BASE-EXCHANGE: AN ANALYTICAL TOOL FOR MIXED-LAYER AGGREGATES

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ABSTRACT

Base-exchange determinations were made on selected clays of the montmorillonite-illite group to test this method as an analytical tool for the analysis of mixed-layer aggregates. The relatively rapid manganese method developed by Bower and Truog was used and its precision determined on monodisperse, monomineralic fractions and monodisperse fractions of prepared mixtures of illite and montmorillonite. The particle size range 1-0.25 micron was chosen for all determinations exclusive of those on bulk samples.

To establish end members, determinations were made on a series of illites, fine-grained muscovite and both natural and synthetic montmorillonites.

In order to test the validity of this method, determinations were made on mixed-layer aggregates on which illite-montmorillonite percentages had been determined by other workers using x-ray techniques and chemical analysis.

INTRODUCTION

The occurrence of illite and montmorillonite together in the same clays has made mineralogical analysis of these materials difficult because of the interactions resulting from their close structural similarities. Bradley (1950, p. 421-427) has pointed out that these materials may occur naturally as discrete minerals (mechanical mixtures), as random-layered intergrowths of mixed species, and as regular alternating intergrowths of two complementary species. In addition, the possibility exists of both interstratification and mixing of discrete minerals in a simple sample.[1] These materials have been studied principally by x-ray diffraction techniques. X-ray evaluations of mixed-layer materials have been based on mathematical treatments of the problem as developed by Hendricks and Teller (1942, p. 147-167) and Mering (1949, p. 371-377). Brown and MacEwan (1951, p. 266-284) have utilized the work of Hendricks and Teller in constructing a series of graphs which depict the type of x-ray diffraction effect one should expect from a material consisting of mixed layers. Bradley (1945, p. 704-713; 1950, p. 421-427) has investigated several mixed-layer aggregates using x-ray techniques and has presented

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[1] For the purpose of the present work a mixed-layer aggregate is regarded as a mixture of illite and montmorillonite. The manner of mixing is not considered.

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criteria for recognizing the various types of structural arrangements. Weaver (1953, p. 921-924) used x-ray diffraction methods in characterizing a mixed-layer metabentonite. Chemical and differential thermal analyses also have been utilized to estimate the proportions of illite and montmorillonite present (Weaver, 1953, p. 921-924; Kerr et al., 1949, p. 38-43; Grim and Rowland, 1942, p. 746-761; 801-818).

In view of the complex nature of the problem, it was felt that a supplementary tool for studying mixed-layer aggregates would be desirable. For this reason the possibility of utilizing base-exchange determinations was investigated.[2] In order to be applicable the base-exchange method must be precise, and the end-member materials (illite and montmorillonite) should have a more limited range of capacities than has been reported in the literature. Furthermore, a well-defined relationship (base-exchange *vs.* composition) must be established.

MATERIALS AND SAMPLE PREPARATION

The materials chosen for study are listed in Table 1.

TABLE 1. — ILLITES, MONTMORILLONITES, AND MIXED-LAYER
AGGREGATES SELECTED FOR STUDY

Illite and Related Materials	*Montmorillonites*	*Mixed-Layer Aggregates*
Fithian (Grim)	Wyoming Montmorillonite	Metabentonite (Weaver)
Oswego	Mississippi Montmorillonite (API no. 19)	M.L.A. (Bradley)
Synthetic Illite	Arizona Montmorillonite (API no. 23)	M.L.A. Cameron (API no. 31)
Fine-grained Muscovite	Nontronite (API no. 33a)	M.L.A. Tazewell (API no. 41)
McAvoy	Synthetic Beidellite (D. M. Roy)	M.L.A. Pioche (API no. 32)

Synthetic illite was prepared by hydrothermal treatment of Wyoming montmorillonite (1-0.25 micron) in an alkaline environment (KOH solution). Synthetic beidellite was prepared hydrothermally by Dr. D. M. Roy.

