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Protocol for measuring cation exchange capacity (CEC) in soils with high calcium content, such as limed, agricultural soils

Purpose
To measure exchangeable cations and cation exchange capacity.

Reagents
1. 0.1M barium chloride $BaCl_2$ (1L)
    a. 20.82 of $BaCl_2$ in 1L DI water
2. 0.002M barium chloride $BaCl_2$ (1L)
    a. 0.416g of $BaCl_2$ in 1L DI water
3. 0.005M* magnesium sulfate heptahydrate $MgSO_4 \cdot 7H_2O$ (1L)
    a. 0.602g $MgSO_4 \cdot 7H_2O$ in 1L DI water

*A 0.01M solution instead (1.2g $MgSO_4 \cdot 7H_2O$ /1L DI water) also works, just adjust the calibration curve

Procedure
1. Write tube number on data sheet and record weight of tube. Tare balance.
2. Weigh 2.00g (±0.01g) of soil in empty centrifuge tube. Record weight.
3. Add 20.0 ml of 0.1M $BaCl_2$.
4. Cap tube. Shake for 1 hour.
5. Centrifuge tubes at 4000 x g (about 6000 rpm on VWR benchtop centrifuges) for 30 minutes (remember to balance the rotor).
6. Decant supernatant liquid (may be saved for exchangeable cation analysis/soil pH measurement). You may use a transfer pipette to remove the last few milliliters of supernatant if needed.
7. Add 20.0mL of 0.002M $BaCl_2$. Disperse solids with vortex mixer. Shake for 10 minutes.
8. Centrifuge for 30 minutes. Decant and discard supernatant.
9. Repeat steps 6, 7, and 8 two times.
10. After decanting 0.002M $BaCl_2$ for the third time, weigh the tube plus soil plus entrained solution.
11. Add 10.0mL 0.005M $MgSO_4 \cdot 7H_2O$. Disperse solids. Shake 30 minutes. NOTE: For critical determinations, the solution ionic strength can be adjusted at this point by matching its electrical conductivity to that of a reference solution. See Gillman 1979 or Rhoades 1982 for a description.
12. Let tubes stand overnight, with occasional hand shaking. This long period of equilibration is necessary to allow the Mg^{2+} ions to completely replace the Ba^{2+} ions on the exchange complex. Displaced barium ions precipitate as $BaSO_4$.
13. Centrifuge 10 minutes. Filter supernatant into a labeled bottle or scintillation vial using Whatman #42 filters.
14. Store in the freezer until ready for analysis.

Analysis
Analyze on atomic absorption spectrophotometer for Mg using the Air-Acetylene flame. Standards can be made in DIW and with the 500 mg Mg/L stock solution with the following standard curve. Run a reagent blank as DIW. Subtract out the concentration of $MgSO_4 \cdot 7H_2O$ in solution blank from the sample concentrations.

Calculations
The total CEC is equivalent to the mass (in millequivalents) of Mg^{++} removed from solution divided by the soil weight.

1. Calculate entrained solution volume:
   Entrained = (weight of tube + soil + entrained) - (weight of empty tube + **oven-dry** soil). This number represents the **mass**; assuming a specific gravity of 1 (close enough), it is also the **volume**, in mL.

2. Convert mg/L to meq Mg^{++} in the extract, for both the blank and the sample (remember, Mass=Concentration*Volume; this step also incorporated unit conversions for Mg meq and mL to L).

$$\text{meq } Mg^{++} = \frac{\text{mg Mg}}{\text{L}} \times \frac{\text{1mmol Mg}}{\text{24.305 mg Mg}} \times \frac{\text{2 meq } Mg^{++}}{\text{1mmol Mg}} \times (\text{10mL + entrained}) \times \frac{\text{1L}}{\text{1000mL}}$$

3. The difference between meq Mg^{++} in the blank and in the sample represents the mass of magnesium ions adsorbed onto the soil exchange complex. Divide by (dry) soil mass, convert meq to cmol (+) and g to kg, and you have CEC.

$$\text{CEC (cmol(+)/kg soil)} = \frac{(\text{meg } Mg^{++}_{\text{blank}} - \text{meq } Mg^{++}_{\text{sample}})}{\text{2g moist soil}} \times \frac{(1+w_d)\text{g moist soil}}{\text{g dry soil}} \times \frac{\text{1 cmol (+)}}{\text{10 meg } Mg^{++}} \times \frac{\text{1000 g soil}}{\text{kg soil}}$$

References

Gillman, G.P. 1979. A proposed method for the measurement of exchange properties of highly weathered soils. Aust. J. Soil Res. 17:129-139.

Hendershot, W.H., and M. Duquette. 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. Soil Sci. Soc. Am. J. 50:605-608.

Rhoades, J.D. 1982. Soluble Salts. In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Agronomy 9: 167-178.