

nia soils by the Salinity Laboratory Staff (1954) using this approach has been criticized as potentially in error due to the effects of ionic strength and complexation on activities of the ions (Sposito & Mattigod, 1977). Complete anion and cation analyses and computer speciation of solutions is needed to accurately calculate activity-based SAR values, which may not always be justified in practice, given that SAR values based on concentration are often within 10% of the activity-based values, and considering the rather wide range of  $K_G$  values reported in the literature for various soil materials (Levy et al., 1988).

The use of equivalent, rather than mole fractions in the Gapon equation also has been criticized as nonthermodynamic, since an activity coefficient ( $f_i$ ) cannot be meaningfully assigned to a "formal" quantity such as an equivalent (Sposito, 1977; Ogwada & Sparks, 1986). Sposito (1977), using the reverse reaction of Eq. [11], derived a new expression for the Gapon equation that is mathematically consistent with the Vanselow equation, and thus thermodynamically correct, as

$$K_G = \frac{SAR}{2E_{NaX}} (1 - E_{NaX}^2)^{1/2} \quad [15]$$

At  $E_{NaX} < 0.2$ , the expression in parentheses on the right hand side of eq. [15] is nearly equal to one, and  $E_{NaX}$  also is approximately equal to  $ESR$  [ $E_{NaX} = ESR / (1 + ESR)$ ]. Thus, this equation reduces to  $K_G = SAR / (2 ESR)$  at low exchangeable Na, which is a linear relation differing only by a factor of two from the "traditional" Gapon equation of Eq. [13].

The question of the "correct" units for expressing exchangeable cations has introduced some confusion in the literature, as other exchange expressions (notably that of Gaines and Thomas, described by Sposito, 1981a) also have used equivalent fractions, and derived thermodynamic parameters (e.g.,  $\Delta G$  values for exchange) based on them. While any correctly formulated exchange coefficient may be used to describe a given cation exchange reaction, it might be argued that the use of moles and mole fractions has greater thermodynamic significance, and any standardization would allow much more ready comparison of coefficients published in the literature. On the other hand, the utility of the equivalent, or mole of charge, concept in CEC has been proven practically and historically, and is not likely to soon disappear.

## PROBLEMS IN MEASUREMENT OF CATION EXCHANGE CAPACITY

### Presence of Soluble Salts and Carbonates

The first step in CEC determinations typically involves the replacement of exchangeable cations by a saturating solution. Cations other than that of the saturating solution may be present, arising from the solubility of the salts and  $CaCO_3$  in the extracting solution. Soluble salts are readily removed during the extraction, but sparingly soluble salts such as  $CaSO_4$  and  $CaCO_3$  will continue to dissolve for prolonged periods. Polemio & Rhoades (1977) have shown that such

dissolution can be appreciable in commonly used saturating solutions. In addition, such salts can be soluble in the washing solution designed to remove the entrained solution. As a result, not all the exchange sites will be occupied by the saturating cation, and this will lead to an underestimation of the CEC. The accurate determination of exchangeable cations in saline and calcareous soils is clearly compromised because of this problem of quantitatively separating soluble or sparingly soluble from exchangeable cations during the extraction procedure by any method. As a result in such cases, CEC cannot be estimated by summing exchangeable cations, and often not by simple saturation techniques.

Soluble cations arising from dissolution reactions also cause errors in selectivity coefficient determinations. Moderately soluble compounds such as gypsum and calcite must either be removed prior to initial cation saturation, or such dissolution accounted for during the measurement (Amrhein & Suarez, 1990). Dissolution of the clay itself also may be a concern if very low ionic strengths are used during washing or equilibration steps, releasing  $Mg^{2+}$ ,  $K^+$  and other cations to the solution phase (Frenkel & Suarez, 1977).

#### Effect of Cation and Anion Type

In soils containing micaceous minerals, problems may arise when cations such as  $K^+$  and  $NH_4^+$  are used in the saturation process due to their fixation in the interlayer positions of the minerals. This can result in underestimation of CEC (Bower, 1950). In addition, some monovalent ions used for extraction are somewhat less efficient than divalent ions in removing  $Al^{3+}$ . Many polyvalent ions such as  $Al^{3+}$  and trace metals form hydroxy ions, which may result in an overestimation of ECEC if they are assumed to be present as the simple ions. However, for  $Ba^{2+}$  at pH values below nine, only very small amounts of hydroxy ions are formed, and thus errors in CEC estimation would be minimized (Bache, 1976). When monovalent ions such as  $NH_4^+$  and  $Na^+$  are used to saturate the CEC, hydrolysis may occur to a considerable extent as the electrolyte concentration is reduced, resulting in a loss of cation and underestimation of CEC.

