Test Procedure for

ANALYSIS OF WATER FOR CHLORIDE AND SULFATE IONS

TxDOT Designation: Tex-619-J
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1. SCOPE

1.1 Use this method to analyze water for chloride and sulfate ions to determine its suitability for concrete, sprinkling, or similar uses. The two procedures described are:

- Part I—Ion Chromatography
- Part II—Wet Chemical.

1.2 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.

2. SAMPLE PREPARATION

2.1 Apparatus:

2.1.1 Erlenmeyer flask, 500 mL.

2.1.2 Filter paper, No. 2, 7.4 in. (185 mm) in diameter.

2.1.3 Gravity filtration funnel, ribbed.

2.2 Water Filtering:

2.2.1 Set up a 500-mL Erlenmeyer flask.

2.2.2 Place a funnel on top of the flask.

2.2.3 Fold and place a No. 2 size filter paper in the funnel.

2.2.4 Filter at least 200 mL of water into the Erlenmeyer flask.
PART I—ION CHROMATOGRAPHY METHOD

3. SCOPE

3.1 This method, for the determination of chloride and sulfate ions in water by chromatography, is similar to the method described in ASTM D 4327. Interferences in this method are the same as discussed in ASTM D 4327.

4. APPARATUS

4.1 *Flasks*, class A volumetric, each with stoppers and the following capacities:
   - 100 mL
   - 500 mL
   - 1000 mL.

4.2 *Ion chromatograph*, with an auto sampler.

4.3 *Pipettes*, class A volumetric, with the following capacities:
   - 1 mL
   - 10 mL
   - 25 mL
   - 50 mL.

4.4 *Vials*, 5 mL, and caps for auto sampler.

5. REAGENTS

5.1 *Certified anion standard reference solution*, containing 100 parts per million (ppm) chloride and sulfate.

5.2 *Deionized or distilled water*, meeting ASTM D 1193, Type II requirements.

5.3 *Sodium bicarbonate eluent concentration*, for ion chromatograph. The concentration of the eluent after 100× dilution should be 8.0 mM sodium carbonate and 1.0 mM sodium bicarbonate.

6. CALIBRATION

6.1 Prepare 6–8 standards using the anion standard solution.

   **Note 1**—The standards should range from 0.1–100 ppm.

6.1.1 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, and dilute to the mark.
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, and dilute to the mark.

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, and dilute to the mark.

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, and dilute to the mark.

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, and dilute to the mark.

The 100-ppm standard needs no dilution.

Ensure the standards are wellmixed.

Set up the ion chromatograph and run the standards according to the manufacturer’s instructions.

Using the results, create a calibration curve for chloride and sulfate ions.

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**7. CHLORIDE AND SULFATE CONTENTS**

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 2**—This dilutes the sample by a factor of 10. If very high concentrations are suspected, it may be necessary to make a larger dilution (e.g., dilution factor of 20, 100).

Follow the manufacturer’s instructions to start the ion chromatograph’s pump and electronic systems. Pump eluent through the column and detector until the ion chromatograph obtains a stable baseline.

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.

Run the samples through the ion chromatograph to determine the concentration of the chloride and sulfate ions.

**Note 3**—Follow the manufacturer’s recommendation for ion chromatograph operation.

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.
8. CALCULATIONS

8.1 Calculate dilution factor:

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

Where:
\( DF \) = dilution factor
\( V_d \) = volume of the flask used for dilution, mL
\( V_p \) = volume of the pipette used to make the dilution, mL.

8.2 Calculate 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, ppm
\( DF \) = dilution factor used.

8.2.1 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:

\[ S_c = \frac{100}{500 / 10} \rightarrow S_c = 2 \text{ ppm} \]

8.3 Calculate concentration of chloride ions in the original water sample:

\[ Cl = R \times DF \]

Where:
\( Cl \) = concentration of chloride ions in the original water sample, ppm
\( R \) = concentration of chloride ions in the sample run through the ion chromatograph, ppm
\( DF \) = dilution factor.
8.4 Calculate concentration of sulfate ions in the original water sample:

\[ SO_4 = R \times DF \]

Where:
- \( SO_4 \) = concentration of sulfate ions in the original water sample, ppm
- \( R \) = concentration of sulfate ions in the sample run through the ion chromatograph, ppm
- \( DF \) = dilution factor.

