratifiée, du quartz, et du matériel non cristallin, et en mesurant la capacité d'échange de cations du bleu de méthylène, la quantité de Ca déplacée par Mg d'un argile saturé de Ca, la quantité de K déplacée par  $\text{NH}_4$  d'un argile saturé de K échauffé à  $110^\circ\text{C}$ , les %  $\text{K}_2\text{O}$ , %  $\text{SiO}_2$ , %  $\text{MgO}$ , et la perte de poids à  $110^\circ\text{--}300^\circ\text{C}$  et  $300^\circ\text{--}950^\circ\text{C}$ , on a trouvé que l'ajustement des valeurs de propriétés avait la valeur résiduelle la plus basse et les résultats les plus consistants. La source d'erreurs analytiques a aussi été localisée par examen de tables de résiduels. Les échantillons qui étaient semblables en composition donnaient les proportions de composés les plus sûrs. [D.J.]