Tex-620-J, Determining Chloride and Sulfate Contents in Soil

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Section 1

Overview


This test method describes the determination of the chloride and sulfate contents in soil. The two methods described are:

♦ ion chromatography
♦ wet chemical.

Units of Measurement

The values given in parentheses (if provided) are not standard and may not be exact mathematical conversions. Use each system of units separately. Combining values from the two systems may result in nonconformance with the standard.
Section 2
Sample Preparation

Use the following apparatus:
♦ balance, calibrated to weigh to nearest 0.1 g
♦ beaker, 400 mL
♦ electric hot plate
♦ filter paper, No. 42, 7.4-in. (185 mm) diameter
♦ flask, class A volumetric, 500 mL capacity, with stopper
♦ gravity filtration funnel, ribbed
♦ jaw crusher
♦ mechanical convection oven, capable of maintaining a temperatures of 140 ±9°F (60 ±5°C)
♦ mechanical pulverizer
♦ sieves, U.S. Standard No. 4 (4.75 mm) and No. 40 (425 μm)
♦ stirring rod
♦ wash bottle
♦ watch glass.

Soil

Pulverizing

The following describes pulverizing soil samples.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Obtain a 300 g representative sample when material top size is smaller than No. 4 (4.75 mm).</td>
</tr>
<tr>
<td>2</td>
<td>Pulverize the 300 g sample to pass the No. 40 (425 μm) sieve.</td>
</tr>
<tr>
<td>3</td>
<td>Weigh to the nearest 0.1 g.</td>
</tr>
<tr>
<td>4</td>
<td>If material top size is larger than No. 4 (4.75 mm), obtain approximately a 3000 g representative sample and crush/grind to pass the No. 4 (4.75 mm) sieve.</td>
</tr>
<tr>
<td>5</td>
<td>Obtain a 300 g representative sample of the minus No. 4 (4.75 mm) material.</td>
</tr>
<tr>
<td>6</td>
<td>Pulverize the 300 g to pass the No. 40 (425 μm) sieve.</td>
</tr>
<tr>
<td>7</td>
<td>Weigh to the nearest 0.1 g.</td>
</tr>
<tr>
<td>8</td>
<td>Dry the sample in a 140 ±9°F (60 ±5°C) oven and cool to 77 ±5°F (25 ±3°C) in a desiccator to constant weight.</td>
</tr>
</tbody>
</table>

Leaching
The following describes the soil leaching procedure to extract the chloride and sulfate ions.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
</table>
| 1    | Prepare samples for leaching.  
     | ♦ Weigh a 30 ±0.1 g portion of the pulverized sample into a clean 400 mL beaker.  
     | ♦ Add 300 mL of deionized water; stir and cover with a watch glass.  
     | ♦ Repeat for multiple samples.  |
| 2    | Leach samples.  
     | ♦ Place the samples on a 150 ±20°F (66 ±11°C) hot plate.  
     | ♦ Stir the samples periodically.  
     | ♦ Maintain the leaching volume at 300 ±25 mL by adding deionized water.  
     | ♦ Remove the samples from the hot plate after 15 – 18 hr. digestion time.  
     | NOTE: Be careful not to boil samples and ensure that no sample solution is lost.  |
| 3    | Set up samples for filtering.  
     | ♦ Set up a 500 mL volumetric flask for each sample solution.  
     | ♦ Place a funnel on top of each flask.  
     | ♦ Fold and place a No. 42 size filter paper in each funnel.  |
| 4    | Filter the samples.  
     | ♦ Use hot, deionized water for all rinsing.  
     | ♦ Rinse any residue left on the stirring rod and on the underside of the watch glass into the funnel.  
     | ♦ Decant as much solution as possible through the filter.  
     | ♦ Transfer the sample material into the filter.  
     | ♦ Rinse any residue left in the beaker into the funnel.  
     | ♦ Repeat washings of the samples until the filtrate is free of chlorides.  
     | NOTE: Test the filtrate for chloride by adding 1 to 2 drops of filtrate from the funnel to a dilute silver nitrate solution. Any turbidity indicates chlorides present.  |
| 5    | Let the solution cool to 77 ±2°F (25 ±1°C).  |
| 6    | Fill the flask to the volumetric mark with deionized water.  |
Section 3

Ion Chromatography Method

This method, for the determination of chloride and sulfate ions in water by chromatography, is similar to the method described in ASTM D 4327, “Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography.” Interferences in this method are the same as discussed in ASTM D 4327.

