Chapter 7

Recommended Soil Sulfate-S Tests

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In the northeastern region of the United States, surface soils are not commonly tested for plant-available sulfur (S) because agricultural crops rarely respond to applied S. Lack of crop response to fertilizer S is most commonly the result of the presence of sulfate-S in subsoils (Kline et al.,1989) or to deposition of atmospheric S from industrial sources, particularly in the vicinity of large metropolitan areas. The addition of S from the air may amount to 3 to 290 kg/ha/yr (Erickson, 1952), relative to typical recommendations for S fertilization of 20-40 kg/ha. The importance of subsoil sulfate in meeting crop S requirements is supported by the fact that some soil testing laboratories will only conduct sulfate soil tests if a subsoil sample is provided with a surface sample. Soil testing methods for S must, therefore, consider the relative extractability and plant availability of the major forms of soil S, including sulfate (SO_4-S) ions in the soil solution (1 to 20 mg/L), sulfate ions adsorbed by inorganic colloids, inorganic compounds in difficultly soluble forms, and organic S compounds.

The sulfate ion is primarily adsorbed by clays and Fe/Al oxides and adsorption increases as pH decreases. Other inorganic forms of soil S are the sulfide minerals pyrite and marcasite (FeS_2), pyrrhotite ($Fe_{1-x}S$) and chalcopyrite ($CuFeS_2$). Some of the strip-mined soils in West Virginia contain pyritic S up to 1% (Singh et al., 1982). Sulfide minerals present in soils are difficultly soluble in water, but can be brought into solution by chemical or biological oxidation. Even though both organic and sulfide forms may contribute to plant nutrition over time, plants primarily absorb S in the sulfate form. Thus, most soil testing solutions estimate plant-available S by extraction and determination of sulfate-S (Tabatabai, 1982). The most widely used extracting solutions are water (Spencer and Freney, 1960; Fox et al., 1964; Walker and Doornenbal, 1972), 0.1 *M* LiCI (Tabatabai, 1972), several phosphate-based extractants [$Ca(H_2PO_4)_2$ or KH_2PO_4 (Fox et al., 1964; Jones et al, 1972)], and acidic solutions, such as 0.5 *M* NH_4OAc + 0.25 *M* acetic acid, and Bray P-1 (Rehm and Caldwell, 1968; Hoeft et al., 1973). The recommended soil test methods for determination of plant available sulfate-S in Northeastern soils are: (I) Acidified NH_4OAc, and (ii) Monocalcium Phosphate.

Extraction Methods for Sulfate-S

0.5 M NH_4OAc + 0.25 M CH_3COOH

***(Rehm and Caidwell, 1968*)**

Equipment:

1. 10 g stainless steel scoop.
2. Reciprocating or rotary shaker capable of 180 oscillations per minute.
3. 50 mL Erlenmeyer flasks.

Reagents:

1. **Acidified 0.5 *M* ammonium acetate**. Dissolve 39 g of NH_4OAc in 1 L of 0.25 M acetic acid (or 702 g NH_4OAc in 18 L of 0.25 *M* acetic acid).

2. **Darco G-6 activated carbon**. Wash the carbon with the extracting solution until free of sulfate. Dry in an oven at 40^0C and store dry carbon in an airtight jar.

Procedure:

1. Weigh or scoop 10 g of air-dried, sieved soil into a 50 mL Erlenmeyer flask. See Chapter 2 for details on sample preparation and scooping techniques.

2. Add 25 mL of acidified ammonium acetate extractant and shake at 200 oscillations per minute for 30 minutes.

3. Add 0.25 g of activated charcoal and shake for 3 minutes.

4. Filter through a sulfate-free filter paper (Whatman No. 42 or equivalent).

Monocalcium Phosphate Extraction
(Schulte and Eik, 1988)

Equipment:

1. 10 g stainless steel scoop.
2. Reciprocating shaker capable of 180 oscillations per minute.
3. 50 mL Erlenmeyer flasks.

Reagents:

1. **Extractant: Monocalcium phosphate:** 500 mg P/L. Dissolve 36.6 g of $Ca(H_2PO_4)_2 \cdot H_2O$ in deionized water and bring to a final volume of 18 L.

2. **Darco G-6 activated carbon**. Wash the carbon with the extracting solution until free of sulfate. Dry in an oven at 40^0C and store dry carbon in an airtight jar.

Procedure:

1. Weigh or scoop 10 g of air-dried, sieved soil into a 50 mL Erlenmeyer flask. See Chapter 2 for details on sample preparation and scooping techniques.

2. Add 25 mL of monocalcium phosphate extracting solution and shake at 200 oscillations per minute for 30 minutes.

3. Add 0.25 g of charcoal to each sample and shake for an additional 3 minutes.

4. Filter through sulfate-free filter paper (Whatman No. 42 or equivalent).

Chapter 7.

