FLORIDA DEPARTMENT OF TRANSPORTATION
State Materials Office
5007 NE 39th Avenue
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March 30, 2023

Florida Method of Test For Determining Low-Levels of Chloride in Concrete and Raw Materials

Designation: FM 5-516

1. SCOPE

This method covers the determination of total chloride content in cement, fine aggregate, coarse aggregate, and concrete. The method is applicable to chloride contents lower than 100 parts per million (about 0.40 lb./yd^3) but will accurately measure contents as high as 625 ppm (about 2.5 lb./yd^3).

2. REFERENCED DOCUMENTS

ASTM C670 – Standard Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials

ASTM E288 – Standard Specification for Laboratory Glass Volumetric Flasks

ASTM E237 – Standard Specification for Laboratory Glass Microvolumetric Vessels (Volumetric Flasks and Centrifuge Tubes)

ASTM E969 – Standard Specification for Glass Volumetric (Transfer) Pipets

ASTM C702 – Standard Practice for Reducing Samples of Aggregate to Testing Size

3. APPARATUS

3.1 Crushing and pulverizing apparatus capable of grinding a sample to pass a No. 50-sieve.

3.2 Analytical balance capable of weighing a sample with a precision of 0.1 mg.

3.3 Hot plate with a heating surface temperature of at least 250°C.

3.4 Glassware:

3.4.1 100-mL and 250-mL beakers.

3.4.2 2,000-mL, 1,000-mL, 500-mL, 100-mL, 50-mL, 30-mL, 10-mL, and 5-mL volumetric flasks (Class A, **ASTM E288/E237**).

3.4.3 50-mL 10-mL, 3-mL, and 1-mL transfer pipets (Class A, **ASTM E969**).

3.4.4 Watch glasses.

3.4.5 Filter glass funnels.

3.4.6 250-mL (Class A) graduated cylinder.

3.5 Glass Stirring Rods.

3.6 Mesh sieves: No. 50 and No. 20.

3.7 Filter paper: No. 41 filter paper, 0.007% maximum ash content, 20 µm pore size. Paper should be checked for chloride content before using.

3.8 Magnetic stirrer and Polytetrafluoroethylene (PTFE) coated stir bar.

3.9 Bottle top dispensers and bottles:

3.9.1 0.50-mL dispensing capacity accuracy within ± 2%; coefficient of variation less than or equal to 0.4%, two required. Brown glass reservoir bottles are required.

3.9.2 35.0-mL dispensing capacity accuracy within ± 2%; coefficient of variation less than or equal to 0.4%. Glass reservoir bottle is required.

3.9.3 5.0-mL dispensing capacity accuracy within ± 2%; coefficient of variation less than or equal to 0.4%. Glass reservoir bottle is required.

3.10 Chloride ion or silver/sulfide ion-selective electrode with manufacturer's recommended filling solutions replaced at the recommended intervals.

3.11 Ion specific electrode/mV meter with a 0.1 mV resolution compatible with electrode in 3.10.

3.12 Wash bottles.

3.13 Lint-free tissue.

3.14 Software, spreadsheet(s), or other means to calculate end points, chloride concentrations, and quality control limits.

Notes: 1) It is the laboratory's discretion to use either volumetric flask or transfer pipet. 2) Laboratories using a chloride auto titration system can use alternative apparatus providing it meets or exceeds specifications stated above.

4. REAGENTS

4.1 5% Nitric Acid (HNO_3) Solution: Prepare this solution under a chemical fume hood. DO NOT ADD WATER TO ACID. Fill half of a 2,000-mL volumetric flask with deionized water. Measure 150 mL of concentrated (~70%) HNO_3 using a 250-mL graduated cylinder. Slowly add HNO_3 to the deionized water. dilute to volume with deionized water. Mix well.

