FLORIDA DEPARTMENT OF TRANSPORTATION
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March 29, 2023

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 (**Method A**) based on a sulfate reagent system or analytical approaches (**Method B** and **Method C**), as found in the **Standard Methods for the Examination of Water and Wastewater (SMEWW)**, **Section 4500-SO_4^{2-} E** or **Section 4110 B**, respectively. These methods can also be used for the determination of sulfate in coarse aggregate.

1.2. Both **Method A** and **Method B** use the reaction of barium chloride and sulfate ions in the sample to form an insoluble white precipitate of barium sulfate. The resulting turbidity of the solution is proportional to the sulfate concentration. **Method C** involves the use of Ion Chromatography (IC) to separate anions in liquid samples using a column and detector. The conductivity is quantified as the ion elutes from column and plotted as a peak. Sulfate concentration is determined by integrating the peak area or height.

2. APPARATUS

Method A:

2.1. Sulfate Reagent System: A colorimeter capable of detecting sulfate concentrations from 2 to 70 mg/L, with a tolerance of ±10 ppm and the ability to allow a user-entered calibration curve. (Hach DR900, Hach Pocket Colorimeter II). Other meters may be used if they meet or exceed these requirements. Additional glass sample cells with a 10-mL mark are needed and are specific to the colorimeter.

2.2. Analytical Balance: An analytical balance with a capacity of 2,000 g or greater and a resolution of 0.1 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 funnel, a filter 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, 1.000 mL transfer pipette and tips, timer (10 min, minimum), 100-mL graduated cylinder, and disposable nitrile gloves.

Method B:

Refer to the **SMEWW Section 4500-SO_4^{2-} E**.

Method C:

Refer to the **SMEWW Section 4110 B**.

3. REAGENTS

Method A:

3.1. Barium chloride ($BaCl_2$) (**Note 1**) and citric acid are required. Barium chloride and citric acid are supplied by several manufacturers in various forms such as: tablets, powder, and powder pillows. Hach DR900 Colorimeter and Hach Pocket Colorimeter II use SulfaVer 4 powder pillows. These are pre-measured, single dose packets (Hach catalog #21067-69) for use with either Hach colorimeter. If using a different colorimeter, check with the manufacturer to determine the type of reagents required.

3.2. Sulfate standard solution, 1,000 ppm (mg/L) as SO42-, that is NIST-traceable.

3.3. Hydrochloric acid (HCl) (Note 1), ~37%, reagent grade.

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.

3.4. Distilled water with a minimum resistivity of 200,000 ohm-cm (**Note 2**).

Note 2: Distilled water stored in containers that are not airtight will absorb ions from acidic and basic gases in the atmosphere resulting in lowered resistivity of the water over time.

Method B:

Refer to the **SMEWW Section 4500-SO42- E** with the following exceptions:

Prepare 1000 ppm Standard Sulfate Solution (Sulfate Calibration Stock)

instead of 100 ppm (**Note 3**).

Weigh 0.3696 g of anhydrous Sodium Sulfate (Na2SO4), place in a 250 mL volumetric flask; add distilled water to bring the solution to 250 mL line on the flask.

Note 3: Using a 1000 ppm solution eliminates the use of a small aliquot from stock that can produce measuring error. If 100 ppm is used as per **SMEWW-4500-SO_4^{2-} E**, **Section 3**, adjust preparation of stock and calibration standards.

Method C:

Refer to the **SMEWW Section 4110 B**.

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 collecting samples. Excessive moisture should be avoided by sampling from areas that have been allowed to gravity drain. If the soil sample has excess free moisture, place 2.2 lb (1 kg) 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. If sampling from ground level, remove the top 12 in. (30 cm) to eliminate vegetation and debris before sampling. The soil sample may be taken from underneath standing water, but free-standing water should not be included with the sample. Soil samples should be placed in plastic (watertight) bags. The bag should be squeezed down snugly around the sample and sealed 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 occur in areas conducive to collecting a representative sample. Care should be observed to avoid sampling from stagnant or pooled water unless a structure will be placed in such an area.

The water sample container shall be clean, at least 1 qt (1 L) in size and be either glass or plastic with an airtight lid. Rinse the container several times with the water to be collected. When possible, submerge the sample container below the surface of the water to avoid 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.

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 and soil samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. 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:

If as-received results are desired, do not dry the sample (**Note 4**).

5.2.1 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 four hours or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per **AASHTO R 76** to obtain 425 g ± 5%.

5.2.2 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 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 R 76** to obtain 425 g ± 5%.

5.3. Preparation of Soil Extract:

5.3.1 Place 100 grams of dried soil in a 500 mL Erlenmeyer flask. Add 300 mL of distilled water, stopper, and shake vigorously for 20 seconds. Let stand for one hour and repeat agitation. Let stand for a minimum of 12 hours. If the soil extract is clear enough to gravity filter skip **Section 5.3.4** (**Note 5**).