In selectivity coefficient determinations, choice of cations is dictated by the study objectives; it should be noted, however, that the theory of cation exchange assumes exchange reactions are reversible, and that there are a fixed number of exchange sites accessible to both cations (assuming fixed ionic strength and pH). Trace metals (Cu, Zn, Mn, etc.) may violate these assumptions on clays with oxidic or organic components, where metals may exchange with protons on uncharged surface functional groups (Sposito & Fletcher, 1985; Sposito, 1981a). As noted above,  $K^+$  and  $NH_4^+$  also are strongly and irreversibly adsorbed by some clay minerals. Such "specific adsorption," by involving proton exchange and limited reversibility, is better modeled using site-binding models which account for the stoichiometry and competing ions (i.e.,  $H^+$ ) involved in such reactions.

Anions such as  $SO_4^{2-}$  and  $PO_4^{3-}$  are specifically adsorbed by variable charge surfaces, which can result in an increase in CEC; hence the preference for  $Cl^-$  or  $ClO_4^-$  salts in CEC measurements (Matsue & Wada, 1985; Hendershot & Duquette, 1986). In addition, formation of soluble complexes with anions may result in errors in both CEC and selectivity coefficient determinations. Sposito et al.

(1983) have suggested that their observed increases in CEC at higher Ca coverages on bentonite may be due to  $\text{CaCl}^+$  complex formation, also which influenced the selectivity of the surface for Ca vs. Na. Suarez & Zahov (1989), however, found no anion effect on CEC using  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{ClO}_4^-$  on montmorillonite, and little difference in Ca-Mg selectivity.

### **pH Effects and the Use of Buffered Solutions**

Almost all topsoils and many subsoils contain variable charge surfaces (organic matter, sesquioxides and clay mineral edges) which can associate and dissociate  $\text{H}^+$  depending on the ambient pH value (Uehara & Gillman, 1981). Thus when a solution buffered at a particular pH value such as 1 M  $\text{NH}_4\text{OAC}$  (pH 7) or  $\text{BaCl}_2\text{-TEA}$  (pH 8.2) is used during the extraction process, the pH of the soil is brought to the pH value of the solution. The magnitude of the error incurred in the CEC measurement depends on the difference in pH values between the soil and extracting solution. Such buffered solutions cannot be used to estimate exchangeable  $\text{Al}^{3+}$ . Thus if estimates of CEC under field conditions are required, methods involving unbuffered salt solutions should be used.

Variation in pH also may affect cation selectivity of soil clays, as functional groups may show differences in selectivity as they dissociate with increasing pH (Miller et al., 1990). Some studies, however, show little effect of pH on  $K_v$  (Sposito & Fletcher, 1985). It is probably desirable to measure selectivity coefficients at near field pH, and to avoid pH levels below 4.5 to 5, where clay dissolution releases  $\text{Al}^{3+}$  to solution to greatly complicate the situation. Buffers containing phosphate or acetate must be avoided due to complex formation with divalent cations.

### **Ionic Strength Effects and Removal of Entrained Electrolyte**

The magnitude of the charge on variable charge surfaces also is a function of the concentration of the equilibrium solution (Uehara & Gillman, 1981). Therefore it is important to fix or measure the ionic strength of the solution at the end of the extraction process during CEC measurement. Usually the ionic strength of the solution is selected to approximate that of the soil solution under field conditions. In methods which involve a water/alcohol wash to remove excess saturating solution, errors in the CEC measured can arise if all the electrolyte is not removed. Such washing also results in an unknown value for EC (electrical conductivity) of the final equilibrating solution. Furthermore, prolonged washing can result in the hydrolysis of adsorbed saturating ions, giving rise to low values for CEC.

Variation in ionic strength has an effect on the distribution of cations between solution and surface for mono-divalent exchange, as predicted by theory (Sposito, 1981b); however, there is no effect on the value of  $K_v$  obtained, provided that activity correction of soluble ions is performed. Many reported  $K_G$  values prior to 1980 did not employ such corrections in mono-divalent exchange at appreciable ionic strengths, and thus may be in error (Sposito & Mattigod, 1977). Most measurements of exchange coefficients are made at 0.01 to 0.05 M ionic

strength, largely in order to provide sufficient solution cations to effect the desired exchange with the solid phase.

## CATION EXCHANGE CAPACITY OF SOILS CONTAINING SALTS, CARBONATES OR ZEOLITES

### Introduction

Arid region soils often contain carbonates and other soluble salts, resulting in complications with respect to the quantities of exchangeable cations extracted. A number of methods have been proposed to overcome these difficulties involving the use of double extractions and LiEDTA (Begheyn, 1987), BaCl<sub>2</sub>-TEA (Mehlich, 1939), CaCl<sub>2</sub> (Papanicolaou, 1976), and NaCl-NaOAc (Gupta et al., 1985).

