

DETERMINATION OF THE CATION EXCHANGE CAPACITY OF CLAYS AND SOILS USING AN AMMONIA ELECTRODE

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Abstract—The ammonia electrode serves as the basis of a simple, accurate method for determination of cation exchange capacity of small (*ca.* 50 mg) samples of clays. The technique is also capable of accurate measurement of CEC values on the order of 0.01 m-equiv/100 g if larger (*ca.* 500 mg) samples are used. The procedure, which requires saturation of the exchange sites with ammonium as in the usual methods, utilizes the electrode in the determination of ammonia released by treatment of the ammonium clay by strong base. For a Wyoming bentonite, the technique gave a CEC of 86 m-equiv/100 g with an S.D. (four determinations) of 0.83 m-equiv/100 g. Duplicate runs on the same sample by the conventional Kjeldahl method gave results of 86.0 and 85.5 m-equiv/100 g.

INTRODUCTION

MANY procedures for the determination of the cation exchange capacities (CEC) of clays have been described in the literature. The most common methods require the saturation of the clays with ammonium ions, followed by determination of the de-sorbed ammonium ions by acid-base titrations, by spectrophotometry, by infrared spectroscopy or other methods. Other index ions have also been used in conjunction with other methods of measurement. For example, a method is described by Hinckley (1962) which utilizes the exchange of strontium ion followed by measurement of the amount by X-ray fluorescence. The method of Pham Thi Hang and Brindley (1970) utilized the saturation of the clay with methylene blue cations for the determination of the CEC and flocculation of the clay suspension for determination of surface area. Some of these procedures suffer from the disadvantages of being time-consuming, or requiring considerable analytical skill or very expensive equipment.

Several papers describe the use of sodium and potassium ion selective electrodes for the determination of CEC and for studying rates of cation exchange reactions. Of particular interest are the publications of Mortland (1961); Kennedy and Brown (1964); Malcolm and Kennedy (1969); Malcolm, Kennedy and Jenne (1969) and Malcolm and Kennedy (1970). The present authors have no experience with these electrodes or methods. In general, these electrodes may be somewhat affected by ions of similar valence if such are present in the

solution. That is, they are subject to interferences, though perhaps not in the procedures referred to.

The method proposed here is simple, rapid, relatively inexpensive, needs only extremely small samples (25 mg) and can be used to measure quite accurately very small cation exchange capacities (0.01 m-equiv/100g using a 500 mg sample). Briefly, the procedure consists of weighing out a sample of ammonium-saturated clay, suspending it in a known volume of water made alkaline with sodium hydroxide solution, inserting an ammonia electrode and reading the potential developed. The ammonium concentration is obtained by comparison with standard solutions of known ammonium concentration. The equipment requires only the ammonia electrode and an expanded scale pH meter. An Orion Model 95-10 Ammonia Electrode and the Orion Model 801 Ionalyzer were used in this work. The ammonia electrode was chosen because it has virtually no interferences, in contrast to almost all other electrodes. In addition, since ammonium ion has most often been the basis of CEC determinations, its use enabled comparison with other methods of measurement.

ION SELECTIVE ELECTRODES

The most commonly used ion electrode is the so-called 'glass electrode' or 'pH electrode', sensitive to hydrogen ions. In recent years, electrodes sensitive to ions other than hydrogen have been developed, and are capable of measuring activities of these ions. Such electrodes are generally referred to as 'specific ion electrodes' or

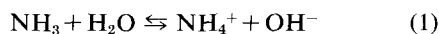
'ion selective electrodes'. General discussions of their principles and uses may be found in Durst (1969) and in Moody and Thomas (1971).

Most ion selective electrodes respond directly to the activity of the desired ion in aqueous solution, but this response may be affected by the presence of other ionic species, especially those of similar charge. The ability of the electrode to discriminate between the desired ion and others is a measure of its efficiency and freedom from interferences.

The ammonia electrode, which operates on a somewhat different principle, merits discussion. What follows is taken (with permission) largely from the *Orion Instruction Manual* (Anonymous, 1972). The Orion ammonia electrode is a gas-detecting electrode, which is able to sense the level of dissolved ammonia (not ammonium) in aqueous solution. Nevertheless, it is used as if it were a specific ion electrode. The electrode can be used to measure ammonium by addition of strong base to convert ammonium to ammonia according to the equation: $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$. Nitrate can be measured after reduction to ammonia, and organic nitrogen can be determined after Kjeldahl digestion of the sample and addition of strong base. The ammonia electrode is free of interferences by cations, anions and other dissolved species, except volatile amines. Sample color and turbidity do not affect the measurement.

