

START

009898

# METHODS OF SOIL ANALYSIS

Part 2

Chemical and Microbiological Properties

Second Edition

A. L. Page, *Editor*

R. H. Miller, *Associate Editor*

D. R. Keeney, *Associate Editor*

*Editorial Committee*

A. L. Page

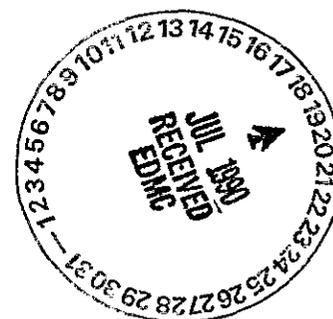
D. R. Keeney

D. E. Baker

R. H. Miller

Roscoe Ellis, Jr.

J. D. Rhoades



*Managing Editor:* RICHARD C. DINAUER

*Assistant Editor:* KRISTINE E. GATES

*Editor-in-Chief ASA Publications:* DWAYNE R. BUXTON

Number 9 (Part 2) in the series

**AGRONOMY**

American Society of Agronomy, Inc.

Soil Science Society of America, Inc.

Publisher

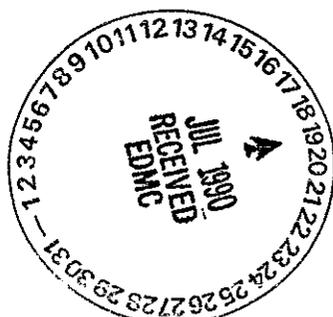
Madison, Wisconsin, USA

9-2-1 2 3 5 3 2 7

# METHODS OF SOIL ANALYSIS

## Part 2, Second Edition

9 2 1 2 5 6 1 1 3 2 8



# Cation Exchange Capacity<sup>1</sup>

J. D. RHOADES

*U.S. Salinity Laboratory  
Riverside, California*

## 8-1 INTRODUCTION

Cation exchange capacity (CEC), usually expressed in milliequivalents per 100 g of soil, is a measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil. These charges may be viewed as being balanced by either (i) an excess of ions of opposite charge and a deficit (or negative adsorption) of ions of like charge, or (ii) the excess of ions of opposite charge over those of like charge. Methods of CEC determination based on either view (when they are correctly carried out) yield identical results, though different proportions of the various exchangeable cations are obtained when such are determined by methods based on the two views (Bolt et al., 1976).

The negative charges in soil constituents are derived from isomorphous substitution within the structures of layer silicate minerals, broken bonds at mineral edges and external surfaces, dissociation of acidic functional groups in organic compounds, and the preferential adsorption (by chemical reaction) of certain ions on the particle surfaces. The first of these four types of matrix charge is permanent charge and is independent of the pH value, the valence of the counter-ion, and the electrolyte level or composition of the bulk solution. The remaining three types of variable charge vary in magnitude depending on the pH value, electrolyte level, valence of the counter-ion, dielectric constant of the medium, and nature of the anion in the solution phase. Another source of variable charge in acid soils is that associated with the neutralization of permanent negative charge by strongly adsorbed aluminum-hydroxy polymers that carry positive charge. As the pH value rises, these polymers are precipitated as bulk  $\text{Al}(\text{OH})_3$ , thereby freeing the negative sites for participation in normal cation exchange reactions. Negative sites can be similarly neutralized by the adsorption of positively charged mineral particles, such as iron oxides. The positive charges on such particles originate from the specific adsorption of protons on the oxide/hydroxide surfaces, and their magnitude depends critically on the ionic strength and pH of the solution. Such charge is substantially neu-

<sup>1</sup> Contribution from the U.S. Salinity Laboratory, USDA-ARS, Riverside, CA 92501.

tralized at  $\text{pH} \geq 7$ . Another kind of neutralization of permanent charge is that caused by highly selective adsorption associated with the mica silicate minerals, such as biotite, vermiculite, and muscovite, which contain  $\text{K}^+$  and  $\text{NH}_4^+$  between the contracted platelets. These interlayer cations are not readily exchangeable, although they can be desorbed with certain chemical treatments and through weathering.