The method of Amrhein & Suarez (1990) which has been selected here, was developed to facilitate the measurement of CEC and the exchangeable cations in calcareous and gypsiferous soils by taking into account the dissolution of calcite and gypsum during the saturation and extraction steps. In addition, it accounts for anion exclusion, but does not correct for primary weathering which is assumed to be negligible in comparison to that of calcite and gypsum. The soil is first saturated with 0.2 M CaCl<sub>2</sub> solution adjusted to pH 8.2 and then extracted with 0.5 M Mg(NO<sub>3</sub>)<sub>2</sub>, correcting for the entrained CaCl<sub>2</sub> solution. Corrections for gypsum and calcite dissolution are made from the SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> contents of the soil solution prior to extraction, and the saturating and extracting solutions.

### Method

#### Apparatus

1. Atomic absorption spectrometer.
2. Centrifuge.
3. Centrifuge tubes (30 mL).
4. Reciprocating or end-over-end shaker.
5. Vortex stirrer.

#### Reagents

1. Saturating solution, 0.2 M CaCl<sub>2</sub>/0.0125 M CaSO<sub>4</sub>. Dissolve 29.41 g CaCl<sub>2</sub> • 2H<sub>2</sub>O and 2.15 g CaSO<sub>4</sub> • 2H<sub>2</sub>O in approximately 900 mL deionized water and adjust to pH 8.2 using saturated Ca(OH)<sub>2</sub> solution. Make up to 1 L with deionized water.
2. Dilute saturating solution, 0.025 M CaCl<sub>2</sub>. Dissolve 3.68 g CaCl<sub>2</sub> • 2H<sub>2</sub>O and make up to 1 L with deionized water.
3. Extracting solution, 0.5 M Mg(NO<sub>3</sub>)<sub>2</sub>. Dissolve 91.19 g Mg(NO<sub>3</sub>)<sub>2</sub> • 2H<sub>2</sub>O and make up to 1 L with deionized water.
4. 0.01 M KH(IO<sub>3</sub>)<sub>2</sub> solution. Dissolve 3.8994 g KH(IO<sub>3</sub>)<sub>2</sub> and make up to 1 L with deionized water.

### Procedure

Weigh 5 g soil into a preweighed 30-mL centrifuge tube and add 20 mL of the saturating solution. Shake for 5 min, centrifuge, decant and save supernatant. The Vortex stirrer is used to resuspend the soil. Repeat this process four times, combining supernatants in a 100-mL volumetric flask for determination of exchangeable Mg, K and Na. Add 20 mL of the dilute saturating solution, shake for 5 min, centrifuge and decant supernatant. Repeat this process twice. Decant and save the last supernatant for determination of Ca, SO<sub>4</sub>, Cl and alkalinity (HCO<sub>3</sub>), and then reweigh the tube plus contents to obtain the weight of entrained solution. Add 20 mL of the extracting solution, shake for 5 min, centrifuge and save supernatant. Repeat this process a further two times. Combine all the supernatants in a 100-mL volumetric flask and determine Ca, SO<sub>4</sub>, Cl and alkalinity (HCO<sub>3</sub>).

The cations Ca, Mg, K and Na are determined by atomic absorption spectrophotometry [Chapters 19 (Helmke & Sparks, 1996), 21 (Suarez, 1996)], Cl by Chloridometer (LABCONCO, Kansas City, MO) [Chapter 31 (Frankenberger et al., 1996)], SO<sub>4</sub> by turbidimetry [Chapter 33 (Tabatabai, 1996)] and alkalinity by titration to pH 4.40 using the 0.01 M KH(IO<sub>3</sub>)<sub>2</sub>.

### Calculations

$$CEC = 10 \times \{T_{Ca} - T_{HCO_3} - T_{SO_4} + V([HCO_3] + [SO_4] - [Ca]) \\ - (T_{Cl} - V[Cl]) - [SO_4] (T_{Cl} - V[Cl])/[Cl] - [HCO_3](T_{Cl} - V[Cl])/[Cl]\}$$

where  $T$  denotes ions in the Mg(NO<sub>3</sub>)<sub>2</sub> extract in millimoles of cation charge per kilogram,  $[ ]$  denotes ion concentration in the final rinse with dilute saturating solution in millimoles of cation charge per liter,  $V$  is the volume of entrained solution/weight of soil in liters per kilogram,  $CEC$  is the cation exchange capacity in centimoles of cation charge per kilogram.

### Comments

The primary advantage of this method is that it permits the estimation of exchangeable cations and CEC simultaneously while correcting for the presence of soluble salts and the dissolution of calcite and gypsum. This method also enables selectivity coefficients to be calculated. The correction for calcite and gypsum is based on the assumption that any HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> found in the extracting solution in excess of that in the entrained solution is due to dissolution. The saturating solution contains saturated gypsum to reduce gypsum dissolution during the saturation process, so that when traces are present they are not removed prior to extraction.

The method avoids the use of barium salts which increase calcite dissolution resulting from the precipitation of BaCO<sub>3</sub>.

