



A semi-quantitative x-ray diffraction technique for estimation of smectite, illite, and kaolinite
by Roger W E Hopper

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Soils

Montana State University

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Abstract:

Two studies are reported.

I. An assessment of the major sources of error in the X-ray diffraction procedure was conducted using a nested design and ANOVA for peak area and clay mineral composition. Clay separation, slide preparation and slide positioning were significant sources of error.

II. Modifications of the factor method for semi-quantitative characterization of clay mineral composition by X-ray diffraction analysis were tested. Samples used in the study were from early Tertiary aged sediments of the Fort Union Formation and associated soils in Southeastern Montana. Estimates of the total CEC of the clay-sized fraction were based on X-ray diffraction results. The accuracy of estimation for each modification was tested by linear regression comparing these estimates with measured CEC values. Variation in measured CEC explained 90% of the variation in estimated CEC, 92% of the variation in smectite composition, and 82% of the variation in kaolinite composition. Percent illite was compared with illite content estimated by total K analysis. Variation in measured illite content accounted for 74% of the variation in estimated illite content.

A modification of the factor method is presented that provides relatively fast and reasonably accurate estimations of percent smectite, illite, and kaolinite for material that does not contain significant portions of vermiculite or chlorite.

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Date

October 28, 1981

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ESTIMATION OF SMECTITE, ILLITE, AND KAOLINITE

by

ROGER W E HOPPER

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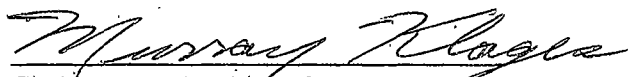
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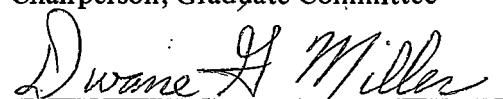
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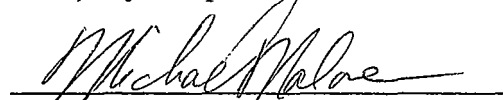
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ABSTRACT

Two studies are reported.

I. An assessment of the major sources of error in the X-ray diffraction procedure was conducted using a nested design and ANOVA for peak area and clay mineral composition. Clay separation, slide preparation and slide positioning were significant sources of error.

II. Modifications of the factor method for semi-quantitative characterization of clay mineral composition by X-ray diffraction analysis were tested. Samples used in the study were from early Tertiary aged sediments of the Fort Union Formation and associated soils in Southeastern Montana. Estimates of the total CEC of the clay-sized fraction were based on X-ray diffraction results. The accuracy of estimation for each modification was tested by linear regression comparing these estimates with measured CEC values. Variation in measured CEC explained 90% of the variation in estimated CEC, 92% of the variation in smectite composition, and 82% of the variation in kaolinite composition. Percent illite was compared with illite content estimated by total K analysis. Variation in measured illite content accounted for 74% of the variation in estimated illite content.

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INTRODUCTION

X-ray diffraction methods are central to studies of the clay fraction of soils with the exception of those soils suspected to contain large amounts of amorphous material. A study of the components of the clay fraction of soil must begin with the proper identification of the minerals present. Quantitative estimations of the clay mineral components have applications to many disciplines.

Several methods have been employed to make quantitative estimations of clay minerals in soil investigations. The factor method used in making the investigations reported here has the advantages of being relatively rapid and precise. However, estimations obtained are relative values. Consequently, the method has been referred to as semi-quantitative. Few investigations report tests of the accuracy of quantitative estimations. McNeal [31] used a combination of chemical and X-ray diffraction methods to make quantitative estimations of the mineralogy of arid and semi-arid land soils.

The objective of this study was to derive a relatively fast and reasonably accurate method of determining clay mineral composition of soils and associated parent material for application to large numbers of samples. Ten modifications of the factor method for semi-quantitative characterization of clay mineral composition by X-ray diffraction analysis were tested for accuracy and precision. Appropriate factors were determined. Estimations of relative mineral composition and cation exchange capacity derived from X-ray diffraction results were tested against cation exchange capacity values obtained by chemical methods. Estimates of the percent illite derived from X-ray diffraction analysis were tested against percent illite values obtained from total potassium analysis.

In addition an attempt was made to assess the major sources of error in the method of X-ray diffraction analysis used in this study, and to identify the diffraction maxima that may be measured with the greatest precision.