Apparatus

Use the following apparatus:

♦ flasks, class A volumetric, each with stoppers and the following capacities:
  * 100 mL
  * 500 mL and
  * 1000 mL.
♦ ion chromatograph with an auto sampler
♦ pipettes, class A volumetric, with the following capacities:
  * 1 mL
  * 10 mL
  * 25 mL and
  * 50 mL.
♦ vials, 5 mL, and caps for auto sampler.

Reagents

Use the following reagents:

♦ certified anion standard reference solution containing 100 parts per million (ppm) chloride and sulfate
♦ deionized or distilled water meeting ASTM D 1193, “Standard Specification for Reagent Water,” Type II requirements
♦ sodium bicarbonate eluent concentrate for ion chromatograph. The concentration of the eluent after 100× dilution should be 8.0 mM sodium carbonate and 1.0 mM sodium bicarbonate.
Calibration

The following table describes how to prepare solutions to calibrate the ion chromatograph.

<table>
<thead>
<tr>
<th>Calibration Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step</td>
</tr>
</tbody>
</table>
| 1    | Prepare 6 to 8 standards using the anion standard solution.  
      | *NOTE:* The 6 to 8 standards should range from 0.1 to 100 ppm. |
| 2    | To prepare a 0.1-ppm standard:  
      | ♦ Use a 1 mL pipette to transfer a 1 mL aliquot of the anion standard solution into a 1000 mL volumetric flask.  
      | ♦ Dilute to the mark. |
| 3    | To prepare a 1.0-ppm standard:  
      | ♦ Use a 1 mL pipette to transfer a 1 mL aliquot of the anion standard solution into a 100 mL volumetric flask.  
      | ♦ Dilute to the mark. |
| 4    | To prepare a 10-ppm standard:  
      | ♦ Use a 10 mL pipette to transfer a 10 mL aliquot of the anion standard solution into a 100 mL volumetric flask.  
      | ♦ Dilute to the mark. |
| 5    | To prepare a 25-ppm standard:  
      | ♦ Use a 25 mL pipette to transfer a 25 mL aliquot of the anion standard solution into a 100 mL volumetric flask.  
      | ♦ Dilute to the mark. |
| 6    | To prepare a 50-ppm standard:  
      | ♦ Use a 50 mL pipette to transfer a 50 mL aliquot of the anion standard solution into a 100 mL volumetric flask.  
      | ♦ Dilute to the mark. |
| 7    | The 100-ppm standard needs no dilution. |
| 8    | Ensure the standards are well mixed. |
| 9    | Set up the ion chromatograph and run the standards according to the manufacturer’s instructions. |
| 10   | Using the results, create a calibration curve for chloride and sulfate ions. |

Chloride and Sulfate Contents

The following table describes the procedure for determining the chloride and sulfate contents by ion chromatography.

<table>
<thead>
<tr>
<th>Determining Chloride and Sulfate Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step</td>
</tr>
</tbody>
</table>
| 1    | Dilute the sample.  
      | ♦ Pipette 50 mL of the filtered sample into a 500 mL volumetric flask and dilute to the mark.  
      | ♦ Shake the dilution well to ensure a homogenous mixture.  
      | *NOTE:* This dilutes the sample by a factor of 10. If a very high concentration are suspected, it may be necessary to make a larger dilution (i.e., dilution factor of 20, 100, etc.). |
Determining Chloride and Sulfate Contents

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
</table>
| 2    | Start up and equilibrate the ion chromatograph.  
♦ Follow the manufacturer’s instructions to start the pump and electronic systems.  
♦ Pump eluent through the column and detector until the ion chromatograph obtains a stable baseline. |
| 3    | Load samples into the auto sampler.  
♦ Pour samples into properly labeled sample vials.  
♦ Run one prepared standard and one deionized water blank after every 4 - 5 samples to check the accuracy of the chromatograph. |
| 4    | Run the samples through the ion chromatograph to determine the concentration of the chloride and sulfate ions.  
**NOTE**: Follow the manufacturer’s recommendation for ion chromatograph operation. |
| 5    | Obtain results.  
♦ Obtain chloride and sulfate contents in ppm as determined by the ion chromatograph.  
♦ Use conversion factors to convert to ppm chloride and sulfate content in the original sample |

**Calculations**

Use the following calculations to determine the chloride and sulfate contents from the ion chromatographic method.