Although the ammonia electrode is functionally simple, the mechanism of its operation is complex. Like other electrodes it follows Nernst's Law and responds logarithmically to the activity of dissolved ammonia in a solution. The activity is proportional to the ammonia concentration, which, in turn, is proportional to the concentration of ammonium ion that was originally present.

The electrode contains a hydrophobic membrane which is permeable to ammonia, but not to any ionic species. Dissolved ammonia in the sample solution diffuses into the electrode until the activity of ammonia is the same on both sides of the membrane. Ammonia which passes through the membrane dissolves in solution contained within the electrode according to the equation:



The potential of an internal sensing element varies in a Nernstian manner with changes in the hydroxide level:

$$E = E_0 - S \log [\text{OH}^-] \quad (2)$$

where S is the slope of the electrode response:

The relationship between ammonia, and ammonium and hydroxide ions is given by the equation:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \text{constant} \quad (3)$$

The internal filling solution contains ammonium chloride at a sufficiently high concentration so that $[\text{NH}_4^+]$ can be considered fixed. Equation (3) then becomes:

$$[\text{OH}^-] = [\text{NH}_3] \cdot \text{constant}' \text{ equations} \quad (4)$$

Combination of (2 and 4) shows that the electrode response to ammonia is also Nernstian.

Each ten-fold increase in ammonia concentration gives rise to a minus 58.5 mV change in electrode potential at room temperature. The potential developed under standard conditions is reproducible to better than ± 0.5 mV, or ± 2 per cent according to the Orion manual (Anonymous, 1972). The ammonia electrode can accurately measure concentrations as low as 10 parts per billion. Ordinary distilled water contains levels of ammonia higher than this. It is also important, therefore, to use ammonia-free water in all experiments. This standard can easily be prepared by passing distilled water through a commercial ion-exchanger which reduces the concentration of ammonia to below the limit of detection of the electrode. Care must also be used to avoid storing or opening ammonia reagent bottles in the same room

EXPERIMENTAL

The ammonium saturated clays were prepared (Chapman, 1965) by allowing the starting sample to stand overnight in 1N ammonium acetate solution which had been adjusted to pH 7, after which the samples were leached with 1N NH_4Cl . Excess ammonium salts were removed by washing with isopropyl alcohol, after which the clays were dried and ready for determination of CEC. An alternate method designed for quantitative recovery of small samples has been described by Mackenzie (1951).

For the measurement of the CEC, a 50–150 mg sample of air-dried, ammonium-saturated clay was weighed out and transferred to a 100 ml Pyrex beaker containing a Teflon-covered stirring bar, $\frac{1}{2}$ in. in length. Exactly 50 ml of ammonia-free, deionized-distilled water were added. Stirring was commenced and maintained at a constant level (a necessary condition) while measuring both samples and standards. A small magnetic stirrer motor, connected to a Powerstat regulator set at a constant value, was used. Air-driven stirrers are not

recommended. The electrode was immersed in the suspension, taking care to prevent entrapment of air bubbles under the concave tip. By means of a syringe, $\frac{1}{2}$ ml of 10 M sodium hydroxide solution was added to the beaker, and a timer was started. This amount of NaOH will quantitatively displace all accessible NH_4^+ and convert it to NH_3 . Electrode readings were taken at $\frac{1}{2}$ -min intervals until a constant potential was recorded for two or three readings. Two to five min were usually required before the electrode reached equilibrium. Longer times were required for lower ammonia concentrations. To determine the CEC of the clay sample, the unknown is compared to two standard solutions of ammonium chloride of concentrations which bracket the unknown concentration. Standards of low concentration ($< 10^{-5}\text{M}$) should be freshly prepared daily by dilution, with ammonia-free water, of a 0.1 M primary standard solution. Solutions of 10^{-4}M are good for 1 week. The known solutions range from 10^{-2} to 10^{-5}M , with most clays falling within the 10^{-3} - 10^{-4}M range.