LITERATURE REVIEW

Quantitative applications are firmly based on sound theoretical considerations. However, almost every procedural step in X-ray diffraction methods may be considered as a potential source of error [16,43,32,39]. In this review of pertinent literature, an attempt is made to briefly survey the major procedural steps in making quantitative clay mineral estimations by X-ray diffraction methods. These steps may be identified as: (1) sample dispersion and particle size segregation, (2) sample preparation and presentation, and (3) quantitative estimation of clay mineral components.

Sample Dispersion and Particle Size Segregation

Day [7], Kunze [27], Kittrick and Hope [23], Jackson [18] and Watson [53] provide reviews of procedures applicable to sample dispersion. It is generally accepted that cementing agents and free oxides and salts should be removed to some extent to aid in dispersion. Apparent disagreement does exist, however, as to the severity of the pretreatment required.

The procedures described by Jackson [18] are generally rigorous. It has been demonstrated that less severe pretreatments are adequate to obtain satisfactory sample dispersion and X-ray diffraction results [23]. Several authors have found that sample pretreatment can seriously affect apparent clay mineral composition. Harward, Theisen, and Evans [17] compared the effects of several different dispersion methods. Generally, they found that, although iron removal enhanced dispersion, it also resulted in significant differences in apparent clay mineral composition. More rigorous iron removal and dispersion treatments generally resulted in a greater number of clay minerals identified, however, this was also dependent upon the soil itself.

The choice of the proper combination of pretreatment and dispersion methods remains to the discretion of the investigator. A combination of methods might be most worthwhile. While it is important to identify the maximum number of mineral components present, it is also advantageous to use those methods which retain the real mineral assemblages as they exist *in situ* [17].

Use of ultrasonic vibrations to obtain sample dispersion may eliminate need for drastic pretreatment. Olmstead [37] found that sonic vibrations could be used in conjunction with chemical treatments to obtain stable dispersed suspensions of soil colloids. However, his work was largely overlooked for almost thirty years. Recently Edwards and Bremner [9,8] found, using soils having a wide range of characteristics, that sample dispersion could be obtained with most soils using only distilled water, thus reducing both the time involved in treating the sample and the possibility of destruction of natural mineral structure. This work has been corroborated by Genrich and Bremner [12]. Vladimirov [52] suggested the value of ultrasonic dispersion methods in studying highly calcareous soils where chemical treatments disallow a particle size investigation of carbonate salts. Emerson [10] found that sodium hexametaphosphate improved dispersion of soils particularly high in organic matter or soluble salts. In most cases it has been reported that abrasion of minerals is lower using ultrasonic methods than with either shaker or mixer methods of mechanical dispersion except in the case of biotite [9].

Particle size segregation may be obtained by settling or centrifugation [18]. Tanner and Jackson [48], in considering settling and centrifugation techniques, have published nomographs by which the sedimentation of particles having a particular effective radius may be predicted according to time temperature, particle density and centrifuge

speed. Procedures employing density gradient centrifugation and heavy liquid techniques have not received much attention in clay mineralogy as yet. Towe [51] suggested these latter techniques while critically considering the use of the less-than-2-micron particle size fraction in making typical clay mineral studies. Towe seriously questioned the ability of current sedimentation and centrifuge techniques to yield accurate representative samples of this size fraction based on inherent differences in particle density and settling times.

Sample Preparation and Presentation

Preferential orientation is rather easily obtained because of the shape of most layer-silicate minerals. Orientation results in the enhancement of basal (001) diffraction maxima and thus permits greater sensitivity to small amounts of the mineral components present [27].

The length of the specimen irradiated and the depth to which the X-ray beam penetrates are functions of the angle at which the X-ray beam intersects with the sample (θ). The length of the irradiated specimen (L) may be calculated by the relationship:

$$L = \alpha R / 2 \sin \theta ,$$

where α represents the divergence slit width (in radians) and R represents the radius of the goniometer [38]. The irradiated specimen length increases rapidly at smaller angles of θ . This results in a maximum d-spacing that may accurately be measured and a minimum sample length. It is interesting to note that the majority of studies reported in the literature use $\text{CuK}\alpha$ radiation in conjunction with a divergence slit width of 1° to study soil clay minerals. According to the values reported by Parrish [38] the maximum d-spacing accurately measured under these conditions is 5.2A, a value well below even the relatively small c dimension of the kaolinite minerals (approximately 7A).

