
Test Procedure for**DETERMINING CHLORIDE IN CONCRETE****TxDOT Designation: Tex-617-J****Effective Date: October 2005**

1. SCOPE

- 1.1 Use this method to determine the concentration of water-soluble chloride and sulfate ions in concrete. Part I describes the ion chromatography method, and Part II describes the wet chemical method.
- 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 *Balance*, Class G2 in accordance with Tex-901-K.
- 2.1.2 *Beaker*, 400 mL.
- 2.1.3 *Diamond-tooth saw*, or other means of segmenting concrete cores and producing a smooth cut surface.
- 2.1.4 *Electric hot plate*.
- 2.1.5 *Filter paper*, No. 2, 7.4-in. (185-mm) diameter.
- 2.1.6 *Flask*, class A volumetric, 500-mL capacity, with stopper.
- 2.1.7 *Gravity filtration funnel*, ribbed.
- 2.1.8 *Jaw crusher*, capable of reducing concrete core segments (4-in. diameter, 1-in. height) to pass a No. 10 (2.00 mm) sieve.
- 2.1.9 *Mechanical convection oven*, capable of maintaining $140 \pm 9^\circ\text{F}$ ($60 \pm 5^\circ\text{C}$).
- 2.1.10 *Mechanical pulverizer*, capable of reducing concrete material passing a No. 10 (2.00 mm) sieve to pass a No. 60 (250 μm) sieve.
- 2.1.11 *Sieve*, U.S. Standard, No. 60 (250 μm).
-

2.1.12 *Stirring rod.*

2.1.13 *Wash bottle.*

2.1.14 *Watch glass.*

2.2 *Pulverizing Concrete Cores:*

2.2.1 Use a core bit to obtain 4-in. (102-mm) diameter concrete core samples. Remove any asphaltic overlay material from the surface of the core. Use the cleaned face as a reference plane for subsequent core segmenting. Use mark guides around the core's circumference at exactly 1 in. (25 mm) and 2 in. (51 mm) from the core surface. Make adjustments for cores that contain steel reinforcing bar segments. Cut the cores into segments with faces parallel to the core surface such that the saw blade cuts through the center of the guide markings. Use water to lubricate and cool the saw blade without leaching the salts.

Note 1—Each core segment is a separate sample.

2.2.2 Towel dry each core segment. Place the core segments in the 140°F (60°C) oven and dry for at least 24 hr.

2.2.3 Crush each sample in the jaw crusher separately. The crushed sample should be able to pass through a No. 10 (2.00 mm) sieve. Grind the crushed segment in the pulverizer. The ground sample should be able to pass through a No. 60 (250 µm) sieve. Shake the powder from each sample by hand through the No. 60 (250 µm) sieve. Place each sieved sample into a labeled container.

Note 2—Ensure that cross-contamination does not occur during the grinding and sieving process.

2.3 *Leaching Samples:*

2.3.1 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.

2.3.2 Place the samples on a $150 \pm 20^\circ\text{F}$ ($66 \pm 11^\circ\text{C}$) 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 8 hr. digestion time.

Note 3—Be careful not to boil samples, and ensure that no sample solution is lost.

2.3.3 Set up a 500-mL volumetric flask for each sample solution. Place a funnel on top of each flask. Fold and place a no. 2 size filter paper in each funnel.

2.3.4 Using 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 4—Test the filtrate for chloride by adding one to two drops of filtrate from the funnel to dilute silver nitrate solution. Any turbidity indicates chlorides present.

2.3.5 Cool the solution to $77 \pm 2^\circ\text{F}$ ($25 \pm 1^\circ\text{C}$).

2.3.6 Fill the flask to the volumetric mark with deionized water.

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, and
- 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, and
- 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 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.

6. CALIBRATION

- 6.1 Prepare six to eight standards using the anion standard solution.
Note 5—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.
- 6.1.2 To prepare a 1.0-ppm standard, use a 1-mL pipette to transfer a 1-mL aliquot of the anion standard solution to a 100-mL volumetric flask, and dilute to the mark.
- 6.1.3 To prepare a 10-ppm standard, use a 10-mL pipette to transfer a 10-mL aliquot of the anion standard into a 100-mL volumetric flask, and dilute to the mark.
- 6.1.4 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.
- 6.1.5 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.
- 6.1.6 The 100-ppm standard needs no dilution.
- 6.2 Ensure the standards are well mixed.
- 6.3 Set up the ion chromatograph and run the standards according to the manufacturer's instructions.
- 6.4 Using the results, create a calibration curve for chloride and sulfate ions.