**Dilution Factor**

\[ DF = \frac{V_d}{V_p} \]

Where:

♦ DF = dilution factor  
♦ \( V_d \) = volume of the flask used for dilution in milliliters  
♦ \( V_p \) = volume of the pipette used to make the dilution in milliliters.

**Concentration of Standard Solution Used for Calibration**

\[ S_c = \frac{C_s}{DF} \]

Where:

♦ \( S_c \) = standard solution concentration  
♦ \( C_s \) = concentration of the ion in the certified reference solution in ppm  
♦ DF = dilution factor used.

Example: If the reference solution contains 100 ppm Cl and a technician dilutes 10 mL of the solution to 500 mL, the resulting concentration is:
Concentration of Chloride Ions in the Original Soil Sample

\[ Cl = \frac{R \times DF \times Fl}{W} \]

Where:
- Cl = concentration of chloride ions in the original soil sample in ppm
- R = concentration of chloride ions in the sample run through the ion chromatograph in ppm
- DF = dilution factor
- Fl = volume of the flask containing undiluted sample in milliliters
- W = weight of the original soil sample in grams.

Concentration of Sulfate Ions in the Original Soil Sample

\[ SO_4 = \frac{R \times DF \times Fl}{W} \]

- SO$_4$ = concentration of sulfate ions in the original soil sample in ppm
- R = concentration of sulfate ions in the sample run through the ion chromatograph in ppm
- DF = dilution factor
- Fl = volume of the flask containing undiluted sample in milliliters
- W = weight of the original soil sample in grams.
Section 4

Wet Chemical Method


Apparatus

Use the following apparatus:

♦ analytical balance, with an accuracy of ±0.5 mg
♦ beaker, 200 mL, tall-form
♦ beaker with the following capacities:
  • 250 mL and
  • 500 mL.
♦ burette, 50 mL
♦ desiccator
♦ drop-dispensing bottles
♦ Erlenmeyer flask, 500 mL
♦ filter paper, No. 42 (ashless)
♦ flask, class A volumetric, 500 mL capacity, with stopper
♦ graduated cylinder with the following capacities:
  • 10 mL
  • 25 mL
  • 50 mL and
  • 100 mL.
♦ heat-resistant tongs
♦ hot plate
♦ magnetic stirrer
♦ Meeker burner
♦ muffle furnace, capable of maintaining temperatures of 1,472 to 2,012°F (800 to 1100°C)
♦ oven, capable of maintaining a temperature of 212°F (100°C)
♦ pH meter, having an accuracy of ±0.1 pH or better with automatic temperature compensation or pH paper, range 8 to 9
Reagents

Use the following reagents, which all must be ACS reagent-grade:

- barium chloride (anhydrous)
- hydrochloric acid (37%)
- nitric acid (70%)
- potassium chromate indicator
- silver nitrate
- sodium chloride
- sodium hydroxide (1 N).

Solutions

Use deionized water to prepare the following solutions.

**Barium Chloride (10%)**

The following describes preparing a 10% by weight barium chloride solution.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>In a 500 mL beaker, weigh 50 ±0.5 g of barium chloride.</td>
</tr>
<tr>
<td>2</td>
<td>Add the deionized water to the barium chloride until a total of 500 g of solution is achieved.</td>
</tr>
<tr>
<td>3</td>
<td>Add a stirring magnet to the beaker and place on a magnetic stirrer. Stir until all the barium chloride is dissolved.</td>
</tr>
<tr>
<td>4</td>
<td>Transfer the solution into an airtight container.</td>
</tr>
</tbody>
</table>

**Dilute Nitric Acid**

The following describes preparing a dilute nitric acid solution.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>In a 10 mL graduated cylinder, measure 2 mL of nitric acid. In a 50 mL graduated cylinder, measure 38 mL of deionized water.</td>
</tr>
<tr>
<td>2</td>
<td>Combine the deionized water and nitric acid in a 200 mL, tall-form beaker.</td>
</tr>
<tr>
<td>3</td>
<td>Add a stirring magnet to the beaker and place on a magnetic stirrer. Stir until the solution is thoroughly mixed.</td>
</tr>
<tr>
<td>4</td>
<td>Transfer the solution into a drop-dispensing bottle.</td>
</tr>
</tbody>
</table>
### Potassium Chromate Indicator

