



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

Designation: FM 5-516

## 1. SCOPE

- 1.1 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<sup>3</sup>), but will accurately measure contents as high as 625 ppm (about 2.5 lb/yd<sup>3</sup>).

## 2. REFERENCED DOCUMENTS

### 2.1 ASTM Standards:

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 Laboratory 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 50 mesh 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 (min. of 3 each).
- 3.4.2 100-mL volumetric flasks (min. of 3, Class A, ASTM E288).
- 3.4.3 2,000-mL, 1,000-mL, 500-mL, and 5-mL volumetric flasks (1 each; Class A, ASTM E288/E237).
- 3.4.4 10-mL, 3-mL, and 1-mL transfer pipets (Class A, ASTM E969).
- 3.4.5 watch glasses (min. of 3).
- 3.4.6 filter funnels (min. of 3).
- 3.4.7 250-mL graduated cylinder.
  
- 3.5 Mesh sieves: #50 and #20.
  
- 3.6 Filter paper: No. 41 filter paper, 0.007% maximum ash content, 20  $\mu$ m pore size, chloride free. Paper should be checked for chloride content before using.
  
- 3.7 Magnetic stirrer and Polytetrafluoroethylene (PTFE) coated stir bar.
  
- 3.8 Bottletop dispensers:
  - 3.8.1 0.50-mL dispensing capacity accuracy within  $\pm 2\%$ ; coefficient of variation less than or equal to 0.4%, two required. Brown glass reservoir bottles are required.
  - 3.8.2 35.0-mL dispensing capacity accuracy within  $\pm 2\%$ ; coefficient of variation less than or equal to 0.4%. Glass reservoir bottle is required.
  - 3.8.3 5.0-mL dispensing capacity accuracy within  $\pm 2\%$ ; coefficient of variation less than or equal to 0.4%.
  
- 3.9 Chloride ion or silver/sulfide ion-selective electrode with manufacturer's recommended filling solutions replaced at the recommended intervals.
  
- 3.10 Ion specific electrode/mV meter with a 0.1 mV resolution for use with electrodes in 4.9.
  
- 3.11 Software package "Chloride 2011" is available for all FDOT-approved chloride laboratories (Figures 1 and 2). Software calculates chloride content in weight %, ppm, lb/yd<sup>3</sup>, kg/m<sup>3</sup> from electrode measurements.




# FLORIDA DEPARTMENT OF TRANSPORTATION

State Materials Office  
5007 NE 39<sup>th</sup> Avenue  
Gainesville, Florida 32609

September 17, 2018

QualityControlDataEntry

Chloride2011



**Florida Department of Transportation**  
**Corrosion Research Laboratory**

Date: Friday, March 09, 2012 Lab Technician: None

LCS ID #: None LCS Unit Weight [lb/yd<sup>3</sup>]: 3800

CCS Volume [mL]: 100 LCS mass[g]: 4


Blank 0.01N AgNO <sub>3</sub>		Blank 0.1N AgNO <sub>3</sub>		Chloride Check Std.		Lab Control Std.	
Volume Silver Nitrate	Voltage Reading [mV]	Volume Silver Nitrate	Voltage Reading [mV]	Volume Silver Nitrate	Voltage Reading [mV]	Volume Silver Nitrate	Voltage Reading [mV]
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
End Point <input type="text"/>		End Point <input type="text"/>		End Point <input type="text"/>		End Point <input type="text"/>	
<input type="button" value="Show Chart"/>		<input type="button" value="Show Chart"/>		<input type="button" value="Show Chart"/>		<input type="button" value="Show Chart"/>	

Record Number: 181

Figure 1. Chloride 2011 software data fields for quality assurance/quality control (QA/QC) samples.

TitrationDataEntry

Chloride2011



**Florida Department of Transportation**  
**Corrosion Research Laboratory**

Date: Friday, March 09, 2012 Lab Technician: None

Sample ID#: Lab Name: SMO Corrosion Lab

Replicate A		Replicate B		Replicate C		Blank Results		Sample Information	
Volume Silver Nitrate	Voltage Reading [mV]	Volume Silver Nitrate	Voltage Reading [mV]	Volume Silver Nitrate	Voltage Reading [mV]	Blank Selection	Volume Silver Nitrate	Voltage Reading [mV]	Unit Weight [lbs/yd <sup>3</sup> ]
						<input checked="" type="radio"/> 0.01 N <input type="radio"/> 0.1 N			3800
							.00	.00	<input checked="" type="checkbox"/> Powder Mass [g]
							.00	.00	<input type="checkbox"/> Solution Vol. [mL]
							.00	.00	Replicate A 4 [g]
							.00	.00	Replicate B 4 [g]
							.00	.00	Replicate C 4 [g]
							.00	.00	<input type="checkbox"/> LCS Added to Sample?
End Point		End Point		End Point		Blank End Point			

