MEASUREMENT OF THE SPECIFIC SURFACE AREA OF CLAYS BY INTERNAL REFLECTANCE SPECTROSCOPY[1]

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Abstract—The specific surface area, S, of a clay is commonly measured by the adsorption of ethylene glycol monoethyl ether (EGME); however, this method can be tedious and time consuming, especially if the clay is saturated with a monovalent, highly hydrated cation. An alternative method for measuring S was developed involving infrared internal reflectance spectroscopy. This method is based on the discovery that the ratio of R_1, the reflectance of a clay-HOD mixture at the frequency of O–D stretching, to R_2, the reflectance of the mixture at the frequency of H–O–D bending, is linearly related to S. The correlation coefficient between R_1/R_2 and S, as measured by the adsorption of EGME, was 0.995. Consequently, a calibration curve of R_1/R_2 versus S was constructed, and the measured values of R_1/R_2 for any clay-HOD mixture were referred to it for the determination of S. Results were obtained in triplicate in about an hour; hence, this method of determining S is more rapid and convenient than that involving the adsorption of EGME. Moreover, it applies to clays in a natural condition, i.e., swollen in water.

Key Words—Ethylene glycol monoethyl ether, Infrared spectroscopy, Internal reflectance spectroscopy, Molar absorptivity, Montmorillonite, Surface area.

INTRODUCTION

The large specific surface area, S, of clays is responsible for many of their unique properties; hence considerable effort has been expended in its measurement. Many methods have been developed, including: the method of S. Brunauer, P. H. Emmett, and E. Teller (1938), commonly called the B.E.T. method, which relies on the adsorption of a vapor; the methods of Dyal and Hendricks (1950), Diamond and Kinter (1958), and Carter *et al.* (1965) which rely on the adsorption of an organic solvent, namely, ethylene glycol, glycerol, and ethylene glycol monoethyl ether (EGME), respectively; and the method of Schofield (1949) which relies on the negative adsorption of anions. In recent years, the EGME method has gained precedence because it is relatively quick and does not suffer from some of the disadvantages associated with the other methods (see, e.g., Mortland and Kemper, 1965). Even this method, however, can be very time consuming if the clay is saturated with Na^+ and if a high degree of accuracy is required (Low, 1980). A quicker method is therefore desirable, especially one in which the measurement is made while the clay layers are separated by water, as they usually are in nature.

During an investigation of the spectroscopic properties of water near the surfaces of clay particles, Mulla and Low (1983) found that the molar absorptivity, ϵ, of HOD in a clay-water system at the frequency of O–D stretching is given by

$$\epsilon = \epsilon^0 e^{k_\epsilon Sm_c/m_w}, \qquad (1)$$

where ϵ^0 is the molar absorptivity of pure bulk water, S is the specific surface area of the clay, m_c/m_w is the mass ratio of clay to water, and k_ϵ is a constant equal to -1.368×10^{-7} g/cm^2. Hence, a spectroscopic measurement of ϵ and a gravimetric measurement of m_c/m_w should allow the determination of S while the clay is mixed with water (a dilute solution of D_2O in H_2O). Unfortunately, however, to determine ϵ the sample thickness must be known precisely and, because infrared radiation is strongly absorbed at the frequency of O–D stretching, the thickness cannot exceed ~0.0025 cm. Although these requirements can be met if great care is exercised, they preclude the routine measurement of S by this method.

Mulla and Low (1983) indicated the feasibility of measuring S quickly and conveniently by infrared spectroscopy provided the problem of sample thickness could be resolved. Internal reflectance spectroscopy (Harrick, 1967) may provide a solution to this problem inasmuch as one of its advantages is that it does not require a knowledge of the thickness of the sample. Other advantages of an internal reflectance spectroscopic method are the ease of sample preparation, the absence of interference fringes (Harrick, 1967), the ease of analyzing samples having large absorption coefficients and, hence, requiring short path lengths (Katlafsky and Keller, 1963), and the lack of scattering in the spectra of mineral powders (Harrick and Riederman, 1965). The present paper reports the results of our investigation of the measurement of S by infrared internal reflectance spectroscopy.

