



Florida Method of Test For Sulfate in Soil and Water

Designation: FM 5-553

1. SCOPE

- 1.1 This method covers the determination of sulfate in soil and water using either a screening approach based on a sulfate reagent system or an analytical approach as found in the Standard Methods for the Examination of Water and Wastewater, Section 4500-SO₄²⁻ E or Section 4110 B(SMEWW). This method can also be used for the determination of sulfate in coarse aggregate.
- 1.2 Both the screening and analytical approaches use the reaction of water-dissolved barium and sulfate to form an insoluble white precipitate of barium sulfate. The concentration (turbidity) of the precipitate is proportional to the sulfate concentration.

2. APPARATUS

- 2.1 Sulfate Reagent System: Sulfate, Pocket Colorimeter II Test Kit (Hach catalog #5870029), 2 to 70 mg/L, or equivalent, may be used for sulfate determinations. Additional glass sample cells with a 10-mL mark are needed (for example, Hach catalog #2427606). Alternatively, the apparatus referred to in the SMEWW may be used for sulfate determinations.
- 2.2 Analytical Balance: An analytical balance with a capacity of 2,000 g or greater and a resolution of 0.01 g or better.
- 2.3 Vacuum Filtration System: A vacuum filtration system is required. Such a system includes a vacuum pump, 0.25 in (6 mm) inner diameter flexible vacuum hose, 300 mL filter funnel/holder for a 47-mm diameter filter, and a 1-liter side arm vacuum filtration flask or similar.
- 2.4 Other: Whatman 41 filter paper (or equivalent), glass or plastic funnel, two or more 500-mL Erlenmeyer flasks, 47-mm diameter 0.45-micron pore size mixed cellulose ester (MCE) membrane filters, transfer pipette (variable pipette from 0.100 to 1.000 mL, capable of delivering increments of 0.01 mL) and tips, timer (10 min, minimum), 100-mL graduated cylinder, and disposable nitrile gloves.



3. REAGENTS

- 3.1 Barium chloride (BaCl_2) (Note 1) and citric acid are required for the sulfate test kit. Barium chloride and citric acid are supplied as SulfaVer 4 powder pillows (for example, Hach catalog #21067-69). For the SMEWW method, reagent purchasing and preparation information is provided in the method procedures.
- 3.2 Sulfate standard solution, 1,000 ppm (mg/L) as SO_4^{2-} , NIST-traceable.
- 3.3 Hydrochloric acid (HCl) (Note 1), ~37%, reagent grade.
- 3.4 Deionized or distilled water (dilution water) with a resistivity equal or greater than 200,000 ohm-cm.

Note 1: Barium chloride and hydrochloric acid are hazardous materials. Refer to the chemical safety data sheets (SDS) regarding the safe storage, handling, and disposal of these hazardous materials. Dispose of hazardous material in accordance with federal, state, and local mandates.

4. SAMPLES

- 4.1 Soil Sampling: Every effort should be made to obtain a soil sample that is representative of the bulk material. Use clean tools for gathering samples. Excessive moisture should be avoided by sampling from an area that has been allowed to gravity drain for a short time. If the soil sample has excess free moisture, place 2.4 pounds (1,075 g) \pm 5% of the soil on top of a suitable sieve and cover with plastic. Allow the sample to drain for a minimum of one hour. This step may be performed in the lab prior to testing.

If the soil sample is obtained from a heap that has been sitting for a long time, take the sample from a depth below the weathered surface where the moisture content appears to have stabilized. Avoid taking the sample from near a weathered soil surface. If sampling from ground level, remove top 12in (30 cm) to eliminate vegetation and debris before sampling. The soil sample may be taken from underneath standing water, but excess water should not be included with the sample. Soil samples should be placed in plastic or plastic-lined bags. Squeeze the bag down snugly around the sample and seal tightly to minimize contact with air.