7. CHLORIDE AND SULFATE CONTENT

- 7.1 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 6—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).
- 7.2 Follow the manufacturer's instructions to start ion chromatograph's pump and electronic systems. Pump eluent through the column and detector until the ion chromatograph obtains a stable baseline.
- 7.3 Pour samples into properly labeled sample vials. Run one prepared standard and one deionized water blank after every four to five samples to check the accuracy of the chromatograph.
- 7.4 Run the samples through the ion chromatograph to determine the concentration of the chloride ions.
Note 7—Follow the manufacturer's recommendation for ion chromatograph operation.

- 7.5 Obtain the chloride and sulfate contents in ppm as determined by the ion chromatograph. Use conversion factors to convert back to 1 lb./cu. yd. of original concrete 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:

$$S_c = \frac{100}{(500/10)} = 2 \text{ ppm}$$

- 8.3 Calculate concentration of chloride ions in the original concrete sample:

$$Cl = \frac{R \times DF \times Fl}{W}$$

Where:

Cl = concentration of chloride ions in the original concrete sample, ppm

R = concentration of chloride ions in the sample run through the ion chromatograph, ppm

DF = dilution factor

Fl = volume of the flask containing undiluted sample, mL

W = weight of the original concrete sample, g.

- 8.4 Calculate pounds of chloride per cubic yard of concrete:

$$P = \frac{Cl \times D_c}{1,000,000}$$

Where:

P = pounds of chloride per cubic yard of concrete

Cl = concentration of chloride ions in the original concrete sample, ppm

D_c = density of concrete = 4,000 lb./cu. yd.

- 8.5 Calculate concentration of sulfate ions in the original concrete sample:

$$SO_4 = \frac{R \times DF \times Fl}{W}$$

Where:

SO_4 = concentration of sulfate ions in the original concrete sample, ppm

R = concentration of sulfate ions in the sample run through the ion chromatograph, ppm

DF = dilution factor

Fl = volume of the flask containing undiluted sample, mL

W = weight of the original concrete sample, g.

- 8.6 Calculate pounds of sulfate per cubic yard of concrete:

$$P = \frac{SO_4 \times D_c}{1,000,000}$$

Where:

P = pounds of sulfate per cubic yard of concrete

SO_4 = concentration of sulfate ions in the original concrete sample, ppm

D_c = density of concrete (4,000 lb./cu. yd.).

PART II—WET CHEMICAL METHOD

9. SCOPE

- 9.1 Interferences may occur for both chloride and sulfate determinations. For the chloride determination, assume that errors in the silver nitrate titration due to interfering substances in concrete are negligible. The equations in this procedure use instrument-specific constants, which may not be applicable to different equipment. For sulfate determination, refer to ASTM D 516 for interferences and the methods of treating them.

10. APPARATUS

- 10.1 *Beaker*, with the following capacities:
- 200 mL, tall-form,
 - 250 mL,
 - 500 mL, and
 - 1 L.
- 10.2 *Burette*, class A volumetric, 50-mL capacity.
- 10.3 *Desiccator*.
- 10.4 *Drop-dispensing bottles*.
- 10.5 *Erlenmeyer flask*, 500 mL.
- 10.6 *Filter paper*, No. 42 (ashless).
- 10.7 *Flask*, class A volumetric, 500-mL capacity, with stopper.
- 10.8 *Funnel*.
- 10.9 *Heat-resistant tongs*.
- 10.10 *Hot plate*.
- 10.11 *Ion meter*, with chloride-selective ion electrode.
- 10.12 *Magnetic stirrer*.
- 10.13 *Meeker burner*.
- 10.14 *Muffle furnace*, capable of maintaining 1,472–2,012°F (800–1100°C).
- 10.15 *Oven*, capable of maintaining 212°F (100°C).
- 10.16 *Pipette*, class A volumetric, 50-mL capacity.
- 10.17 *Platinum crucible*.
- 10.18 *Stirring magnets*.
- 10.19 *Graduated cylinder*, with the following capacities:
- 10 mL,
 - 25 mL,
 - 50 mL,

- 100 mL, and
- 1 L.

