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Available Soil Sulfate-Sulfur

1. Application

This method covers the extraction of sulfur in the form of sulfate ($SO_4^{=}$-S) and turbidimetric analysis of the extracted $SO_4^{=}$.

2. Summary of Methods

Sulfate-S is extracted with Ca (H_2PO_4) in 2 N HOAc. Sulfate in the extract is precipitated as $BaSO_4$ and measured turbidimetrically.

3. Safety

Each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should be made available to all personnel involved in the chemical analysis.

4. Interferences

In solutions containing small amounts of sulfate, dissolved organic matter acts as a sulfur protective colloid and causes low results. At high concentrations of sulfate, organic matter coprecipitates with barium sulfate and causes high results. The interference of organic matter can be removed by the addition of activated charcoal.

5. Apparatus and Materials

5.1 Soil scoop calibrated to hold 10 g of light-colored silt loam soil.
5.2 Charcoal scoop calibrated to hold 0.1 g.
5.3 Erlenmeyer flask (50 ml).
5.4 25 ml filter tubes.
5.5 Nephelometer tubes (25 ml).
5.6 Constant suction pipette bank (25 ml).
5.7 Activated charcoal, SO_4= free, prepared as follows:
    - Boil approximately 20 g of charcoal in 200 ml of 6 N HCl for 10 min.
    - Filter under suction
    - Wash with deionized water until free of Cl^-
    - Dry at 105° C.
5.8 Time-controlled oscillating shaker (Eberbach) set at 160 excursions per minute.
5.9 Acid washed filter paper (11 cm Whatman No. 2 or equivalent).
5.10 Filter paper (24 cm Whatman #2 and Whatman #8 or equivalent).

5.11 Filtering Apparatus: 27 cm buchner funnel, 4000 ml Erlenmeyer flask, vacuum pump.
5.12 Turbidimeter (HF Scientific, DRT 100B, model # 20052).
5.13 Nephelometer tubes (50 ml) matched.

6. Reagents

6.1 Extracting solution (500 ppm P in 2 $\underline{N}$ HOAc): dissolve 2.03 g of $Ca(H_2PO_4)_2\cdot H_20$ in about 800 ml of deionized water. Add 115 ml of glacial acetic acid and dilute to liter.
6.2 Gum Arabic ($BaCl_2$ –HOAc): dissolve 5 g of gum Arabic in about 500 ml of hot deionized water. Cool slightly, then filter with filtering apparatus. Put 24 cm filter papers into buchner funnel one at a time #2 on the bottom, and #8 on the top and wet them down with deionized water. Add 50 g of $BaCl_2\cdot 2H_2O$ and 450 ml of glacial acetic acid, and dilute to 1 liter.
6.3 Sulfur stock solution (1000 ppm)
6.4 Working S standards (0, 2, 4, 6, 8, and 10 ppm S).
Dilute from sulfur stock solution (1000 ppm) as follows:
0 ppm: Sulfur extracting solution (6.1).
2 ppm: 0.5 ml of 1000 ppm S stock solution diluted to 250 ml with extracting solution.
4 ppm: 1 ml of 1000 ppm S stock solution diluted to 250 ml with extracting solution.
6 ppm: 1.5 ml of 1000 ppm S stock solution diluted to 250 ml with extracting solution.
8 ppm: 2 ml of 1000 ppm S stock solution diluted to 250 ml with extracting solution.
10 ppm: 2.5 ml of 1000 ppm S stock solution diluted to 250 ml with extracting solution.

7. Methods

7.1 Transfer a 10 g scoop of soil to a 50-ml Erlenmeyer flask.
7.2 Add 25 ml of extracting solution by means of constant suction pipette bank.
7.3 Add a 0.1 g scoop of activated charcoal.
7.4 Shake the sample for 15 minutes on an oscillating shaker.
7.5 Filter through S-free filter paper into a clean, dry 50 ml Erlenmeyer flask.
7.6 Transfer a 10-ml aliquot of filtrate to a 25 ml nephelometer tube.
7.7 Rinse pipette bank with deionized water before adding gum Arabic solution.
7.8 Add 10 ml of $BaCl_2$-gum Arabic-HOAc solution. Dip the pipette a few centimeters below the surface of the solution in the nephelometer tube, and bubble the mixture for 5 seconds.
7.9 Read NTU (National Turbidity Units) on turbidimeter, with the instrument adjusted to 0 with the zero S standard.
7.10 Preparation of standard curve: (Prepare a new standard curve each day)
-Take a 10 ml aliquot of each working standard and treat as with samples

(steps 7.6-7.8).

- Plot ppm S against NTU. Alternatively, regress NTU against ppm S, and use the resulting regression equation to calculate ppm S in unknown solutions.

8. Calculations

The concentration of $SO_4^{=}$-S in the working standards (0, 2, 4, 6, 8, 10) is equivalent to 0, 5, 10, 15, 20, and 25 ppm of $SO_4^{=}$-S in the soil when put through the following equation:

$$\text{ppm } SO_4^{=}\text{-S in soil} = \text{ppm } SO_4^{=}\text{-S in the solution} \times 2.5$$

9. Quality Control

9.1 Laboratory Reagent Blank (LRB) – At least one LRB is analyzed with each batch of samples to asses contamination from the laboratory environment. Contamination from the laboratory or reagents is suspected if LB values exceed the detection limit of the method. Corrective action must be taken before proceeding.

9.2 Standard soil – One or more of the standard soils of known extractable SO4=-S content are analyzed with each batch of samples to check instrument calibration and procedural accuracy.

9.3 Precautions: Pipette all of the sample extracts (step 7.6) and the working standard solutions before rinsing the pipettes in the pipette bank with water. Then pipette the $BaCl_2$-gum Arabic-HOAc solution (step 7.7). Otherwise, a film of $BaSO_4$ will coat the inside of the pipette and will be difficult to remove, and may contaminate subsequent samples. The $BaCl_2$-gum Arabic-HOAc solution should be added to all samples and standards at the same rate. That is, the delivery rate of each pipette in the bank should be the same. The rate of addition influences the size of the $BaSO_4$ particles that develop. Large particles will give a different nephelometer / turbidometer reading than the same amount of S in fine particles.

10. Reporting

Results are reported as ppm $SO_4^{=}$-S in soil.

11. References

11.1 Combs, S.M., J.L. Denning, and K.D. Frank. 1998 Sulfate-Sulfur. Pp. 35-40. In J.R. Brown (Ed.), Recommended Chemical Soil Test Procedures for the North Central Region. NCR Publ. No. 221 (revised). Missouri Agr. Exp. Sta. SB 1001. Columbia, MO.

11.2 Hoeft, R.G., L.M. Walsh, and D.R. Keeney. 1973. Soil Sci. Soc. Am. Proc. 37:401-404.

11.3 Hesse, P.R. 1957. The effect of colloidal organic matter on the precipitation of barium sulfate and a modified method for determinant soluble sulfate in soils. Analyst 82:710-712