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A QUANTITATIVE METHOD FOR THE DETERMINATION OF MONTMORILLONITE IN SOILS*

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Abstract—A quantitative method for determination of montmorillonite in the soil clay fraction, using X-ray spectrometry, is proposed. The method is based on the fact that polyvinylpyrrolidone (PVP) is adsorbed on the interlayer surfaces of montmorillonite, giving a first order *c*-axis spacing of 26 Å, while it is not adsorbed on other swelling clays. The experimental conditions to obtain a maximum height of the X-ray diffraction peak, and the effect of the mass adsorption coefficient of vermiculite on the intensity of montmorillonite, were investigated. Soil montmorillonite was determined by the method of known additions, measuring the intensity of the X-ray diffraction peak before and after the addition of small and known amounts of Wyoming montmorillonite.

Several methods have been proposed for the quantitative determination of montmorillonite in soil clays (Mehra and Jackson, 1959; McNeal and Sansoterra, 1964; Barshad, 1965; Alexiades and Jackson, 1965, 1966). These methods involve the simultaneous determination of montmorillonite and vermiculite, because these clays often occur together in the soil clay fraction, especially in arid and semi-arid soils (McNeal and Sansoterra, 1964; Levy *et al.*, 1972). The methods proposed by Jackson and co-workers are direct ones viz. they involve measuring either mono- and duo-interlayer glycerol adsorption (Mehra and Jackson, 1959), or reduction in the cation exchange capacity (CEC) due to potassium fixation by vermiculite (Alexiades and Jackson, 1965). The main source of error in the two methods originated in their inability to separate these clays from amorphous material (Mehra and Jackson, 1959; Van Reeuwijk and de Villiers, 1968). The methods proposed by McNeal and Sansoterra and by Barshad are indirect. For example the first authors estimated the amount of montmorillonite and vermiculite through the use of simultaneous equations involving measurements of surface area, CEC and hydroxyl water loss after correction for the presence of the other constituents. Barshad based his estimation on CEC measurements of the soil clay and specifically assigned CEC values for montmorillonite and vermiculite (100 and 150 m-equiv/100 g clay, respectively). In the indirect methods, all errors in the determinations of the other clay minerals were transferred to the calculated ones.

X-ray spectrometry has been used for quantitative analysis of powder mixtures of inorganic crystallites (Klug and Alexander, 1954) and clay minerals (Brindley, 1961). Talvenheimo and White (1952) reported quantitative determinations for kaolinite, bentonite and illite using a direct-reading Geiger counter X-ray spectrometer. Accuracy of the quantitative measurements was quite good for standards of the individual clay minerals. However, accuracy of measurements in mixtures of the clays was relatively poor. In the case of mixtures, two error terms should be taken into consideration—overlap of the diffraction peaks and the difference in the mass absorption coefficients of the clay minerals. In using X-ray spectrometry for quantitative analysis of soil clays, an additional obstacle arises. The mass adsorption coefficient of the soil clay may differ appreciably from that of a reference clay mineral.

It was recently shown that the monoionic polymer polyvinylpyrrolidone (PVP) was adsorbed on the interlayer surfaces of sodium and potassium montmorillonite (Francis, 1973; Levy and Francis, 1975), giving a first-order *c*-axis spacing of 26 Å. However, this polymer did not adsorb on the interlayer surfaces of vermiculite (Francis, 1973), leaving the first-order *c*-axis spacing of 11 Å unchanged. The difference between the Bragg angle of diffraction of vermiculite and montmorillonite–PVP complex was large enough to eliminate overlapping of the two X-ray maxima. This fact incited the development of a quantitative method for determination of soil montmorillonite by X-ray spectrometry. Quantitative determination of soil clays by X-ray diffraction analysis is sometimes not very accurate, because it depends on many uncontrolled variables (Whittig, 1965). However, an increase in the number of methods for evaluation of soil clays (even a semi-quantitative one) to the already existing ones, can improve the possibility for better characterization of the soil clay fraction (Barshad, 1965).

The purpose of this research was to develop a method that uses X-ray spectrometry and the non-ionic polymer PVP for quantitative determination of montmorillonite in the soil clay fraction.

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MATERIALS AND METHODS

Two reference clays were used in this study: (1) Wyoming bentonite, API No. 26, supplied by Wards Natural Science Establishment; and (2) vermiculite from Traveller's Rest, South Carolina, supplied by the W. R. Grace Co. Flakes of the vermiculite were dispersed by ultrasonic vibration (Watson, 1971) so that particles of 2 μm could be obtained. The dispersion was carried out for 5 min only, to avoid possible lattice alterations (Gata, 1964). The 2 μm fractions of the two clays were separated by sedimentation.