The concentration of ammonia released from the clay by the sodium hydroxide can be determined graphically (Fig. 1), or can be read directly from the previously calibrated scale of the ion-analyzer, which is simply a pH meter with an expansible scale. The ion-analyzer is calibrated by bracketing

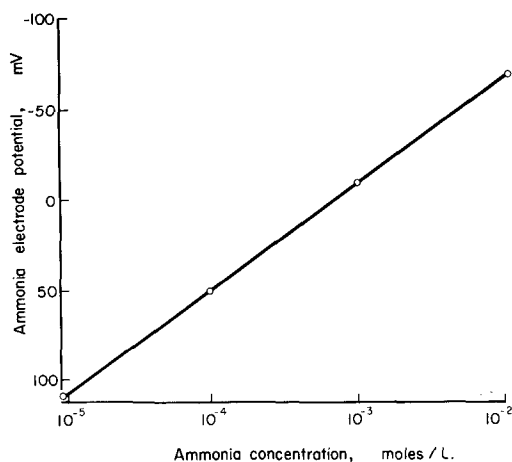


Fig. 1. Graph used to determine ammonia concentration from electrode potential. (Adapted with permission of Orion Research Inc. from *Instructional Manual for Ammonia Specific Ion Electrode*, p. 6).

the unknown with two standard ammonium chloride solutions, a procedure analogous to the standardization of a pH meter by using two buffer solutions of known pH.

The CEC of the sample is obtained from the following equation:

$$\text{CEC} = \frac{(c)(v)}{(w)(f)} \quad (5)$$

where

CEC = the cation exchange capacity of the sample expressed in m-equiv per 100g of clay, and
 c = concentration of ammonia in moles per l.
 v = volume of water added (50 ml in this case)
 w = weight of the sample in mg
 f = a conversion factor, in this case a constant equal to 10^{-5} .

With careful technique, this method is capable of accurate measurement of exchange capacities as low as 0.01 m-equiv/100g with a sample of only 500 mg. For higher exchange capacities, smaller samples are used. The manual for the ammonia electrode (Anonymous, 1972) states that the reproducibility of the electrode under standard conditions is $\pm 0.5\text{ mV}$ or ± 2 per cent of the concentration measured. In order to establish the precision obtainable on replicate samples using this method, four determinations of CEC were made on each of the following samples: kaolinite, S.C.; illite, Ill.; illitic soil, Ill; and montmorillonite, Wyo. The S.D. found for each material was 0.06, 0.25, 0.75 and 0.83 m-equiv/100g, respectively.

RESULTS AND DISCUSSION

The CEC of 6 clays and 1 soil were determined by the procedure described in this paper and also by 4 other common methods of ammonia recovery. The other methods used were: the aeration method of Potter and Snyder as modified by Vanselow (in Chapman, 1965); Mackenzie's (1951) procedure, and by two variations of the Kjeldahl method. In the usual Kjeldahl digestion, the sample is boiled in 36N sulfuric acid for 1 hr, then 50 per cent NaOH is added until the solution is alkaline. The ammonia is then distilled off and collected (in the variation of the method used for this study) in an excess of saturated boric acid solution. The boric acid fixes the ammonia. However, since boric acid is neutral to methyl red, use of this indicator permits direct titration of the ammonia with standardized HCl. The samples were run using this method. Then for comparison, the same Kjeldahl distillation procedure was used to separate the ammonia, but the ammonia was determined using the ammonia electrode instead of by titration. With the other methods, the ammonia electrode was used to determine the ammonia concentration.

Table 1. Comparison of results of cation-exchange capacity determinations on 5 clays, 1 clay soil and 1 macro-crystalline vermiculite which was ground to -200 mesh. Numbers are expressed in m-equiv/100g of sample and are the average of 4 determinations, with the exception of the numbers in the last row, where lack of sample prevented multiple determinations. Those marked with an asterisk in the last row indicate a single determination, while those with two numbers were run in duplicate, the two numbers giving the individual results