The following describes preparing a potassium chromate indicator solution.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>In a 250 mL beaker, weigh 50 ±0.5 g of potassium chromate powder.</td>
</tr>
<tr>
<td>2</td>
<td>In a 100 mL graduated cylinder, measure 100 mL of deionized water.</td>
</tr>
<tr>
<td>3</td>
<td>Add the deionized water to the beaker with the potassium chromate.</td>
</tr>
<tr>
<td>4</td>
<td>Add a stirring magnet to the beaker and place on a magnetic stirrer.</td>
</tr>
<tr>
<td></td>
<td>Stir the solution until all of the potassium chromates dissolves.</td>
</tr>
<tr>
<td>5</td>
<td>Transfer the solution into a drop-dispensing bottle.</td>
</tr>
</tbody>
</table>

### Silver Nitrate (0.1 N)

The following describes preparing a silver nitrate solution.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mix the silver nitrate solution.</td>
</tr>
<tr>
<td></td>
<td>On a balance, weigh 17 ±0.5 g of silver nitrate powder.</td>
</tr>
<tr>
<td></td>
<td>In a graduated cylinder, measure 1 L of deionized water.</td>
</tr>
<tr>
<td></td>
<td>Combine the silver nitrate and deionized water in a 1 L beaker.</td>
</tr>
<tr>
<td></td>
<td>Add a stirring magnet, place the beaker on a magnetic stirrer, and stir until all of the silver nitrate dissolves.</td>
</tr>
<tr>
<td></td>
<td>Transfer the solution into a 1 L light protective storage bottle.</td>
</tr>
<tr>
<td>2</td>
<td>Determine the normality of the silver nitrate solution.</td>
</tr>
<tr>
<td></td>
<td>Dry approximately 5 g of sodium chloride at 212°F (100°C) for at least 1 hr.</td>
</tr>
<tr>
<td></td>
<td>Use an analytical balance, weigh 0.2 g of sodium chloride to the nearest 0.0005 g into a tared 200 mL, tall-form, beaker.</td>
</tr>
<tr>
<td></td>
<td>In a graduated cylinder, measure 100 mL of deionized water.</td>
</tr>
<tr>
<td></td>
<td>Add the deionized water to the beaker with the sodium chloride, add a stirring magnet, and place the beaker on a magnetic stirrer.</td>
</tr>
<tr>
<td></td>
<td>Stir until the sodium chloride completely dissolves.</td>
</tr>
<tr>
<td></td>
<td>Add 10 drops of potassium chromate indicator to the solution.</td>
</tr>
<tr>
<td></td>
<td>Fill a 50 mL burette with the silver nitrate solution.</td>
</tr>
<tr>
<td></td>
<td>Titrate the sodium chloride solution with the silver nitrate to the first color change.</td>
</tr>
<tr>
<td></td>
<td>Use the results from the titration to calculate the normality to at least 3 significant digits.</td>
</tr>
</tbody>
</table>

#### Calculations for Silver Nitrate

Use the following calculation to determine the normality of the silver nitrate solution:

\[
N = \frac{W}{(0.05844) V}
\]

Where:

- \(N\) is the normality of the silver nitrate solution.
- \(W\) is the mass of sodium chloride used in the titration.
- \((0.05844)\) is the volume of silver nitrate solution used in the titration.
- \(V\) is the volume of sodium chloride solution used in the titration.
♦ N = normality of the silver nitrate solution
♦ W = mass of sodium chloride used for the titration in grams
♦ V = volume of silver nitrate used for the titration in milliliters.

**Dilute Sodium Hydroxide**

The following describes preparing a dilute sodium hydroxide solution.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>In a 10 mL graduated cylinder, measure 5 mL of 1 N sodium hydroxide solution. In a 50 mL graduated cylinder, measure 35 mL of deionized water.</td>
</tr>
<tr>
<td>2</td>
<td>Combine the deionized water and the sodium hydroxide in a 200 mL, tall-form, beaker.</td>
</tr>
<tr>
<td>3</td>
<td>Add a stirring magnet to the beaker and place on a magnetic stirrer. Stir until the solution is thoroughly mixed.</td>
</tr>
<tr>
<td>4</td>
<td>Transfer the solution into a drop-dispensing bottle.</td>
</tr>
</tbody>
</table>