Replicate A Results		Replicate B Results		Replicate C Results		Sample Average		Sample Range	
%Cl	ppm	%Cl	ppm	%Cl	ppm	%Cl	ppm	%Cl	ppm
lb/yd <sup>3</sup>		lb/yd <sup>3</sup>		lb/yd <sup>3</sup>		lb/yd <sup>3</sup>		lb/yd <sup>3</sup>	
Kg/m <sup>3</sup>		Kg/m <sup>3</sup>		Kg/m <sup>3</sup>		Kg/m <sup>3</sup>		Kg/m <sup>3</sup>	

Record Number: 1067

Add/Update Record Previous Screen Print Report Clear

Figure 2. Chloride 2011 software data fields for sample replicates.

#### 4. REAGENTS

- 4.1 5% Nitric Acid (HNO<sub>3</sub>) Solution: Fill a 2,000-mL volumetric flask with 1,800 mL of deionized water. Under a chemical fume hood, measure 150 mL of concentrated (~70%) HNO<sub>3</sub> into a 250-mL graduated cylinder. Slowly add HNO<sub>3</sub> to the deionized water. Do NOT add the water to the acid. Still under the hood, rinse the graduated cylinder with ~50 mL of deionized water (the acid residue will fume) and add the rinsate to the volumetric flask to bring the total solution volume up to 2,000 mL.

- 4.2 0.100 N Silver Nitrate ( $\text{AgNO}_3$ ) Solution: Weigh 16.987 g of reagent grade  $\text{AgNO}_3$  and transfer to a 1,000-mL volumetric flask. Add enough deionized water to the flask to dissolve the  $\text{AgNO}_3$ , then fill to the mark with deionized water and mix thoroughly. Alternately, obtain a 0.100 N  $\text{AgNO}_3$  standard solution from a reputable supplier. Store the solution in a cabinet in an opaque and chemically-resistant bottle away from any light source. Silver nitrate solutions will deteriorate when exposed to light, so a dark storage place is essential for stability. Evaporation of water from silver nitrate solution will tend to concentrate the silver nitrate over time.
- 4.3 0.0100 N Silver Nitrate Solution: Prepare a 1:10 dilution of 0.100 N  $\text{AgNO}_3$  by transferring 50.0 mL of 0.100 N  $\text{AgNO}_3$  from a 50-mL volumetric flask into a 500-mL volumetric flask. Rinse the 50-mL flask several times with deionized water into the 500-mL flask; fill the 500-mL flask to the appropriate mark with deionized water. Prepare fresh each week. Store the solution in a cabinet in an opaque and chemically-resistant bottle away from any light source.  $\text{AgNO}_3$  solutions will deteriorate when exposed to light, so a dark storage place is essential for stability. Evaporation of water from silver nitrate solution will tend to concentrate the  $\text{AgNO}_3$  over time.
- 4.4 Low-Level Ionic Strength Adjuster (ISA) Solution: Weigh 15.0 g of reagent grade potassium nitrate ( $\text{KNO}_3$ ) and dissolve it in 100 mL of deionized water. Store this solution in an opaque and chemically-resistant bottle.
- 4.5 1,000 mg/L Chloride Standard Solution: Dry reagent grade NaCl for 2 hours in an oven at 105 °C. Cool in a desiccator, and once cooled weigh out 1.649 g, dissolve in deionized water, and transfer to a 1,000-mL volumetric flask. Fill to the mark with deionized water. Transfer to a suitable storage container. Alternately, obtain a 1,000 mg/L chloride standard solution from a reputable supplier. Use this standard solution for the electrode calibration curve when needed.
- 4.6 100 mg/L Chloride Standard Solution: Obtain a NIST-traceable 1,000-mg/L chloride standard solution from a reputable source. Prepare a 1:10 dilution by transferring 10.0 mL of the NIST-traceable 1,000 mg/L chloride standard solution to a 100-mL volumetric flask and fill the flask with deionized water up to the mark. Use this 100 mg/L chloride standard solution to prepare a 3.00 mg/L (ppm) chloride check standard (CCS) prior to testing and after every 30 analyses (10 samples) or a lapse in use of more than 1 hour.

## 5. SAMPLE PREPARATION

- 5.1 Hardened Concrete: A concrete field sample should be approximately 650  $\text{cm}^3$  (40  $\text{in}^3$ ) comparable to a half filled 10x20 cm (4x8 in) standard cylinder

mold. 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 sample has dried, pulverize the material until the entire sample will pass a 50-mesh sieve.