Thus, it is obvious that CEC is not a soil property that is independent of the conditions under which it is measured. Different results will be obtained with different methods. Ideally the method to use is one that measures the soil's capacity to adsorb cations from an aqueous solution of the same pH, ionic strength, dielectric constant, and composition as that encountered in the field, since CEC varies (especially in tropical soils) with these parameters. It is seldom practical to determine the CEC of each soil sample with reagents appropriate to its specific field solution conditions, since the latter information is not easily obtained and each CEC determination would require unique reagents. For this reason CEC determinations are generally based on reference solution conditions that must be standardized to obtain data that can be applied and interpreted universally. The method used should always be reported with the data.

Many methods for determining CEC are provided by using different combinations of soil pretreatment, saturation, washing, and extraction procedures, and different saturation and replacing cations, washing solvents, and pH control. Most methods used may be categorized as one of four:

- 1) The exchangeable cations can be displaced with a saturating salt solution and the CEC taken as equivalent to the sum of exchangeable cations present in the reacted "leachate" (summation method).
- 2) After the CEC has been saturated with an index cation, the adsorbed cation and the small amount of solution entrained by the soil after centrifuging can be displaced directly by another salt solution without further treatment of the soil. The saturating cation and anion are then determined in the resulting extract, and their difference is taken as equal to the CEC of the soil (direct displacement method).
- 3) When the exchange sites have been saturated with an index cation, the soil can be washed free of excess saturating salt, and the amount of the index cation adsorbed by the soil can then be displaced and determined (displacement after washing method).
- 4) Following saturation of the soil CEC with an index cation, the saturating solution can be diluted and labeled with a radioactive isotope of the saturating cation. The concentration of the index cation in the solution is then determined, and the distribution of the isotope (and hence of the total cation) between the two phases is given by measuring the radiation in the solution and soil plus solution (radioactive tracer method).

Variations in results are not surprising in view of the many possible complicating interactions between saturating, washing, and extracting solutions and soil constituents during the analysis and the fact that CEC is not an independent, single-valued soil property. The complications arising from the dissolution of  $\text{CaCO}_3$  and gypsum and the presence of salt in the soil

during CEC determinations are particularly troublesome for arid land soils. Determination of CEC of acid soils, on the other hand, is complicated because of their variable charge character and relatively high content of the more difficultly exchangeable aluminum-hydroxy "cations." For these reasons, different methods of CEC determination are recommended for arid and acid soils. For arid land soils, a modification of the method of Polemio and Rhoades (1977) is recommended. For acid soils, the method of Gillman (1979) is recommended. These methods were chosen because they are reasonably simple and accurate.

Methods of CEC determination, mechanisms of cation exchange, and issues involved in selecting a suitable method are given in reviews by Kelley (1948), Jackson (1958), Coleman and Thomas (1967), Bache (1976), and Thomas (1977). Theory of CEC and effects of anion exclusion on its determination are discussed by Bolt et al. (1976).

Ammonium acetate (pH 7) and NaOAc (pH 8.2) have been employed widely for determining soil CEC. Significant errors result when CEC is determined with these methods on soils that contain calcium carbonate, gypsum, zeolites, feldspathoids, or vermiculite minerals. These methods are described by Chapman (1965).

## 8-2 SOURCES OF ERROR IN CONVENTIONAL CEC METHODS

Either two or three steps are commonly used in the conventional methods of determining the CEC of soils, and potential errors exist in each step. The three steps are (i) saturation of cation exchange sites with a specific cation, (ii) removal of excess saturating solution (this step is eliminated in two-step methods), and (iii) replacement of saturating cation. Possible sources of error in these steps include the following:

- 1) In the saturation step, the exchange sites may not be completely saturated with the saturating cation because other cations in the saturating solution compete for adsorption sites or because the saturating cation's replacing power is insufficient to replace the more strongly adsorbed cations (e.g., exchangeable Al and its hydroxy forms). Other cations may be present in the saturating solution because of the dissolution of  $\text{CaCO}_3$ , gypsum, and silicate minerals during saturation. Such dissolution may be appreciable in certain commonly used saturating solutions (Rhoades & Krueger, 1968; Polemio & Rhoades, 1977). Exchangeable Al and its hydroxy forms are not readily exchanged with monovalent cation saturating solutions. This error would result in an underestimate of CEC.
- 2) In the washing step, there are four potential sources of error. The adsorbed cation may be removed by hydrolysis and replaced by the H ion. It may be replaced by cations (especially  $\text{Ca}^{2+}$ ) brought into solution in the washing solvent from the dissolution of  $\text{CaCO}_3$ , gypsum, and silicates. Cation exchangers (especially fine clay particles and organic matter) may be lost during decantation because they tend to disperse as the excess electrolyte is removed during washing. Some of the original saturating solution may be retained

in the sediment and subsequently extracted as an exchangeable cation if the washing is incomplete or if salt is retained. All but the last of these error sources cause underestimates of CEC.