- 4.2 Water Sampling: Water samples should be obtained from the main channel of rivers and streams. Sampling from other bodies of water such as lakes or ponds should be obtained from areas conducive to the capture of representative samples. Care should be observed not to sample from stagnant or pooled water, unless a structure will be placed in such an area. Sample the water just below the surface to alleviate introduction of floating



debris such as leaves, sticks, foam or trash. Fill the sample container to the top to eliminate introducing air into the sample and tightly seal the lid. The sample container shall be clean, at least 1 quart (1 liter) in size, and be either glass or plastic with an airtight lid. When possible, submerge the sample container below the surface of the water to completely fill and secure lid underwater.

- 4.3 Transporting Samples: Maintain test samples in a cool dark area after sampling and during transport to the test facility.
- 4.4 Storing Samples: Store water samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Dry soil samples without delay per section 5.2 and store dried soil at room temperature prior to analysis. Analyze samples within seven (7) days of collection.

5. SAMPLE PREPARATION

5.1 Preparation of Water:

Allow test sample to reach room temperature. If water sample contains suspended solids or color, gravity filter the water sample through a Whatman 41 filter (or equivalent), and if necessary, vacuum filter the water sample through a 0.45-micron pore size MCE membrane filter.

5.2 Preparation of Soil:

- A. Loose Granular Soils: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hours or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per AASHTO R76 to obtain 425 g ± 5%.

Muck and Soils with Clay: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hours or until a constant mass is achieved. Using a rawhide mallet or other suitable device pulverize the sample and sieve through a No. 10 mesh (2 mm) sieve. Split the sample per AASHTO R76 to obtain 425 g ± 5%.

5.3 Preparation of Soil Extract:

Place 100 grams of dried soil in a 500 mL Erlenmeyer flask (Note 2).



Add 300 mL of dilution water, stopper, and shake vigorously for 20 seconds. Let stand for one hour and repeat agitation. Let stand for a minimum of 12 hours.

- A. Suspended particles (turbidity) or color will interfere with the sulfate determination. If the extract is cloudy or colored due to the suspension of fine particles, add a few (3-5) drops of hydrochloric acid.
- B. Allow the acidified extract to stand for one to four hours as the suspended particles settle (Note 3).
- C. Filter by gravity the soil extract through a Whatman 41 filter into a 500-mL Erlenmeyer flask. Slowly decant into the filter the water layer followed by the soil slurry from the sample extract and allow the liquid to drain until the liquid stops dripping.
- D. Filter by vacuum the soil extract through a 0.45-micron pore size membrane filter (Note 4) into a filtration flask; repeat if necessary to get a clear extract.

5.4 Preparation of Coarse Aggregate:

Split the sample per AASHTO T248 to obtain 1,300 g \pm 5% and place aggregate in a suitable container. Add 1,200 mL of dilution water, cover and let stand for 24 hours at room temperature. Collect the leachate using clean equipment to avoid contamination. If leachate contains suspended solids or color, gravity filter the water sample through a Whatman 41 filter (or equivalent), and if necessary, vacuum filter the water sample through a 0.45-micron pore size MCE membrane filter.

Note 2: Prepare separate soil extracts for sulfate and chloride analyses. If after 12 hours of settling both extracts are clear enough to filter, only one of the extracts needs to be filtered for both sulfate and chloride analysis.

Note 3: More than a few drops of concentration hydrochloric acid will acidify the sample to less than pH 2, upon which the sample becomes hazardous material.

Note 4: The MCE membrane filter is white; spacers are blue.

