Department of Sustainable Natural Resources

SOIL SURVEY STANDARD TEST METHOD

CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS BY SILVER THIOUREA

ABBREVIATED NAME	CEC
TEST NUMBER	C5
TEST METHOD TYPE	A
VERSION NUMBER	4

SCOPE

Cation Exchange Capacity (CEC) is a general indicator of soil storage capacity for available positively-charged plant nutrients such as calcium, magnesium, potassium and sodium. In some instances, this method appears to overestimate exchangeable magnesium in some saline and alkaline soils and can overestimate exchangeable potassium in some mica-rich soils.

PRINCIPLE

This method for the simultaneous measurement of CEC and exchangeable cations is based on the very high affinity of the silver-thiourea complex for occupying exchange sites on soil colloids. Residual silver is measured in a silver-thiourea extract by atomic absorption spectrometry to determine the total CEC. The displaced cations are also measured in the same extract by AAS.

SPECIAL APPARATUS

- Atomic absorption spectrophotometer with hollow cathode lamps to measure Ag, Na, K, Ca, Mg and Al.

- Diluter/Dispenser (Brand Diluette® Cat No 7046 54).

REAGENTS

General Reagents

(a) Glycol-Ethanol

Mix 100 mL ethylene glycol (ethanediol) with 36 mL deionised water and make to 1L with ethanol.

(b) 0.01 M Ag-Thiourea

Dissolve 7.5 g thiourea in about 250 mL deionised water in a 1 L beaker. Dissolve 1.699 g $AgNO_3$ (AR) in 500 mL deionised water in a beaker. Slowly add the $AgNO_3$ solution to the Thiourea solution under vigorous stirring. Transfer the Ag-Th. to a 1 L volumetric flask and make to volume with deionised water. (See Note 1).

(c) Thiourea (0.75 g/L)

Dissolve 0.75 g of thiourea and dilute to 1 L with deionised water. Dilute 1:10 for preparation of silver standards and samples.

(d) Potassium (20 000 mg/L)

Dissolve 38.14 g of KCl (AR) and dilute to 1 L with deionised water.

(e) Potassium (2 000 mg/L)

Dissolve 3.81 g KCl (AR) and dilute to 1 L with deionised water.

(f) Sodium (15 000 mg/L)

Dissolve 38.13 g of NaCl (AR) and dilute to 1 L with deionised water.

(g) Sodium (1 500 mg/L)

Dissolve 3.81 g NaCl (A.R.) and dilute to 1 L with deionised water.

Standard Reference Solutions

Sodium 1 000 mg/L Std. Soln.

Dissolve 2.542 g of oven-dried sodium chloride (AR) in deionised water, transfer to a 1 L volumetric flask and make to volume with deionised water.

Potassium 1 000 mg/L Std. Soln.

Dissolve 1.907 g of oven-dried potassium chloride (AR) in deionised water, transfer to a 1 L volumetric flask and make to volume with deionised water.

Calcium 1 000 mg/L Std. Soln.

Disperse 2.497 g of oven-dried calcium carbonate (AR) in 50 mL deionised water. Add drop wise a minimum volume of HCl to effect complete solution of the $CaCO_3$. Transfer to a 1 L volumetric flask and make to volume with deionised water.

Magnesium 1 000 mg/L Std. Soln.

Dissolve 1 g of magnesium (AR) in a minimum quantity of 1 N HCl, transfer to a 1 L volumetric flask and make to volume with deionised water.

Aluminium 1 750 mg/L Std. Soln.

Dissolve 1.750 g of aluminium (AR) in minimum quantity of 1 N HCl (containing trace HNO_3), transfer to a 1 L volumetric flask and make to volume with deionised water.

Working Standard Solutions

Silver

Pipette 25 mL of 0.01M Ag-Thiourea reagent into a 200 mL volumetric flask and bulk to volume with 0.75 g/L Thiourea solution.

$$concentration\ Ag \equiv 134.8\ mg/L$$

Prepare a range of calibration standards using the Diluter/Dispenser and Table 1 (below) as a guide:

Table 1. Preparation of calibration solutions of silver

Standard No. →	1	2	3	4	5	6
Mls. 134.8 mg/LAg. Std. Soln.	0.05	0.10	0.20	0.30	0.40	0.50
Mls. 0.075 g/L Thiourea Soln.	4.95	4.90	4.80	4.70	4.60	4.50
Final Concentration of Ag (mg/L)	1.35	2.70	5.39	8.09	10.78	13.48

Sodium, Calcium and Magnesium

Transfer by pipette 20 mL of 1 000 mg/L Na, 25 mL of 1 000 mg/L Ca, and 2.5 mL of 1 000 mg/L Mg, into a 500 mL volumetric flask and make to volume with deionised water.

Concentrations:
Na ≡ 20 mg/L
Ca ≡ 50 mg/L
Mg ≡ 5 mg/L

Prepare a range of calibration standards using the diluter/dispenser and Table 2 as a guide.

Table 2. Preparation of calibration solutions of Na, Ca and Mg

Standard No. →	1	2	3	4	5	6
Mls. Na, Ca & Mg Working Standard	0.05	0.10	0.20	0.30	0.40	0.50
Mls. 2 000 mg/L Potassium Soln.	4.95	4.90	4.80	4.80	4.70	4.50
Final Concentration of ion (mg/L) Na	0.20	0.40	0.80	1.20	1.60	2.00
Ca	0.50	1.00	2.00	3.00	4.00	5.00
Mg	0.05	0.10	0.20	0.30	0.40	0.50

Potassium

Pipette 10 mL of 1 000 mg/L potassium std. into a 500 mL volumetric flask and make to volume with deionised water.

$$concentration\ K \equiv 20\ mg/L$$

Prepare a range of calibration standards using the diluter/dispenser and Table 3 as a guide:

Table 3. Preparation of calibration solutions of potassium.