- 3) In the replacement step, there are two potential sources of error. First, the adsorbed cation may be trapped between interlayers by contraction of expandable 2:1 layer silicates (especially vermiculites and weathered micas) if the replacing solution contains  $\text{NH}_4^+$  or  $\text{K}^+$ . This entraps the saturating cation and prevents its replacement during extraction. This is a common problem with many arid land soils (Bower, 1950) and results in an underestimate of CEC. Second, nonexchangeable cations may be extracted from zeolite, feldspathoid, feldspar, and mafic minerals by the replacing solution. This error also is common with arid land soils (Rhoades & Krueger, 1968), especially if  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  is the saturating cation, if  $\text{NH}_4\text{OAc}$  is the replacing solution, and if the soils are calcareous, gypsiferous, and relatively unweathered. This error results in high CEC values.

Methods described herein minimize these errors. Still, the appropriateness of the methods depends on the particular soils of interest, and the suitability of these methods should be evaluated with respect to these soil properties.

### 8-3 CATION EXCHANGE CAPACITY OF ARID LAND SOILS

The method of Polemio & Rhoades (1977) is particularly suited to arid land soils, including those containing carbonates, gypsum, and zeolites. The two-step procedure involves (i) saturation of cation exchange sites with Na by "equilibration" of the soil with pH 8.2, 60% ethanol solution of 0.4N  $\text{NaOAc}$ -0.1N  $\text{NaCl}$ ; and (ii) extraction with 0.5N  $\text{MgNO}_3$ . Total Na and Cl are subsequently determined in the extracted solution so that the soluble Na from the excess saturating solution, carried over from the saturation step to the extraction step, may be deducted from the total Na to obtain exchangeable Na, which is equivalent to the CEC.

#### 8-3.1 Apparatus

1. Atomic absorption spectrometer.
2. Centrifuge.
3. Round-bottom, narrow-neck centrifuge tubes, 50 ml.
4. Ultrasonic disperser with microtip focusing horn.
5. Reciprocating shaker.

#### 8-3.2 Reagents

1. Saturating solution, 0.4N  $\text{NaOAc}$ -0.1N  $\text{NaCl}$ , 60% ethanol, pH 8.2 solution: Combine 544.32 g of sodium acetate trihydrate ( $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ ), 58.44 g of sodium chloride ( $\text{NaCl}$ ), and 6 liters of ethanol, and

dilute to 10 liters with distilled water. Adjust the pH by stirring and dropwise addition of 6*N* sodium hydroxide (NaOH). Determine the Na/Cl ratio of this solution.

2. Extracting solution, 0.5*N* magnesium nitrate [Mg(NO<sub>3</sub>)<sub>2</sub>]: Weigh out 641.1 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and dilute to 10 liters.

### 8-3.3 Procedure

Weigh out samples of 4 to 5 g of air-dry soil (correct to oven-dry moisture content as determined using a separate subsample), and place in centrifuge tube.

Step 1. Add 33 ml of saturating solution, stopper the tube, and shake for 5 min. Unstopper, and centrifuge at relative centrifugal force of 1,000 until the supernatant liquid is clear (about 5 min). Decant the supernatant liquid and discard. Add fresh saturating solution, insert sonifier tip, and "sonify" for 10 to 30 sec to disperse sediment, then continue as above. Make four successive "equilibrations," discarding the supernatant liquid each time.

Step 2. Add 33 ml of extracting solution, shake for 5 min, centrifuge until the supernatant liquid is clear, and decant the extracted solution into a 100-ml volumetric flask. Repeat the extraction steps two more times with fresh extracting solution, and make to volume. Determine Na (Na<sub>t</sub>) and Cl (Cl<sub>t</sub>) in dilutions of this extracted solution using standards made up in the same batch of extracting solution (sections 10-3.4 and 10-3.5). Chloride is determined so that the soluble Na (Na<sub>sol</sub>) carried over from the saturation step to the extraction step can be deducted from the total Na to obtain exchangeable Na (Na<sub>exch</sub>):

$$\text{CEC} = (\text{Na}_t - \text{Na}_{\text{sol}}) = \text{Na}_t - (\text{Cl}_t) (\text{Na/Cl})_{\text{sat sol}}$$