6. TEST PROCEDURE

- 6.1 Low Range: For the SMEWW analytical approach, refer to the SMEWW step-by-step instructions. For the screening approach using the sulfate test kit (2-70 ppm), follow these instructions:



- A. Check the Reagents and Glassware: Check that the SulfaVer 4 reagent powder pillows have not reached their expiration date. Check and clean as necessary glass sample cells so that cells are free of scratches, stains, deposits, or films that could affect light transmission through the glass.
- B. Prepare a Reagent Blank: Fill one sample cell with dilution water to the 10-mL mark. Prepare a blank at least once per day on days in which samples are tested.
- C. Prepare a 30 ppm Check Standard: Add to a second sample cell 0.30 g of 1,000-ppm (mg/L) sulfate standard solution and fill the sample cell to the 10-mL mark with dilution water. Prepare a check standard at least once per day on days in which samples are tested.
- D. Prepare two Test Samples (water, soil extract, and coarse aggregate leachate): Fill the third and fourth cells with sample to the 10-mL mark. Use one of these cells as a blank to exclude (zero) any remaining turbidity or color.
- E. React the Blank, Standard, and Samples: Add one SulfaVer 4 powder pillow to each of these: the reagent blank, the 30 ppm check standard, and only one of the two cells that contain the test sample. Cap all four sample cells and gently invert each cell 10 times to mix. Treat each of the four sample cells the same, as the mixing action may entrain air bubbles that will interfere with the measurement. Wipe the glass cells clean of fingerprints. Wait for a 5-minute reaction period with the sample cells undisturbed. Test the blank, check standard, and test samples within 10 minutes of adding the SulfaVer 4 reagent.
- F. Select a Range for the Measurements (see Note 5 and Figure 1): Select a range on the photometer that gives the best results for the reagent lot number. To switch from Range 1 to Range 2, press the Menu key, then the Read key. Note the small arrow under the Range label. Use the same range for blanks, check standard, and both test samples.
- G. Measure the Check Standard: Place the reagent blank into the sample cell holder and cap the holder. Press the photometer Zero key. After a few seconds the digital display should read 0. Remove the reagent blank and place the 30 ppm check standard into the sample cell holder and cap the holder. Press the photometer Read key. After a few seconds the digital display should read 30 (25 to 35).



Record the reading. If the measured concentration is less than 25 ppm or greater than 35 ppm, check first for scratched or dirty glassware or a light leak through the cell holder; otherwise suspect the potency of SulfaVer 4 reagent; purity or volume of sulfate standard, or purity of dilution water. Troubleshoot and correct the problem before testing the sample extract

- H. Measure the Test Sample: Place the test sample without the SulfaVer 4 reagent into the sample cell holder and cap the holder. Press the photometer Zero key. After a few seconds the digital display should read 0. Remove the test sample without the SulfaVer 4 reagent and place the reacted test sample into the sample cell holder and cap the holder. Press the photometer Read key. After a few seconds a reading will appear. If reading is 2 ppm or less, record reading as below detection. Otherwise, record the photometer reading and multiply the reading by the dilution factor, which may be 1 for a water sample or coarse aggregate but 3 to account for the initial dilution of a soil sample (100 grams of soil to 300 mL water). Report the dilution factor and the sulfate concentration in units of ppm.

- 6.5 Sample Dilution: Dilution of the test sample will be necessary if the sulfate concentration is greater than the maximum limit of the photometer (digital display will flash if reading is too high). To dilute by a factor of 10, mix in a 100-mL graduated cylinder 10 mL of sample and 90 mL of dilution water. Repeat steps 6.1 E, F, and H for the sample. The dilution factor for water and coarse aggregate will be 10, for a soil extract, multiply the sulfate concentration by 3 for the initial dilution, then by 10 for the final dilution (factor of 30 for the total dilution).

Note 5: The Hach photometer includes a pre-programmed calibration curve on each range, Range 1 and Range 2. To check the built-in calibration curves, use a series of check standards from 0 to 70 ppm and plot the results. An example plot is shown below. Re-check the curves if the photometer is repaired or replaced, for each new lot of SulfaVer 4 powder pillows, and if a problem with the curve is suspected. Add in sequence to eight sample cells 0.00 g, 0.10 g, 0.20 g, 0.30 g, 0.40 g, 0.50 g, 0.60 g, and 0.70 g of 1,000 ppm (mg/L) sulfate standard solution. Fill each sample cell to the 10-mL mark with dilution water to obtain sulfate concentrations of 0, 10, 20, 30, 40, 50, 60, and 70 ppm. Test the calibration curve standards as described in the above procedures (6.1 E, F, and G). The Hach photometer also accepts a user-generated calibration curve as outlined in the instrument's instruction manual.

