Department of Sustainable Natural Resources

SOIL SURVEY STANDARD TEST METHOD

CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS BY AMMONIUM CHLORIDE

ABBREVIATED NAME	CEC
TEST NUMBER	C5
TEST METHOD TYPE	B
VERSION NUMBER	1

SCOPE

The methods for determination of Cation Exchange Capacity and Exchangeable Cations are those of Tucker (1974) and Tucker & Beatty (1974) with modifications to suit the Soil Conservation Service done by Craze & Doust (1980). This procedure is suitable for soils of pH $\geq$7.5.

The sample is washed with ethanol/glycol mixture to remove soluble salts, and the cations are displaced with alcoholic 1M NH_4Cl @ pH 8.5, followed by 0.05MNH_4Cl, then displacement of NH_4^+ & Cl^- with 15% KNO_3 + 6% $Ca(NO_3)_2$ solution.

The combined nitrate extract is analysed to determine the Cation Exchange Capacity (CEC) and the combined chloride extract is analysed to determine the Basic Exchangeable Cations.

SPECIAL APPARATUS

- Atomic Absorption Spectrophotometer fitted with an Air/Acetylene burner and Hollow Cathode lamps to measure calcium, magnesium, sodium and potassium.
- Shaker – a slow speed mixing machine rotating at 10 rpm with clips to hold the tubes at 30-40° to the horizontal.
- Magnetic Stirrer.
- pH Meter with temperature compensator.
- Diluter/Dispenser.
- Centrifuge, 3000 rpm.
- Centrifuge Tubes (120 $\times$ 15 mm diameter and 15 mL capacity). High strength polythene with caps.

REAGENTS

(a) **Glycol/Ethanol Mixture**

Mix 100 mL Ethylene Glycol (Ethanediol) with 36 mL deionised water and bulk to 1 L with ethanol or methylated spirit.

(b) **Alcoholic 1M NH_4Cl Solution (1 L)**

Dissolve 54 g NH_4Cl A.R. in 310 mL deionised water, add 665 mL ethanol. Stir or shake to expel dissolved air. Adjust to pH 8.5 with concentrated ammonia solution A.R. Store in pyrex with a plastic stopper to exclude access of CO_2. Check the pH before use or prepare sufficient solution for immediate use only by proportioning the above quantities.

(c) **Alcoholic 0.05M NH_4Cl Solution**

Dissolve 2.70 g NH_4Cl (A.R.) in 330 mL deionised water and add 670 mL ethanol. Proceed as for 1M NH_4Cl.

(d) **K/Ca Nitrate Solution**

Dissolve 150 g KNO_3 A.R. in 800 mL deionised water, add 60 g $Ca(NO_3)_2.4H_2O$ A.R., dissolve and bulk to 1 L with deionised water.

(e) **4M HCl Solution**

Mix 200 mL concentrated HCl with 300 mL deionised water.

(f) **0.05M $AgNO_3$ Solution**

Dissolve 8.5 g $AgNO_3$ A.R. in deionised water, add 1 drop conc. HNO_3 and bulk to 1 L with deionised water.

(g) **10% w/w K_2CrO_4 Solution**

Dissolve 10 g K_2CrO_4 in 90 mL deionised water.

(h) **Formol Reagent**

Mix 500 mL 35% formaldehyde with 500 mL deionised water. Adjust to pH 8.2 with NaOH solution. Check the pH of this solution before use and adjust if necessary.

(i) **Aqueous Acetone**

Mix 500 mL Acetone with 1 L deionised water.

(j) **0.02M NaOH Solution**

Weigh 12 g NaOH A.R. into a 250 mL beaker. Add 50 mL deionised water, mix, decant and repeat until the pellets are reduced by one third. Dissolve pellets in recently boiled and cooled deionised water and bulk to 1 L ($\approx$ 0.2M). Dilute this solution 1:10 with deionised water (treated as above) to prepare 0.02M NaOH.

(k) **0.05M NH_4Cl Standard Solution**

Dissolve 2.675 g NH_4Cl A.R. in deionised water, transfer to a 1 L volumetric flask and bulk to volume with deionised water.

(l) **Flaming Solution**

Dissolve the following in order in 800 mL deionised water:

12 g	Urea A.R.
20 mL	Perchloric Acid (70%)
1.25 g	$La(NO_3)_3.6H_2O$ A.R.
0.67 g	CsCl A.R.
50 mL	Ethanol

Bulk to 1 L with deionised water.

PROCEDURE

Removal of Soluble Salts

1. Dispense 10 mL glycol/ethanol mixture to the oven-dry equivalent of 1 g of air-dry (<2 mm) soil contained in a centrifuge tube. Stopper the tube and mix on the shaker for 30 minutes. (Include at least one tube without soil for a blank.)

2. Centrifuge for 5 minutes at 3000 rpm. Discard supernatant.

3. Repeat (1) and (2) using fresh glycol/ethanol mixture. Ensure the soil pad is dispersed before mixing.

Preparation of Extracts

1. Add 10 mL 1M Alcoholic NH4Cl, stopper the tube and mix for 30 minutes. Ensure the soil pad is dispersed before mixing.
2. Centrifuge for 5 minutes @ 3000 rpm and decant the clear supernatant into a 50 mL volumetric flask. Add the extracts from (3) and (4) to the same flask.
3. Repeat (1) and (2) with fresh 1M NH4Cl solution.
4. Repeat (1) and (2) using 0.05M alcoholic NH4Cl solution.
5. Add 5 mL 4M HCl to the combined chloride extracts, bulk to 50 mL with 0.05M alcoholic NH4Cl and mix.
6. Add 10 mL K/Ca nitrate solution to the centrifuge tube, disperse the soil pad and mix for 30 minutes. Centrifuge for 5 minutes @ 3000 rpm and decant the supernatant into a 50 mL volumetric flask.
7. Repeat (6), add the extract to the same flask, bulk to volume with the K/Ca nitrate solution and mix.