A much simpler method, requiring fewer analyses, but which measures the CEC only of soils containing carbonates, gypsum and zeolites was presented in the previous edition of this volume (Rhoades, 1982).

## CATION EXCHANGE CAPACITY OF ALL OTHER SOILS

## Compulsive Exchange Method

## Introduction

This method was originally proposed by Gillman (1979) and subsequently modified by Gillman & Sumpter (1986a) to measure  $CEC_{CE}$  (compulsive exchange CEC). It has been shown to be a measure of the basic cation exchange capacity ( $CEC_B$ ), which is defined as the capacity of the soil to retain basic cations under field conditions (simulated by a standard ionic strength of 0.006 M) (Gillman & Hallman, 1988; Gillman & Sumpter, 1986b). For over 200 soils of widely varying origin and for 22 Andisols, the relationship between  $CEC_B$  and  $CEC_{CE}$  was very similar for the two cases

$$CEC_B = -0.14 + 1.09 CEC_{CE} \quad r^2 = 0.82 \quad (200 \text{ soils}) \quad [14]$$

$$CEC_B = -0.09 + 1.05 CEC_{CE} \quad r^2 = 0.88 \quad (22 \text{ Andisols}) \quad [15]$$

The total cation exchange capacity ( $CEC_T$ ) is obtained by adding exchangeable Al obtained by extraction with 1 M KCl (Bertsch & Bloom, 1996; see Chapter 18) to the value for  $CEC_B$  (Gillman & Sumpter, 1986b). In addition, the anion exchange capacity (AEC) also can be estimated. This method has been successfully applied to all types of soil including saline and calcareous versions although originally developed for use on highly weathered, variable charge soils.

The soil is initially saturated with  $Ba^{2+}$  and then brought to an equilibrium solution ionic strength similar to that of the original soil solution. The  $Ba^{2+}$  is then exchanged by  $Mg^{2+}$  by addition of  $MgSO_4$ , which precipitates  $BaSO_4(s)$ . After readjustment of the ionic strength to a value comparable to that of the soil solution, the quantity of  $Mg^{2+}$  adsorbed (= CEC) is estimated as the loss of  $Mg^{2+}$  from the  $MgSO_4$  solution added.

## Apparatus

1. Bench-top centrifuge equipped for 30-mL polypropylene centrifuge tubes with caps.
2. pH meter with combination electrode.
3. Conductivity meter, preferably with the facility to operate in "ratio mode" using two electrodes.
4. Vortex stirrer.
5. End-over-end shaker or reciprocating shaker.
6. Top loading balance reading to 0.01 g.
7. Dispensers and micropipettes.

## Reagents

1. Saturating solution, 0.2 M  $BaCl_2/0.2$  M  $NH_4Cl$ . Dissolve 48.9 g  $BaCl_2 \cdot 2H_2O$  and 10.7 g  $NH_4Cl$  and make up to 1 L with deionized water.

2. 0.05 M BaCl<sub>2</sub> solution. Dissolve 12.2 g BaCl<sub>2</sub> • 2H<sub>2</sub>O and make up to 1 L with deionized water.
3. Equilibrating solution, 0.002 M BaCl<sub>2</sub>. Dissolve 0.4889 g BaCl<sub>2</sub> • 2H<sub>2</sub>O and make up to 1 L with deionized water.
4. Reactant solution, 0.005 M MgSO<sub>4</sub>. Dissolve 1.2324 g MgSO<sub>4</sub> • 7H<sub>2</sub>O and make up to 1 L with deionized water.
5. 0.05 M MgSO<sub>4</sub> solution. Dissolve 12.3240 g MgSO<sub>4</sub> • 7H<sub>2</sub>O and make up to 1 L with deionized water.
6. Ionic strength reference solution, 0.0015 M MgSO<sub>4</sub>. Dissolve 0.3697 g MgSO<sub>4</sub> • 7H<sub>2</sub>O and make up to 1 L with deionized water.
7. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 0.1 M.

### Procedure

Weigh a 30-mL centrifuge tube (Column A, Table 40-1), add approximately 2 g soil, and reweigh to determine the exact soil mass (Column B). Add 10 mL deionized water and shake for 1 h. Measure the suspension electrical conductivity (EC) and pH. If the soil contains soluble salts as indicated by EC, wash with 20 mL 70% ethanol in water and then 20 mL 10% ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) in water and discard solutions. Add 10 mL 0.2 M BaCl<sub>2</sub>/0.2 M NH<sub>4</sub>Cl solution, shake for a further 2 h, centrifuge and retain supernatant for estimation of exchangeable cations [Chapter 19 (Helmke & Sparks, 1996) and 20 (Suarez, 1996)]. Add 20 mL 0.05 M BaCl<sub>2</sub> to the tube, mix thoroughly with Vortex stirrer, centrifuge and discard supernatant. Care should be taken to avoid loss of soil material, which can be effected by removal of the supernatant by suction. To bring the soil to the standard 0.006 M ionic strength, wash three times with 20-mL portions of 0.002 M BaCl<sub>2</sub> solution. During the last washing after thorough mixing, measure the suspension pH (pH<sub>BaCl<sub>2</sub></sub>) prior to centrifugation. If AEC is to be determined, retain the supernatant for Cl<sup>-</sup> determination (Variable C<sub>2</sub>). Weigh the tube and contents (Column C) to estimate the volume of entrained BaCl<sub>2</sub> solution. Add 10 mL 0.005 M MgSO<sub>4</sub> solution to begin the compulsive exchange of

Table 40-1. Worksheet for computation of CEC by the compulsive exchange method.