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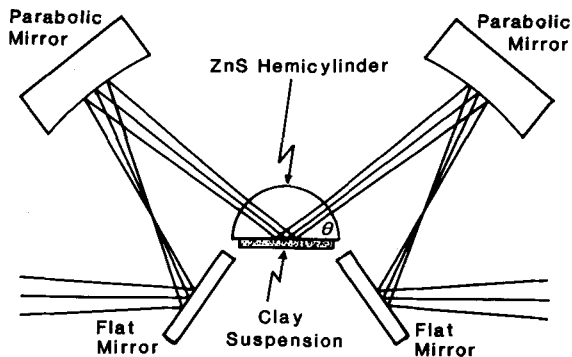
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Figure 1. Diagram illustrating the principle of internal reflectance spectroscopy (θ = angle of incidence).

MATERIALS AND METHODS

The following clays were used: nine <2-μm, Na-saturated montmorillonites (Belle Fourche, California Red Top, Czech #650, Italian, Nevada, Rio Escondido, Romanian, Texas, and Upton) prepared by Low (1980); five <2-μm, Na-saturated soil clays (nos. 128, 207, 208, 210, and 217) prepared by Romkens et al. (1977); kaolinite (Hydrite 10) from the Georgia Kaolin Company; and six <2-μm, homoionic samples of Upton montmorillonite saturated with Li^+, K^+, Cs^+, Rb^+, Mg^{2+}, and Ca^{2+}. The last samples were prepared from Na-saturated clay by washing it with chloride solutions of these ions, dialyzing out the excess electrolyte, and freeze-drying the products.

The value of S for each of the clays was determined by the EGME method of Carter et al. (1965) as modified by Low (1980).

A stock solution of 8% D_2O in H_2O was prepared by pipeting 8 ml of pure D_2O into a 100-ml volumetric flask and adding distilled, deionized water to volume. This solution was mixed with the various clays to yield samples for spectroscopic analysis having accurately known values of m_c/m_w, the mass ratio of clay to water. Before being analyzed, the samples were allowed to equilibrate for one day in sealed weighing bottles.

A grating, ratio-recording infrared spectrophotometer (Perkin-Elmer Model 180) was used for the spectroscopic analyses. It included a wire grid-AgBr, common-beam polarizer and a single pass, variable angle, internal reflectance accessory manufactured according to our specifications by Harrick Scientific Corporation, Ossining, New York. A simplified diagram of this accessory is presented in Figure 1. Radiation from the source of the spectrophotometer passes through the hemicylinder of ZnS (diameter = 2.54 cm) and strikes the sample. A common-beam polarizer on the spectrophotometer allows only that radiation properly polarized relative to the plane of the hemicylinder to pass on to the detector. Depending on its frequency and angle of incidence, different fractions of the radiation

Table 1. Specific surface area, S, of clay minerals as estimated by the adsorption of EGME.

Mineral	Source	S (m^2/g)
Na-Belle Fourche	Belle Fourche, South Dakota	771
Na-California Red Top	Red Top, California	605
Na-Czech #650	Unknown	438
Na-Italian	Ponza, Italy	696
Na-Nevada	Lovelock, Nevada	487
Na-Rio Escondido	Unknown	664
Na-Romanian	Unknown	753
Na-Texas	Sierra Blanca, Texas	568
Li-Upton	Upton, Wyoming	800
Na-Upton	Upton, Wyoming	800
K-Upton	Upton, Wyoming	480
Rb-Upton	Upton, Wyoming	470
Cs-Upton	Upton, Wyoming	540
Ca-Upton	Upton, Wyoming	800
Mg-Upton	Upton, Wyoming	720
Soil Na-clay #128	Romkens et al. (1977)	205
Soil Na-clay #207	Romkens et al. (1977)	335
Soil Na-clay #208	Romkens et al. (1977)	340
Soil Na-clay #210	Romkens et al. (1977)	411
Soil Na-clay #217	Romkens et al. (1977)	303
Kaolinite (Hydrite 10)	Georgia Kaolin Company	35

are absorbed, refracted, and reflected. Hence, the intensity of the reflected radiation differs from that of the incident radiation and can be used to determine the spectroscopic and optical properties of the sample. The recommended procedure follows:

1. Warm up the spectrophotometer for at least 30 min.
2. Set the spectrophotometer for 1.5-cm^{-1} resolution at 2600 cm^{-1}.
3. With the ZnS hemicylinder, support, and goniometer mounted in the sample compartment, set the goniometer at 51°.
4. Set the polarizers to a setting of 90° for maximal absorption by the sample.
5. Adjust the 100% readings on the recorder using a reference beam attenuator in the reference compartment.
6. Place a drop of the HOD solution on the support that holds the sample against the flat surface of the hemicylinder, carefully bring the support and hemicylinder together, and gently tighten the connecting screws. When the solution (sample) is viewed through the hemicylinder, no air bubbles should be visible.
7. Place the assembled hemicylinder and sample support containing the HOD solution in the reflectance assembly and adjust the goniometer until the reflectance reading on the recorder chart is 72%. (For our instrument, this reading was attained when the goniometer was set at 51°.)
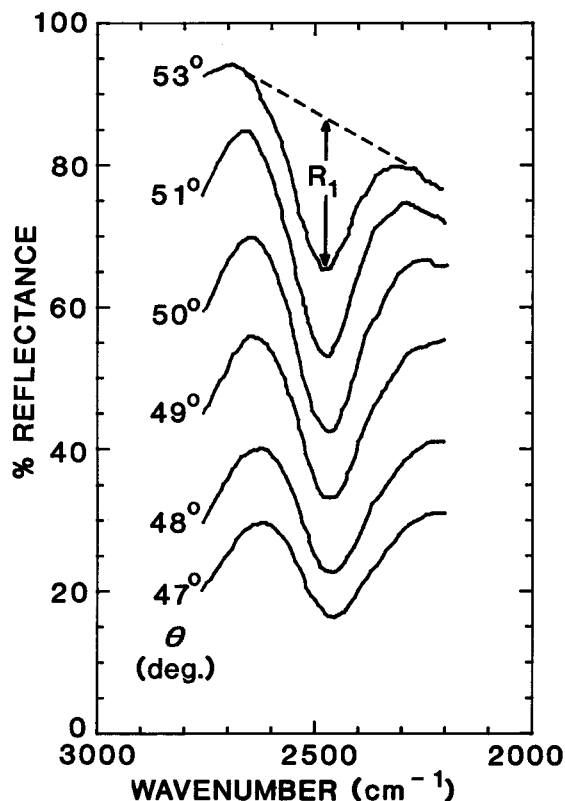
Figure 2. Infrared reflectance spectra for the O–D stretching mode of HOD as a function of the angle of incidence, θ. (R_1 represents the maximal height of the reflectance band.)
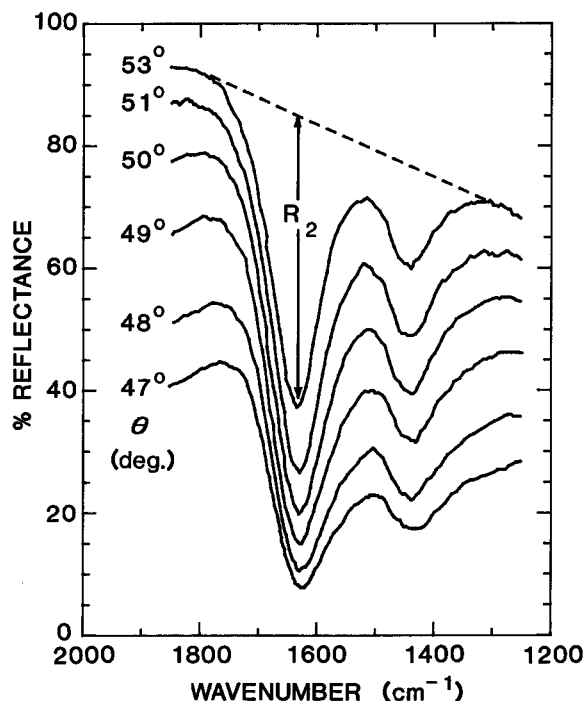

Figure 3. Infrared reflectance spectra for the bending mode of HOD as a function of the angle of incidence, θ. (R_2 represents the maximal height of the reflectance band.)

8. Record the spectrum of the HOD solution in the range 2800 to 1200 cm^{-1}.

9. From the heights of the peaks at wavenumbers corresponding to O–D stretching ($\sim$2450 cm^{-1}) and H–O–D bending ($\sim$1625 cm^{-1}), determine R_1 and R_2, the respective reflectances.

10. Repeat steps 6 through 9 with a clay-water sample (but do not readjust the goniometer as described in step 7).

11. Remove the sample from the hemicylinder and sample support with a soft cleaning tissue and water, taking care to avoid scratching the surface of the hemicylinder.