Air-dry samples of the clays were crushed in a mortar to pass 60 mesh and dispersed in an ammoniacal solution using a Waring blendor. In most cases, ammonium hydroxide (added to give a solution approximately 0.01 N in NH_4^+) provided adequate dispersion. Sodium oxalate or sodium tetraphosphate was used as a dispersant for clays which did not disperse well in ammonium hydroxide. A very dilute suspension (about 0.05 percent solids) of muscovite was disaggregated in a Manton-Gaulin type homogenizer. This treatment served to break down most of the muscovite particles to less than two microns. The homogenized sample was in a well-

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[2] This type of approach has been used by Dyal and Hendricks (1950, p. 421-432) and Hendricks and Alexander (1940, p. 95).

dispersed condition at this point and subsequent fractionation was accomplished without difficulty.

The clay suspensions were diluted with distilled water and fractionated by centrifuging (International Type No. 2 and Sharples supercentrifuge) to obtain 1 to 0.25 micron fractions. The fractionated samples were dried at 90°C, ground to pass 60 mesh and stored in a desiccator. One-quarter gram samples of Fithian illite and Wyoming montmorillonite were prepared in the following proportions: illite 100, 75-25, 50-50, 25-75, and montmorillonite 100. Each sample was prepared in triplicate. One-quarter gram samples of each of the remaining materials were prepared in duplicate.

EXPERIMENTAL PROCEDURE

A base-exchange technique was selected for use in the present investigation because it offered an additional means for the study and characterization of mixed-layer aggregates. The manganese-saturation method described by Bower and Truog (1940, p. 411-413) was chosen because it is relatively rapid, accurate, and simple, and requires only small amounts of sample.

For a detailed description of the analytical procedure used, the reader is referred to the work of Bower and Truog. Briefly, the procedure is as follows: a 0.25-gram sample of dried material is saturated with normal manganous chloride solution, the exchangeable manganese removed by leaching with normal ammonium acetate, and an aliquot taken. The dried aliquot is treated to oxidize Mn^{2+} to MnO_4^- and the managanese content is determined colorimetrically. The manganese is determined by the classical method of Willard and Greathouse (1917, p. 2366) as adapted to photoelectric colorimetry by Mehlig (1939, p. 274).

RESULTS

Precision Experiments

The base-exchange determinations made on prepared mixtures of illite and montmorillonite are listed in Table 2 and shown graphically in Figure 1. These results show a linear relationship (base-exchange vs. composition) for the mixtures of illite and montmorillonite and indicate the precision obtainable using the manganese method.

TABLE 2. — BASE-EXCHANGE RESULTS ON PREPARED
ILLITE-MONTMORILLONITE MIXTURES
(Fithian Illite — Wyoming Montmorillonite)

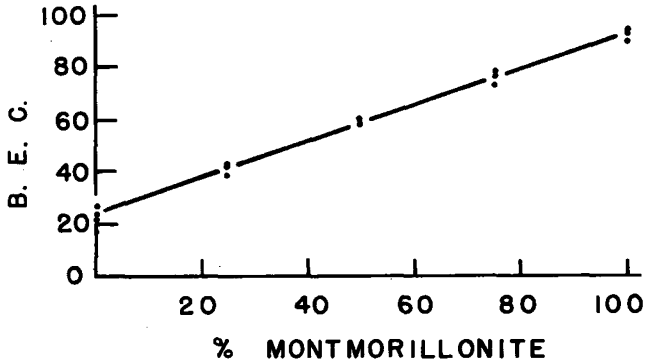| Montmorillonite (percent)	0	25	50	75	100
Base-Exchange Capacity (meq Mn^{2+}/100 g)	25.8	42.4	58.8	77.5	95.1
	24.4	40.7	61.0	75.4	94.5
	23.8	43.1	58.8	77.8	89.4
average	24.7	42.0	59.5	76.9	93.0

FIGURE 1. — Results of precision experiments on fractionated (1 - 0.25 micron) Fithian illite — Wyoming montmorillonite.

Determinations on Selected Clays

Base-exchange capacity values obtained for natural and synthetic materials are tabulated in Table 3.