### 8-3.4 Calculation

$$\text{CEC in meq/100 g} = (10/\text{weight soil sample in g})$$

$$\left[ (\text{Na concentration in meq/liter}) (\text{DF}_{\text{Na}}) - (\text{Cl concentration in meq/liter}) (\text{DF}_{\text{Cl}}) (\text{NaCl})_{\text{sat sol}} \right]$$

where DF represents the dilution factor, i.e., (final analytical volume in milliliters)/(aliquot volume in milliliters).

### 8-3.5 Comments

If the soil is initially high in salts (EC ≥ 4 mmho/cm), wash the soil with one 33-ml increment of water before beginning saturation (avoid excessive washing to prevent loss of particles during decantation). The pH adjustment of the extracting solution has been eliminated from the procedure (Polemio & Rhoades, 1977) because it is not easy to adjust a relatively con-

centrated  $\text{Mg}(\text{NO}_3)_2$  solution to pH 7 without adding considerable electrolyte. This added electrolyte may cause burner clogging and background interference problems during the atomic absorption spectrometric determination of Na (section 2-5.1) with some instruments. For the same reason, it is recommended that 0.5 rather than 1N  $\text{Mg}(\text{NO}_3)_2$  be used as the extractant. This concentration of  $\text{Mg}(\text{NO}_3)_2$  is sufficient to ensure complete desorption of Na during the replacement step. Quite satisfactory determinations of Na in 0.5N  $\text{Mg}(\text{NO}_3)_2$  solution are obtained using an air-acetylene flame and a single-slot burner set at  $45^\circ$  to the optic path with the wavelength set at 295 nm. The concentration range of 0 to 1 meq/liter of Na may be covered linearly in this manner. Any dilutions should be made in such a way that the standards and unknowns have the same final  $\text{Mg}(\text{NO}_3)_2$  concentration.

The amount of carryover of entrained saturating solution should be determined by direct analytical determination of  $\text{Cl}^-$  as described in section 10-3.5.3 and not by weight of solution retained. The latter is an inaccurate measure of  $\text{Cl}^-$  carryover because of the anion exclusion phenomenon. Indeed, this phenomenon can be used to estimate surface area of soil particles with the information collected during the CEC determination by using the method of Bower and Hatcher (1966).

The major advantages of this method are its simplicity, elimination of important sources of error inherent in other methods for certain soils, and its appropriateness for all kinds of soils, including saline and sodic soils and soils containing zeolites, feldspathoids,  $\text{CaCO}_3$ , and gypsum. The method should work equally well with acid soils for determining their permanent total negative charge.

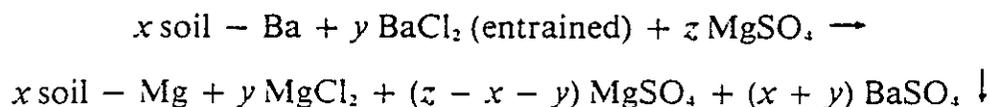
Another method likely suited for determining the CEC of soils that are calcareous, gypsiferous, and relatively unweathered is that of Papanicolaou (1976). In the Papanicolaou CEC method, 1N  $\text{CaCl}_2$  (pH 7.0) is used as the saturating solution; adsorbed Ca is replaced by extraction with 1N  $\text{NaNO}_3$  (pH 7.0). Total ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ),  $\text{Cl}^-$ , and ( $\text{CO}_3^{2-} + \text{HCO}_3^-$ ) are determined in the combined extract. The CEC is calculated as  $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{Cl}^- + \text{CO}_3^{2-} + \text{HCO}_3^-)$ . This method could probably be used for soils containing gypsum if  $\text{SO}_4^{2-}$  were determined. The method, however, requires numerous analyses.

#### 8-4 CATION EXCHANGE CAPACITY OF ACID SOILS

The method described above for determining the CEC of arid-land soils should be applicable to acid soils for determining their permanent charge, but it will not yield a valid value of the capacity of highly weathered tropical soils, which consist primarily of variably charged matrices, to adsorb cations from an aqueous solution at a pH and ionic strength similar to that encountered in the field. Hence, a different method is needed for such soils. The method of Gillman (1979) is recommended because it is appropriate, simple, and inexpensive, and because it can be extended to determine the anion exchange capacity, which is often of equal interest for

such soils. Also, the exchangeable cations can be estimated with the method (Chapt. 9).

