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A METHOD FOR DETERMINING THE EXCHANGE
CAPACITY OF ORGANIC MATTER IN THE
PRESENCE OF NITROGEN AND
CALCIUM¹

H. C. MILLAR, F. B. SMITH AND P. E. BROWN

Many methods have been used for determining the base exchange capacity of soils and certain advantages have been claimed by each investigator for his particular method. Fewer studies on the base exchange reactions of organic matter have been made and the nature of the material makes many of the methods used for soils impracticable and inaccurate when applied to organic matter. According to McGeorge (1) the monovalent lignin salts are soluble in alcohol and the use of alcohol in base exchange studies on organic matter is of questionable value. The removal of excess soluble salt from the base exchange complex preparatory to determining the amount of base fixed, by the use of water, allows too great a hydrolysis of monovalent salts and, therefore, will lead to low results. Then again, the monovalent lignin salts are soluble under certain conditions in salt solution, and especially in acetate solutions which hydrolyze and yield OH ions.

The procedure adopted in these base exchange studies involved placing a two-gram sample of the organic matter to be tested into 35 cc. of neutral, normal solution of the particular salt which was being used to saturate the exchange complex for the quantitative measurement. After remaining in this solution 16 to 24 hours, the organic material was transferred to a percolation tube which was fitted with an asbestos-covered, perforated porcelain disk.

Above these tubes 250 c.c. volumetric flasks were supported inverted in order to supply solution to the leaching tube as fast as it was leached through. In order to prevent the organic matter from rising to the top of the volumetric flasks 10 grams of clean white quartz sand were placed on the plant material. The rate of percolation was controlled by the thickness of the asbestos pad, by suction or by closing the extending arm of the suction flasks thereby allowing a pressure to be created which decreased the leaching process.

The method which was studied first involved placing 2 and 4

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grams of finely-ground alfalfa into 35 cc. of neutral, normal calcium acetate or neutral, half-normal calcium acetate. The material remained in these solutions for 12 hours and then was leached with fresh 250 cc. portions of the respective solution.

Each sample was then leached with distilled water until calcium was no longer detected in the leachate. The fixed calcium was replaced with neutral, normal ammonium acetate and calcium was determined quantitatively in the leachate. The results obtained are given in Table I.

Table I. Effect of Strength of Calcium Acetate Solution upon the Exchange Capacity of Alfalfa

Sample	Wt. of Sample	First Leached with neutral Ca-acetate	Millequivalents per 100 gms. of alfalfa
1	2 gms.	Normal	51.00
2	2 "	"	51.00
3	4 "	"	52.00
4	4 "	"	52.00
5	2 "	"	40.00
6	2 "	"	43.00
7	4 "	"	44.50
8	4 "	"	47.00

The results are higher and more consistent in the case of the normal solution of Ca acetate than with the one-half normal solution. For this reason normal solutions were adopted in all subsequent determinations.

The next step involved attempting to use this method to test the exchange capacity of soils, which had received CaCO_3 at the rate of one and a half times the lime requirement, and to determine the exchange capacity of plant materials which had decomposed in the presence of 2.5 per cent of calcium cyanamide. In these experiments difficulty was encountered because it was not possible to leach either the soils or the plant materials free of calcium with distilled water. Twenty-five hundred cc. of distilled water were leached through the samples and calcium still continued to appear in the filtrate. Since the use of this method in the presence of CaCO_3 apparently gives high results it can only be used by making a correction for this compound. In order to do this it has been advocated that a second volume of solution equal to the first one in which the exchangeable calcium is determined, be leached through the sample, and the calcium content of this solution be subtracted from that of the first. This attempts to correct for the solubility of the CaCO_3 by assuming that the same amount of CaCO_3 is soluble in the first 500 cc. of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ as in a second 500 cc. portion. This assumption very probably is not true, and

consequently the determination of the exchange capacity by a calcium determination on material containing CaCO_3 was not followed. The ammonium acetate method (2) was considered next but before adopting the method it was decided to study the influence of the base used for neutralizing the alcohol upon the exchange capacity of the plant material as indicated by the nitrogen determinations.