TABLE 3. — BASE-EXCHANGE CAPACITIES (meq Mn^{2+}/100 g) OF ILLITES, MONTMORILLONITES AND RELATED MATERIALS (1-0.25 micron fractions)*

Illites and Related Materials		Montmorillonites		Mixed-Layer Aggregates	
Fithian	24.7	Wyoming	93.0	Metabentonite (Weaver)	27.2
Oswego	13.5	Mississippi	112.1	M.L.A. (Bradley)	43.0
Synthetic Illite	11.2	Arizona	101.2	M.L.A. (API no. 31)	80.5
Muscovite	16.6	Nontronite	111.0	M.L.A. (API no. 32)	83.9
McAvoy	21.8	Synthetic Beidellite	96.0	M.L.A. (API no. 41)	30.8

* All samples were fractionated with the exception of the mixed-layer material supplied by Dr. Bradley.

Figure 2 shows a working graph constructed with end members having assigned values of 15 meq/100 g (illite) and 95 meq/100 g (montmorillonite). Implications involved in these selections are considered later (see discussion). Figure 2 also shows the positions assumed by the various mixed-layer materials investigated.

This figure was constructed on the basis of the linear relationship which was obtained for mixtures of discrete particles. It may be possible that this relationship does not hold for interstratified aggregates but sufficient samples were not available to investigate this aspect. However, using the straight line relationship, reasonably good agreement was obtained with Bradley and Weaver on two analyzed mixed-layer aggregates.
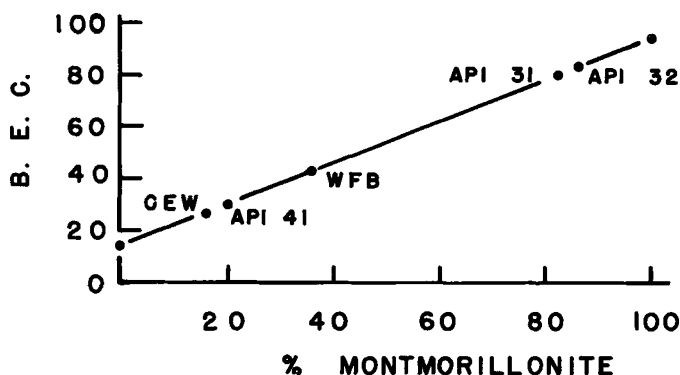
B. E. C.

100
80
60
40
20
0

API 31 • •API 32

WFB

CEW • •API 41

20   40   60   80   100

% MONTMORILLONITE

FIGURE 2. — Composition of some mixed-layer aggregates as determined from base-exchange capacities.

DISCUSSION

If this base-exchange method is to be used as an analytical tool in evaluating mixed-layer aggregates, the selection of representative end members is critical. For the illite end member a possibility is Fithian illite which has been regarded as one of the better illites, but the base-exchange value falls in the middle of the range of values given by Grim (1953, p. 129) for illites. Weaver (1952, p. 119-130) reports an unusually pure and well-formed illite from an Oswego graywacke. In his opinion the Oswego material was an end member illite. This sample had a base-exchange capacity of 14 which is considerably lower than most of the values reported for illite. Another material used to fix the end member illite was fine-grained muscovite. The base-exchange capacity obtained for this material (17 meq/100 g) is of the same order of magnitude as Oswego illite and probably represents a value close to an end member of this series. It has been suggested that the large difference in base-exchange capacity between illite and montmorillonite may be due solely to particle size. For this reason, Wyoming bentonite (1-0.25 micron) was treated hydrothermally for a period of 24 hours at a temperature of 380°C and 15,000 p.s.i. water pressure in a potash solution to convert the bentonite to an illite. X-ray and differential thermal analyses of this converted bentonite showed the characteristic reactions of illite and an electron micrograph of the material showed no change in morphology. This material had approximately the same ultimate particle size as the original bentonite and its base-exchange capacity was 11 meq/100 g. This value is compatible with those of Oswego illite and fine-grained muscovite. On the basis of these three determinations the value for the end member illite was placed at 15 meq Mn^{2+} per 100 grams of clay. With regard to Fithian illite and other illites reported, it is felt that there is sufficient montmorillonite present in the illite to raise the base-exchange capacities. These should then be considered as mixed-layer aggregates.