- 5.2 **Aggregates:** A coarse aggregate field sample should be approximately 3 kg (7 lb). A fine aggregate sample should be approximately 2 kg (5 lb). Reduce the aggregate field 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 sample has dried, pulverize the material until the entire sample will pass a 50-mesh sieve.
- 5.3 **Cement:** The cement field sample should fill a 2,000-mL container (half gallon can). Pass the sample through a 20-mesh sieve in order to mix the sample, break up lumps, and remove foreign materials.
- 5.4 **Laboratory Control Sample (LCS):** Prepare both a hardened concrete and cement LCS with chloride content near 0.1 lb/yd<sup>3</sup> as described in 6.1 and 6.3, respectively, in sufficient quantity for routine monitoring of method performance over the course of one or more years. Once a concrete LCS and cement LCS are selected, 25 samples of each must be run to establish valid control charts prior to sample chloride determination.
- 5.5 **Storage:** Store the powdered samples in chemically-inert covered containers that are clean and dry.

## 6. PROCEDURE

### 6.1 Total Chloride Extraction:

- 6.1.1 **Cementitious Materials:** Prepare each of triplicate samples by weighing the mass of material shown in Table 1 onto a watch glass and transfer mass to a 100-mL beaker.

Table 1. Mass of Cementitious Material

Material	Mass, g
Cement	2.0000 (±0.0005)
Concrete	4.0000 (±0.0005)

6.1.2 Aggregate Materials: Prior to weighing out samples, place a watch glass under the chemical hood and add ~ 0.5 g of sample followed by a few drops of 5% HNO<sub>3</sub>. If aggregate fails to froth with the addition of acid, prepare triplicate samples by weighing 3.0000 (±0.0005) g of material with 2.0000 (±0.0005) g of cement LCS onto a watch glass; otherwise prepare each of triplicate samples by weighing 3.0000 (±0.0005) g of material onto a glass.

6.1.3 Add 5.0 mL of deionized water to each beaker. Slowly add 35.0 mL of the 5% HNO<sub>3</sub> to each beaker (care should be exercised to avoid excessive frothing). Use a clean stir 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 (at a minimum of 250°C (482°F) until they boil. Allow samples 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<sub>3</sub> to the sample due to the emission of a sulfur smell. Prior to boiling, add 1-2 mL of concentrated HNO<sub>3</sub> to drive the sulfide ions off as hydrogen sulfide. Boil the sample for a total of 10 to 12 minutes.

6.1.4 Remove beakers from the hot plate and filter the extract from each beaker through the specified filter paper into a 100-mL volumetric flask. Rinse residue from the beaker into the filter and residue on the filter sides with approximately 30 mL of hot deionized water. Allow the sample to cool to room temperature (about 1 hour), then add deionized water to the mark on the flask.

6.2 Electrode Maintenance: Prior to testing and after every 30 analyses (10 samples) or a lapse in use of more than 1 hour perform the following:

6.2.1 Restore and condition the electrode as described in the manufacturer's manual. The electrode can be restored more often if the response appears sluggish.

6.2.2 Flush the filling solution from the electrode and refill the electrode with fresh solution prior to conditioning.

Follow the manufacturer's guidance for both short-term (<2 weeks) and long-term electrode storage.



If the electrode is suspect in its performance, 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. To a 250-mL beaker, add 100 mL of deionized water and 1 mL of low-level ISA. Place the beaker on a magnetic stirrer, put a clean stir bar in the beaker and stir at a moderate and constant rate. With the meter in the 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.

- 6.3 Check AgNO<sub>3</sub> Dispenser Calibration: Daily at the start of sample analyses and for every 30 analyses (10 samples), dispense ten 0.50-mL aliquots of AgNO<sub>3</sub> 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-test.
- 6.4 Blank Sample: Prior to testing and after every 30 analyses (10 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. To 100 mL of deionized water in a 250-mL beaker, add 1.00 mL of low-level ISA. Place the beaker on the magnetic stirrer, and a clean stir bar in the beaker. Immerse electrode in the solution. Stir the solution at a moderate and constant speed. Add 1.00 mL of 0.0100 N AgNO<sub>3</sub> titrant and record the potential. This potential is hereafter referred to as the scaling potential. Make four 0.500-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 with deionized water, and pat dry with lint-free tissue. Using the FDOT chloride software or alternative, enter the blank data in the space provided (Figure 1). Once the data is entered, the FDOT chloride software will indicate the end point for the blank and whether or not it is within the acceptable range. If the intercept does not fall between -0.100 mL and +0.100 mL, the software will indicate the failure. Likewise, the end point for the blank should 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, otherwise the software will indicate a failure. If failure is indicated and data entries are correct, perform the appropriate electrode maintenance per the manufacturer recommendations and then re-run the blank. If samples are run with 0.100 N AgNO<sub>3</sub>, determine the blank chloride end point with 0.100 N AgNO<sub>3</sub> as well.