Standard No. →	1	2	3	4	5	6
Mls. 20 mg/L K std. Soln.	0.05	0.10	0.20	0.30	0.40	0.50
Mls. 1 500 mg/L Sodium Soln.	4.95	4.90	4.80	4.70	4.60	4.50
Final Concentration of K (mg/L)	0.20	0.40	0.80	1.20	1.60	2.00

Aluminium

Pipette 20 mL of 1 750 mg/L Aluminium Std. into a 250 mL volumetric flask and make to volume with deionised water.

$$concentration\ Al \equiv 140\ mg/L$$

Prepare a range of calibration standards using the diluter/dispenser and Table 4 as a guide:

Table 4. Preparation of calibration solutions of aluminium

Standard No. →	1	2	3	4	5	6
Mls. 140 mg/L Al Std. Soln.	0.05	0.10	0.20	0.30	0.40	0.50
Mls 2 000 mg/L Potassium Soln.	4.95	4.90	4.80	4.70	4.60	4.50
Final Concentration of Al (mg/L)	1.40	2.80	5.60	8.40	11.2	14.0

PROCEDURE

Removal of Soluble Salts

1. Weigh accurately 1 g of air-dry soil (<2 mm) into a small plastic shaking bottle.

2. Add about 15–20 mL of glycol-ethanol and shake for 1 hour at 15 rpm.

3. Filter through a Whatman No 42 filter paper, retaining as much of the soil as possible in the shaking bottle. Discard the filtrate.

4. Rinse the soil retained in the bottle with a further 15–20 mL of glycol-ethanol and pass through the filter paper. (See Note 2.)

5. Allow the soil to air-dry. Brush any soil particles adhering to the rim of the bottle into the filter paper and then return the filter paper and soil to the bottle.

Extraction for Cation Exchange Capacity and Exchangeable Cations

1. Add 50 mL of 0.01 M Ag-Thiourea and shake for 4 hours at 15 rpm.

2. Filter through a Whatman No 42 filter paper.

3. Retain the filtrate in a sealable glass container.

Measurement of Cation Exchange Capacity

1. Dilute the unknown sample by 100 with 0.75 g/L thiourea solution.

2. Set up the atomic absorption spectrophotometer to measure Ag according to the manufacturer's instructions. Measure the absorption of each of the standard solutions and diluted unknown samples.

Measurement of the Exchangeable Na, Ca, Mg, Al

1. Dilute the unknown sample by 10 with 2 000 mg/L potassium solution.

2. Set up the atomic absorption spectrophotometer to measure sodium according to the manufacturer's instructions. Measure the absorption of each of the standard solutions and diluted unknown samples.

3. Carry out the measurement of Ca, Mg and Al concentration in the same manner. A dilution ratio of 50 is suggested for calcium and magnesium, and a dilution ratio of 3 for aluminium.

Measurement of Exchangeable K

1. Dilute the unknown sample by 10 with 1 500 mg/L sodium solution.

2. Set up the atomic absorption spectrophotometer to measure potassium according to the manufacturer's instructions. Measure the absorption of the standard solutions and diluted unknown samples.

CALCULATIONS

Cation Exchange Capacity

From the working standards, draw a calibration curve of absorption versus Ag concentration. Read the Ag concentration of the unknown sample extract from the graph.

Calculate the Cation Exchange Capacity (CEC).

$$CEC = \frac{53\ 490 - (A\ x\ DF\ x\ 50\ mL)}{B\ x\ 1\ 078.8}$$

Where:

A	=	Ag concentration in diluted extract from graph (mg/L)
B	=	Oven-dry weight of sample (g)
DF	=	Dilution factor

Exchangeable Cations

From the working standards, draw a calibration curve of absorption versus cation concentration. Read the cation concentration of the unknown sample extract from the graph.

Calculate Exchangeable Cations.

$$Cation\,(mg/kg) = \frac{A\ x\ DF\ x\ 50mL}{B}$$

Where:

A	=	Cation concentration in diluted extract from graph (mg/kg)
B	=	Oven-dry weight of sample (g)
DF	=	Dilution factor

$$Cation\,(me/100g) = \frac{Cation\,(mg/kg)}{E}$$

Where:

E	=	Equivalent weight of cation $\times$ 10

i.e.

Na	=	229.9
K	=	391.0
Ca	=	200.4
Mg	=	121.6
Al	=	89.9

REPORTING THE RESULTS

Report CEC to one decimal place and exchangeable cations to one decimal place for meq/100 g or to the nearest whole number for mg/kg.

REFERENCES

Pleysier, JL & Juo, ASR 1980, A single-extraction method using silver-thiourea for measuring exchangeable cations and effective CEC in soils with variable charges. *Soil Science,* 129:4, 205-211.

Searle, PL 1984, The single-extraction silver thiourea method for measuring the cation exchange capacity of soil: Some preliminary comments. *New Zealand Soil News,* 32:4, 133-136.

NOTES

1. The volume of 0.01M Ag-Thiourea prepared should be adjusted according to the amount required for extraction and use in standard solutions.

2. The drying time is reduced if the final wash is done with water/ethanol mixture (36 mL deionised water/964 mL ethanol).

3. If the concentration in the samples is greater than that of the standards, carry out a further dilution with Na, Ca, Mg diluting solution by taking 25 mL of 0.01M Ag-Thiourea, 25 mL of 20 000 mg/L K and dilute to 250 mL with deionised water.

4. If the concentration in the samples is greater than that of the standards, carry out a further dilution with K diluting solution.

5. To prepare K diluting solution, take 25 mL of 0.01M Ag-Thiourea, 25 mL of 15 000 mg/L Na and dilute to 250 mL with deionised water.