The selection of the montmorillonite end member was more difficult owing to the large number of existing montmorillonites and the iso-morphous substitutions in the lattice apparently affecting the base-exchange capacities. This observation has been made by many workers (Foster, 1951, p. 717-730; Ross and Hendricks, 1945, p. 23-79; Earley et al., 1953, p. 707-714). Since their results are based almost exclusively on chemical analyses, which are subject to a fair amount of error, it was thought best to select the members of the montmorillonite group which are most com-monly found in nature. These varieties were thought to be montmoril-lonite and beidellite. These two minerals probably comprise the bulk of the montmorillonites occurring in mixed-layer aggregates. For example, Ross and Hendricks (1945, p. 61) have noted that beidellite commonly occurs in mixed-layer materials. The value for montmorillonite (Wyoming) was found to be 93 meq and the synthetic beidellite was found to have a base-exchange capacity of 96 meq. On the basis of these two values, which are the same within experimental error and are believed to be typical for these two varieties, 95 meq/100 grams was selected as the value for the end member montmorillonite. If it can be determined by another means that another variety of montmorillonite is present, then the values reported in Table 3 for those particular montmorillonites can be used as the end member. It is believed, however, that for general use the base-exchange value of 95 meq should be utilized.

Since this method is proposed as a sensitive tool, it is pertinent to emphasize the precision which can be obtained. There has been criticism in the literature (MacKenzie, 1952, p. 203) that excessively high values are obtained using the manganese saturation method owing to the forma-tion of $Mn(OH)^+$ groups. In the first experimental work done by the present authors using this method, these excessively high base-exchange values also were obtained; this resulted from not carefully controlling the pH of the test solutions. More specifically, before saturation with man-ganous chloride the clay sample should have a pH below 7. Any bases used for dispersion should be removed. When neutral or slightly acid solutions were used, no difficulty was encountered in arriving at repro-ducible and accurate base-exchange values. No values higher than 112 meq were obtained for any variety of montmorillonite in the particle size range tested. Since values up to 160 or more meq have been reported in the literature (Lewis, 1950, p. 91-124), it can be stated definitely that this method of determination does not give abnormally high values if the necessary precautions are taken. The precision of the method was good (± 3 percent) over the whole range of determinations. Bower and Truog (1940, p. 411-413) have compared the method with other methods of determination and have found it to check satisfactorily.

In determining the applicability of this method, the work was handi-capped by the lack of a number of good natural mixed-clay aggregates in which the proportions of illite and montmorillonite had been determined

by other methods. The only two analyzed samples that could be had were obtained from Drs. C. E. Weaver and W. F. Bradley. Other mixed-clay aggregates studied, viz., A.P.I. samples 31, 32 and 41, had not been analyzed in any detail, but from differential thermal analysis evidence they were considered to be mixtures of illite and montmorillonite. The results obtained in the present study are compared in Table 4 with those of the other workers.

TABLE 4. — MINERAL COMPOSITION OF MIXED-LAYER AGGREGATES

Material	Montmorillonite : Illite	Percent Montmorillonite From B.E. Determination
Metabentonite (Weaver) (X-ray and chemical analysis)	1:3 or 1:4	16
M.L.A. (Bradley) (X-ray)	1:1	36
M.L.A. (API no. 41) (DTA)	Illite dominant	20
M.L.A. (API no. 32) (DTA)	ca. 1:1	86
M.L.A. (API no. 31)	Illite dominant	82

It should be emphasized that the compositions derived from differential thermal analysis studies on bulk materials (A.P.I. samples) are only qualitative. It is not surprising that agreement between two methods (base-exchange and DTA) was obtained on only one sample (API no. 41).