- 6.5 Chloride Check Standard (CCS): Prior to testing and after every 30 analyses (10 samples), obtain the chloride titration end point for a 3.00 mg/L (ppm) CCS. Rinse the electrode with deionized water and pat dry with lint-free tissue. 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. Transfer the contents of the volumetric flask to a 250-mL beaker and add 1.00 mL of low-level ISA. Place the beaker on the magnetic stirrer and a clean stir bar in the beaker. Immerse electrode in the solution. Stir the solution at a moderate and constant speed. Add 0.0100 N AgNO<sub>3</sub> titrant in 0.500-mL increments until the scaling potential determined in Section 7.4 is reached or just exceeded. Record the total volume of titrant and the potential. Make four more 0.500-mL additions of titrant and record the potential after each addition. Remove and rinse electrode with deionized water, and pat dry with lint-free tissue. Enter the volume and potential data in the FDOT chloride software (Figure 1) or alternative. After blank correction, the observed concentration should be within 3.33% ( $\pm 0.100$  ppm) of the CCS concentration and within the upper control limit (UCL) and lower control limit (LCL) based on a sequential record of at least 25 CCS end points; otherwise, the software will indicate a failure. If failure is indicated, prepare fresh reagents as necessary and test again.
- 6.6 Laboratory Control Sample (LCS): Prior to testing and after every 30 analyses (10 samples), run one replicate of a LCS by the procedures described in Sections 7.1, 7.7 and 7.8; either a concrete or a cement LCS, as appropriate. Enter the volume and potential data in the FDOT chloride software (Figure 1) or alternative. After blank correction, the observed concentration should be within the upper control limit (UCL) and lower control limit (LCL) based on a sequential record of at least 25 LCS chloride end points; otherwise, the software will indicate a failure. If failure is indicated, prepare fresh reagents and test again.
- 6.7 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 7.1 into a 250-mL beaker. Place the beaker on the magnetic stirrer and a clean stir bar in the beaker. Immerse electrode in the solution. Stir the solution at a moderate and constant speed. If the potential is less than what would be measured in a 10 ppm standard solution then use 0.100 N AgNO<sub>3</sub> anywhere the method asks for 0.0100 N AgNO<sub>3</sub>.
- 6.8 Add 0.0100 N AgNO<sub>3</sub> titrant in 0.500-mL increments until the scaling potential determined in Section 6.4 is just exceeded. Record the total volume of titrant and the potential. Make four more 0.500 mL additions of titrant and record the potential after each addition. Remove and rinse

electrode with deionized water, and pat dry with lint-free tissue. Enter the volume and potential data in the space provided by the chloride software for replicate A (Figure 2). Repeat the procedure for replicates B and C with the same  $\text{AgNO}_3$  normality as used with replicate A. Check the block on the entry page (not shown) to indicate if samples were run with the cement LCS added. The computer software will subtract the contribution of chloride from the cement LCS from the total chloride to obtain the chloride concentration of the aggregate material.

## 7. CALCULATIONS

- 7.1 The chloride software will perform all the calculations required based on the normality, unit weight, and sample mass. Once all the pertinent data have been entered into the appropriate field, the results are displayed for the sample. If the sample range exceeds  $0.080 \text{ lbs/yd}^3$  when titrating with  $0.0100 \text{ N AgNO}_3$  ( $0.80 \text{ lbs/yd}^3$  when titrating with  $0.100 \text{ N AgNO}_3$ ) the software will indicate a failure and the sample must be re-analyzed in triplicate.

## 8. DISPOSAL OF PROCESS WASTE

- 8.1 Disposal of Process Waste: Dispose of process waste in accordance with the most stringent of local, state, or national regulations.

## 9. PRECISION AND BIAS STATEMENTS

### 9.1 Precision:

The multi-laboratory standard deviation of a single test result has been found to be  $0.0326 \text{ lbs/yd}^3$  for chloride content below  $1.0 \text{ lbs/yd}^3$ . Therefore, results of two properly conducted tests in two different laboratories on identical samples of a material are not expected to differ from each other by more than  $0.0922 \text{ lbs/yd}^3$  for chloride content below  $1.0 \text{ lbs/yd}^3$ . These numbers represent the (1s) and (d2s) limits as described in ASTM C670.

The multi-laboratory standard deviation for chloride contents above  $1.0 \text{ lbs/yd}^3$  is  $0.3243 \text{ lbs/yd}^3$ . Therefore, results of two properly conducted tests in two different laboratories are not expected to differ by more than  $0.9178 \text{ lbs/yd}^3$ .

### 9.2 Bias:



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