Method	Kaol. S.C.	Kaol. Ga.	Mont. Wyo.	Mont. Miss.	Illite Ill.	Illitic Soil Ill.	Vermiculite Transvaal (ground to -200 mesh)
Ammonia electrode method (this paper)	2.8	3.0	86	81	23	13	83
Mackenzie (1951) distillation method (using electrode)	2.7	3.3	86	81	23	13	85
Aeration method (Chapman, 1965) (using electrode)	2.8	3.3	84	80	25	13	83
Standard Kjeldahl digestion method (using electrode)	2.8	3.4	88	83	24	14	88
Standard Kjeldahl digestion method (by titration)	3.0*	3.3*	86.0, 85.5	80.0, 81.0	24*	13.3*	86.0 86.0

*Lack of sample prevented running multiple analyses

The results obtained by the five methods are shown in Table 1. All methods are in good agreement for the two kaolinites, the two montmorillonites, the illite and the illitic soil. For the vermiculite, the Kjeldahl digestion gave slightly higher results than the other three methods. The discrepancy is thought to be caused by fixation of ammonia by the vermiculite, and only the Kjeldahl method, which completely destroys the clay structure, frees all the ammonia. The other methods thus give slightly lower results.

CONCLUSIONS

The obvious advantages of this method are simplicity, speed, accuracy, ability to utilize small sample sizes (50 mg) and freedom from interferences. CEC determinations can be made as easily as the determination of pH and almost as rapidly, once the ammonia-saturated clay has been prepared. The results compare extremely well with standard methods. Another attractive feature is the capability of accurate measurement of extremely small CEC, on the order of 0.01 m-equiv/100g if larger samples (500 mg) are used. The method should be easily adaptable for measurement of ammonium present on clays and soils in the field, if a field procedure for drying and accurately

weighing a sample can be found, since suitable portable pH meters are available.

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Résumé — L'électrode à ammoniacque sert de base à une méthode simple et précise pour la détermination de la capacité d'échange de petits échantillons d'argile (environ 50 mg). La technique permet également de mesurer avec précision les valeurs de CEC de l'ordre de 0,01 meq/100 g si des échantillons plus importants (environ 500 mg) sont utilisés. Ce procédé, qui nécessite la saturation des sites d'échange avec l'ammonium comme dans le cas des méthodes habituelles, utilise l'électrode dans le but de doser l'ammoniacque libérée par l'argile ammonium lors d'un traitement par une base forte. Pour une bentonite du Wyoming, cette technique a donné une CEC de 86 m-equiv./100 g avec une déviation standard (quatre dosages) de 0,83 m-equiv./100 g. Des doubles effectués sur le même échantillon par la méthode Kjeldahl conventionnelle ont donné comme résultats 86,0 et 85,5 m-equiv./100 g.

Kurzreferat — Die Ammoniumelektrode dient als Grundlage einer einfachen, genauen Methode zur Bestimmung der Kationenaustauschkapazität kleiner (ca 50 mg) Tonproben. Die gleiche Technik ist auch zur genauen Bestimmung von Austauschkapazitätswerten in der Größenordnung von 0,01 mval/100 g geeignet, wenn größere Probenmengen (ca 500 mg) benutzt werden. Bei dem Verfahren, das eine Sättigung der Austauschplätze mit Ammoniumionen wie bei den üblichen Methoden erfordert, wird die Elektrode zur Bestimmung des durch Behandlung des Ammonium-Tons mit starken Basen freigesetzten Ammoniums eingesetzt. Für einen Wyoming-Bentonit ergab die Methode eine Austauschkapazität von 86 m-val/100 g mit einer Standardabweichung (4 Bestimmungen) von 0,83 m-val/100 g. Parallelbestimmungen an der gleichen Probe mit der konventionellen Kjeldahl-Methode ergaben 86,0 und 85,5 m-val/100 g.

Резюме — Аммиачный электрод служит основанием простого и точного метода определения способности катионообмена небольших образцов глины (ca 50 мг). Этим способом можно также аккуратно вымерять значения СЕС порядка 0,01 мек/100 г, если использовать более крупные образцы (ca 500 мг). Процедура, требующая насыщения аммиаком обменных узлов как и по обычным методам, применяет электрод для определения выделенного аммиака обработкой аммиачной глины крепким основанием. Этот способ для вайомингского бетонита дал СЕС порядка 86 мек/100 г со стандартными отклонениями (четыре определения) 0,83 мек/100 г. Дублированные опыты с этим же образцом стандартным методом кжелдала дали следующие результаты: 86,0 и 85,5 мек/100 г.