PART II—WET CHEMICAL METHOD

9. SCOPE

9.1 Interferences may occur in both methods. Refer to ASTM D 512 and ASTM D 516 for interferences in the wet chemical method and the methods of treating them.

10. APPARATUS

10.1 *Analytical balance*, Class A in accordance with Tex-901-K.

10.2 *Beakers*, with the following capacities:
- 200 mL, tall-form
- 250 mL
- 500 mL.

10.3 *Burette*, 50 mL.

10.4 *Desiccator*.

10.5 *Drop-dispensing bottles*.

10.6 *Erlenmeyer flask*, 500 mL.

10.7 *Filter paper*, No. 42 (ashless).

10.8 *Flask*, class A volumetric, 500-mL capacity, with stopper.

10.9 *Graduated cylinders*, with the following capacities:
- 10 mL
- 25 mL
- 50 mL
- 100 mL.
10.10 *Gravity filtration funnel,* ribbed.
10.11 *Heat-resistant tongs.*
10.12 *Hot plate.*
10.13 *Magnetic stirrer.*
10.14 *Meeker burner.*
10.15 *Muffle furnace,* capable of maintaining temperatures of 1,472–2,012°F (800–1100°C).
10.16 *Oven,* capable of maintaining a temperature of 212°F (100°C).
10.17 *pH meter,* with an accuracy of ± 0.1 pH or better, with automatic temperature compensation or pH paper, range 8 to 9.
10.18 *Pipette,* class A volumetric, 50-mL capacity.
10.19 *Platinum crucible.*

11. **REAGENTS**

11.1 All reagents must be American Chemical Society (ACS) reagent-grade.
   - *Barium chloride,* anhydrous
   - *Hydrochloric acid,* 37%
   - *Nitric acid,* 70%
   - *Potassium chromate indicator*
   - *Silver nitrate*
   - *Sodium chloride*
   - *Sodium hydroxide,* 1 N
   - *Deionized or distilled water,* meeting ASTM D 1193, Type II requirements.

12. **SOLUTIONS**

12.1 *Silver Nitrate (0.1 N):*
12.1.1 On a balance, weigh 17 ± 0.5 g of silver nitrate powder.
12.1.2 In a graduated cylinder, measure 1 L of deionized water.
12.1.3 Combine the silver nitrate and deionized water in a 1-L beaker.
12.1.4 Add a stirring magnet and stir on a magnetic stirrer.
12.1.5  Once all of the silver nitrate dissolves, transfer the solution into a 1-L light-protective storage bottle.

12.1.6  Dry approximately 5 g of sodium chloride at 212°F (100°C) for at least 1 hr. Using an analytical balance, weigh 0.2 g of sodium chloride to the nearest 0.0005 g into a tared 200-mL tall-form beaker.

12.1.7  In a graduated cylinder, measure 100 mL of deionized water.

12.1.8  Add the deionized water to the beaker with the sodium chloride.

12.1.9  Add a stirring magnet and stir on a magnetic stirrer.

12.1.10 Once the solution is thoroughly mixed, add 10 drops of potassium chromate indicator to the solution.

12.1.11 Fill a 50-mL burette with the silver nitrate solution and titrate the sodium chloride solution with the silver nitrate to the first color change.

12.1.12 Use the results from the titration to calculate the normality to at least 3 significant digits:

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

Where:
\(N\) = normality of the silver nitrate solution
\(W\) = mass of sodium chloride used for the titration, g
\(V\) = volume of silver nitrate used for the titration, mL.

