

A METHOD FOR THE DETERMINATION OF THE CATION EXCHANGE CAPACITY OF CLAY MINERALS AND SOILS *

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ABSTRACT

For many purposes it is desirable to have a method for the determination of the cation exchange capacity of clay minerals based on principles as free from ambiguity as possible. Most of the many methods previously proposed have the drawback of entailing a great deal of work if one is to make sure that the mineral is completely saturated with the reagent in use, or that an excess of the reagent is absent. What might be called the complete chromatographic method by its very nature does not suffer from this difficulty. A known weight of clay is suspended on an appropriate inert filter aid (such as Gooch asbestos), packed into a glass tube, and the exchangeable ions eluted with a solution of cesium chloride traced with radioactive Cs 137. The effluent is collected in a series of appropriately sized samples, and the specific radioactivity of each of these determined. When the activity of the effluent has risen to that of the influent solution, one is certain that complete exchange has taken place. A simple computation gives the total cesium holdup of the column, and if the column was initially dry, the exchange capacity of the clay sample.

As a routine method, particularly when results of the highest precision are not needed, the effluent may be collected in only two samples, one large sample and finally one small sample to check for complete exchange. This procedure requires a minimum of work and attention but suffers from the disadvantage that the result depends upon the difference of the two counting rates measured and is thus subject to greater uncertainty.

These methods have been compared with the Bower-Truog method (Ind. and Eng. Chem., Anal. Ed., 12, 411 (1940)) on Chambers, Arizona, montmorillonite, a nontronite, and an attapulgite. Generally the Bower-Truog method gave more variable and somewhat lower results. Thus for the Chambers montmorillonite the Bower-Truog method gave 0.97 meq./gm.; the chromatographic method, 1.054 meq./gm.

The method has been further tested by initially saturating columns with manganous ion, determining the weight of solution held up in the column, and then eluting with traced CsCl. Effluent Mn was determined colorimetrically and the Cs in the Geiger counter. The results agreed within experimental error for the following clays of the API series: montmorillonites H19, H23, H24; illite H36; and nontronite H33b.

A great variety of methods has been proposed for the determination of the exchange capacities of the clay minerals. A review of these methods is given by Piper (1944), and a new method together with references to more recent literature is given by Perkins (1952, p. 446). Generally the methods proposed involve treatment of the mineral by a specific reagent and do not allow much freedom of modification to approximate special conditions which may arise in practice, such as a determination of the proportions of

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a pair of ions taken up by a clay in contact with a definite solution. The method described here, which involves no new principles, simulates the conditions which are found in the motion of dilute solution through beds of soils. It is therefore felt that its possibilities will be of interest to those working in the earth sciences.

The method relies upon the replacement of exchangeable ions by cesium. It has been shown by ourselves and by others that cesium is more strongly held on montmorillonite and attapulgite clays than a large number of uni- and divalent ions: Li^+ , Na^+ , K^+ , NH_4^+ , Rb^+ , Ca^{++} , Sr^{++} , Ba^{++} , Mn^{++} . The behavior of cesium in conjunction with trivalent ions and ions of higher valence has been very little investigated. Undoubtedly the behavior will be found to be more complex, particularly because of effects due to hydrolysis of polyvalent ions. It is not possible at this time to make any general statements in this connection.

Essentially the method consists in running an elution chromatogram with cesium chloride solution from a mineral sample distributed on an appropriate inert filter aid. The chromatogram is mapped, more or less roughly as may be desired, by following the cesium content of the eluate with a tracer of radioactive $\text{Cs } 137$. Cesium being more strongly adsorbed than any of the ions commonly found in clays and soil minerals, the "break-through" of the chromatographic column is always relatively sharp and the effluent activity rises rapidly to its input value. When this stage is reached one may be certain that the exchange process is complete.

Insofar as the determination of a capacity is concerned, the shape of the elution curve is of no consequence, provided only that it is sufficiently steep so that the area above it can be determined with adequate accuracy. For if the column was initially dry, the area above this curve is a direct measure of the amount of cesium left on the mineral. The actual shape of the curve will depend on many factors entering into the operation of the column. The rate of flow of the solution and the degree of subdivision of the mineral are the most important of these. Any channeling in the column will cause the curve to flatten. None of these effects, however, has any effect on the area above the curve. It is this fact, together with the easy method of noting the completion of the exchange, that makes for the unambiguity of the present method.

The determination of the area above the curve may be done in any manner that suits the fancy of the operator. The simplest method of all is the least subject to error. One has only to sum the product of the counting rates (activities) and volumes (or weights) of the samples collected and subtract this from the product of the initial activity of the solution and the total volume (or weight) of the effluent. This difference multiplied by the normality of the cesium solution and divided by the weight of the mineral is the exchange capacity sought. For a simple capacity determination when one is not interested in the detailed shape of the elution curve, only two samples need be collected: one large sample of volume V_1 (See Fig. 1) which corresponds to some point after the effluent activity has risen to its

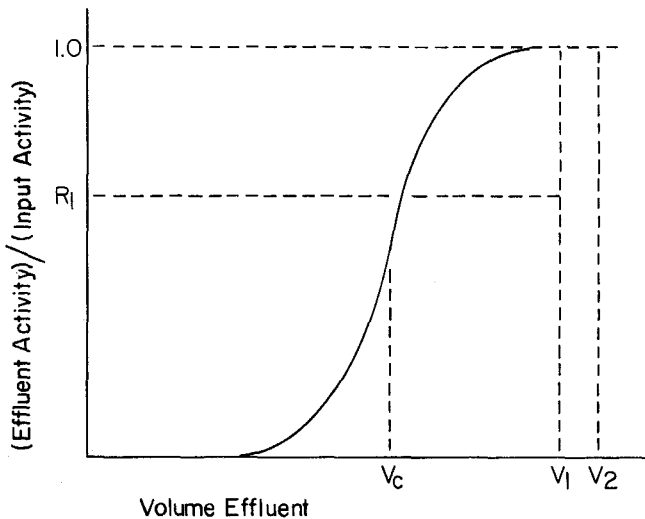


FIGURE 1.—Elution chromatogram.

input value, and one small sample to check this fact. The area above the break-through curve is given by $1 \times V_1 - R_1 \times V_1 = V_1(1 - R_1)$ where R_1 is the relative activity of the large sample V_1 ; provided, of course, the relative activity of the small sample $V_2 - V_1$ is $R_2 = 1.000$.

While it is obvious that the easiest way to ensure that $R_2 = 1.000$ is to take V_1 very large, this affects adversely the accuracy of the result. The larger V_1 the more nearly R_1 approaches unity and the less accurate is the difference $1 - R_1$. The R 's can be determined to an accuracy of 1 percent without too much difficulty; hence to obtain results consistent to 2 percent, R_1 should be no larger than 0.5. Evidently the larger the capacity of the column and the steeper the break-through, the easier will it be to obtain a small R_1 . These factors are at least partially under the control of the operator. The magnitude of V_1 can be adjusted by properly selecting the normality of the cesium solution with respect to the total exchange capacity of the column. For a nearly symmetrical break-through curve such as is generally obtained with cesium the area above the curve will be nearly equal to $1 \times V_c$, where V_c is the volume corresponding to $R = 0.5$. Thus $V_c = (\text{Total Capacity}) / (\text{Normality of cesium solution})$, and since $V_1 > V_c$ it is quite simple to adjust conditions to give a convenient value for V_1 . Only a rough estimate of the exchange capacity of the mineral is needed for this purpose.

The above discussion makes it apparent that the present method is impractical for minerals of very low capacity. It will evidently be unsatisfactory for the kaolin clays.

The steepness of the break-through curve is at least partially under the control of the operator. Fine subdivision of the material is conducive to

rapid exchange reaction and so to steep break-through. Within limits the curve can be made steeper by lowering the flow rate. This adjustment cannot be carried to extremes; at very low flow rates the effect of longitudinal diffusion in the column becomes of importance and prevents further sharpening of the break-through. We have used with success flow rates of 0.1-0.2 ml./min. (cm². of column cross section).

Some idea of the precision of the method can be gained from an inspection of the results given in Table I.† Other methods in our hands have generally given lower values for the capacity and have shown less satisfactory agreement. Thus for the Chambers montmorillonite the method described by Bower and Truog (1940, p. 411) gave 0.97 meq./gm. rather than the value 1.054 meq./gm. produced by the chromatographic method.

The data of Table I are given first as milliequivalents per gram of clay as weighed. The average values are converted to milliequivalents per gram of clay "backbone," a method of expressing the results entirely independent of the variable water content of the clay minerals and of the particular content of exchangeable ion. The "backbone" of a clay is determined by igniting a weighed sample in air to constant weight at 1,100-1,200° C. From

† For some of these results we are indebted to Drs. G. L. Gaines and C. N. Merriam, working in the Sterling Chemistry Laboratory.

TABLE I. — EXCHANGE CAPACITIES OF VARIOUS CLAYS BY CHROMATOGRAPHIC CESIUM REPLACEMENT

(All results are in meq./gm. and the averages have been converted to meq./gm. backbone. See text)

Montmorillonites			Attapulgite
Chambers, Ariz. API 23	Polkville, Miss. API 19	Otay, Calif. API 24	Quincy, Fla. API 46-1
1.050	0.960	1.102	0.280
1.044	.978	1.109	.283
1.066	1.002	1.084	.287
1.046	—	—	.277
1.062	0.980	1.098	.287
—	1.321	1.439	—
1.054	—	—	0.283
1.381	—	—	0.349
Nontronite		Metabentonite	Illite
Spokane, Wash. API 33b		High Bridge, Ky. API 42	Morris, Ill. API 36
0.945		0.270	0.176
.959		.289	.169
.940		.286	.160
—		—	—
0.948		0.282	0.168
1.225		0.320	0.188

the weight of the residue the weight of the exchangeable ions is deducted, and capacity results are computed per unit weight of this backbone. It is worth remarking that even for a high capacity montmorillonite an exact knowledge of the composition of the exchangeable ions is not necessary in order to be able to make a sufficiently accurate backbone determination. Since the proportion of exchangeable ions is small, one may take for a natural clay the value 0.025 gm. as an average milliequivalent weight of these ions. Of course, if a backbone determination is made on a clay of known composition, the true milliequivalent weight should be used; indeed, for cesium clays the difference is of significance.

The chromatographic method has been further tested by initially saturating clay columns with manganous ion followed by eluting with traced CsCl. Effluent manganese was determined colorimetrically after periodate oxidation and the results compared with the radioactive cesium analyses. The two sets of results agreed within experimental error for the following clays of the A.P.I. series: montmorillonites H19, H23, H24; illite H36; and nontronite H33 b. It should be noted that this comparison is made slightly more complex by the necessity of knowing the hold-up volume of the column in use. This information, which is generally somewhat difficult to obtain with high accuracy, is unnecessary in a simple capacity determination.

An additional experiment has been done with the view of checking directly the completeness of the recovery of exchangeable ions in the elution experiments. Portions of the montmorillonite API 23 and of the attapulgite API 46-1 were made into stiff pastes with distilled water and extruded under high pressure (through a die carrying a $\frac{3}{8}$ -inch hole) into water-filled columns. Under these conditions the extruded filaments break up into short lengths, but disintegrate very little if any further, on the passage of solutions of cesium chloride upward through the columns. By this means it is easy to convert a clay to the monoionic form.‡ Difficulties are encountered if the clay swells appreciably in the exchange, as does a montmorillonite with sodium. The conversion to the cesium form, with labeled Cs, was checked for completeness by the usual comparison of influent and effluent activities. The columns were then washed with water until free of dissolved cesium chloride, as checked both by confirming the absence of radioactivity and of chloride ion in the eluate. The resulting clays were dried under mild conditions (the montmorillonite at 45°-50° and the attapulgite at 30°-35°) and preserved in well-stoppered containers. Two weighed samples of each were submitted to J. Lawrence Smith decompositions. The alkali fraction, after double precipitation of the calcium, was brought to a definite volume and its activity determined. Samples of each of the two clays were eluted with "dead" cesium solutions in the manner of capacity determinations, and the total activity of the eluate deter-