Determination of Sulfate-S in Soil Test Extracts

Sulfate-S in soil extracts can be determined by several methods, including turbidimetry, atomic absorption spectrophotometry, inductively coupled plasma spectroscopy (ICP), potentiometry, and high-performance liquid chromatography. The method selected will depend upon the amount of sample, chemical constituents in the extract, instrumentation available, and concentration of sulfate in the extracts.

In samples containing high levels of sulfate, (e.g., acidic subsoils, minesoil extracts), the turbidimetric method gives satisfactory results. Ion chromatography or HPLC with conductivity detectors are very sensitive instrumental methods for determination of low concentrations of sulfate in soil extracts. These procedures are especially useful when simultaneous measurements of nitrate, chloride, fluoride, and sulfate are made. However, HPLC measurements of sulfate alone can be time consuming and, because the soil extracts must be filter-sterilized, expensive.

The procedure of Johnson and Nishita (1952) is the most sensitive and accurate colorimetric method used for determination of sulfate. However, since this method involves reduction of sulfate to sulfide and then measurement of sulfide by colorimetry, it is also time consuming and depends greatly upon operator skill. Sulfide produced by the Johnson and Nishita (1952) procedure can also be measured electrochemically, i.e. a sulfide specific electrode. For electrochemical measurements, sulfate is reduced by the Johnson and Nishita procedure, sulfides generated are adsorbed onto a sulfide anti-oxidant buffer (2*M* NaOH + 0.2 *M* Na_2EDTA) and the activity of sulfide is then measured by a sulfide electrode. The electrochemical measurement is also time consuming and requires careful attention to detail on the part of the analyst.

Turbidimetric Determination of Sulfate-S:

The turbidimetric method described below, when carefully performed, provides reproducible results with relatively simple instrumentation requirements, which is particularly useful when samples are not analyzed for sulfate on a routine basis. In this procedure, sulfate is converted to a $BaSO_4$ suspension under controlled conditions. The resulting turbidity is determined by a spectrophotometer and compared with a curve prepared from standard sulfate solutions (Anonymous, 1980). For accurate and reproducible results with turbidimetric techniques, it is critical that factors such as temperature, time and rate of stirring, and time of standing of suspension before measurements, be as uniform as possible.

Equipment:

1. 50 mL Erlenmeyer flasks.
2. Magnetic stirrer.
3. Wrist-action shaker
4. Spectrophotometer.

Reagents:

1. **Acid "seed" solution:** A 6 *M* solution of HCl containing 20 mg S/L as K_2SO_4. Thoroughly mix 50 mL of a 40 mg S/L standard solution (see below) with 50 mL of concentrated HCl.

2. **Standard solution, 100 mg S/L**: Dissolve 0.543 g of reagent grade K_2SO_4 in the extracting solution (either acidified NH_4OAc or monocalcium phosphate) in a 1 L volumetric flask and make to volume with more extracting solution.

3. **Working S standard solutions**: Using different proportions of the appropriate extracting solution and the 100 mg S/L standard, make standards that contain either 0, 2, 5, 10, 20, 25, 30, or 40 mg S/L (Table 7-1). Add 0.25 g of activated carbon to the standards and shake each for 3 minutes. Filter the solution through dry Whatman No. 42 filter paper previously washed with extracting solution.

Table 7-1. Working standards for turbidimetric determination of sulfate in soil extracts.

Volume of 100 mg S/L Stock Solution	Distilled Water	Final Volume	SO4-S In Solution	SO4-S In Soil
mL	mL	mL	mg/L	mg/kg
0	100	100	0	0
2	98	100	2	5
5	95	100	5	12.5
10	90	100	10	25
20	80	100	20	50
30	70	100	30	75
40	60	100	40	100

Procedure:

1. Treat the working standard solutions in an identical manner as the soil extracts in steps 2 through 7.

2. Pipette 10 mL of the filtrate from the extraction process selected into a 50 mL Erlenmeyer flask, and add 1 mL of acid "seed" solution.

3. Swirl the solution, and then add 0.5 g of $BaCl_2 \cdot 2H_2O$ crystals.

4. Let the mixture stand one minute, then swirl the solution in the flask frequently until the crystals are dissolved (use magnetic stirrer if available).

5. Within the time interval of 3 to 8 minutes, read the transmittance or optical density using a spectrophotometer or colorimeter at a wavelength of 420 nm.

6. Plot the percent transmittance reading vs. concentration on semi-log paper. If absorbance readings are taken, plot absorbance vs. concentration on a linear graph paper. Find the S concentration in the sample from the standard curve.

7. **Calculations**: Based on a 10 g sample of soil, 25 mL of extracting solution, and a 10 mL aliquot:

$$\text{mg SO}_4\text{-S/kg of soil} = \frac{\text{mg S /L x 0.025L}}{\text{0.010 kg soil}} = \text{mg S/L x 2.5}$$

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