Sample	pH <sub>BaCl<sub>2</sub></sub>	Weighings				Entrained volume	Number of 0.5-mL increments of 0.05 M MgSO <sub>4</sub>	Volume MgSO <sub>4</sub> expressed as 0.005 M	Final volume	CEC <sub>CE</sub> ‡
		Tube	Tube + soil†	Tube + soil + BaCl <sub>2</sub>	Final					
		A	B	C	E	V <sub>1</sub> = C - B	D	V <sub>2</sub> = 10 + 5 × D	V <sub>3</sub> = E - B	
1589	5.37	13.00	15.01	16.56	40.82	1.55	5	35	25.81	13.56
1625	4.82	13.18	15.23	16.86	33.18	1.63	0	10	17.95	2.24
1696	5.14	13.19	15.26	17.54	28.37	2.28	2	20	13.11	7.76

† If contents have been transferred to a beaker, substitute "wt. beaker + soil" for "wt. tube + soil."  
 AEC (cmol<sub>e</sub> kg<sup>-1</sup>) = 50(C<sub>1</sub>V<sub>3</sub> - C<sub>2</sub>V<sub>1</sub>); where C<sub>1</sub> = concentration of Cl<sup>-</sup> in final solution, and C<sub>2</sub> = concentration of Cl<sup>-</sup> in entrained solution millimoles per milliliter.

‡ CEC<sub>CE</sub> (cmol<sub>e</sub> kg<sup>-1</sup>) = 100(Mg added - Mg remaining)/weight soil = (100/wt. soil) • (0.01 V<sub>2</sub> - 0.003 V<sub>3</sub>)

Mg for Ba. Mix thoroughly and allow to stand for 1 h. Compare the EC of the suspension with that of the reference 0.0015 *M* MgSO<sub>4</sub> solution. If the conductivity ratio ( $CR = EC_{\text{susp}}/EC_{\text{ref}}$ ) < 1.0, add 0.5-mL increments of 0.05 *M* MgSO<sub>4</sub> and record the number of such additions. If initial  $CR > 1.0$ , take no further action. Measure pH of the suspension. If  $\text{pH}_{\text{susp}} > \text{pH}_{\text{BaCl}_2}$  by more than 0.2 to 0.3 units, add 0.1 *M* H<sub>2</sub>SO<sub>4</sub> dropwise until  $\text{pH} = \text{pH}_{\text{BaCl}_2}$  and allow to stand for at least 1 h. Reduce CR to 1.0 by adding deionized water and allow to stand overnight. Recheck  $\text{pH}_{\text{susp}}$  and CR. If necessary, readjust to  $\text{pH}_{\text{BaCl}_2}$  with 0.1 *M* H<sub>2</sub>SO<sub>4</sub>, and CR to  $1.0 \pm 0.05$  with deionized water. When satisfied that the appropriate conditions of pH and ionic strength have been established, reweigh the tube (Column E). If AEC is to be determined, centrifuge and determine Cl<sup>-</sup> concentration in the supernatant (Variable *C*<sub>1</sub>) and in the solution retained above (Variable *C*<sub>2</sub>) [Chapter 31 (Frankenberger et al., 1996)].

### Calculation

The worksheet shown in Table 40-1 gives example calculations for this method, and its use considerably simplifies the record-keeping necessary with the procedure. Such a table might readily be constructed in a computer spreadsheet application, greatly facilitating computations.