In this method the soil is saturated with Ba, subsequently equilibrated with  $\text{BaCl}_2$  solution of a concentration about equivalent in ionic strength to the soil solution, and then reacted with  $\text{MgSO}_4$  to replace Ba with Mg. The resultant  $\text{MgSO}_4$  concentration is adjusted to achieve an ionic strength comparable with that of the soil solution. The use of unbuffered solutions throughout ensures that natural soil pH is not significantly altered. The loss of Mg from the reactant  $\text{MgSO}_4$  solution is determined by analysis of the equilibrium solution and is equivalent to that adsorbed and hence to CEC. Thus, for 100 g of soil:



where  $x$ ,  $y$ , and  $z$  are expressed in milliequivalents; hence:

$$\begin{aligned} \text{CEC} &= \text{Mg lost from reactant solution} \\ &= z - [y + (z - x - y)] \\ &= x \text{ meq/100 g.} \end{aligned}$$

#### 8-4.1 Apparatus

1. Use the same as that described in section 8-3.1.

#### 8-4.2 Reagents

1. Saturating solution, 0.1M barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ): Dissolve 24.4 g of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , and make to 1-liter volume with distilled water.
2. Equilibrating solution, 0.002M barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ): Dissolve 0.4889 g of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , and make to 1-liter volume with distilled water. Adjust the pH to 7.0 or other specified pH using  $\text{Ba}(\text{OH})_2$  or HCl.
3. Reactant solution, 0.005M magnesium sulfate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ): Dissolve 1.232 g of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and make to 1-liter volume with distilled water.
4. Ionic strength reference solution, 0.0015M magnesium sulfate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ): Dissolve 0.3700 g of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and make to 1 liter with distilled water.

#### 8-4.3 Procedure

Place 2 g of air-dry (correct to oven-dry moisture content as determined using a separate subsample) plus 20 ml of 0.1M  $\text{BaCl}_2$  saturating solution in a preweighed centrifuge tube; stopper and shake for 2 hours. Centrifuge and decant solution. Equilibrate soil with three successive 20-ml

increments of 0.002M BaCl<sub>2</sub>, equilibrating solution by "sonifying" for 10 to 30 sec to disperse sediment and shaking each for 1 hour between centrifugations, and discard the supernatants. Weigh the centrifuge tube plus soil and entrained 0.002M BaCl<sub>2</sub> of solution following the last decantation of supernatant. Add 10 ml of 0.005M MgSO<sub>4</sub> reactant solution, and shake gently for 1 hour. Adjust the EC of the reactant suspension to that of the 0.0015M MgSO<sub>4</sub> ionic strength reference solution at the ambient laboratory conditions by the addition of 0.005M MgSO<sub>4</sub> reactant solution or distilled water. Shake gently overnight, and again adjust the reactant suspension conductivity, if necessary. Weigh the centrifuge tubes plus contents to determine the volume of MgSO<sub>4</sub> or water added. Centrifuge and decant the supernatant, retaining it for analysis. Determine pH and Mg concentration of this supernatant solution (also its Cl<sup>-</sup> concentration if anion exchange capacity is desired).

#### 8-4.4 Calculation

1. If only distilled water was added:

$$\text{CEC in meq/100 g} = 100 (0.1 - C_1 V_3) / \text{oven-dry weight soil sample in g.}$$

2. If more MgSO<sub>4</sub> reactant solution had to be added:

$$\text{CEC in meq/100 g} = 100 (0.01 V_2 - C_1 V_3) /$$

(oven-dry weight soil sample in g)

where  $V_2$  and  $V_3$  are volume (milliliters) of added MgSO<sub>4</sub> reactant solution and final supernatant solution, respectively, and  $C_1$  is concentration of Mg in supernatant (milliequivalents/milliliter).

The CEC obtained is appropriate to the pH measured in the final MgSO<sub>4</sub> solution supernatant and is a close estimate of the soils CEC under natural field conditions of pH as measured in a 1:5 soil/water extract (Gilman, 1979).