Monoionic montmorillonites and vermiculites in the sodium and potassium forms were prepared by batch exchange with 1 N chloride solutions of the respective cations. Excess salt was removed by successive water washes.

The clay fractions of three soils were prepared for mineralogical analysis by the methods recommended by Kunze (1965). Carbonates, soluble salts, organic matter and free ion oxides were removed from the soils prior to separation of the 2 μm fractions by sedimentation. The soil clay fraction thus obtained was already sodium saturated because sodium salts were used in the preparations (Na–acetate for carbonate removal, $NaHCO_3$, $Na_2S_2O_4$, NaCl and Na–citrate for free iron oxide removal, respectively). Some characteristics of the soils are listed in Table 1.

The research was performed in three stages:

(1) Finding the experimental conditions under which maximum height of the X-ray diffraction peak of the montmorillonite–PVP complex was obtained. The height and width at half-maximum intensity were measured as functions of time of contact between the montmorillonite and the PVP solutions, the weight ratio of PVP to clay and desorption of PVP from the montmorillonite surfaces. Twenty-five mg of montmorillonite was mixed with 5 ml PVP aqueous solutions and left in contact for 4, 24 and 48 hr, while shaking the samples occasionally. For the different PVP:clay ratios, the PVP solutions varied from 0·25 to 10 per cent by weight. After a given time of contact the samples were centrifuged, deposited on glass slides, dried at room $T°$ and humidity, and X-rayed (Levy and Francis, 1975). Some of the samples were washed twice with distilled water after the decantation of the PVP solution, and then deposited on the glass slides.

(2) The effect of vermiculite on the montmorillonite–PVP X-ray diffraction peak was studied by obtaining intensity–concentration curves of the two clays. Depending on the values of the mass adsorption coefficients of the two minerals, the intensity–concentration curves can be linear, concave or convex (Klug and Alexander, 1954). Clay mixtures of the two clays ranging in weight fraction from zero to one were prepared. Twenty-five mg of the mixtures was equilibrated with 5 ml per cent PVP aqueous solutions for 24 hr, centrifuged, decanted, washed with water, deposited on glass slides, dried at room $T°$ and humidity, and X-rayed.

(3) The method of known additions was used for the determination of soil montmorillonites (Brindley, 1961) in order to eliminate corrections for the mass adsorption coefficients of the soil and the reference montmorillonite. "By adding a known weight of a pure component to a sample containing this component, and measuring the reflected intensity before and after the addition, I_1 and I_2, respectively, one can determine approximately the weight proportion of that component in the original sample

$$\frac{I_1}{I_2} = \frac{W_p}{(W_p + W_t)/(1 + W_t)} \times \frac{\mu_1}{\mu_1},$$

where: W_p = weight fraction of the component before the addition; W_t = weight fraction of the added component; and μ_1 and μ_2 are the average mass adsorption coefficients before and after the addition.

According to Brindley (1961) "if W_t is sufficiently small so that μ_2/μ_1 does not depart appreciably from unity, then on rearranging the above equation the following expression is obtained.

$$W_p = \frac{W_t(I_1/I_2)}{1 + W_t - (I_1/I_2)}. \quad (1)$$

If $(\mu_2/\mu_1) > 1$ the value derived for W_p will be too large and conversely if $(\mu_2/\mu_1) < 1$, W_p will be too small. By taking several values of W_t, one can extrapolate the measured value of W_p to $W_t = 0$ and thus eliminate a correction for the adsorption ratio".

Twenty-five mg of soil clay and appropriate amounts of soil clay (22·5, 20·0, 17·5 mg) containing 0·1, 0·2, 0·3 fractions by weight of Wyoming montmorillonite, were equilibrated with 5 ml 1% PVP aqueous solution for 24 hr, centrifuged, the PVP solution decanted, and the clay washed twice with distilled water by centrifugation and decantation. The clays were deposited on glass slides, dried and X-rayed.

Table 1. Some characteristics of the soils in which montmorillonite was determined

Soil type	Site	Dominant clay mineral	Cation exchange capacity of soil (cm/100 g)	Clay in soil (%)
Clay loam	Jordan Valley Israel	Montmorillonite	42	55
Silt loam	Elba, Wisc. U.S.A.	Montmorillonite	31	32
Silt loam	Dodge, Wisc. U.S.A.	Montmorillonite and kaolinite	24	27

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Quantitative and uniform deposition of the clays on the glass slides was difficult. Each result was the mean value of at least triplicates. Integrated intensities, defined as the product of the peak height and peak width at half-maximum intensity were used in all the calculations (Norrish and Taylor, 1962). The accuracy of the measurements attained was about 10 per cent.