Analysis of Ammonium Chloride Extract (See Note.)

1. Set up and calibrate the AAS according to the manufacturer's instructions.
2. Dilute an aliquot of the chloride extract with flaming solution to adjust the concentration of the cation being measured to the linear concentration range of the instrument.
3. Aspirate the diluted extract into the flame of the AAS burner and record the absorbance reading. Determine cation concentration in mg/L from the calibration graph.

Analysis of K/Ca Nitrate Extract

(a) Procedure for Chloride Analysis

1. Pipette 20 mL of nitrate extract into a 250 mL conical flask.

2. Add 3 drops of 10% potassium chromate solution.

3. Titrate with 0.05M AgNO3 solution until the appearance of a permanent red-orange tint.

4. Record the volume of titrant consumed.

5. Determine reagent blank by repeating (1) to (5) and substituting 20 mL K/Ca nitrate solution for soil extract.

6. Add 20 mL 0.05M NH4Cl standard solution by pipette and repeat (3) and (4) to determine the concentration of the $AgNO_3$ solution.

(b) Procedure for Ammonium Analysis

1. Pipette 20 mL of nitrate extract into a 250 mL beaker.

2. Add 8 mL formol reagent then 50 mL acetone/water reagent. Place the beaker with a small mixing bar on the stirrer.

3. Insert pH electrode, activate the stirrer and allow the pH to stabilise (approximately 2–3 minutes).

4. Titrate with 0.02M NaOH to pH 8.2 endpoint.

5. Record the volume of titrant consumed.

6. Determine reagent blank by repeating (1) to (5) but substituting 20 mL K/Ca nitrate solution for soil extract.

7. Add 10 mL 0.05M NH_4Cl standard solution by pipette and repeat (3) to (5) to determine the concentration of the NaOH solution.

CALCULATIONS

(a) Reagent Standardisation

Calculate and record concentration of the $AgNO_3$ solution.

$$Molarity\ AgNO_3 = \frac{V\ x\ M}{T - B}$$

Where:

V	=	Volume of standard NH_4Cl solution (mL)
M	=	Concentration of NH_4Cl solution (mol/L)
T	=	Volume of $AgNO_3$ solution (mL)
B	=	Reagent blank (mL)

Calculate and record concentration of the NaOH solution.

$$Molarity\ NaOH = \frac{V\ x\ M}{T - B}$$

Where:

V	=	Volume of standard NH_4Cl solution (mL)
M	=	Concentration of NH_4Cl solution (mol/L)
T	=	Volume of NaOH solution (mL)
B	=	Reagent blank (mL)

(b) Analysis of Nitrate Extract

Calculate and record the ammonium ion concentration.

$$NH\,(meq) = (A-B)\,x\,M\,x\,2.5$$

Where:

A	=	Volume of NaOH solution (mL)
B	=	Reagent blank (mL)
M	=	Concentration of NaOH solution (mol/L)
2.5	=	Sampling factor

Calculate and record the chloride ion concentration.

$$Cl^{-}\,(meq) = (A-B)\,x\,M\,x\,2.5$$

Where:

A	=	Volume of $AgNO_3$ solution (mL)
B	=	Reagent blank (mL)
M	=	Concentration of $AgNO_3$ solution (mol/L)
2.5	=	Sampling factor

(c) Cation Exchange Capacity

Calculate and record the Cation Exchange Capacity.

$$CEC\,(meq/100g) = \frac{(A-B)}{W}\frac{x\,100}{}$$

Where:

A	=	Concentration of ammonium ion in extract (meq)
B	=	Concentration of chloride ion in extract (meq)
W	=	Oven-dry sample weight (g)

(d) Exchangeable Cations

Calculate and record the Exchangeable Cation concentration.

$$M\ (meq/100g) = \frac{C\ x\ D\ x\ 5}{E\ x\ W}$$

Where:

M	=	Concentration, in soil, of cation under test
C	=	Concentration of Cation in solution (mg/L)
D	=	Dilution factor. (See Analysis of Ammonium Chloride Extract, Step 2 on page 4.)
E	=	Equivalent weight of Cation under test (g)
W	=	Oven dry sample weight (g)

REPORTING THE RESULTS

Report the Cation Exchange Capacity and Exchangeable Cations results in meq/100 g to one decimal place.

REFERENCES

Craze, B & Doust, R 1980, *A Close Look at Tucker's Procedure for Determining Exchangeable Cations and Exchange Capacity,* Cowra Research Centre Technical Bulletin No 14.

Tucker, BM 1974, *Laboratory Procedures for Cation Exchange Measurement on Soils,* CSIRO Division of Soils Technical Paper No 23.

Tucker, BM & Beatty, HJ 1974, Exchangeable Cations and Cation Exchange Capacity, in Loveday, J (ed), *Methods for Analysis of Irrigated Soils*, Commonwealth Bureau of Soils Technical Communication No 54.

NOTE

AAS Instruments vary in sensitivity and degree of automation, so it is not possible to give detailed instructions on setting up for concentrations of standard solutions or for calibration procedures at each installation.