**Chloride Ion Content**

The following describes the steps required to determine chloride ion content by titration method.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pipette 50 mL of the filtered sample into a 200 mL, tall-form, beaker.</td>
</tr>
<tr>
<td>2</td>
<td>Determine the pH of the sample. Use the pH meter or pH paper. Add either dilute nitric acid or dilute sodium hydroxide to adjust the sample pH to between 8 and 9.</td>
</tr>
<tr>
<td>3</td>
<td>Prepare to titrate the solution with silver nitrate. Add 11 drops of potassium chromate indicator to the sample. Stir the solution until a solid yellow color persists throughout the sample. Fill a 50 mL burette with the 0.1 N silver nitrate solution.</td>
</tr>
<tr>
<td>4</td>
<td>Titrate the sample to determine chloride ion content. Stir the solution with a magnetic stirrer. Add the silver nitrate drop by drop until a brick-red color persists throughout the sample. Record the amount of silver nitrate used.</td>
</tr>
<tr>
<td>5</td>
<td>Determine the chloride ion concentration as indicated under 'Calculations.'</td>
</tr>
</tbody>
</table>

**Sulfate Ion Content**

The following describes the steps required to determine sulfate ion gravimetrically.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pipette 50 mL of the filtered sample into a 250 mL beaker.</td>
</tr>
<tr>
<td>Step</td>
<td>Instruction</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
</tr>
<tr>
<td>2</td>
<td>Add 10 mL of concentrated hydrochloric acid to the sample.</td>
</tr>
<tr>
<td>3</td>
<td>Heat the sample on a hot plate to near boiling.</td>
</tr>
<tr>
<td>4</td>
<td>Add 25 mL of barium chloride solution and continue to heat the solution for 10 min.</td>
</tr>
<tr>
<td>5</td>
<td>Remove the sample from the hot plate. Allow the sample to cool at room temperature for 15 min.</td>
</tr>
</tbody>
</table>
| 6    | Filter the samples.  
  ♦ Set up an Erlenmeyer flask and funnel with a No. 42 filter paper.  
  ♦ Decant the solution through the No. 42 filter paper to catch the precipitate.  
  ♦ Wash the precipitate with hot water until the washings are free of chlorides.  
  NOTE: Test for chlorides by adding 1 to 2 drops of the filtrate to approximately 2 mL of the 0.1 N silver nitrate solution. Any turbidity indicates chlorides are present. |
| 7    | Dry the captured sulfates in the filter paper.  
  ♦ Weigh a platinum crucible on an analytical balance.  
  ♦ Record the mass to the nearest 0.0005 g.  
  ♦ Carefully fold the filter paper with the precipitate and place in the crucible.  
  ♦ Dry the crucible in a 212°F (100°C) oven for at least 1 hr. |
| 8    | Burn off the filter paper using a Meeker burner.  
  ♦ Set up the Meeker burner with gas and air.  
  ♦ Adjust the gas and airflow to obtain a bright blue flame.  
  ♦ Using heat-resistant tongs, slowly char the filter paper in the crucible to a white ash residue.  
  NOTE: Be careful not to let any of the sample blow out of the crucible. |
| 9    | Place the crucible with the residue into the muffle furnace at a temperature of 1,472 to 2,012°F (800 to 1100°C) for 1 hr. |
| 10   | Using heat-resistant tongs, remove the crucible from the muffle furnace.  
  ♦ Place the crucible into a desiccator.  
  ♦ Allow the crucible to cool to room temperature. |
| 11   | Using an analytical balance, weigh the crucible to the nearest 0.0005 g. |
| 12   | Determine the concentration of sulfate ions in the original soil sample as indicated under ‘Calculations.’ |

### Calculations

Use the following calculations to determine chloride and sulfate concentrations.

**Chloride Ion Concentration**

\[
ppm \text{ Chloride} = \frac{3.5433 \times N \times V \times A \times (10,000)}{S}
\]

Where:

- N = normality of silver nitrate (AgNO₃)
- V = volume of AgNO₃ in milliliters
- A = aliquot factor
- S = sample weight in grams
Sulfate Ion Concentration

\[
ppm \text{ Sulfate} = \frac{41.15 \times RA \times 10,000}{S}
\]

Where:

- R = residue weight in grams
- A = aliquot factor
- S = sample weight in grams.
Section 5

Archived Versions

Archived versions of "Tex-620-J, Determining Chloride and Sulfate Content in Soils" are available through the following links:

♦ Click on 620-0899 for the test procedure effective August 1999 through July 2002.
♦ Click on 620-0802 for the test procedure effective August 2002 through July 2005.