Six grams of red clover which had decomposed in the presence of 2.5 per cent of calcium cyanamide were placed in 35 cc. of neutral, normal ammonium acetate solution for 12 hours. The clover samples were then transferred to the percolation tubes and leached with 250 cc. of neutral, normal ammonium acetate solution. Eighty per cent ethyl alcohol was used to remove the excess ammonium acetate. Two samples were leached with the slightly acid 80 per cent alcohol, two with alcohol neutralized with calcium hydroxide and two with alcohol neutralized with ammonium hydroxide. The alcohol was brought to the same pH as the ammonium acetate solution as shown by bromthymol blue. After the alcohol leaching the receiving flasks were emptied and cleaned and 10 cc. of a one-to-one solution of hydrochloric acid were placed in them as a precaution against losing any ammonia. The fixed ammonium was replaced by neutral, normal barium chloride and total nitrogen was determined in this leachate. The results obtained are given in Table II.

Table II. Neutralization of the Alcohol with Different Bases

2 Grams Red Clover	Barium Acetate Method	Leached with 80% Alcohol		
		Alcohol not Neutralized	Alcohol $\text{Ca}(\text{OH})_2$	Neutralized with NH_4OH
M. E. Per 100 Gms. of Material				
A.	45.98	25.60	23.10	56.50
B.	45.98	25.10	24.10	56.00

It may be noted that the results differ materially according to whether or not the alcohol was neutralized and according to the base used for neutralization. It appears that the results obtained were not in agreement with those obtained by the barium acetate method. In view of these difficulties it was decided to use a divalent cation for measuring the exchange capacity of the organic materials. A calcium determination was objectionable, and so it was decided to try the barium acetate method. Since many determinations were to be made in a relatively short period of time it was imperative that a volumetric rather than a gravimetric method be employed. Scott (3) lists three methods for determining bar-

ium volumetrically. These were tested and the potassium iodide method was found to give a very definite and distinct end-point and was rapid and convenient as well.

In employing the potassium iodide method the solution containing the barium is neutralized, heated to boiling and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is added slowly with stirring as the precipitate comes down. With very small amounts of barium it sometimes requires a few moments before any precipitation occurs. A slight excess of the chromate is added and the solution is allowed to simmer a short time. It is then allowed to cool and is filtered through a good grade of filter paper. (Prolonged heating of the solution after precipitation favors the production of a coarse precipitate which makes filtering easier; otherwise the precipitate may pass through the paper.) The precipitate is washed with 0.5 per cent $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution until the filtrate is colorless or until no test for the chromate ion is obtained. The BaCrO_4 precipitate is dissolved on the filter paper by adding 50 to 100 cc. of dilute hydrochloric acid. This filtrate is collected in the beaker in which the precipitation was made. After the precipitate is completely dissolved the paper is broken and is washed with water until the volume in the beaker becomes 300 to 400 cc.

Two grams of iodate-free KI salt are added and allowed to react about 10 minutes. The liberated iodine is now titrated with N/10 $\text{Na}_2\text{S}_2\text{O}_3$. At the beginning of the titration the solution has a deep brown color due to the iodine, and as the titration proceeds the color becomes a pale yellow. When the color of the iodine can barely be detected 5 cc. of a freshly prepared starch solution are added and the titration continued until the blue color disappears.

The starch solution is conveniently made by adding 1 gm. of soluble starch to a little distilled water. This is then emptied into 1 liter of boiling distilled water and boiled for a few minutes. The suspension is cooled and is ready for use. (Adding the starch in the beginning of the titration when a high concentration of free iodine is present will give low results as a deep blue flocculate appears which carries iodine out of solution.) In testing the potassium iodide method for determining barium, 0.1740 grams of barium were put into solution and precipitated as the chromate. Analysis of the solution with the potassium iodide method showed a 0.1737 grams of barium to be present.

In the barium acetate method the system which was first used involved leaching the material with neutral, normal barium acetate, leaching with boiled distilled water and then replacing the barium with neutral, ammonium acetate and precipitating the barium as

a chromate in this ammonium acetate solution. However, BaCrO_4 is appreciably soluble in ammonium salts. When the 500 cc. of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ are reduced in volume before the precipitation is made the concentration of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ approaches a 16 per cent solution. This of course gives low results and some other procedure is necessary.