12.2  Potassium Chromate Indicator:

12.2.1 In a 250-mL beaker, weigh 50 ± 0.5 g of potassium chromate powder.

12.2.2 In a graduated cylinder, measure 100 mL of deionized water.

12.2.3 Add the deionized water to the beaker with the potassium chromate.

12.2.4 Add a stirring magnet to the beaker and stir on a magnetic stirrer.

12.2.5 Once all of the potassium chromate dissolves, transfer the solution into a drop-dispensing bottle.

12.3  Dilute Nitric Acid:

12.3.1 Measure 2 mL of nitric acid in a 10-mL graduated cylinder, and measure 38 mL of deionized water in a 50-mL graduated cylinder.

12.3.2 Combine the deionized water and nitric acid in a 200-mL tall-form beaker.
12.3.3 Add a stirring magnet to the beaker and stir on a magnetic stirrer.
12.3.4 Once the solution is thoroughly mixed, transfer into a drop-dispensing bottle.

12.4 Dilute Sodium Hydroxide:
12.4.1 Measure 5 mL of 1 N sodium hydroxide solution into a 10-mL graduated cylinder, and measure 35 mL of deionized water in a 50-mL graduated cylinder.
12.4.2 Combine the deionized water and the sodium hydroxide in a 200-mL tall-form beaker.
12.4.3 Add a stirring magnet to the beaker and stir on a magnetic stirrer.
12.4.4 Once the solution is thoroughly mixed, transfer into a drop-dispensing bottle.

12.5 Barium Chloride (10%):
12.5.1 In a 500-mL beaker, weigh 50 ± 0.5 g of barium chloride.
12.5.2 Add deionized water to the barium chloride until reaching a total of 500 g of solution.
12.5.3 Add a stirring magnet to the beaker and stir on a magnetic stirrer.
12.5.4 Once all the barium chloride dissolves, transfer the solution into an airtight container.

13. CHLORIDE ION CONTENT
13.1 Tare a 200-mL tall-form beaker on an analytical balance. Weigh 50 g of the filtered sample into the beaker. Record the mass of the sample to the nearest 0.0005 g.
13.2 Using 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.
13.3 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.
13.4 Stir the solution with a magnetic stirrer. Add the silver nitrate drop by drop until a brick-red color persists throughout the sample.
13.5 Determine the chloride ion concentration as indicated under Section 15.

14. SULFATE ION CONTENT
14.1 Tare a 200-mL tall-form beaker on an analytical balance. Weigh 80 g of the filtered sample into the beaker. Record the mass of the sample to the nearest 0.0005 g.
14.2 Add 10 mL of concentrated hydrochloric acid to the sample.
14.3 Heat the sample on a hot plate to near boiling.

14.4 Add 25 mL of barium chloride solution and continue to heat the solution for 10 min.

14.5 Remove the sample from the hot plate. Allow the sample to cool at room temperature for 15 min.

14.6 Set up an Erlenmeyer flask and funnel with a No. 42 filter paper. Decant the solution through the No. 42 paper to catch the precipitate. Wash the precipitate with hot water until the washings are free of chlorides.

**Note 4**—Test for chlorides by adding 1–2 drops of the filtrate to approximately 2 mL of the 0.1 N silver nitrate solution. Any turbidity indicates chlorides are present.

14.7 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.

14.8 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 5**—Be careful not to let any of the sample blow out of the crucible.

14.9 Place the crucible with the residue into the muffle furnace set at 1,472–2,012°F (800–1,100°C) for 1 hr.

14.10 Using heat-resistant tongs, remove the crucible from the muffle furnace. Place the crucible in a desiccator. Allow the crucible to cool to room temperature.

14.11 Using an analytical balance, weigh the crucible to the nearest 0.0005 g.

14.12 Determine the concentration of sulfate ions in the original sample as indicated under Section 15.

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15. **CALCULATIONS**

15.1 Calculate chloride ion concentration:

\[
ppm \text{ Chloride} = \frac{3.545 \times V \times N}{10,000} \times \frac{1}{S}
\]

Where:
- \(V\) = volume of silver nitrate solution, mL
- \(N\) = normality of silver nitrate solution
- \(S\) = sample weight, g.
15.2 Calculate sulfate ion concentration:

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

Where:

\[ R = \text{residue weight, g} \]
\[ S = \text{sample weight, g} \]

16. ARCHIVED VERSIONS

16.1 Archived versions are available.