### Comments

Matsue & Wada (1985) criticized this method on the grounds that it could not be applied to soils which specifically adsorb SO<sub>4</sub><sup>2-</sup>. They proposed using 0.01 *M* SrCl<sub>2</sub> instead of BaCl<sub>2</sub> and extracting with 0.5 *M* HCl or 1 *M* NH<sub>4</sub>OAc. Hendershot & Duquette (1986) found that the CEC of predominantly variable charge soils measured by compulsive exchange with MgSO<sub>4</sub> was higher than when the Ba was replaced by MgCl<sub>2</sub>, suggesting that specific adsorption of SO<sub>4</sub><sup>2-</sup> may be responsible. Subsequently, Wada & Matsue (1987) questioned Gillman & Sumpter's (1986a) use of H<sub>2</sub>SO<sub>4</sub> to reduce the pH of the MgSO<sub>4</sub> soil suspension to its value in BaCl<sub>2</sub>, and calculated that the CEC may be overestimated by 10 to 15% using this method. Gillman & Hallman (1988) addressed these criticisms by using CaCl<sub>2</sub> instead of BaCl<sub>2</sub> and extracting with 1 *M* NH<sub>4</sub>OAc; their results showed that on a range of Andisols, specific adsorption of SO<sub>4</sub><sup>2-</sup> was not a problem. As far as the use of H<sub>2</sub>SO<sub>4</sub> is concerned, they indicated that the magnitude of the error was small and would only be significant when a soil had >5 cmol<sub>c</sub> kg<sup>-1</sup> of both CEC and AEC. None of the soils they studied showed any of these characteristics even remotely.

If this method is to be used to estimate exchangeable cations, care should be taken to prepare standards in the same matrix as the unknown solutions; Ca<sup>2+</sup> in particular suffers some interference from SO<sub>4</sub><sup>2-</sup> with air-acetylene atomic absorption determination. When soils contain soluble salts, pretreatment should be used to remove them, but this can cause errors in the estimation of exchangeable cations. However the presence of soluble salts will have little or no effect on the measurement of CEC<sub>CE</sub>.

The reason for the use of an equilibrating solution of divalent cations of ionic strength equal to 0.006 *M* is because it approximates that of the "soil solu-

tion" of many highly weathered soils (Gillman & Bell, 1978). In soils where the ionic strength of the soil solution differs substantially from 0.006 *M*, an appropriate value should be used.

Although  $\text{BaCl}_2$  is not usually used as an electrolyte to measure soil pH,  $\text{pH}_{\text{BaCl}_2}$  should be a reliable estimate except for saline soils where the removal of soluble salts generally results in an increase in pH.

For greater convenience, a conductivity meter which has the capability of being operated in a ratio mode is preferred, although a meter with a single electrode will suffice.

With experience, it becomes possible with highly buffered soils to overadjust  $\text{pH}_{\text{BaCl}_2}$  with 0.1 *M*  $\text{H}_2\text{SO}_4$ , knowing that an upward drift will occur. Similarly, adjustment of CR to 1.0 by the addition of deionized water is soil-dependent. Should the capacity of the centrifuge tube be exceeded, simply transfer the contents to a weighed beaker and continue. A modification to the procedure which makes it less time-consuming has been proposed by Sumner et al. (1994), in which instead of dilution with water to bring the CR to 1.0 in the final step, the sample is centrifuged prior to water addition and the EC of the supernatant is measured. From a calibration curve relating EC of the supernatant to water added, the amount of water that would have been added can be estimated.

Cation exchange capacity values obtained by the compulsive exchange method are similar to those obtained by the silver thiourea method (Searle, 1986; Gillman et al., 1983), sum of exchangeable cations (ECEC) (Gillman et al., 1983; Grove et al., 1982), and 0.2 *M*  $\text{NH}_4\text{Cl}$  (Grove et al., 1982) methods.

### Unbuffered Salt Extraction Method

#### Introduction

This method is based on the original proposal of Schofield (1949) which enabled the measurement of the CEC of a soil at its "field pH" value. An unbuffered salt solution is used in place of the buffered solutions such as  $\text{NH}_4\text{OAc}$  and  $\text{BaCl}_2$ -TEA which were in vogue at that time for saturating the exchange complex. The method presented here is a modification of the procedure described by Grove et al. (1982). It involves the saturation of the exchange sites with  $\text{NH}_4^+$  using an unbuffered  $\text{NH}_4\text{Cl}$  solution, reducing the ionic strength to an appropriate value (or removing the entrained salt with water), assessing the volume of the solution which is entrained and then displacing  $\text{NH}_4^+$  with a solution of  $\text{KNO}_3$ . The quantities of  $\text{NH}_4^+$  and  $\text{Cl}^-$  in the final extract are corrected for the amounts in the entrained solution. If the volume of entrained solution is measured, this method also permits the estimation of the anion exchange capacity from the quantity of  $\text{Cl}^-$  adsorbed.

#### Apparatus

1. Bench-top centrifuge.
2. 50-mL centrifuge tubes with caps.
3. Vortex stirrer.
4. End-over-end or reciprocating shaker.

5. Top-loading balance reading to 0.01 g.
6. Dispensers.
7. 250-mL volumetric flasks.

### Reagents

1. Saturating solution, 0.2 *M* NH<sub>4</sub>Cl. Dissolve 10.7 g NH<sub>4</sub>Cl and make up to 1L with deionized water.
2. Equilibrating solution, 0.04 *M* NH<sub>4</sub>Cl. Dissolve 2.1 g NH<sub>4</sub>Cl and make up to 1 L with deionized water.
3. Extracting solution, 0.2 *M* KNO<sub>3</sub>. Dissolve 20.2 g KNO<sub>3</sub> and make up to 1 L with deionized water.

