

Scope and Application

This method semiquantitatively determines the amount of sulfate-sulfur ($\text{SO}_4\text{-S}$) in soils by extraction with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ with subsequent determination of $\text{SO}_4\text{-S}$ by turbidimetric measurement. Calcium phosphate is utilized to suppress the dissolution of organic matter and for the removal of sulfate that may be absorbed. Turbidimetric analysis is based on the formation of BaSO_4 crystals in a suspension and subsequent measurement of optical density. The turbidimetric method will require practice to become proficient. It is sensitive to high concentrations of dissolved soil organic carbon which may lead to an under estimation of $\text{SO}_4\text{-S}$ (Ajwa and Tabatabai, 1993). Sulfate-sulfur can also be determined using ion chromatography using an AS4A column. Soil $\text{SO}_4\text{-S}$ is only an index of plant available sulfur since sulfur is also available from the mineralization of organic matter, irrigation water and atmospheric deposition. The method has a detection limit of 2.0 mg kg^{-1} (dry basis) and is generally reproducible to within $\pm 15\%$.

Equipment

1. Analytical balance: 250 g capacity, resolution $\pm 0.01 \text{ g}$.
2. Reciprocating horizontal mechanical shaker, capable of 180 oscillations per minute.
3. Erlenmeyer flasks, 125 mL.
4. Magnetic stirrer.
5. Whatman No. 42, S&S 597 or equivalent highly retentive filter paper.
6. Repipette dispenser calibrated to $25.0 \pm 0.2 \text{ mL}$.
7. Pipette 10.0 mL.
8. Nephelometer, Turbidimeter or spectrophotometer 420 nm filter.

Reagents

1. Deionized water, ASTM Type I grade.
2. Calcium phosphate extraction solution, 0.08 M (containing $500 \text{ mg L}^{-1} \text{PO}_4\text{-P}$): Dissolve 2.03 g of analytical grade $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ in 1000 mL of deionized water (see Comment #1).
3. Activated Charcoal (See Comment #2). Mix 100 g of Darco G-6 activated carbon with calcium phosphate extraction solution and thoroughly wet carbon. Cap container, shake, and filter slowly through buchner funnel. Wash three times with deionized water and verify removal of $\text{SO}_4\text{-S}$.
4. Acid "seed" solution, $20 \text{ mg L}^{-1} \text{S}$ in 5.8 N HCl: Dissolve 0.1087 g analytical grade K_2SO_4 in 500 mL of deionized H_2O and add 500 mL of concentrated HCl. Add Teflon coated magnetic stir bar and place on stirrer. Add 5.0 g of powdered gum acacia, or gelatin (See Comment #3) suspension agent slowly add 400 mL of 40°C deionized water, dissolve lumps and bring to 500 mL. Bring to 1000 mL final volume with acetic acid, CH_3COOH (99%), slowly stirring.
5. Barium chloride crystals. Parr turbidimetric grade, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals 20-30 mesh. Use high purity BaCl_2 , as low purity may result in low recovery of $\text{SO}_4\text{-S}$ (See Comment #4).
6. Standard $\text{SO}_4\text{-S}$ calibration solutions. Prepare $100 \text{ mg L}^{-1} \text{SO}_4\text{-S}$ calibration solution, dissolve 0.5434 g of oven dry K_2SO_4 in 500 mL of deionized water and dilute to one liter. Prepare six 100 mL calibration solutions of: 0.5, 1.0, 2.0, 4.0, 6.0, and $8.0 \text{ mg L}^{-1} \text{SO}_4\text{-S}$ and diluted to final volume with calcium phosphate extraction solution.

Procedure

1. Weigh 10.0 ± 0.1 g of air dry soil pulverized to pass 10 mesh sieve (< 2.0 mm) into 125 mL Erlenmeyer extraction flasks (See Comment #5). Add 25 mL of calcium phosphate extraction solution using a pipette dispenser and place on reciprocating mechanical shaker for thirty (30) minutes. Include a method blank.
2. Add 0.15 g of activated charcoal and shake for an additional three (3) minutes. Repeat with 25 mL aliquot of $\text{SO}_4\text{-S}$ calibration solutions.
3. Filter extract through paper, refilter if filtrate is cloudy.
4. Place 10.0 mL aliquot of soil extract in 25 mL flask, and add 1.0 mL of seed solution and swirl. Repeat with $\text{SO}_4\text{-S}$ calibration solution and method blank (See Comment #6 and #7).
5. Place flask on magnetic stirrer and add 0.3 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals. Stir for five (5) minutes and then read optical density (or percent transmittance) on a nephelometer, turbidimeter or spectrophotometer at 420 nm (See Comment #8). Zero optical density with deionized water. Repeat with $\text{SO}_4\text{-S}$ calibration solutions and method blank. Using standard calibration solutions determine $\text{SO}_4\text{-S}$ concentration of soil extracts and method blank by plotting log of transmittance versus standard concentration. Record as mg L^{-1} of analyte in extract solution to the nearest 0.5 mg L^{-1} .

Calculations

Report soil sulfate-sulfur ($\text{SO}_4\text{-S}$):

$$\text{mg kg}^{-1} = (\text{mg L}^{-1} \text{SO}_4\text{-S in soil extract} - \text{method blank}) \times (2.5)$$

Comments

1. For acidic soils ($\text{pH} < 5.5$) add 10 mL of concentrated HCl to extractant solution. Acidified phosphate extraction solutions are more reliable for use on acid soils which may contain absorbed sulfate.
2. For soils containing low concentrations of $\text{SO}_4\text{-S}$ labile organic matter may prevent the formation of barium sulfate crystals resulting in a low bias $\text{SO}_4\text{-S}$ concentration. Labile organic matter may be removed by the addition of activated charcoal or hydrogen peroxide. For organic soils the volume of extraction (1:5) solution must be increased to account for high potential $\text{SO}_4\text{-S}$ concentrations.
3. A number of suspension agents have been reported in the literature which include: gum acacia, gelatin, glycerol, PVP-K30 (polyvinylpyrrolidone), and Tween 80 which have proven effective in turbidimetric analysis. Each of these will require experimentation and practice using $\text{SO}_4\text{-S}$ spiking to fully refine the technique. For use of PVP-K30 (polyvinylpyrrolidone) add 10 g to 700 mL and dilute to 1000 mL final volume.
4. Use BaCl_2 specifically designated for turbidimetric determination of sulfate-sulfur. Sources: J.T. Baker Cat. Parr Turbidimetric BaCl_2 , JT0974-5; VWR JT0974-5; and GFS Chemicals Reagent Grade ACS #602.
5. Pre-rinse all extraction flasks, turbidimetric and spectrometer cuvette in hot water followed by 0.5 N HCl rinse.
6. Check pipette volume, calibrate using an analytical balance.
7. HCl is included in the turbidimetric "seed" solution to prevent the precipitation of alkali metals with carbonate and phosphate and provide nucleus for initiating precipitation.
8. Development of BaSO_4 suspension requires continuous mixing and development may require from 1-10 minutes. It is essential that time of development be equivalent for both standards and unknown samples.

Literature

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