The diffraction work with the reference clays was carried out with a Norelco X-ray diffraction unit with a copper tube and nickel filter, at 35 kV and 20 mA. The diffraction work with the soil clays was carried out with a Philips X-ray diffraction unit with a cobalt tube, at 40 kV and 20 mA. A Geiger counter attached to a chart recorder was used for direct readings of intensity and angle of diffraction. A scanning speed of 1°/min and a receiving slit of 0·2° were used. The background intensity was subtracted by using relative heights above the background.

RESULTS AND DISCUSSION

The difference between the X-ray diffraction patterns of montmorillonite and vermiculite in a mixture containing 50% montmorillonite and 50% vermiculite dried from PVP solutions and those from glycerol or water solutions, is presented in Fig. 1. It is evident that the overlapping of the diffraction maxima for the clays dried from glycerol or water was avoided by drying from PVP solutions.

The height and width of the first-order *c*-axis spacing (26 Å) of potassium–montmorillonite as functions of time of contact with the PVP solution, the weight ratio of PVP:clay, and number of washes, were measured (Table 2). Similar results were obtained with sodium-montmorillonite. The results revealed that a maximum height was obtained after 24 hr. Only the height of the X-ray diffraction maximum increased, as time of contact with the PVP solution increased, indicating that the penetration of the polymer between interlayers is not a rapid process. For qualitative measurements, the 26 Å peak can be measured after contact with the PVP for a shorter time. The increase in peak height after 48 hr of contact was within experimental error.

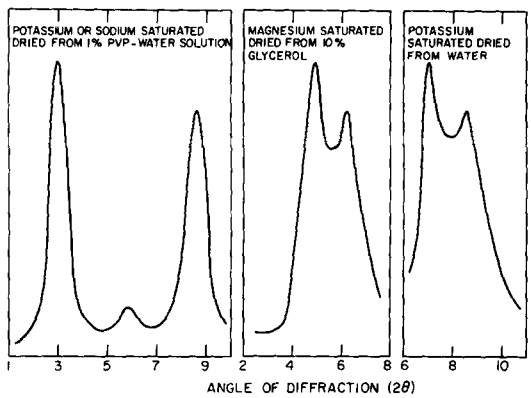


Fig. 1. Smoothed traces of X-ray diffraction patterns of a mixture containing 50% montmorillonite and 50% vermiculite.

Table 2. Heights* and widths* of the first-order *c*-axis spacing (26 Å) of potassium montmorillonite as functions of the different treatments

	Time of contact (2:1 PVP:clay)		
	4 hr	24 hr	48 hr
Height	86	120	125
Width	1·3	1·4	1·4

	PVP:clay ratio (by weight)						
	0·5:1	1:1	2:1	4:1	8:1	10:1	20:1
Height	30	120	125	60	49	30	6
Width	1·5	1·3	1·3	1·4	1·5	1·5	1·6

	PVP:Clay (by weight) and number of H_2O washes			
	No washes		Two H_2O washes	
	2:1	8:1	2:1	8:1
Height	109	49	125	130
Width	1·3	1·5	1·4	1·4

* Arbitrary units.

To ascertain the optimal amount of PVP needed to give the maximum intensity, the diffraction maximum was measured as a function of the weight ratio between PVP and clay (Table 2). At PVP:clay ratios less than one, there was a decrease in the peak height as compared with ratios of 1:1 and 2:1. At a PVP:clay ratio below one, a maximum of 12·8 Å appeared, indicating that there was not sufficient PVP to penetrate all interlayers. As the PVP:clay ratio increased, the 12·8 Å maximum disappeared, with a corresponding increase in the height of the 26 Å maximum. At a PVP:clay ratio above two, there was again a decrease in the height of the peak; apparently, PVP accumulated on the external surfaces, coating the montmorillonite and reducing the X-ray diffraction peak's height.

The externally accumulated polymer could be easily washed with water (Table 2). After two H_2O washes maximum height of the peak was obtained. The PVP adsorbed on the interlayer surfaces could not be desorbed by water (Francis, 1973), leaving the 26 Å spacing unchanged. The above results indicated that the optimal conditions for quantitative measurement were the following: 24 hr of contact,

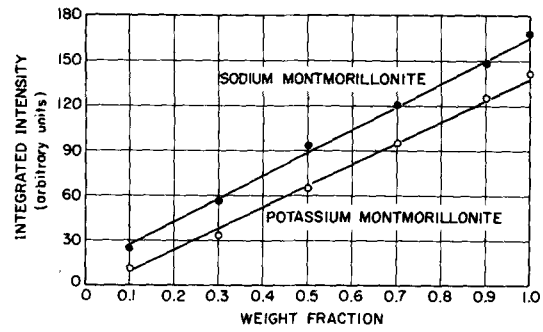


Fig. 2. Integrated intensities of sodium and potassium montmorillonite diffraction peaks in a mixture with vermiculite, as functions of the weight fraction of montmorillonite.