### Procedure

Weigh 5 g of soil into a preweighed 50-mL centrifuge tube. Add 30 mL of 0.2 *M* NH<sub>4</sub>Cl and shake for 5 min, centrifuge and decant supernatant into a 250-mL volumetric flask, being careful to avoid loss of soil. Add 30 mL of 0.2 *M* NH<sub>4</sub>Cl, resuspend the soil using the Vortex stirrer (Scientific Industries, Bohemia, NY), shake for 5 min, centrifuge and decant supernatant into volumetric flask. Repeat this process three more times, combining supernatants prior to making up to volume with 0.2 *M* NH<sub>4</sub>Cl. Save this solution for the determination of exchangeable Na, K, Ca, Mg and Al [Chapter 18 (Bertsch & Bloom, 1996), 19 (Helmke & Sparks, 1996), and 20 (Suarez, 1996)]. Two options are possible at this point: EITHER wash three times with deionized water and discard the supernatant, OR add 3 × 30-mL portions of 0.04 *M* NH<sub>4</sub>Cl, resuspend, shake for 5 min, centrifuge and discard the supernatant each time, and then weigh tube to determine volume of entrained solution. Add 30 mL 0.2 *M* KNO<sub>3</sub>, resuspend, shake for 5 min, centrifuge and collect supernatant in a 250-mL volumetric flask. Repeat this process a further four times, combining the supernatants. Analyze this solution for NH<sub>4</sub><sup>+</sup> [Chapter 38 (Mulvaney, 1996)] and, if entrained solution was measured and AEC is desired, for Cl<sup>-</sup> [Chapter 31 (Frankenberger et al., 1996)].

### Calculations

With water wash,

$$CEC = (NH_4^+ \times 5)/18$$

where NH<sub>4</sub><sup>+</sup> = NH<sub>4</sub><sup>+</sup> in KNO<sub>3</sub> extract in milligrams per liter.

CEC = cation exchange capacity in centimoles of cation charge per kilogram.

With correction for entrained solution,

$$CEC = 0.2775 \times NH_4^+ - 0.80 \times V_{En}$$

where NH<sub>4</sub><sup>+</sup> = NH<sub>4</sub><sup>+</sup> in KNO<sub>3</sub> extract in milligrams per liter.

V<sub>En</sub> = volume of entrained solution in milliliters

$$AEC = 0.14 \times Cl^- - 0.8 \times V_{En}$$

where  $Cl^-$  =  $Cl^-$  in  $KNO_3$  extract in milligrams per liter

AEC = anion exchange capacity in centimoles of anion charge per kilogram

### Comments

When water washes are used instead of estimating the volume and concentration of the entrained solution, the soil may begin to disperse, and a higher speed centrifuge may be necessary to separate the phases. The concentration of 0.04 *M*  $NH_4Cl$  was selected as that which would prevent the deflocculation of the clay in most soils. It is in the middle of the range used by Matsue & Wada (1985). The values of CEC obtained at this concentration are similar to those obtained in the compulsive exchange method at a concentration of 0.001 *M*  $BaCl_2$ . Grove et al. (1982) suggested that the net charge on the soil was given by the value for CEC obtained using the water wash, which was essentially equal to the value obtained when the AEC was subtracted from the CEC. This value also was equal to the sum of exchangeable cations (ECEC).

## Ammonium Acetate (pH 7) Method

### Introduction

Although this method has been used for many years, it overestimates the "field" CEC of soils with a pH <7. Nevertheless, it is a standard method used in the classification of soils (Soil Surv. Lab. Staff, 1992) and consequently warrants citation here. Because the  $NH_4OAc$  used during the procedure is buffered at pH 7, the method causes variable charge sites in acid soils not active at the field pH to become ionized and consequently measured. There are a number of variants of this method using both batch and continuous leaching techniques. The methodology selected here is a leaching tube method proposed by the Soil Survey Laboratory Staff (1992).

### Apparatus

1. Mechanical vacuum extractor (Centurion International, Inc., Lincoln, NE Model 24).
2. 100-mL volumetric flasks.
3. Top-loading balance weighing to 0.01 g.

### Reagents

1. Saturating solution, 1 *M*  $NH_4OAc$  pH 7.0. Mix 68 mL  $NH_4OH$  (sp gr. 0.90) and 57 mL 99.5%  $CH_3COOH$  per liter of solution desired. Cool, adjust to pH 7.0 with  $CH_3COOH$  or  $NH_4OH$  and dilute to 1 L with deionized water.
2. Ethanol, 95%.
3. Replacing solution, 1 *M*  $KCl$ . Dissolve 74.5 g  $KCl$ , dilute to 1 L of deionized water.