#### 8-4.5 Comments

If centrifuge tubes of 30-ml capacity are used, the use of 0.005M MgSO<sub>4</sub> is limited to soils with CEC values of < 10 meq/100 g. For higher CEC values, stronger MgSO<sub>4</sub> solution is required, e.g., 0.01M MgSO<sub>4</sub> for CEC values between 10 to 20 meq/100 g.

The volume of entrained 0.002M BaCl<sub>2</sub> equilibrating solution is determined (from the centrifuge tube plus contents weight after centrifugation and decantation) so that the dilution of the final MgSO<sub>4</sub> solution can be estimated.

The unbuffered 0.002M BaCl<sub>2</sub> and 0.0015M MgSO<sub>4</sub> solutions are used because their ionic strengths ( $\mu = 0.006$ ) approximate that found in the soil solutions (at near field capacity) of highly weathered soils (Gillman & Bell,

1978). This ionic strength can be altered at the discretion of the analyst for soils that differ in this respect.

Overnight equilibration is necessary for the complete replacement of Ba by Mg.

Variation in the ratio of soil to 0.002M BaCl<sub>2</sub> from 1:5 to 1:20 produces no change in CEC since the ionic strength and equilibrium pH are constant. Thus, flexibility in the choice of sample weights for soils with high and low CEC values is permitted.

The CEC values obtained for soils with this method are much lower than those obtained with conventional methods (such as the method in section 8-3.3) for the reasons discussed in section 8-1.

This method is suitable for routine determinations and for research needs where effects due to pH and ionic strength are to be studied. The desired pH can be attained during washings with 0.002M BaCl<sub>2</sub> using Ba(OH)<sub>2</sub> or HCl, and the reference MgSO<sub>4</sub> solution can be set at any desired ionic strength. Magnesium concentration in the supernatant is suitably determined by atomic absorption spectrometry (Chapt. 2 and section 10-3.4).

## 8-5 LITERATURE CITED

- Bache, B. W. 1976. The measurement of cation exchange capacity of soils. *J. Sci. Food Agric.* 27(3):273-280.
- Bolt, G. H., M. G. M. Bruggenwert, and A. Kamphorst. 1976. Adsorption of cations by soil. p. 54-90. *In* G. H. Bolt and M. G. M. Bruggenwert (ed.) *Soil chemistry A. Basic elements.* Elsevier North-Holland, Inc., New York.
- Bower, C. A. 1950. Fixation of ammonium in difficultly exchangeable forms under moist conditions by some soils of semi-arid regions. *Soil Sci.* 70:375-383.
- Bower, C. A., and J. T. Hatcher. 1966. Simultaneous determination of surface area and cation-exchange capacity. *Soil Sci. Soc. Am. Proc.* 30:525-527.
- Chapman, H. D. 1965. Cation exchange capacity. *In* C. A. Black et al. (ed.) *Methods of soil analysis.* Agronomy 9:891-901. Am. Soc. of Agron., Inc., Madison, Wis.
- Coleman, N. T., and G. W. Thomas. 1967. The basic chemistry of soil acidity. *In* R. W. Pearson and F. Adams (ed.) *Soil acidity and liming.* Agronomy 12:1-41. Am. Soc. of Agron., Inc., Madison, Wis.
- Gillman, G. P. 1979. A proposed method for the measurement of exchange properties of highly weathered soils. *Aust. J. Soil Res.* 17:129-139.
- Gillman, G. P., and L. C. Bell. 1978. Soil solution studies on weathered soils from tropical north Queensland. *Aust. J. Soil Res.* 16:67-77.
- Jackson, M. L. 1958. *Soil chemical analysis.* Prentice-Hall, Inc., Englewood Cliffs, N.J. p. 57-81.
- Kelley, W. P. 1948. Cation exchange in soils. A.S.C. Monogr. 109.
- Papanicolaou, E. P. 1976. Determination of cation exchange capacity of calcareous soils and their percent base saturation. *Soil Sci.* 121:65-71.
- Polemio, M., and J. D. Rhoades. 1977. Determining cation exchange capacity: A new procedure for calcareous and gypsiferous soils. *Soil Sci. Soc. Am. J.* 41:524-528.
- Rhoades, J. D., and D. B. Krueger. 1968. Extraction of cations from silicate minerals during the determination of exchangeable cations in soils. *Soil Sci. Soc. Am. Proc.* 32:488-492.
- Thomas, G. W. 1977. Historical developments in soil chemistry: Ion exchange. *Soil Sci. Soc. Am. J.* 41:230-238.