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Table 3. Heights and widths before and after the addition of 0·1, 0·2, 0·3 weight fractions of sodium montmorillonite (Wyoming)

	Jordan valley				Elba				Dodge			
	Before addition	After addition of 0·1 w.f.	After addition of 0·2 w.f.	After addition of 0·3 w.f.	Before addition	After addition of 0·1 w.f.	After addition of 0·2 w.f.	After addition of 0·3 w.f.	Before addition	After addition of 0·1 w.f.	After addition of 0·2 w.f.	After addition of 0·3 w.f.
Height*	12·8	21·7	26·7	31·1	17·0	24·3	27·3	32·2	10·2	18·2	24·4	30·6
Width*	2·0	1·2	1·0	0·9	1·4	1·1	1·1	1·0	1·6	1·1	1·0	1·0

* Arbitrary units.

2:1 PVP:clay weight ratio, and two H_2O washes before deposition of the clay on the glass slide.

The effect of the mass adsorption coefficient of vermiculite on the intensity of X-ray diffraction of the montmorillonite–PVP complex was observed on the intensity–concentration curves (Fig. 2). Sodium or potassium montmorillonite in mixtures with sodium or potassium vermiculite, as functions of the weight fraction of montmorillonite (Fig. 2), reveal a linear dependence of the integrated intensity on the concentration of montmorillonite. The presence of vermiculite affected only slightly this linear relationship. The integrated intensity of potassium montmorillonite was lower than that of sodium montmorillonite, possibly due to the higher mass adsorption coefficient of the potassium ion. From these results it was concluded that the presence of vermiculite in the soil clay fraction will not affect appreciably the X-ray diffraction peak of montmorillonite.

The height and width at half-maximum intensity of the three soil clays before and after the addition of Wyoming montmorillonite (sodium-saturated) were measured (Table 3). From these results the integrated intensities before the addition, I_1, and after the addition of 0·1, 0·2 and 0·3 weight fractions of montmorillonite ($I_2^{0\cdot1}$, $I_2^{0\cdot2}$, $I_2^{0\cdot3}$), were calculated. These intensities were inserted in equation (1) and the weight fractions of montmorillonite in the soil clays, W_p, were calculated as functions of the added weight fraction, W_t (Fig. 3). It is evident from Fig. 3 that the calculated weight fractions of the three soil montmorillonites were linear functions of the added montmorillonite, indicating that at low fractions of the added montmorillonite the mass adsorption coefficients ratio of the soil montmorillonite and the added montmorillonite did not deviate appreciably from unity.

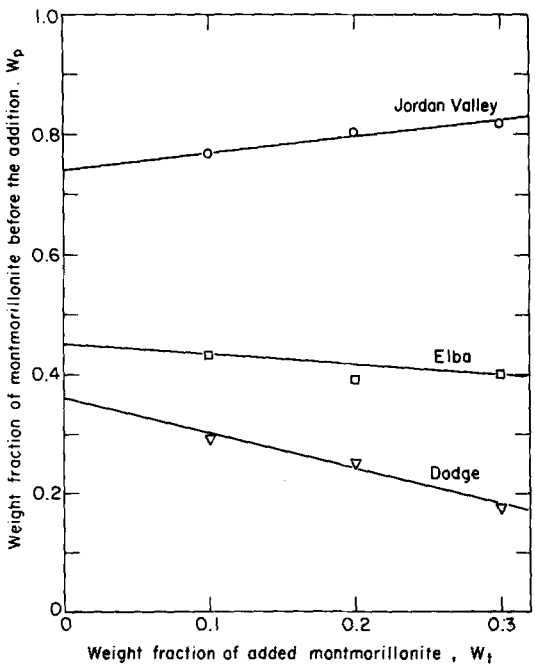


Fig. 3. Weight fractions of soil montmorillonites as functions of added montmorillonite (Wyoming).

However, W_p was not constant and independent of W_t. For the Jordan Valley soil, W_p was overestimated, while that of the Elba and Dodge soils were underestimated, indicating that the mass adsorption coefficient of the soil montmorillonites differs from that of the added one. By extrapolating to $W_t = 0$, the real weight fraction of the soil's montmorillonites was determined.

It should be emphasized that the proposed method may fail to give good results in cases where the soil fraction contains large amounts of amorphous matter and the size of the soil clay particles differs appreciably from that of the added montmorillonite.

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