Since barium chromate is insoluble and calcium chromate is soluble, one is able to use a calcium salt to replace the barium. A normal CaCl_2 solution was tried but it was found to be practically impossible to control the pH of a CaCl_2 solution while a solution of calcium acetate did not present this difficulty. In view of this fact neutral, normal calcium acetate was employed to replace the barium.

A comparison of the barium acetate and calcium acetate methods for determining the base exchange capacity of red clover was made in order to see how well the two methods checked. Two 2-gram samples of undecomposed red clover were submerged in each of normal barium and calcium acetate solutions for 12 hours. The samples were transferred to the percolation tubes and leached with 250 cc. of the respective solutions. They were then leached with boiled distilled water until free of the cations. The absorbed barium was replaced by neutral, normal calcium acetate, while the fixed calcium was replaced by neutral, normal ammonium acetate. The amounts of barium and calcium absorbed were determined and are shown in Table III.

Table III. Base Exchange Capacity of Undecomposed Red Clover by Barium and Calcium Acetate Methods

Sample	M. E. Per 100 grams Red Clover	
	Barium Acetate	Calcium Acetate
1	37.22	37.13
2	37.22	37.13

It is seen that the results by the two methods are in agreement on samples of undecomposed red clover.

A comparison of the barium acetate, calcium acetate and electro-dialysis was also made on an unlimed, Dickinson fine sandy loam soil having a pH of 6.33 and a lime requirement of one ton per acre. Twenty grams of the soil were leached with the respective acetate solutions then with boiled distilled water until the leachate was free of the cation. The barium was replaced with calcium acetate solutions while the calcium was replaced with ammonium acetate. One hundred grams of soil were used in deter-

mining the base exchange capacity by the method of electro dialysis. The results are given in Table 4.

Table IV. Base Exchange Capacity of Dickinson Fine Sandy Loam

Sample	M. E. Per 100 grams of Soil		
	Barium Acetate	Calcium Acetate	Electrodialysis
1	13.86	14.05	14.00
2	13.88	14.05	14.00

The results obtained with the three methods indicate that they are in agreement. The precipitation of barium as barium chromate and its determination by the potassium iodide method can be made in the presence of calcium and nitrogen and, therefore, has this advantage over other methods which are either slower or subject to interference by these elements.

SUMMARY

Considerable difficulty was encountered in attempting to determine the base exchange capacity of organic matter which was decomposed in the presence of added calcium and nitrogen compounds. Methods which involved calcium or nitrogen determinations were not applicable but a quantitative barium acetate method was found to give reliable results in the presence of these elements. The details of the procedure finally adopted are:

Two gram samples of organic matter are placed in 400 cc. beakers and 35 cc. of neutral, normal barium acetate are added. The plant material is stirred well and allowed to remain in the solution for 16 to 24 hours. It is then transferred to a percolation tube which is fitted with an asbestos covered, perforated porcelain disk. Above these tubes 250 cc. volumetric flasks were supported, inverted in order to supply solution to the leaching tube as rapidly as it leached through. The organic matter is prevented from rising to the top of the volumetric flask by placing clean quartz sand on the plant material. The material is leached with 250 cc. of neutral, normal barium acetate, and then leached with boiled and cooled distilled water until no barium is found in the percolate. The fixed barium is replaced by neutral, normal calcium acetate. The filtrate contains the barium that was fixed in the exchange complex of the organic matter. This filtrate is transferred to 600 cc. beakers and heated to boiling. Ammonium bichromate is then added with constant stirring until complete precipitation is effected. The precipitate is allowed to settle until cold and the solution is filtered through a good grade of filter paper. The precipitate is washed with distilled water until the excess chromate is removed. The $BaCrO_4$ is dissolved in 50 to 100 cc. of dilute hydrochloric acid and about 2 grams of solid potassium iodide are added and allowed to react about 10 minutes. The liberated iodine is titrated with N/10 sodium thiosulfate.

At the beginning of the titration the solution has a deep brown

color due to the iodine. As the titration proceeds the color becomes a pale yellow. When the color of the iodine can barely be detected, 5 cc. of a freshly prepared starch solution are added and the titration continued until the blue color disappears.

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