12. Follow the procedure described in step 10 with additional clay-water samples.

13. During prolonged periods of measurement, periodically check the standardization of the instrument with the HOD solution and restandardize as necessary.

RESULTS AND DISCUSSION

Table 1 reports values of S for the different clay minerals as determined by the adsorption of EGME. Additional values of S were obtained by mixing kaolinite and Na-saturated Upton montmorillonite in different proportions. The values of S for the montmorillonite-kaolinite mixtures, calculated from the weight fractions and specific surface areas of the two components, were 90, 149, 227, 301, 364, 436, 450, 532, and 695 m^2/g.

Initially, the values of R_1 and R_2 were determined for the HOD solution at different values of θ, the angle of incidence. The results are presented in Figures 2–4. Note that R_1, R_2, and R_1/R_2 depend sensitively on θ and that R_1/R_2 is a maximum at $\sim$51°. Therefore, this value of θ was used for all determinations.

In earlier work, Low (1979) found that the thermodynamic and spectroscopic properties of water in clay-water systems are described by the equation

$$J_i = J_i^0 e^{\beta_i m_c/m_w}, \qquad (2)$$

where J and J^0 are the values of any property, i, in the clay-water system and in pure bulk water, respectively, and β is a constant. The logarithmic form of this equation is

$$\ln(J/J^0) = \beta m_c/m_w. \qquad (3)$$

The theory of internal reflectance spectroscopy (Harrick, 1967) indicates that the reflectance is a complicated function of several variables, including the attenuation constant and refractive index of the sample. The same must be true of R_1/R_2. Nevertheless, we wanted to see if R_1/R_2, being dependent on the nature
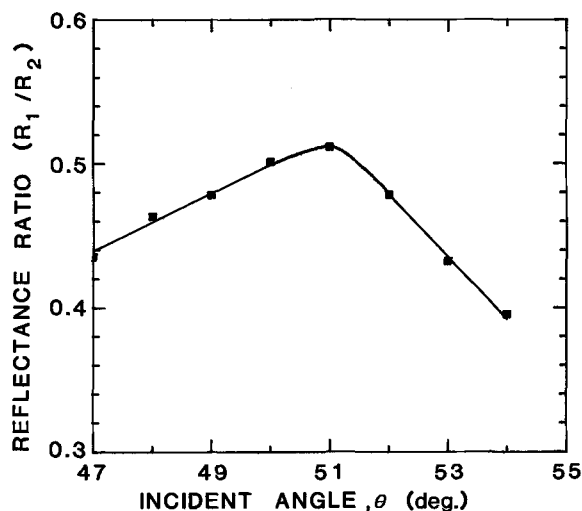
Figure 4. Plot of reflectance ratio, R_1/R_2, for HOD vs. angle of incidence, θ.

Figure 5. Plot of $-\ln[(R_1/R_2)/(R_1/R_2)^0]$ vs. m_c/m_w for mixtures of Na-saturated Upton montmorillonite and HOD.

of the interparticle water, obeyed Eq. (2). For this purpose, we measured R_1/R_2 for pastes of Na-saturated Upton montmorillonite at different values of m_c/m_w and constructed the plot shown in Figure 5. Each datum point in this figure is the average of at least three replicates. Obviously, $-\ln[(R_1/R_2)/(R_1/R_2)^0]$ is linearly related to m_c/m_w, but both the slope and intercept of this relation change abruptly at $m_c/m_w \cong 0.3$. The necessary conclusion is that R_1/R_2 obeys Eq. (2), but that the constants in the equation are different on opposite sides of $m_c/m_w \cong 0.3$. Because S for the Upton clay is 800 m²/g, and because the density of the interparticle water is ~ 1.0 g/cm³, the average thickness of the water films on the particle surfaces is ~ 40 Å when $m_c/m_w = 0.3$. It is interesting to note that, according to the results of Mulla and Low (1983), this value is the thickness of the water film in which its spectroscopic properties differ from those of pure bulk water.

In view of this evidence,

$$R_1/R_2 = (R_1/R_2)^0 e^{\beta m_c/m_w}; \qquad (4)$$

however, because $\beta \ll 1.0$,

$$R_1/R_2 = (R_1/R_2)^0[1 + \beta m_c/m_w]. \qquad (5)$$

Mulla and Low (1983) found that when Eq. (2) was applied to the molar absorptivity for O–D stretching in the interparticle water, β was proportional to S. Hence, they arrived at Eq. (1). If, in general,

$$\beta = kS + b, \qquad (6)$$

in which k is a constant and b either equals zero or is another constant, Eq. (5) transforms to

$$R_1/R_2 = (R_1/R_2)^0[1 + (kS + b)m_c/m_w]. \qquad (7)$$

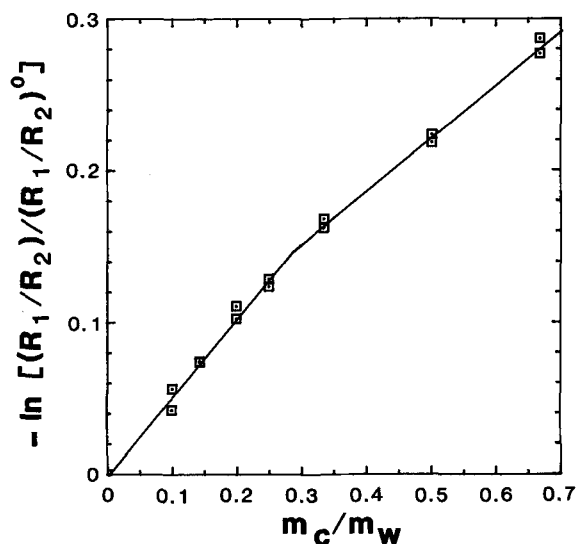According to Eq. (7), R_1/R_2 should be a linear function

of m_c/m_w at any value of S and should be a linear function of S at any value of m_c/m_w. Figures 6 and 7 show that both these predictions are realized. The data in Figure 6 were obtained at different values of m_c/m_w and a constant value of S, namely, that of Na-saturated Upton montmorillonite; whereas, the data in Figure 7 were obtained at many values of S, provided by different Na-saturated clays and mixtures of clays, at a constant value of m_c/m_w. Every datum point in each figure is the average of at least three replicates. Note that Figure 6 is consistent with Figure 5 in regard to the break at $m_c/m_w = 0.3$ because both were derived from the same data.

From Figure 7 it is evident that R_1/R_2 is a linear function of S over the range of values of S that would normally be encountered with clays. Therefore, by using Figure 7 as a calibration curve, it is possible to determine S by measuring R_1/R_2. Alternatively, the value of S can be calculated from the statistical regression equation

$$R_1/R_2 = -7.28 \times 10^{-5}S + 0.4662, \qquad (8)$$

in which S is expressed in m²/g. Note that this equation holds only if $m_c/m_w = 0.5$. The correlation coefficient for the data in Figure 7, which were used to obtain Eq. (8), is 0.995.

In clay-water systems, unexpanded layers, partially expanded layers with a fixed c-axis spacing, fully expanded layers with a variable c-axis spacing depending on the water content, or a mixture of all of these kinds of layers may be present. The water between the partially expanded layers should have a different R_1/R_2 than the water between the fully expanded layers because, on the average, it is closer to the surfaces of the
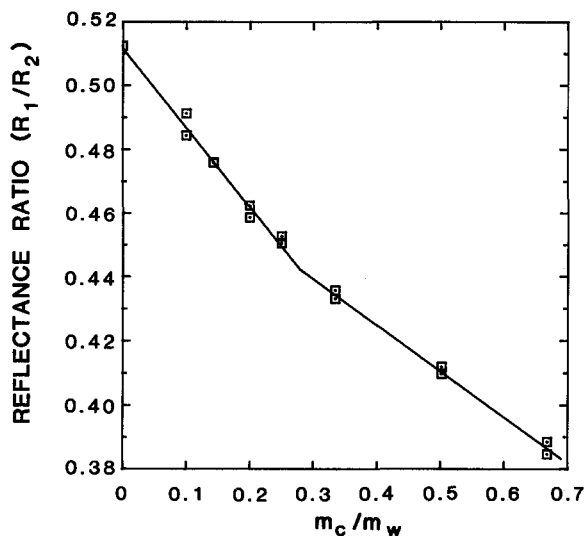
Figure 6.   Plot of reflectance ratio, R_1/R_2, vs. mass ratio of clay to water, m_c/m_w, for mixtures of Na-saturated Upton montmorillonite and HOD.

Figure 8.   Plot of specific surface area, S, measured by EGME adsorption vs. S measured by reflectance for several homoionic samples of Upton montmorillonite at $m_c/m_w = 0.5$.

layers. Therefore, R_1/R_2 should depend on the relative proportions of these layers in addition to m_c/m_w and S. This means that the curve in Figure 7, having been obtained with clays in which the expandable layers were fully expanded (i.e., with Na-saturated clays), applies only to such clays. To establish this fact, Figure 8 was prepared to compare the results obtained by reflectance with those obtained by EGME adsorption for homoionic samples of Upton montmorillonite. The c-axis spacings of the samples, which were taken from
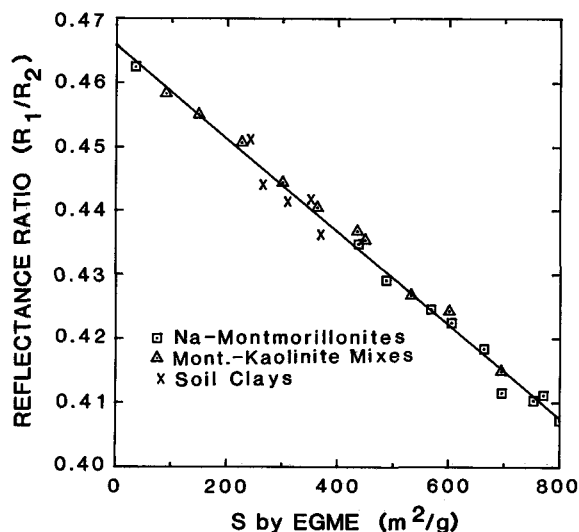

Figure 7.   Plot of reflectance ratio, R_1/R_2, vs. EGME specific surface area for mixtures of Na-saturated clays and HOD when $m_c/m_w = 0.5$.
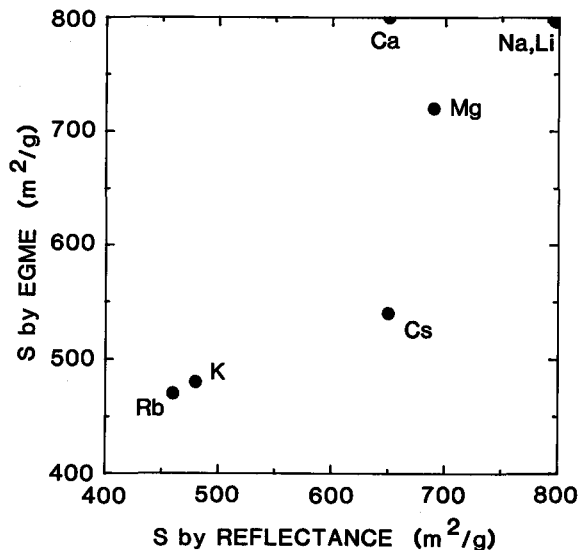
unpublished X-ray powder diffraction data obtained by B. E. Viani (Agronomy Department, Purdue University, West Lafayette, Indiana, 1982), were 13, 13, 20, and 20 Å for the Cs-, Rb-, Mg-, and Ca-saturated samples, respectively, and 35–100 Å for the Li-, Na-, and K-saturated samples. Based on these c-axis spacings, the agreement for the Li-, Na-, and K-saturated samples and the disagreement for the Ca- and Cs-saturated samples was expected. The agreement for the Rb- and Mg-saturated samples, however, was unexpected and, at the present time, is inexplicable. In this regard, it should be noted that disagreement between the two methods is not necessarily ascribable to errors in the reflectance method. If the adsorption of EGME is similar to the adsorption of glycerol or ethylene glycol, the degree of adsorption is affected by the exchangeable cation (MacEwan and Wilson, 1980; McNeal, 1964) and not entirely by the magnitude of S.

We recommend the reflectance method for measuring S when the clay is saturated with an ion like Na^+ that promotes full expansion of the expandable layers. This method is quick and convenient. It requires only that the sample be mixed in a given proportion with HOD, pressed against the hemicylinder of the reflectance accessory by means of the sample support, and allowed to reflect infrared radiation at two frequencies. The value of S for any sample can be determined in triplicate in less than one hour. Moreover, S is determined while the sample is wet with water, as it is in a soil or sediment. Therefore, the reflectance method for measuring S should have great utility.

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