4.2 0.1 N Silver Nitrate (0.1 N $AgNO_3$) Solution: Weigh 16.987 g of reagent grade $AgNO_3$ and transfer to a 1,000-mL volumetric flask. Add enough deionized water to the flask to dissolve the $AgNO_3$, then dilute to volume with deionized water and mix thoroughly. Alternately, obtain a 0.1 N $AgNO_3$ standard solution from a reputable supplier.

4.3 0.01 N Silver Nitrate (0.01 N $AgNO_3$) Solution: Transfer 50.0 mL of 0.1 N $AgNO_3$ into a 500-mL volumetric flask. Dilute to volume with deionized water. Prepare fresh each week.

Note: Store silver nitrate solutions in a cabinet in a brown, chemically resistant bottle away from any light source. $AgNO_3$ solutions will deteriorate when exposed to light, so a dark storage place is essential for stability. Evaporation of water from solution will tend to concentrate the $AgNO_3$ over time.

4.4 Low-Level Ionic Strength Adjuster (ISA) Solution: Weigh 15.0 g of reagent grade potassium nitrate (KNO_3) and transfer to a 100-mL volumetric flask. Dissolve with deionized water and dilute to 100 mL. Mix well. Store in a chemically resistant bottle.

4.5 1,000 ppm Chloride Standard Solution: Dry reagent grade NaCl for 2 hours in an oven at 140 °C. Cool in a desiccator. Weigh 1.649 g, of dried NaCl and transfer to a 1,000-mL volumetric flask. Dissolve with deionized water and dilute to volume. Mix well. Store in a chemically resistant bottle. Alternatively, obtain a 1,000 mg/L reagent grade chloride standard solution. Use this standard solution to calibrate the electrode.

4.6 100 ppm Chloride Standard Solution: Transfer 10.0 mL of the NIST-traceable 1,000 mg/L chloride standard solution to a 100-mL volumetric flask and dilute to volume with deionized water. Mix well. Use this 100 ppm chloride standard solution to prepare a 3.00 ppm Chloride Check Sample (CCS). Store in a chemically resistant bottle.

4.7 10 ppm chloride solution: Transfer 10.0 mL of 100 ppm chloride standard solution into a 100-mL volumetric flask and add deionized water to bring up to volume. Mix Well. Use this solution to identify the voltage potential threshold for determining which titrant concentration should be used to analyze a sample. Typically, this only needs to be done one time.

5. SAMPLE PREPARATION

5.1 Hardened Concrete: A concrete sample should be approximately 650 cm^3 (40 in^3) comparable to a half filled 10x20 cm (4x8 in) standard cylinder mold. A core obtained from a concrete element is acceptable and should be at least 5 cm (2 in) in diameter. Crush the sample such that the largest particles are no larger than 1.3 cm (0.5 in) in diameter. Reduce the sample size down to approximately 400 g in accordance with **ASTM C702**. Dry the sample in an oven at 110°C (230°F) for 4 hours or until constant mass is achieved. After the sample has dried, pulverize the material until the entire sample will pass a No. 50 sieve.

5.2 Aggregates: A coarse aggregate sample should be approximately 3 kg (7 lb.). A fine aggregate sample should be approximately 2 kg (5 lb.). Reduce the aggregate sample to approximately 400 g (14 oz). If the aggregate is larger than 1.3 cm (0.5 in) in diameter, first crush the sample. Dry the sample in an oven at 110°C (230°F) for 4 hours or until constant mass is achieved. After the sample has dried, pulverize the material until the entire sample will pass a No. 50 sieve.

5.3 Cement: The cement field sample should fill a 2,000-mL container (half gallon can). Pass the sample through a No. 20 sieve to mix the sample, break up lumps, and remove foreign materials.

5.4 Chloride Check Sample (CCS): Transfer 3.00 mL of 100 ppm chloride standard solution into a 100-mL volumetric flask and add deionized water to bring up to volume. To prepare the CCS in bulk, transfer 30.0 mL of 100 ppm chloride standard solution to a 1,000-mL volumetric flask and add deionized water to bring to volume. Mix well. Store in a chemically resistant bottle.