5.3.2 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 (**Note 4**). Allow the acidified extract to stand for one to four hours until the suspended particles settle.

Note 4: An "as-received" sample is one that is tested without drying and most closely represents the in-situ conditions at the time of sampling.

5.3.3 Filter, by gravity, the soil extract through a Whatman 41 (or equivalent) filter into a 500-mL Erlenmeyer flask. Slowly decant into the funnel (containing a filter) the water layer followed by the soil slurry from the sample extract and allow the liquid to drain until the liquid stops dripping. If the extract is clear after gravity filtering, skip **Section 5.3.4**.

5.3.4 Vacuum filter the soil extract through a 0.45-micron pore size membrane filter (**Note 5**) into a clean 1-liter vacuum filtration flask; repeat, if necessary, to get a clear extract.

Note 5: The soil extract for sulfate analysis may also be used for chloride analysis provided that after 12 hours of settling the extract is clear enough to filter (skipping **Section 5.3.2**). The same soil extract cannot be used if **Section 5.3.2** is performed to remove suspended fines because it would affect chloride analysis.

5.4. Preparation of Coarse Aggregate:

Split the sample per **AASHTO R 76** to obtain 1,300 g ± 5% and place aggregate in a suitable container. Add 1,200 mL of distilled water, cover, and let stand for 24 hours at room temperature. Collect the leachate using clean equipment to avoid contamination.

5.5. Preparation of Coarse Aggregate Leachate:

If the leachate is clear enough to gravity filter skip **Section 5.5.1** (**Note 6**).

Note 6: The leachate for sulfate analysis may also be used for chloride analysis provided that after 12 hours of settling the extract is clear enough to filter (skipping **Section 5.5.1**). The same leachate cannot be used if **Section 5.5.1** is performed to remove suspended fines because it would affect chloride analysis.

5.5.1 Suspended particles (turbidity) or color will interfere with the sulfate determination. If the leachate is cloudy or colored due to the suspension of fine particles, add a few (3-5) drops of hydrochloric

acid (**Note 7**). Allow the acidified leachate to stand for one to four hours until the suspended particles settle.

Note 7: More than a few drops of concentrated hydrochloric acid will acidify the sample to less than pH 2, upon which the sample becomes a hazardous material.

5.5.2 Filter, by gravity, the leachate through a Whatman 41 filter or equivalent into a 500-mL Erlenmeyer flask. Slowly decant the water into a funnel (containing a filter) followed by any particulate and allow the liquid to drain until it stops dripping. If the leachate is clear after gravity filtering, skip **Section 5.5.3**.

5.5.3 Vacuum filter the leachate sample through a 0.45-micron pore size MCE membrane filter (**Note 8**) into a clean 1-liter vacuum filtration flask; repeat, if necessary, to get a clear extract.

Note 8: The MCE membrane filter is white, the spacers are typically blue.

6. TEST PROCEDURE

Method A:

6.1. Low Range: Low range is 2 to 70 ppm when using either model of Hach colorimeter.

6.1.1 Check the Reagents and Glassware: Check that the reagents have not reached their expiration date. Only use sample cells that are clean and free of scratches, stains, deposits, or films that could affect light transmission.

6.1.2 Prepare a Reagent Blank: Fill one sample cell with distilled water to the 10-mL mark. Prepare a blank at least once per day on days in which samples are tested.

6.1.3 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 distilled water. Prepare a check standard at least once per day on days in which samples are tested.

6.1.4 Prepare two Test Samples (water, soil extract, or coarse aggregate leachate): Fill the third and fourth cells with sample to the 10-mL mark. Use one of these cells as a sample blank to exclude (zero) any remaining turbidity or color.

6.1.5 React the reagent Blank, check standard, and one test sample: Add the reagent(s) required for the colorimeter (both Hach colorimeters use SulfaVer 4 powder pillow) to each of these: the reagent blank, the 30-ppm sulfate 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 reagent blank, check standard, and test samples within 10 minutes of adding the reagent(s).

6.1.6 Remaining steps are specific to the Hach Pocket Colorimeter II and may not be applicable to other meters. Follow specific colorimeter instructions to obtain turbidity measurement. Select a Range (see **Note 9** and **Figure 1**) 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.

6.1.7 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 ± 10. Record the reading. If the measured concentration is less than 20 ppm or greater than 40 ppm, check for scratched or dirty glassware or a light leak through the cell holder; otherwise suspect the potency of the reagent(s); purity or volume of sulfate standard, or purity of the distilled water. Troubleshoot and correct the problem before testing the sample extract.