Cullity [6, pp. 269-272] described the effective depth of X-ray penetration in terms of the fraction (G_x) of the total diffracted intensity contributed by a surface layer of a certain thickness (x) by the relationship:

$$G_x = (1 - e^{-2\mu x/\sin\theta}),$$

where μ represents an appropriate mass absorption coefficient. Gibbs [13] used this equation to calculate penetration values. The need for a uniform sample in which no particle segregation has occurred is imperative.

In a comparison of several techniques Gibbs [13] found that particle segregation was best avoided by smear-on-glass techniques as described by Theisen and Harward [50] and suction-on-ceramic tile techniques described by Kinter and Diamond [22]. Centrifuge methods for deposition on either ceramic tiles or glass were found to cause particle size segregation and thus bias estimates toward the finer grained smectite minerals.

An additional consideration in preparing oriented samples is the degree of orientation that is actually achieved. Departure from the preferred orientation can cause a reduction in the peak intensity. Taylor and Norrish [49], using the suction-on-ceramic tile method reported significant variations in the degree of preferred orientation between specific minerals. They also found that variations in the degree of orientation for specific minerals may vary between duplicates. Quakernaat [41] reported relatively low absolute orientation for all minerals studied using a suction-on-plastic membrane technique. Schultz [44], in a study of kaolinite-illite mixtures using a smear-on-glass technique, found that the degree of preferred orientation in pure kaolinite samples was greater than the orientation of either kaolinite or illite in mixed samples. However, for any one mixture,

the preferred orientation of the kaolinite and illite was about the same. He concluded that the effect of orientation was eliminated within a single slide.

At present no clear advantage is held by either the smear-on-glass or the suction-on-ceramic tile techniques in comparison with each other [50].

Quantitative Estimation of Clay Mineral Components

Quantitative X-ray diffraction methods fall into three basic approaches described here as: (1) the Theoretical Method, (2) the Standard Clay Mixture Methods, and (3) the Factor Method.

The Theoretical Method. The work reported by Alexander and Klug and their associates [1,24,25] form the theoretical basis for current quantitative methods. In its simplest form, the method of Alexander and Klug [1] reduces to:

$$I_p/I_{o,p} = w_p,$$

where I_p equals the diffraction intensity of the P component in a multiphase mixture, $I_{o,p}$ equals the diffraction intensity of the P component in pure form (the external standard), and w_p equals the weight fraction of the P component in the mixture. This method assumes that the mass absorption coefficient of the P component (μ_p^*) is equal to the mass absorption coefficient of the matrix containing the rest of the components of the mixture (μ_m^*). This assumption is not strictly true and can lead to large errors. Leroux, Lennox, and Kay [28] attempted to correct for this by extending Eq. 1 to include a ratio of the mass absorption coefficient of the P component to the average mass absorption coefficient of the mixture ($\bar{\mu}_m^*$):

$$I_p/I_{o,p} = w_p(\mu_p^*/\bar{\mu}_m^*).$$

Tabulated values of μ_p^* for several minerals are available [3]. Assuming an investigator has previously determined $I_{o,p}$, the application of this technique requires only a measurement of I_p and $\bar{\mu}_m^*$. Williams [57] provided an improved method for determining the average mass absorption coefficient.

The Standard Clay Mixtures Method. Methods using mixtures of standard clays have been applied through two basic avenues for quantification: (1) the calibration curve approach and (2) the empirical factor approach.

The calibration curve approach uses mixtures of known weighed amounts of standard clay minerals to calibrate the method. Probably the most extensive use of this technique was that of Willis, Pennington, and Jackson [58]. They used 141 standard clay mixtures containing either 2, 3, 4, 5, or 6 components based on their conception of the weathering sequence of clay size material. Talvenheimo and White [47] used a diffractometer in developing a standard clay mixture method for multiphase system containing kaolinite, illite, and bentonite. With this technique they reported 5 to 10% accuracy.

Internal standards have been employed in the calibration curve approach. Compounds such as MgO, LiF, and CaF₂ having low absorption coefficients and high symmetry are normally used [3] so that small amounts may be incorporated in the sample to be measured without disrupting the desired degree of orientation. The internal standard method of quantitative analysis is based upon the ratio of the integrated intensity of a component in a clay mixture with the integrated intensity of an internal standard added to the mixture in a constant amount. Calibration curves are normally prepared using synthetic mixtures of standard clay samples together with a constant amount of the internal standard. The use of an internal standard circumvents the need to know mass absorption

coefficients or crystal lattice parameters. Because of this advantage the method has been applied to the study of soil clays by several investigators. Many of these investigations were done using photographic techniques on random powder mounts [55,19]. In a more recent study, Glenn and Handy [15] applied the internal standard method using a diffractometer.