The relative percentages of montmorillonite and illite obtained by base-exchange studies were 16:84 (Weaver) and 36:64 (Bradley) as opposed to their previously determined ratios of 1:4 and 1:1, respectively. The approximate correspondence of these two sets of values suggests that the base-exchange method can be of supplemental value in studying mixed-layer aggregates.

The advantages of the base-exchange technique may be summarized as follows:

(1) The method is precise; accuracy of the method was established by Bower and Truog.

(2) A wide spread of values between end members gives high sensitivity to the method.

(3) The interpretation is simple and is not based on theoretical assumptions which may or may not be of general application.

CONCLUSIONS

On the basis of a number of base-exchange determinations made on montmorillonites, illites, and mixed-layer aggregates, it is believed that this method offers a sensitive and relatively rapid technique for the analysis of mixed-layer aggregates. A good degree of precision was established on determinations of prepared artificial mixtures of illite and montmorillonite, and the values are believed to be accurate.

ACKNOWLEDGMENTS

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APPENDIX

Recent work has demonstrated the usefulness of base-exchange determinations in characterizing mixtures of clay materials. Webber and Shivas (Soil Sci. Soc. Am. Proc. *17* (2) 96 (1953)) correlated chemical and thermal analyses with base-exchange determinations in the study of some illite-bearing Ontario soils ($<$ 1 micron fractions). Chemical analyses revealed a high K_2O content for these materials and an exchange capacity higher than that normally associated with illite. Seven of the nine samples studied showed a linear relationship between base-exchange capacity and percent K_2O. Chemically determined potash contents and base-exchange capacities agreed very well with calculated values of base-exchange and K_2O based on estimated compositions. The values of 20 meq Mn^{2+}/100 g and 90 meq/100 g were used for reference materials (illite and montmorillonite, respectively).

Roy and Das (Soil Sci. *76* (2) 97 (1953)) used electrometric titration curves, cation-exchange capacities, viscosity behavior and chemical composition in studying the clay fractions of several Indian soils. They showed that the base-exchange capacities of mixtures of illite and montmorillonite were additive. A value of 15 meq Ba^{2+}/100 g was obtained for the base-exchange capacity of illite and 101 meq Ba^{2+}/100 g for montmorillonite (source of minerals not specified). These workers successfully evaluated the composition of the soils using the four previously mentioned techniques.

DISCUSSION

R. C. Vanden Heuvel. — Montmorins exhibit wide ranges of base-exchange capacity depending upon the particular isomorphous charge of the particular sample examined. For example, montmorin extracted from California bentonite exhibits a base-exchange capacity of approximately 125 meq/100 g whereas montmorin from Wyoming bentonite exhibits a lesser exchange capacity. Therefore, montmorin is not represented by one particular end member but by a range of materials of varied chemical composition showing also a range of base-exchange capacities. This range is even more extensive in complex soil systems and therefore the application of the method to soil systems may lead to great uncertainties.

W. C. Ormsby. — The variability of the exchange capacities of pure montmorillonites is felt to be less than is commonly believed. Factors other than isomorphous substitutions may well contribute to differences in the saturation capacity. Impurities certainly affect the total exchange capacity

and may increase or decrease the ability of the clay to adsorb ions. By working with pure fractionated samples and using a standardized method of determination, the differences will be minimized.

In this investigation, several types of montmorillonites (including nontronite and synthetic beidellite) were found to have exchange capacities between 93 and 112.1 meq per 100 grams of clay. Wyoming montmorillonite and synthetic beidellite had exchange capacities of 93 and 96 meq, respéctively. It has been observed that mixed layer materials tend to contain a beidellite-type mineral. For this reason it seems justifiable to select 95 meq as an end member value. It is not suggested that montmorillonites can be represented by a single end member but for the purposes of mixed-layer studies, beidellite seems the logical choice.

Because a range of capacities does exist for montmorillonites, the suggested method is limited and should be applied in conjunction with other techniques. Properly applied, the method should relieve rather than create uncertainties.