10.20 *Light protective storage bottle, 1-L capacity.*

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

11. REAGENTS

11.1 All reagents must be American Chemical Society (ACS) reagent-grade.

- *Barium chloride, anhydrous*
- *Deionized or distilled water, meeting ASTM D 1193, Type II requirements*
- *Ethanol, 60% by volume*
- *Hydrochloric acid, 37%*
- *Methyl red*
- *Nitric acid, 70%*
- *Reference chloride ion selective electrode outer filling solution, 10% KNO₃*
- *Reference chloride ion selective electrode inner filling solution*
- *Silver nitrate*
- *Potassium chromate indicator*
- *Sodium chloride*

12. SOLUTIONS

12.1 *Barium Chloride:*

12.1.1 In a 500-mL beaker, weigh 50 ± 0.5 g of barium chloride.

12.1.2 Add deionized water to the barium chloride until achieving a total of 500 g of solution.

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

12.1.4 Once all the barium chloride dissolves, transfer the solution into an airtight container.

12.2 *Methyl Red Indicator Solution:*

12.2.1 Weigh 0.1 ± 0.05 g of methyl red powder into a tared 200-mL, tall-form beaker.

12.2.2 In a 50-mL graduated cylinder, measure 50 mL of ethanol.

12.2.3 Add the ethanol to the beaker with the methyl red powder.

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

- 12.2.5 Once the solution is thoroughly mixed, transfer 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 *Silver Nitrate:*
- 12.4.1 Weigh 1.7 ± 0.05 g of silver nitrate powder.
- 12.4.2 Measure 1 L of deionized water in a graduated cylinder.
- 12.4.3 Combine the silver nitrate and deionized water in a 1-L beaker.
- 12.4.4 Add a stirring magnet and stir on a magnetic stirrer.
- 12.4.5 Once all of the silver nitrate dissolves, transfer the solution into a 1-L light-protective storage bottle.
- 12.4.6 Dry approximately 5 g of sodium chloride at 212°F (100°C) for at least 1 hr. Weigh 0.02 g of sodium chloride to the nearest 0.0005 g into a tared 200-mL, tall-form beaker.
- 12.4.7 In a graduated cylinder, measure 100 mL of deionized water.
- 12.4.8 Add the deionized water to the beaker with the sodium chloride.
- 12.4.9 Add a stirring magnet and stir on a magnetic stirrer.
- 12.4.10 Once the solution is thoroughly mixed, add ten drops of potassium chromate indicator to the solution.
- 12.4.11 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.
- 12.4.12 Use the results from the titration to calculate the normality of the solution to at least three 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.

13. CHLORIDE ION CONTENT

13.1 *Discussion of Method:*

13.1.1 This method is based on the constant response slope of a chloride ion selective electrode to increasing concentration.

13.1.2 Record the initial millivolt (mV) response of the probe for each sample.

13.1.3 Titrate one of the samples with silver nitrate to determine its chloride concentration.

13.1.4 Compare the mV responses of the titrated sample to the other samples.

13.1.5 Knowing the response slope of -56 mV per decade, calculate the concentrations of the rest of the samples.

13.2 *Initial Millivolt Readings:*

13.2.1 Ensure the level of the filling solutions in the ion meter's reference electrode chamber is adequate. Fill the reference electrode chamber with the appropriate filling solutions if the solution levels are low. Rinse and towel dry the electrode surfaces. Place the electrodes in a beaker of deionized water. Turn on the ion meter and place controls in the mV readout setting. Allow the mV reading to stabilize by coming to a constant value or a net change of 0.1 mV in no less than 5 sec.

13.2.2 Transfer 50 ± 5 mL of solution to a clean, dry 200-mL, tall-form beaker. Stir the sample with a magnetic stirring bar. Add three to four drops of methyl red indicator solution to the sample. Add the nitric acid solution drop by drop to the sample until a pale pink color persists throughout the solution.

13.2.3 Rinse the electrode surfaces in deionized water. Towel dry the electrode surfaces and immerse the electrodes in the sample solution. Allow the mV reading to stabilize by coming to a constant value or a net change of 0.1 mV in no less than 5 sec. Record the mV readings as the initial mV reading for the sample.

13.2.4 Remove and rinse the electrodes with deionized water. Turn off the magnetic stirrer and discard the sample.

13.2.5 Repeat Sections 13.2.2–13.2.4 for the rest of the samples.

Note 8—Place the electrodes in deionized water when not in use.