### Procedure

Prepare the leaching tubes by placing either filter paper or filter paper pulp into the syringe barrels and compressing it with the plunger. Weigh 5.0 g soil into the tube and place on mechanical vacuum extractor. Add 25 mL 1 M NH<sub>4</sub>OAc, stir and leach. Add an additional 25 mL 1 M NH<sub>4</sub>OAc and allow to stand overnight by using a pinch clamp or by stoppering the leaching tube. Leach and make up to volume and save for determination of exchangeable cations if required [Chapter 19 (Helmke & Sparks, 1996) and 20 (Suarez, 1996)]. Add about 10 mL ethanol to the soil pad, stir and leach. Leach with 100 mL ethanol and check for NH<sub>4</sub><sup>+</sup> in leachate. If NH<sub>4</sub><sup>+</sup> is present, leach with an additional 100 mL ethanol. Discard leachate. Now leach with a total of 60 mL 1 M KCl and make up to 100 mL. Determine NH<sub>4</sub> in the leachate by an appropriate method [Chapter 38 (Mulvaney, 1996)].

### Calculations

$$\text{CEC in cmol}_c \text{ kg}^{-1} = (10^6 \times \text{NH}_4)/9$$

where NH<sub>4</sub> is the concentration in the leachate in milligrams per liter

## Summation of Cations (Effective Cation Exchange Capacity)

### Introduction

The concept of effective cation exchange capacity (ECEC) was first formalized by Coleman et al. (1959) as the sum of the exchangeable Ca, Mg and Al displaced from the soil using 1 M KCl but has evolved to include Na and K. There is considerable evidence to show that the quantities of exchangeable cations extracted from nonsaline noncalcareous soils by any of the common extracting solutions are very similar (Grove et al., 1982). Thus it is possible to use this technique to estimate cation exchange capacity in soils which do not contain salts and carbonates.

### Apparatus

As listed under "Preparations" for "Cation Exchange Capacity of All Other Soils," or "Apparatus" for "Unbuffered Salt Extraction Method."

### Reagents

As listed for "Reagents" for "Cation Exchange Capacity of All Other Soils," or "Reagents" for "Unbuffered Salt Extraction Method."

### Procedure

Determine Ca, Mg, K, Na and Al by atomic absorption spectrometry as outlined in Chapters 19 (Helmke & Sparks, 1996), 20 (Suarez, 1996), and 18 (Bertsch & Bloom, 1996).

### Calculations

Calculate exchangeable ions ( $M^{n+}$ ) in centimoles of cation charge per kilogram as

$$M^{n+} = (M^{n+} \times V \times n) / (W \times A)$$

where  $M^{n+}$  = concentration of cation in extract in milligrams per liter

$V$  = volume of extract (mL)

$n$  = valence of cation

$W$  = weight of soil (g)

$A$  = atomic weight of cation

$$ECEC = Ca + Mg + K + Na + Al$$

where Ca = exchangeable Ca in centimoles of cation charge per kilogram

Mg = exchangeable Mg in centimoles of cation charge per kilogram

K = exchangeable K in centimoles of cation charge per kilogram

Na = exchangeable Na in centimoles of cation charge per kilogram

Al = exchangeable Al in centimoles of cation charge per kilogram

### Comments

For soils containing salts and carbonates, this procedure results in highly inflated values for cation exchange capacity because of the appreciable solubility of these materials in the extracting solutions. For all other soils, the values obtained are very similar to those measured by the methods designed to determine the CEC at "field pH" as described in "Unbuffered Salt Extraction Method" and "Compulsive Exchange Method" above. This agreement is to be expected on theoretical grounds.

Over a wide variety of soils, values for the sum of basic cations extracted by a variety of extractants such as 1 M  $\text{NH}_4\text{OAc}$ , 0.2 M  $\text{NH}_4\text{Cl}$ , 0.2 M  $\text{BaCl}_2$ , 0.2 M  $\text{CaCl}_2$ , 1 M  $\text{BaCl}_2\text{-TEA}$  and 0.01 M  $\text{SrCl}_2$  (Bache, 1976; Grove et al., 1982; Gillman & Hallman, 1988; Hendershot & Duquette, 1986; Matsue & Wada, 1985) plus Al extracted with 1 M  $\text{KCl}$  or 0.2 M  $\text{NH}_4\text{Cl}$  [Skeen & Sumner, 1967a,b; Chapter 18 (Bertsch & Bloom, 1996)] were essentially the same, indicating that almost any extractant is suitable for estimation of ECEC.

## MEASUREMENT OF SELECTIVITY COEFFICIENTS

### Introduction

A wide range of methods and computational approaches have been used in measurements of selectivity coefficients, despite a common objective: to bring solutions containing varying ratios of two competing cations into equilibrium with an exchanger phase at fixed pH and ionic strength, and to measure both solution and exchanger compositions. In arriving at a method to suit a particular objective, several choices must be made: