

Use of Cesium-137 in the Determination of Cation Exchange Capacity

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ION EXCHANGE ON MINERAL MATERIALS

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ABSTRACT

Separate determinations of the exchange capacity of 5 American Petroleum Institute standard clay samples and 7 soil samples were made using cesium, ammonium, and manganese ions, respectively, to saturate the exchange sites of the samples. The cesium method was found to be more rapid and the results obtained more precise than those obtained using either the ammonium or the manganese method. Using the cesium method, an accurate measurement of the exchange capacity of two soil samples was obtained even when the sample analyzed weighed as little as 30 milligrams.

INTRODUCTION

For more than 50 years, cation exchange capacity has been used in the prediction of soil properties, and numerous methods for determining cation exchange capacity of soils and clay minerals have been developed. In these methods, various cations, including ammonium (Lewis, 1950, p. 91-124), cesium (Frysingher and Thomas, 1955, p. 239-245), manganese (Bower and Truog, 1940, p. 411-413), and sodium (Bower and others, 1952, p. 251-261), have been used to saturate the exchange sites of the soil or clay. Of these, the ammonium ion has had the widest acceptance. Frysingher and Thomas (1955) described an ion exchange capacity determination that consisted of "running an elution chromatogram with cesium chloride solution from a mineral sample distributed on an inert filter aid." The chromatogram is mapped and the area above the curve is used to calculate the exchange capacity of the sample. They reported that precise results could be obtained for samples having high exchange capacities, but that reduced precision could be expected when the exchange capacity of the sample is small.

As part of an investigation of equilibria between dilute aqueous solutions containing radioactive substances and clay minerals, a procedure was needed for the rapid and accurate measurement of the cation exchange capacities of the clay minerals. The "batch" method described by Lewis (1950, p. 91-92) was chosen as the most applicable to the problem. "Batch" procedures for the determination of cation exchange capacity of clays and soils were evaluated for relative precision and speed using ammonium, cesium, and manganese cations.

This work was conducted under the supervision of F.B. Barker, succeeded by J.H. Baker, project chief.

EXPERIMENTAL WORK

DESCRIPTION OF SAMPLES

Twelve samples, including 5 American Petroleum Institute (A.P.I.) reference clays and 7 soil samples, were used in this investigation. The locations of the deposits from which the A.P.I. standard clay samples were obtained are described by Kerr and Kulp (1949). The soil samples were dug within 25 miles of Denver.

Soil sample descriptions and locations follow:

- | Soil | Description and location |
|------|--|
| 1 | A grayish clayey soil obtained on the golf course approximately 100 feet SE of the lake at Rolling Hills Country Club, Denver, Colo., SE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 30, T. 3 S., R. 69 W. |
| 2 | A sample of Pierre Shale obtained from railroad cut at intersection with highway 93 just south of Rocky Flats, Colo., SW $\frac{1}{4}$ sec. 21, T. 2 S., R. 70 W. |
| 3 | Clay sample from the Fox Hills Sandstone in railroad cut as described in No. 2. Sample taken approximately 200 feet stratigraphically above the contact of the Pierre Shale and Fox Hills Sandstone, SW $\frac{1}{4}$ sec. 21, T. 2 S., R. 70 W. |
| 4 | Yellowish bentonitic layer in the Benton Shale from a stream cut approximately 6 miles north of Boulder, Colo., on route 7, NE $\frac{1}{4}$ sec. 25, T. 2 N., R. 71 W. |
| 5 | Sample of black Benton Shale from same location as No. 4, NE $\frac{1}{4}$ sec. 25, T. 2 N., R. 71 W. |
| 6 | Soil sample taken from a slump on switchback approximately 3 miles south of the Rocky Flats intersection of routes 93 and 72, approximately 6 miles north of Golden, Colo., SE $\frac{1}{4}$ sec. 33, T. 2 S., R. 70 W. |
| 7 | A light grayish shaly sample from the Morrison Formation exposed on the west slope of the Dakota hogback just north of Morrison, Colo. Sample taken approximately 25 feet below the Morrison-Dakota contact, NW $\frac{1}{4}$ sec. 26, T. 4 S., R. 70 W. |

The major clay minerals in the soil samples were identified by X-ray diffraction techniques (table 1). After separation of the clay-sized fractions from the soil, oriented aggregates were prepared on porous tile plates. X-ray diffraction patterns were made of each sample after each of the following steps:

1. The clay as deposited from a water suspension and then air drying while maintaining suction to prevent curling and flaking.
2. Glycolated sample obtained by heating the clay in a desiccator over a free surface of ethylene glycol at 60°C for a period of 16-20 hours (overnight).

3. The clay after having been heated at 300°C for approximately 2 hours.
4. The clay after having been heated at 550°C for approximately 1 hour.

The identification of clay minerals by X-ray diffraction techniques is facilitated by the changes in patterns obtained by subjecting the samples to the four steps outlined. A basic pattern for a given sample is obtained from the air dried deposit (step 1). Glycolation (step 2) causes the mixed layer minerals to expand giving a more or less broadened 17 Å (Angstrom) peak. The broadness of the peak is an indication of the degree of mixed layering. A relatively pure montmorillonite with little mixed layering gives a sharper peak than a clay with greater degree of mixed layering. The term "mixed layer" refers to the random arrangement of expanding and non-expanding layers in some clays. A 10 Å peak that does not show a broadening of the peak on glycolation is indicative of "illite." Heating the samples to 300°C (step 3) collapses the layers that are expanded due to hydration or glycolation. The collapsed clays give sharper peaks and further indications as to the degree of mixed layering, hydration, etc. Heating to 550°C destroys the kaolinite crystalline structure and consequently the 7 Å peak disappears.

TABLE 1.—*Clay minerals in soil samples*

[_, not detected; X, present; XX, predominant]

Soil	Montmorillonite	"Illite"	Kaolinite
1-----	XX	X	—
2-----	X	—	—
3-----	—	X	X
4-----	X	—	X
5-----	X	—	—
6-----	X	X	—
7-----	—	X	X

DESCRIPTION OF METHODS

The "batch" method was used for each of the cations. The general procedure in a "batch" method is to treat the sample of clay or other exchange material with a 0.50–3.00*N* solution of the chosen salt until all the available exchange positions are occupied by cations from the salt solution. The excess salt solution adhering to the sample is removed by washing the sample with a suitable solvent, such as ethyl alcohol, which will not remove ions from the exchange sites. The amount of the cation retained by the sample is then determined.

CESIUM METHOD

Place a 200-mg sample of the clay or soil in a test tube, approximately 16 x 150 mm in size, and add 5 ml of a 1.00*N* cesium chloride

solution containing about 38 microcuries of cesium-137 per liter of the 1.00*N* cesium chloride solution. Shake the test tube by hand until the clay is thoroughly dispersed, and then shake by mechanical shaker for at least 4 hours. Separate the phases by centrifuging, and decant the supernatant liquid. Add another 5 ml of the 1.00*N* cesium chloride solution to sample. After shaking the sample for at least 4 hours, centrifuge and decant the supernatant liquid. Repeat this procedure one additional time. Remove the excess cesium chloride from the sample by repeated washing with approximately 10-ml portions of 95 percent ethyl alcohol, agitating thoroughly (10 to 15 minutes), centrifuging completely, and decanting the supernatant liquid after each additional centrifugation until the decanted alcohol is free of chloride.

When the washing is completed, stopper the test tube and clean the outside by dipping the tube in dilute HCl and rinsing with distilled water. Dry the tube and place it in a well-type gamma scintillation counter and determine the counting rate of the adsorbed cesium-137.

Using the same gamma counter, count an aliquot of the solution used to saturate the samples with cesium. (The effect of self absorption on the counting rate of cesium-137 was found to be negligible.) Calculate the exchange capacity by comparing the counting rate of the sample with that of the equilibrating solution, using the following equation:

$$\begin{aligned} \text{Exchange capacity} &= \frac{\text{sample counts per minute}}{\text{counts per minute/milliequivalent of cesium}} \\ &\times \frac{100}{\text{sample weight expressed in grams}} \quad \text{or} \\ &\frac{\text{sample cpm}}{\text{cpm/milliequivalent}} \times \frac{100}{\text{sample wt in grams}} \\ &= \text{milliequivalents per 100 grams} \end{aligned}$$

AMMONIUM METHOD

Disperse a 2.000-g sample in 15 ml of 1.00*N* ammonium chloride solution and shake for at least 4 hours. Clarify the suspension by centrifuging, and decant the supernatant liquid. Repeat the above procedure twice. Remove the excess ammonium chloride solution adhering to the sample by washing repeatedly with ethyl alcohol as in the cesium method until the discarded alcohol is free of chloride. Transfer the washed sample to a 500-ml Kjeldahl flask, using approximately 150 ml of distilled water. Add 30 ml of 50 percent sodium

hydroxide solution and distill the evolved ammonia into a measured volume of standard acid.

Determine the excess acid by titration with a standard base and calculate the milliequivalents of ammonia evolved. Calculate exchange capacity using the following equation:

$$\begin{aligned}\text{Exchange capacity} &= \frac{\text{milliequivalents of NH}_3}{\text{sample weight in grams}} \times 100 \\ &= \text{milliequivalents per 100 grams}\end{aligned}$$

MANGANESE METHOD

Place a 2.000-g sample in a test tube and add 15 ml of a 1.00*N* manganous chloride solution. After shaking the sample for at least 4 hours, centrifuge the suspension and decant the supernatant solution. Repeat this procedure twice. Remove the excess manganous chloride solution by washing the sample with ethyl alcohol as described in the cesium method. Transfer the sample to a sintered glass filter using 25 ml of 1:9 nitric acid, and leach the sample with 5 additional 25-ml portions of the 1:9 nitric acid to remove all of the adsorbed manganese ions. Evaporate the combined filtrate to dryness and, using the bismuthate method described by Kolthoff and Sandell (1952, p. 677-679), determine the amount of manganese extracted from the sample. Calculate the exchange capacity using the following equation:

$$\begin{aligned}\text{Exchange capacity} &= \frac{\text{milliequivalents of Mn}}{\text{sample weight in grams}} \times 100 \\ &= \text{milliequivalents per 100 grams}\end{aligned}$$

RESULTS AND DISCUSSION

Two analysts made triplicate determinations of the exchange capacity of each sample by all three methods. All 12 samples were air dried, ground to pass a 100 mesh sieve ($<.125\text{mm}$), and thoroughly mixed in preparation for the exchange capacity determinations. Exchange capacity values obtained by this laboratory on the 4 types of clay tested, using the ammonium, cesium, and manganese ions, agree very well with published values for similar clays (Fryssinger and Thomas, 1955; Grim, 1953). The mean value of the exchange capacity, its standard deviation, and the coefficient of variation¹ were

¹ Coefficient of variation = $\frac{100 \times \text{standard deviation}}{\text{arithmetic mean}} = \frac{100\sigma}{\bar{x}}$

computed for each method and are given in table 2. Even though smaller samples are used, the precision of the cesium method compares favorably with that of the other methods. The radiocesium method, therefore, is adaptable to semimicro determinations. Moreover, it is suitable for a broad range of exchange capacities. Using a well-type scintillation counter (thallium activated NaI crystal) and a 1.00*N* cesium chloride solution containing a "spike"² of 38 microcuries of cesium-137 per liter, cation exchange capacities in the range from 10 to 120 milliequivalents per 100 g can be measured precisely.

TABLE 2.—Comparison of cation exchange capacities determined by the ammonium, cesium, and manganese methods

Sample	Ammonium		Cesium		Manganese	
	Average exchange capacity (meq per 100 g)	Coefficient of variation	Average exchange capacity (meq per 100 g)	Coefficient of variation	Average exchange capacity (meq per 100 g)	Coefficient of variation
Kaolinite 4-----	10	3. 2	10	1. 3	9	2. 9
Montmorillonite 11---	81	. 7	87	1. 3	76	1. 3
Montmorillonite 21---	95	1. 3	98	1. 2	83	1. 5
Halloysite 21-----	14	4. 2	15	1. 7	13	2. 6
"Illite" 35-----	19	2. 5	20	. 9	20	3. 7
Soil 1-----	27	3. 6	27	2. 0	25	1. 7
Soil 2-----	21	1. 1	26	1. 6	30	. 1
Soil 3-----	5. 4	11. 3	5. 5	2. 0	6. 6	3. 2
Soil 4-----	39	1. 4	40	1. 1	39	7. 4
Soil 5-----	19	. 9	18	1. 3	18	. 9
Soil 6-----	23	3. 2	24	3. 2	25	1. 8
Soil 7-----	18	3. 2	19	2. 1	17	1. 4
Average-----		3. 1		1. 6		2. 4
Medium-----		2. 85		1. 45		1. 75

Exchange capacities in the range from 1 to 20 milliequivalents per 100 g can be determined by increasing the radioactive "spike" to 200 microcuries of cesium-137 per liter in 1.00*N* cesium chloride solution. Not only can the specific activity of the cesium chloride solution be adjusted, but the sample weight can be chosen to permit determination of even wider exchange-capacity ranges. The pH of the sample should be a relatively insignificant factor as the leaching solutions outweigh the sample by a factor of approximately 60:1. The cesium chloride leaching solution has a pH of approximately 5.

Soil samples 3 and 5 were selected arbitrarily for a study of the effect of sample weight on exchange capacity. Occasionally, exchange capacity values are desired when the amount of sample available for analysis is very minute. Results obtained by using the cesium method

² "Spike" is a term used to denote the minute amount of radioactive material added as a tracer to the bulk of inactive material enabling the analyst to make a quantitative determination.

are presented in table 3. Within the limits of the measurements attempted, good data were obtained even when the samples weighed as little as 30 mg. The results obtained with 10-mg samples were not in accord with the other determinations. With very small samples a very slight loss of sample or adsorption of radioactivity by the test tube can result in wide variations in the expected exchange-capacity values.

TABLE 3.—*Effect of sample weight on the cation exchange capacity determination by the cesium method*

Sample	Sample weight (g)	Cation exchange capacity (meq per 100 g)
Soil 3-----	1. 000	5. 5
	. 200	5. 1
	. 030	5. 5
	. 010	16. 2
Soil 5-----	1. 000	19. 0
	. 200	18. 8
	. 030	19. 5
	. 010	41. 0

CONCLUSIONS

The precision of the radiocesium method for determining cation exchange capacity is generally superior to both the ammonium and manganese methods. Because the cesium is determined instrumentally in a single analytical step, considerably less time is needed per analysis. This method can be used to determine cation exchange capacity of samples weighing as little as 30 mg. By adjusting the specific activity of the cesium ion, either very high or very low exchange capacities can be determined precisely.

REFERENCES CITED

- Bower, C. A., and Troug, E., 1940, Base-exchange capacity determination of soils and other materials: *Indus. Eng. Chemistry, Anal. Ed.*, 12, no. 7, p. 411-413.
- Bower, C. A., Reitemeier, R. F., and Fireman, M., 1952, Exchangeable cation analysis of saline and alkali soils: *Soil Sci.* 73, p. 251-261.
- Frysingher, G., and Thomas, H. C., 1955, A method for the determination of the cation-exchange capacity of clay minerals and soils, in Milligan, W. O., (ed.), *Natl. Conf. on Clays and Clay Minerals, Proc.*, 3d, Houston, 1954: Natl. Research Council Pub. 395, p. 239-245.
- Grim, R. E., 1953, *Clay mineralogy*: New York, McGraw-Hill Book Co., 384 p.
- Kerr, P. F., and Kulp, J. S., 1949, *Reference clay locations*. United States. American Petroleum Inst. Project 49. Clay Mineral Standards Preliminary Report No. 2: New York, Columbia University Press.

- Kolthoff, I. M., and Sandell, E. B., 1952, *Textbook of quantitative inorganic analysis*: 3d ed., New York, The MacMillan Co., 759 p.
- Lewis, D. R., 1950, Base-Exchange Data. American Petroleum Institute Project 49. Clay Mineral Standards Preliminary Report No. 7, Section 3: New York, Columbia University Press.