13.3 *Silver Nitrate Titration:*

- 13.3.1 Out of the batch of samples, choose the sample with the lowest mV response. Use this sample in the silver nitrate titration analysis.
- 13.3.2 Using a volumetric pipette, place 50 mL of the sample into a clean, dry 200-mL, tall-form beaker. Stir the solution with a magnetic stirring bar. Add three to four drops of methyl red indicator solution. Add the nitric acid solution, drop by drop, to the sample until a pale pink color persists throughout the solution. Fill a 50-mL burette with the 0.01 N silver nitrate solution. Set up a burette and the sample for a titration.
- 13.3.3 Refill the ion meter's electrodes, if necessary. Ensure the ion meter is on and stabilized in deionized water.
- 13.3.4 Immerse the electrodes in the sample solution and stir. Allow the mV reading to stabilize. Record this as the sample initial mV reading.
- 13.3.5 Repeat the following steps to titrate the solution with silver nitrate. Stop titrating after reaching the endpoint:
- 13.3.5.1 Zero the ion meter.
- 13.3.5.2 Add approximately 0.2 mL of the silver nitrate solution to the sample.
- 13.3.5.3 Allow the mV reading to stabilize.
- 13.3.5.4 Record the mV reading and the amount of silver nitrate added.
Note 9—The endpoint occurs at the greatest mV reading. Perform at least two additions after the endpoint. If the endpoint is not reached within 50 mL, stop the analysis and reanalyze with 0.1 N silver nitrate solution.
- 13.3.6 Use the titration data to determine the chloride ion content in all of the solutions. Use the calculations listed under Section 15.
- 13.4 *Endpoints:*
- 13.4.1 After completing the titration, construct a table with the resulting data as shown in Table 1.

Table 1—Titration Result Example

Titrant Volume (mL)	mV	DmV	D ² mV
4.0	220.5	9.6	---
4.2	230.1	16.2	+6.6
4.4	246.3	26.5	+10.3
4.6	272.8	22.7	-3.8
4.8	295.5	12.9	-9.8
5.0	308.4	---	---

- 13.4.2 The endpoint is located where D²mV equals zero. Determine this point graphically or by linear interpolation using one point on either side of zero as shown in Table 2.

Table 2—Endpoint Location

Volume (mL)	D ² mV
4.4	+10.3
4.6	3.8

- 13.4.3 Using the points from Table 2, the total change in volume is:

$$\Delta V = 0.2 \text{ mL}$$

- 13.4.4 By interpolation, the volume at the endpoint is:

$$\text{Endpoint} = 4.4 \text{ mL} + 0.2 \text{ mL} \left(\frac{10.3}{10.3 + 3.8} \right) = 4.4 \text{ mL} + 0.146 \text{ mL}$$

$$\text{Endpoint} = 4.55 \text{ mL}$$

- 13.4.5 Use the endpoint volume as the silver nitrate volume in Section 15. The accuracy of the method allows determining of the endpoint to the nearest 0.05 mL.

14. SULFATE ION CONTENT

- 14.1 Pipette 50 mL of the filtered sample into a 250-mL beaker.
- 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. 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 a 500-mL 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 10—Test for chlorides by adding one to two drops of the filtrate to approximately 2 mL of the 0.01 N silver nitrate solution. Any turbidity indicates that 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 11—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 at a temperature of 1,472–2,012°F (800–1100°C) for 1 hr.
- 14.10 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.
- 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 soil sample as indicated under Section 15.

15. CALCULATIONS

- 15.1 Calculate percent chloride by weight in the standardizing solution:

$$C_s = \frac{35.453 AVN}{1000 W} (100)$$

Where:

C_s = chloride concentration in standardizing solution in percent by weight

35.453 g/mol = chloride molecular weight

$$A = \text{Aliquot factor} = \frac{500\text{mL}}{50\text{mL}} = 10$$

V = volume of silver nitrate solution, mL

N = normality of silver nitrate solution (equivalents/L)

W = original concrete sample weight, g.

- 15.2 Calculate chloride concentration in the test samples:

$$C_x = C_s (10^{\Delta E/S})$$

Where:

C_x = chloride concentration in samples in percent by weight

C_s = chloride concentration in standardizing solution in percent by weight

ΔE = Initial mV_x - Initial mV_s = Difference in initial mV readings

S = electrode response slope (mV_s per decade).

- 15.3 Calculate pounds of chloride per cubic yard of concrete:

$$P = \frac{C_x D_c}{100}$$

Where:

P = pounds of chloride per cubic yard of concrete

C_x = chloride concentration in samples in percent by weight

D_c = Density of concrete (4,000 lb./cu. yd.)

- 15.4 Calculate concentration of sulfate ions in the original concrete sample:

$$SO_4 = \frac{41.15 RA (10,000)}{S}$$

Where:

SO_4 = concentration of sulfate ions in the original concrete sample, ppm

R = residue weight, g

A = Aliquot factor

S = sample weight, g.

- 15.5 Calculate pounds of sulfate per cubic yard of concrete:

$$P = \frac{SO_4 \times D_c}{1,000,000}$$

Where:

P = pounds of sulfate per cubic yard of concrete

SO_4 = concentration of sulfate ions in the original concrete sample, ppm

D_c = density of concrete (4,000 lb./cu. yd.)

16. ARCHIVED VERSIONS

- 16.1 Archived versions are available.