Orientation problems have been approached by Quakernaat [41] by the use of molybdenite as an orientation indicator. Compensating for deviations from preferred orientation, he set up quantity intervals using standard mineral mixtures. In determining quantities of kaolinite, illite, and smectite, he claimed an accuracy of about 7 percent. Estimations of chlorite, vermiculite, and pyrophyllite were within about 10 percent accuracy.

The empirical factor approach is best exemplified by the work of Schultz [44,45]. Basically this method uses standard clay minerals in binary combinations to obtain ratios of integrated diffraction intensities for two minerals. These ratios were then applied to a multiphase mixture to characterize the peak intensities to obtain relative clay mineral compositions. As stated previously, Schultz recognized that such factors not only resulted from characteristics of the composition and lattice structure of the minerals, but from orientation effects as well. Schultz reported that in 50/50 mixtures by weight of several kaolinites to Pithian Illite, the ratio of the integrated intensities was approximately 1/1. He found no consistent ratio for chlorite minerals. In a similar study Moore [33] reported the accuracy to be within 2 percent of the actual values.

The major problem shared by the methods employing mixtures of standard clays is the difficulty faced in obtaining mineral standards that are comparable to the clays naturally occurring in soils. Gibbs [14], however, has reported a technique in which he

obtained standard minerals directly from the samples to be studied. Coupling the approach of Schultz as described above together with an internal standard method, he avoided the problems of absorption and crystallinity differences between the standards and the unknowns.

The Factor Method. The factor method incorporates the use of an empirical multiplication factor by which measured peak intensities or integrated intensities are characterized. These factors may be derived experimentally as in the case of studies reported by Weaver [54] and Freas [11], or by calculations based on chemical and crystal lattice parameters [4,42]. The method has several advantages in that it is relatively rapid and generally has good precision. Any of the diffraction maxima may be used in the calculations along with a careful and reasonable choice of multiplication factors.

The method as outlined by Johns, Grim, and Bradley [20] is probably the most often cited of all quantitative procedures. Basically it uses illite somewhat like an internal standard. The integrated intensities of the diffraction maxima of the other minerals are then related to the integrated intensity of the illite peak by appropriate multiplication factors. They used two illite peaks for comparison purposes. The 10A illite peak was multiplied by 4 to allow direct comparison with the 17A peak of smectite. The 3.3A peak was compared directly with the 3.5A maximum for chlorite and kaolinite. Heat treatments were used to discern minerals which occur concurrently in a peak. An apparently arbitrary correction for quartz was applied with the 3.3A peak of illite.

Similar applications of this method have been reported by several authors and differ from the method of Johns *et al.* by either the method used to determine peak intensity

or integrated intensity, in the multiplication factors used, and/or in the diffraction maxima being measured. Weaver [54] used a factor of 2.5 in comparing the 7A peak with the 10A peak for the determination of kaolinite. Freas [11], on the other hand, in comparing all minerals present to the (001) diffraction maximum of kaolinite at 7A, used factors of 3, 3, and 1 for comparison with the (001) reflections of illite, chlorite, and smectite, respectively. Biscayne [2] in comparing all minerals to the 17A peak of montmorillonite used a factor of 4 for the 10A peak of illite and a factor of 2 for a comparison with the 7A peak. The relative composition of chlorite and kaolinite was further discerned by using the doublet occurring near 3.5A. Meade [29] assumed that smectite, kaolinite, and illite reflected X-rays at the same intensity. In addition, he used different intensity factors for Type A chlorite (x2) and Type B chlorite (x 1.5) at 7A for comparison with the 10A peak of illite. The method of Keller and Richards [21] is closely similar to that of Johns *et al.* with the exception that a factor of 3 was used to compare the 17A peak to the 10A peak. Neihsel and Weaver [34] used a factor of 2 for comparing the 17A and 7A peaks with the 10A peak.

MATERIALS AND METHODS

MAIN STUDY—QUANTIFICATION

Samples

The fifty samples used in this study were obtained from the Decker Coal Company, Decker, Montana. The material consists of early Tertiary aged sediments of the Fort Union Formation, together with soil formed on this moderately indurated material.