5.5 Laboratory Control Sample (LCS): Prepare both a hardened concrete and cement LCS with chloride content near 0.1 lb./yd^3 as described in 5.1 and 5.3, respectively, in sufficient quantity for routine monitoring of method performance over the course of one or more years.

5.6 Storage: Store the powdered samples in chemically inert covered containers that are clean and dry.

6. PROCEDURE

6.1 Sample Weighing:

6.1.1 Cementitious Materials: Use a watch glass to weigh each sample of material in triplicate as shown in **Table 1**. Transfer samples to 100 mL beakers.

Table 1. Mass of Cementitious Material

Material	Mass, g
Cement	2.0000 (±0.0005)
Grout *	2.5000 (±0.0005)
Concrete	4.0000 (±0.0005)
* pH should be verified to be between 2 and 9 prior to titration. Increase mass if necessary to raise pH into proper range.	

6.1.2 Aggregate Materials: Prior to weighing samples, place a watch glass under the chemical hood and add approximately 0.5 g of sample followed by a few drops of 5% HNO_3. If aggregate fails to froth with the addition of acid, use a watch glass to weigh each sample in triplicate by weighing 3.0000 (±0.0005) g of material with 2.0000 (±0.0005) g of cement LCS. If aggregate froths, prepare each sample in triplicate by weighing 3.0000 (±0.0005) g of material. Transfer samples to 100 mL beakers.

6.2 Sample Digestion:

Dispense 5.0 mL of deionized water to each beaker. Slowly add 35.0 mL of 5% HNO3 to each beaker using a dispenser (care should be exercised to avoid excessive frothing). Use a clean glass rod for each sample to mix thoroughly. Stir until there is no more frothing. Place watch glasses on the beakers and place the beakers on the hot plate. Heat the samples over medium heat (a minimum of 250˚C (482˚F)) until they boil. Allow to boil for 3 to 5 minutes.

Note: Samples that contain blast furnace slag have significant levels of sulfides. Sulfide ions will interfere with the operation of the electrodes and may cause erroneously high chloride results. These samples can be detected after adding the deionized water and 5% HNO_3 to the sample due to the emission of a sulfur smell. Prior to boiling, add 1-2 mL of concentrated HNO_3 to drive the sulfide ions off as hydrogen sulfide. Boil the sample for a total of 10 to 12 minutes.

6.3 Remove beakers from the hot plate. Place a No. 41 filter paper in glass funnel and filter the extract from each beaker into a 100-mL volumetric flask. Using a wash bottle rinse residue from the beaker into the filter. When liquid drains, rinse residue on the filter sides using small portions of hot deionized water making sure not to reach the final mark volume. Allow the sample to cool to room temperature (about 1 hour), then add deionized water to bring to volume.

6.4 Electrode Maintenance: Prior to testing and after every 36 analyses (12 samples) or a lapse in use of more than 1 hour restore and condition the electrode as described in the manufacturer's manual. The following steps may be followed if deemed appropriate:

6.4.1 Polish the electrode tip for 30 seconds. Using the manufacturers recommended solution, thoroughly flush and refill the electrode.

6.4.2 Add 100 mL of deionized water, 1 mL of Low-Level ISA, and 2.5 mL of 0.01N $AgNO_3$ to a 250 mL beaker. Place the beaker on a magnetic stirrer, insert a stir bar and lower the electrode into the solution. Stir at a moderate and constant rate for 10 minutes. Remove and rinse the electrode and stir bar with deionized water. Keep the electrode in a beaker of clean deionized water when not in use.