‡ For this useful technique we are indebted to Mr. L. P. Hatch of Brookhaven National Laboratory, who has applied the principle to an important method of segregating the fission fragments of uranium.

mined. All activity measurements were done in the same counter, the reproducibility of which was confirmed. After taking into account the volumes of solutions and weights of samples the comparable activities (on an arbitrary scale) were found to be: for the montmorillonite, by J. L. S. Method, 33.5, 35.2; by elution, 34.8; for the attapulgite, by J. L. S. Method, 18.8, 18.5; by elution, 18.3. Thus within the precision of the experiments, the two methods give the same result. The capacities of these samples of mono-ionic clays were determined by resaturation with traced cesium, giving for the montmorillonite 1.258 meq./gm. backbone and for the attapulgite 0.33 meq./gm. backbone. These results are seen to be lower than those given in the Table. In the case of the attapulgite only a very small amount of material was available and the discrepancy is not considered significant. In the case of the montmorillonite, however, the discrepancy confirms previous similar work in this laboratory and seems to represent a real effect. If the results of the J. Lawrence Smith decomposition are taken at face value, the effect cannot be due to fixation. We are at present unable to account for it, since it appears improbable that a significant amount of high capacity material could have been washed away in the preparation of the clay.

EXPERIMENTAL DETAILS

Little special material is needed for the determination except a supply of cesium chloride, a sample of Cs137, and apparatus for making the activity determinations. A satisfactory filter aid for the columns is ordinary Gooch asbestos. This material should be tested for its exchange capacity. A large batch which we have used for some years shows a cation capacity of no more than 0.002 meq./gm.

The preparation of the clay columns is carried out by weighing into a dry, 250-ml. bottle appropriate amounts of clay and asbestos. With a montmorillonite, four grams of clay weighed to the nearest milligram, and six grams of asbestos, weighed to the nearest tenth of a gram, gives a satisfactory mixture. The clay and asbestos are mixed by shaking the dry materials, and the mixture is transferred quantitatively to a glass tube of convenient size. For the ten gram mixture a tube 2.5 cm. in diameter and 8-9 cm. long is used. These tubes are drawn to tubulations at one end and reamed for rubber stoppers at the other. The cesium solution is passed through the clay column down-flow, using a siphon from a reservoir a foot or two above the column. A screw clamp on a rubber connection in the siphon is useful for adjusting flow rates. Samples may be collected directly in volumetric flasks, but it is preferable to collect in weighed bottles and determine sample sizes by weight, as less attention to the operation is thereby required.

For columns of the size mentioned a convenient flow rate is 0.5-1.0 ml./min. Thus with a column containing 4 meq. of exchangeable ion being eluted with 0.02 N CsCl the time required for the mid-point volume will be about $4/0.02 \times 0.5 \times 60 = 6.7$ hrs. Since it may be necessary to collect

twice this volume to ensure complete elution, it is convenient to set up several columns and allow them to flow unattended overnight, variations in flow rate being of no consequence. When a small sample shows the activity of the input solution, the volume of the large sample is determined and its activity measured with care.

It is convenient to prepare a stock solution of cesium chloride of strength about 0.5 N and to dilute measured amounts of this for individual determinations, an appropriate volume of Cs137Cl solution being added in the dilution. A millicurie of Cs137Cl diluted to a liter with water affords activity for very many determinations. The volume of this solution to take for an analysis is best determined with respect to the apparatus available for the radioactivity measurements.

The determinations of activity are most accurately done with the liquid samples directly. If glass-jacketed Geiger-Müller counters are used in conjunction with a high speed counting circuit, no further chemical operations are necessary, and with very little trouble results with the expected reproducibility of the counting can be obtained. The techniques of this work are simple and are well described by Bleuler and Goldsmith (1952, pp. 16-34, pp. 49-79). It is usually necessary to take into account the finite resolving time of the counter tube, and it is always essential to measure standard (that is, input solution) and unknown in the same counter at nearly the same time. The glass-jacketed tubes have the advantage of ensuring reproducible geometry. The self-absorption of the radiation in the dilute solutions used can be considered constant and so may be neglected.

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