The samples were chosen on the basis of clay mineral composition estimated from preliminary X-ray diffraction analysis in an effort to obtain a wide range of clay mineral composition. The description of those samples used in this study appeared in Table 1.

Sample Preparation

The samples were first ground to pass a 2mm sieve. Sample dispersion was obtained by using a probe-type ultrasound machine (120 volts, 4 amps, 60 cycles) manufactured by Blackstone Ultrasonics, Inc. Ten grams of each sample were placed in 50 ml of 0.01% Na_2CO_3 and subjected to ultrasound for 2 minutes. Excessive heating of the samples was experienced using longer periods of dispersion.

Stock clay-sized ($< 2\mu$) particle suspensions were prepared for each sample by five washings using 0.01% Na_2CO_3 , centrifuging at 500 RPM according to the nomographs of Tanner and Jackson [48], and saving the supernatant from each wash. Four 25 ml subsamples were removed from these stock suspensions and prepared for X-ray diffraction analysis as described below. The remaining stock suspensions were saturated with calcium by centrifuge washing three times with $N \text{CaCl}_2$. Excess salt was removed by simple dialysis until a test for chloride was negative. Upon completion of dialysis the samples were air dried and hand ground with an agate mortar and pestle to pass a 60 mesh sieve.

Table 1. Sample Identification and Description

Sample No.	Lab. Ident. No.	Description (Depth in Feet)	Sample No.	Lab. Ident. No.	Description (Depth in Feet)
1	44518	0 - 2	26	45257	54 - 60
2	44519	2 - 5	27	45258	60 - 65
3	44520	5 - 11	28	45261	75 - 77
4	44521	11 - 15	29	45262	129 - 135
5	44522	15 - 20	30	45263	135 - 140
6	44523	20 - 23	31	45264	140 - 145
7	44524	23 - 27	32	1235-4	55 - 60
8	44525	27 - 29	33	1235-5	60 - 66
9	44528	40 - 45	34	1235-6	73 - 78
10	44529	45 - 50	35	1235-8	103 - 107
11	44530	50 - 55	36	1235-9	107 - 117
12	44531	55 - 60	37	1235-10	117 - 126
13	44532	60 - 65	38	1237-1	5 - 10
14	45245	0 - 2	39	1237-2	10 - 20
15	45246	2 - 5	40	1237-3	20 - 25
16	45247	5 - 11	41	1237-4	25 - 35
17	45248	11 - 15	42	1237-5	35 - 45
18	45249	15 - 20	43	1237-6	45 - 50
19	45250	20 - 25	44	1237-8	60 - 70
20	45251	25 - 28	45	1237-10	98.8 - 105.3
21	45252	28 - 34	46	1237-11	105.3 - 110.0
22	45253	34 - 40	47	1237-12	111.8 - 120
23	45254	40 - 44	48	1237-13	120 - 130
24	45255	44 - 49	49	1256-2	42 - 52
25	45256	49 - 54	50	1256-12	138 - 142

Total Potassium Determination

Duplicate 0.0500 g clay samples were weighed. The HF-HClO₄ decomposition method was employed as suggested by Pratt [40]. The extract was diluted to 100 ml. so that the resulting solution contained 0.5% Sr as SrCl₂. The concentration of potassium ions in solution was determined by atomic absorption. The results were reported in terms of illite, expressed as a percentage of the total clay fraction as calculated assuming 8.3%

[30] and 5.1% [54] elemental potassium per unit cell illite. The resulting estimations of the percent illite were tested against the percent illite estimated by X-ray diffraction analysis using linear regression methods.

Cation Exchange Capacity Determination

Free carbonates were removed from the dry Ca-saturated clay samples by a modification of the method described by Jackson [18]. The modification involved four centrifuge washings with normal sodium acetate buffer (pH 5.0) without heating the sample. Following carbonate removal air-dried Ca-saturated clay samples were prepared by the method previously described.

The cation exchange capabilities of the clay samples were determined by a Ca//Mg exchange system. Duplicate 0.050 g samples were centrifuge washed four times using 10 ml aliquots of *N* MgCl₂, saving the supernatant following each wash. The resulting extract was diluted to 50 ml so that the resulting solution additionally contained 0.5% Sr as SrCl₂. The concentration of Ca in the extract was determined by atomic absorption and the results reported in terms of meq/100 gm of clay.