6.1.8 Measure the Test Sample: Place the test sample without the reagents 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 reagent(s) 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 reading and multiply the reading by the dilution factor, which may be 1 for a water sample or coarse aggregate or 3 to account for the initial dilution of a soil sample. Report the dilution factor and the sulfate concentration in units of

ppm.

6.2 High Range: Dilution of the test sample will be necessary if the sulfate concentration is greater than the maximum limit of the colorimeter (digital display will flash if reading is too high). To dilute by a factor of 10, mix in a 100-mL volumetric flask 10 mL of sample and 90 mL of distilled water. Repeat steps 6.1.4, 6.1.5, and 6.1.8. The dilution factor for water and coarse aggregate will be 10, and 30 for a soil extract.

Note 9: The Hach Pocket Colorimeter II 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 in **Figure 1**. Re-check the curves if the colorimeter is repaired or replaced, for each new lot of reagent(s), 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 distilled 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 (**Section 6.1.4**, **Section 6.1.5**, and **Section 6.1.8**. The Hach colorimeter also accepts a user-generated calibration curve as outlined in the instrument's instruction manual. Some colorimeters allow adjustments to the pre-programed calibration curve or the input of a custom calibration curve that is unique to the batch of reagents. Refer to the user's manual for specific instructions.

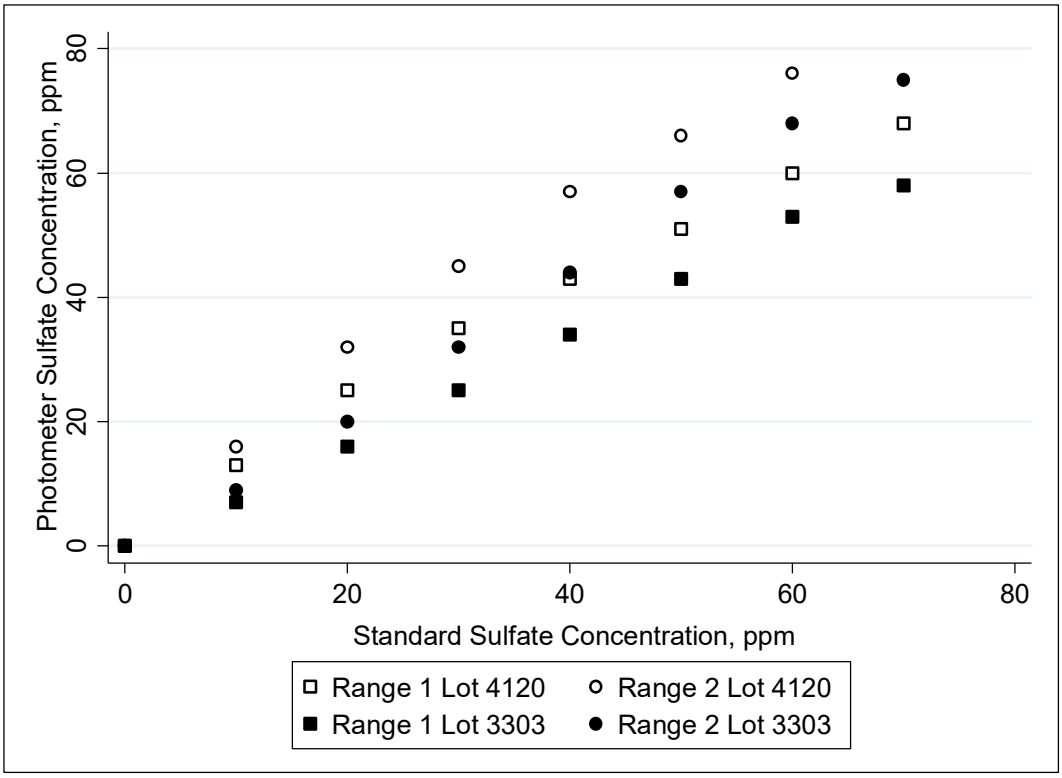

Figure 1. Plot of a Hach Pocket Colorimeter II response to sulfate standard solutions.

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.

Method B:

Refer to the **SMEWW Section 4500-SO_4^{2-} E** with the following exceptions:

In the calculations section, Subtract the sample blank absorbance from the sample absorbance. Enter the result into the Sulfate Calibration worksheet to determine mg SO_4^{2-}/L.

For soil samples, multiply the results by 3 for the sulfate concentration in the original sample.

Method C:

Concentration is calculated by the response of the sample against IC standard calibration curve and is determined by instrument software. Dilution factors, if required, are included in the sequence before sample analysis. For soil samples, multiply the result by 3 for the sulfate concentration in the original

sample.

7. REPORT

The following information should be reported.

Sulfate content of the sample in ppm.

8. PRECISION AND BIAS

Method A:

8.1 Precision: 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.

8.2. 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%).