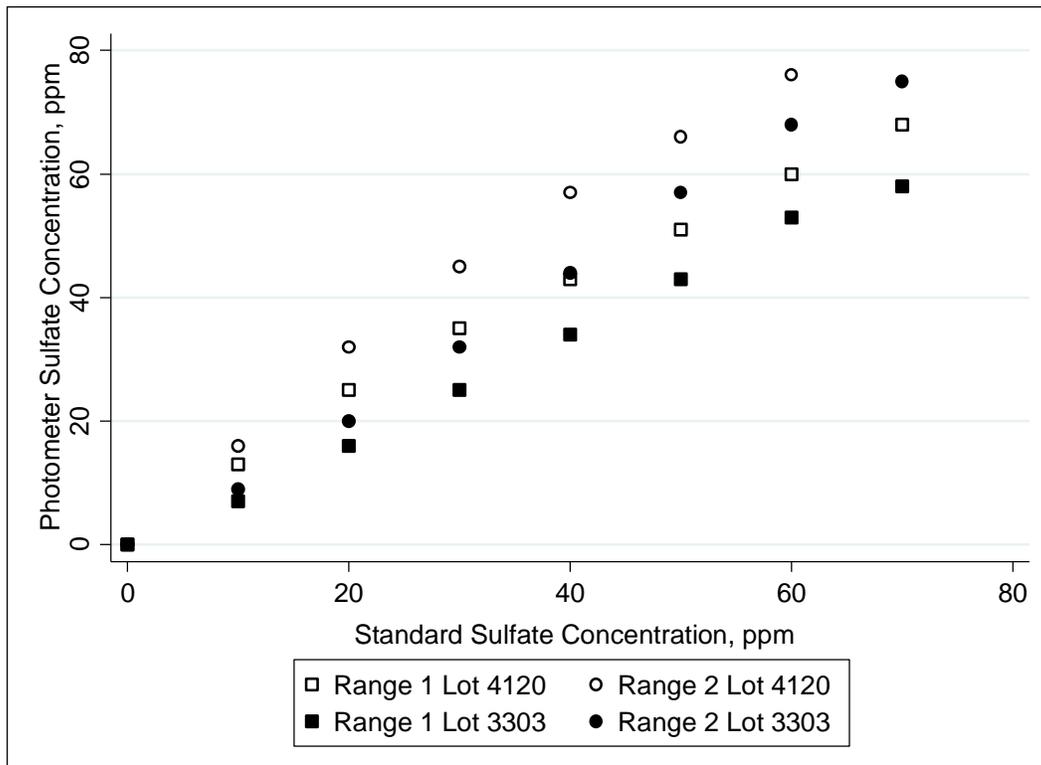


Figure 1. Plot of a Hach photometer response to sulfate standard solutions. For this photometer, the measured sulfate concentration was consistently higher on Range 2 than on Range 1. Moreover, for both Range 1 and Range 2, the measured sulfate concentration was lower for SulfaVer 4 Lot 3303 than for Lot 4120, even though both lots were within their expiration dates.

7. PRECISION AND BIAS

7.4 Bias: Single-operator, single laboratory bias for this method was evaluated using a Hach Sulfate, Pocket Colorimeter II Test Kit and repeated measures of a 100-ppm aqueous standard, which was diluted by a factor of three to be in the target range of the test kit. Six replicate standards were tested, three with one lot number and three with a different lot number of SulfaVer 4 reagent. The average bias was -0.5 ppm (-0.5%).

7.5 Reproducibility: For a test material (sand, A-3) with an average sulfate concentration of 67 ppm, the multi-laboratory standard deviation of a single test result has been found to be 16 ppm. Therefore, results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than 45 ppm.