X-ray Diffraction Analysis

One subsample of each clay sample was saturated with Mg by centrifuge washing three times with 25 ml aliquots of *N* MgCl₂. Excess salt was removed by washing twice with distilled water. A second subsample was saturated similarly with potassium using *N* KCl. Excess salt was removed by washing once with distilled water followed by a second wash with 50% ethanol. Subsamples were duplicated for each clay sample.

Parallel oriented samples were prepared by the paste method of Theisen and Harward [50]. The Mg-saturated samples were ethylene glycol solvated by the condensation method described by Kunze [26]. K-saturated samples were heated to both 350°C and 550°C for three hour periods.

X-ray diffraction analysis was carried out on a General Electric XRD-5 diffractometer using Ni filtered $\text{CuK}\alpha$ radiation at 45Kv and 18ma with beam and detector slit widths of 1° and 0.2°, respectively. Medium range collimating assemblies were used for both the incident and reflected beams. Scanning speed of the goniometer was 2° 2θ per minute and the chart speed was 1 inch per minute, giving a 2° 2θ per inch diffractogram scale for all samples. All Mg-saturated, ethylene glycol solvated samples were scanned through a 2θ range of 2°-30°. A 2°-15° 2θ range was used for K-saturated samples for both heat treatments.

The criteria used to identify the clay minerals present in the samples were taken from [18], [56], and [5] and are as follows:

Mineral Group

Identification Characteristics

Smectite

d(001) maximum at approximately 17A under Mg-saturation and glycol solvation. K-saturation together with heat treatments cause progressive collapse of interlayer space resulting in a d(001) maximum at approximately 10A for the K-saturated, 550°C heat treatment.

Vermiculite

d(001) maximum at approximately 14A under Mg-saturation and ethylene glycol solvation. Total collapse of the interlayer space and a consequent d(001) maximum of approximately 10A result from K-saturation together with heat treatments.

Chlorite

d(001) maximum at approximately 14A for all treatments. d(002) maximum may or may not be present in the K-saturated, 550°C heat treatment.

Illite

d(001) maximum at approximately 10A for all treatments.

Kaolinite

d(001) maximum at approximately 7A and a d(002) maximum at 3.5A for all treatments except K-saturated, 550°C heat treated samples. On heating to approximately 550°C the mineral reported here as kaolinite becomes amorphous to X-rays due to the collapse of crystalline structure.

Quartz

a diffraction maximum at approximately 3.3A and coincides with an accompanying d(003) maximum of illite.

Peak intensities of the d(001) reflections were measured to a hand-drawn background line. The areas under the peaks were estimated by multiplying the peak height by the width of the peak at half the peak height [36], as illustrated in Fig. 1.

Characterization of the minerals followed the factor method of Johns, Grim, and Bradley [20] as modified by Wilding [59]. Modifications in this method involved both the peaks and factors used to characterize the minerals considered. First order basal reflections were used in the characterization of all clay minerals. The 3.3A reflection was used to characterize quartz. Often the 14A peak of the Mg-saturated, ethylene glycolated slide appears as a shoulder on the high angle side of the 17A peak. In such cases the low angle side of the 14A peak was estimated, as in Fig. 1, and the area calculated. The area of the 17A peak was then corrected by subtracting the area of the 14A peak from the area of the 17A peak.

Ten modifications were tested involving different factors for smectite and kaolinite. Computer programs were used to complete the characterization. The following computations were used to calculate characterized peak areas:

Modification I.

$$\begin{aligned}
 &17A \text{ Mg-sat. E.G.}/4 &&= \text{Smec. Peak Area} \\
 &(14A \text{ Mg-sat. E.G. minus } 14A \text{ K-sat. } 350^\circ\text{C})/2 &&= \text{Verm. Peak Area} \\
 &14A \text{ K-sat. } 350^\circ\text{C}/2 &&= \text{Chlor. Peak Area} \\
 &10A \text{ Mg-sat. E.G.}/1 &&= \text{Ill. Peak Area} \\
 &(7A \text{ Mg-sat. E.G. minus } 7A \text{ K-sat. } 550^\circ\text{C})/4 &&= \text{Kaol. Peak Area} \\
 &(3.3A \text{ Mg-sat. E.G. minus } 3/4(10A \text{ Mg-sat. E.G.})/4 &&= \text{Quar. Peak Area}
 \end{aligned}$$