Note: If the electrode performance is suspect, check the slope of the calibration curve to see if it is within the manufacturer's suggested mV range. Slope is defined as the change in mV observed when the concentration changes by a factor of 10. Add 100 mL of deionized water and 1 mL of Low-Level ISA to a 250 mL beaker. Place the beaker on a magnetic stirrer, insert a stir bar and stir at a moderate and constant rate. With the meter in mV mode, lower the electrode tip into the solution. Using a transfer pipet, add 1 mL of 1,000 mg/L chloride standard solution to the beaker. Once the reading is stable, record the reading. Using a transfer pipet, add 10 mL of 1,000 mg/L chloride standard solution to the beaker. Once the reading is stable, record the reading. If the difference is outside the manufacturer's suggested range, refer to the troubleshooting instructions in the electrode manual.

6.5 Check $AgNO_3$ Dispensers Calibration: Prior to sample analysis and after every 36 analyses (12 samples), dispense ten 0.50-mL aliquots of $AgNO_3$ into a 5-mL volumetric flask and verify the solution volume is at the mark. If the solution volume is above or below the mark, adjust the dispenser setting and re-check.

6.6 Blank Sample: Prior to sample analysis and after every 36 analyses (12 samples), obtain the chloride titration end point for deionized water amended with ISA. Rinse the electrode with deionized water and pat dry with lint-free tissue. Add 1.00 mL of Low-Level ISA to 100 mL of deionized water in a 250-mL beaker. Place the beaker on a magnetic stirrer, insert a stir bar and stir at a moderate and constant rate. Immerse electrode in the solution. Add 1.00 mL of 0.01 N $AgNO_3$ titrant and record the potential. This potential is hereafter referred to as the scaling potential. Make four 0.50-mL additions of titrant, recording the potential and total volume of titrant after each increment. After all titrant additions have been made, remove, and rinse electrode and stir bar with deionized water, and pat dry with lint-free tissue. Keep the electrode in a beaker of clean deionized water when not in use. Determine the end point and verify it is 0 ± 0.100. The end point should also be within the upper control limit (UCL) and lower control limit (LCL) based on a sequential record of at least 25 blank chloride end points. If it is not, and data entries are correct, perform the appropriate electrode maintenance per the manufacturer recommendations and re-run the blank. If samples will be tested with 0.1 N $AgNO_3$, determine the blank end point for 0.1 N $AgNO_3$ by following **Section 6.5** substituting 0.1 N $AgNO_3$ anywhere 0.01 N $AgNO_3$ is specified.

6.7 Chloride Check Sample (CCS): Prior to sample analysis and after every 36 analyses (12 samples), obtain the chloride titration end point for the CCS. Rinse the electrode with deionized water and pat dry with lint-free tissue. Transfer 100 mL of the CCS to a 250-mL beaker and add 1.00 mL of low-level ISA. Place the beaker on a magnetic stirrer, insert a stir bar and stir at a moderate and constant rate. Immerse electrode in the solution. Add 0.01 N $AgNO_3$ titrant in 0.50-mL increments until the scaling potential (determined in **Section 6.5**) is reached or just exceeded. Record the total volume of titrant and the potential. Make four more 0.50-mL additions of titrant and record the potential after each addition. Remove and rinse electrode and stir bar with deionized water, and pat dry with lint-free tissue. Keep the electrode in a beaker of clean deionized water when not in use. Determine the end point and subtract the blank end point to obtain the CCS end point. Determine the concentration in ppm and verify it is within ± 0.15 ppm of 3 ppm. The CCS end point should also be within the upper control limit (UCL) and lower control limit (LCL) based on a sequential record of at least 25 CCS end points. If it is not, prepare fresh reagents or solutions as necessary and re-run the CCS.

6.8 Laboratory Control Sample (LCS): Prior to sample analysis and after every 36 analyses (12 samples), run a LCS sample by the procedures described in **Sections 6.1, 6.2, 6.8, and 6.9**, either a concrete or a cement LCS, as appropriate. Determine the end point and subtract the blank end point to obtain the LCS end point. The LCS end point should be within the upper control limit (UCL) and lower control limit (LCL) based on a sequential record of at least 25 LCS end points; If it is not, prepare fresh reagents or solutions as necessary and re-run the LCS.

6.9 Sample Chloride Determination: Rinse the electrode with deionized water and pat dry with lint-free tissue. Empty the contents of one of the 100-mL volumetric flasks prepared in **Section 6.1 and 6.2** into a 250-mL beaker. Place the beaker on a magnetic stirrer, insert a stir bar and stir at a moderate and constant rate. Immerse electrode in the solution. If the potential is less than what would be measured in a 10-ppm chloride solution, substitute 0.01 N $AgNO_3$ with 0.1 N $AgNO_3$ in **Section 6.9**.

6.10 Add 0.01 N $AgNO_3$ titrant in 0.50 mL increments until the scaling potential determined in **Section 6.5** is reached or just exceeded. Record the total volume of titrant and the potential. Make four more 0.50 mL additions of titrant and record the potential after each addition. Remove and rinse electrode and stir bar with deionized water, then pat dry with lint-free tissue. Keep the electrode in a beaker of clean deionized water when not in use. Determine the end point and subtract the blank end point to obtain the sample end point. Repeat the procedure for remaining replicates.

7. CALCULATIONS

This method utilizes Gran's plotting to determine the titration end point. To determine the chloride concentration of a sample in lbs\yd^3, use the following formula:

$$C = \left(\frac{EP_S * N * 3.5453}{m}\right) * \frac{UW}{100} \qquad (1)$$

where,

C = chloride concentration (lbs./yd^3)
N = normality of the $AgNO_3$ used for the titration
EP_S = sample end point
m = mass of the sample (g)
UW = unit weight of the sample (lbs./yd^3)

If an aggregate sample required the addition of cement LCS material prior to performing the analysis, use the following formulas:

$$C = \left(\frac{EP_f * N * 3.5453}{m}\right) * \frac{UW}{100} \qquad (2)$$

$$EP_f = EP_S - EP_{avgLCS_c} \qquad (3)$$

where,

C = chloride concentration (lbs./yd^3)
N = normality of the $AgNO_3$ used for the titration
EPS = sample end point
$EP_{avgLCSc}$ = average cement LCS endpoint as determined from at least 25 cement LCS end points used to establish the control limits
m = mass of the sample (g)
UW = unit weight of the sample (lbs./yd^3)

If the range of chloride concentrations is greater than 0.080 lb./yd^3 when titrating with 0.01 N $AgNO_3$, or greater than 0.80 lb./yd^3 when titrating with 0.1 N $AgNO_3$, the test is invalid, and the sample should be re-analyzed in triplicate.

8. REPORT

The following information should be reported.

8.1 Unit weight of the sample.

8.2 $AgNO_3$ concentration used for titration.

8.3 Chloride content in lbs./yd^3 for each replicate.

8.4 Range of the replicates.

8.5 Average chloride content for the sample.

9. DISPOSAL OF PROCESS WASTE

Dispose of process waste in accordance with the most stringent local, state, or national regulations.

10. PRECISION AND BIAS STATEMENTS

10.1 Precision:

The multi-laboratory standard deviation of a single test result has been found to be 0.0326 lbs./yd³ for chloride contents below 1.0 lbs./yd³. Therefore, results of two properly conducted tests in two different laboratories on identical

samples are not expected to differ from each other by more than 0.0922 lbs./yd³ for chloride contents below 1.0 lbs./yd³.

The multi-laboratory standard deviation of a single test result has been found to be 0.3243 lbs./yd³ for chloride contents above 1.0 lbs./yd³. Therefore, results of two properly conducted tests in two different laboratories on identical samples are not expected to differ from each other by more than 0.9178 lbs./yd³ for chloride contents above 1.0 lbs./lb./yd³.

These numbers represent the (1s) and (d2s) limits as described in **ASTM C670**.

10.2 Bias:

When experimental results are compared with known values from accurately compounded specimens, the test method is found to have no bias.