Recommend Approval: Assistant Division Chief — Vicki K Stewart — Date 12-12-12 Division Chief — Date 12/17/12 Approved: Director — Tim Smith — Date 01/17/13	Maryland Department of Transportation State Highway Administration Office of Materials Technology MARYLAND STANDARD METHOD OF TESTS	
	TEST FOR CHLORIDE IN PORTLAND CEMENT CONCRETE	MSMT 610

SCOPE:

This procedure describes a rapid method of determining chloride ion content in any material where large quantities of chloride are expected. It has been developed particularly for the analysis of bridge deck drillings, in order that the corrosion of the structural steel (such as rebar) may be evaluated and/or projected. The titrant, Silver Nitrate ($AgNO_3$), changes the potential of the solution containing ions from the digested concrete drillings. The ions are detected by a "potentiometer". However, sulfides react in the same manner as chlorides and interfere with the analysis, therefore the test is limited to materials not containing sulfides.

REFERENCE DOCUMENT:

Mettler DL25 Manual

I. AUTOMATIC POTENTIOMETRIC TITRATION OF BRIDGE DECK DRILLINGS

MATERIALS AND EQUIPMENT:

A. APPARATUS:

1. Combination solid state chloride ion selective electrode, reference electrode, stirrer, and burette dispensing units.
2. Mettler DL25 Automatic Titrator.
3. Hot plate.
4. Drying oven, capable of maintaining a temperature of 105 □3 C.
5. Balance, conforming to M 231, Class A.
6. Glassware; including funnels, 50 mL graduates, 250 mL Erlenmeyer flasks, and 150 mL beakers.
7. #54 filter paper.

B. SOLUTIONS/REAGENTS:

1. Standard sodium chloride solutions, 0.00705 N, 0.0141 N, and 0.0282 N.

a. For 0.00705 N sodium chloride solution (250 ppm): Dissolve 4.1215 g sodium chloride (NaCl), dried at 105 C into a 500 mL volumetric flask and dilute to the mark with distilled water. The solution contains 0.25 mg chloride (Cl^-) per 1.0 mL solution.

b. For 0.0141 N sodium chloride solution (500 ppm): Dissolve 8.243 g sodium chloride (NaCl), dried at 105 C, into a 500 mL volumetric flask and dilute to the mark with distilled water. The solution contains 0.50 mg chloride (Cl^-) per 1.0 mL solution.

c. For 0.0282 N sodium chloride solution (1000 ppm): Dissolve 16.486 g sodium chloride (NaCl), dried at 105 C, into a 500 mL volumetric flask and dilute to the mark with distilled water. The solution contains 1.00 mg chloride (Cl^-) per 1.0 mL solution.

2. Standard silver nitrate solutions: 0.00705 N, 0.0141 N, and 0.0282 N.

a. For 0.00705 N silver nitrate solution: Dissolve 1.20 g silver nitrate ($AgNo_3$), dried at 105 C, into a 1000 mL volumetric flask and dilute to the mark with distilled water.

b. For 0.0141 N silver nitrate solution: Dissolve 2.40 g silver nitrate ($AgNo_3$), dried at 105 C into a 1000 mL volumetric flask and dilute to the mark with distilled water.

c. For 0.0282 N silver nitrate solution: Dissolve 4.80 g silver nitrate ($AgN0_3$), dried at 105 C, into a 1000 mL volumetric flask and dilute to the mark with distilled water.

3. Nitric acid (HNO_3) solution:

a. Add 120 mL of concentrated nitric acid to 2350 mL of distilled water.

b. To standardize silver nitrate solutions, choose METHOD 1 or METHOD 2.

METHOD 1: (using the automatic titrator station)

1. Add 10.0 mL standard sodium chloride (NaCl) solution of the same normality as the silver nitrate solution ($AgN0_3$) into a 250 mL beaker.

2. Dilute to 150 mL and add 2.0 mL concentrate nitric acid (HNO_3). Place the beaker under the electrodes, dispensing units, and stirrer.

3. Follow the procedures in as outlined in the Mettler DL25 Manual titled- Operating Instructions (pg. 34).

METHOD 2: (using the manual titrator station)

1. Add 10.0 mL standard sodium chloride (NaCl) solution of the same normality as the silver nitrate solution ($AgNo_3$) into a 250 mL beaker.

2. Dilute to 100 mL and add 2.0 mL concentrated nitric acid (HNO_3). Place the beaker on a stir plate and stir.

3. Set the pH meter on "REL MV" and insert the electrode in the beaker.

4. Titrate with the standard silver nitrate ($AgNO_3$) solution using a burette or a repipette dispenser to the "isoelectric endpoint". The endpoint is defined as the greatest change in the instrument reading per unit addition of titrant (the $AgNO_3$ solution).

5. Normality (N) of the solution is determined in the **CALCULATIONS** section. Adjust the normality of the standard silver nitrate solution to match that of the standard sodium chloride solution.

TEST PROCEDURE:

1. Dry the chloride samples overnight in an oven set at 105 C.

2. Remove samples and allow to cool for 15 to 30 minutes.
Preheat hot plate - allow time for hot plate to reach adequate temperature. Weigh 2.0000 to 2.0300 g into a 250 mL Erlenmeyer flask. Record the sample I.D. and weight on worksheet.

3. Add 50 mL of nitric acid solution to each flask and heat at a temperature just below boiling for 30 minutes.

CAUTION: **Do Not Allow Samples to Boil**

4. Filter through #54 filter paper into a 150 mL beaker. Rinse each flask twice with distilled water. Dilute to 105 mL.

5. Turn on the printer. It is important that there are no operating radios or headsets in the immediate vicinity of the titrator.

6. Enter date: press 10, then mode,
enter number of month, press run,
enter day, press run,
enter year, press run.

7. Make sure all electrodes are in holder and place in sample.

8. Press #2, then pH/calib. Wait for the number to stabilize. This number is the initial millivolt reading and it will be printed when the titration begins. For a given titration, the initial millivolt reading will specify which burette and method you will use. Refer to the current chart to select the method to be used to run the titration.

NOTE: Be sure to loosen thumb screw before moving burettes and tighten them when burettes are in place.

9. Press reset.

10. Press run and look for the light to blink next to **"WEIGHT"**.

11. Enter the weight value and press run again. The light will blink next to **"INDENT"**.

12. Enter the identification number (1 through 18) and press run. The light will blink next to **"BUSY"**. At this point, you may press reset and return to step 8 if you have made a mistake. If everything looks fine, proceed to step 13.

13. Press run. After an initial stirring delay time (1 to 1 1/2 minutes), the titration will proceed. Your results will be printed out when the titration is complete. **Titration may only be aborted during the initial stirring time. Otherwise all data will be lost.**

NOTE: If you come up with an error message, or something is wrong, **DO NOT PRESS BUTTONS.** Stop what you are doing and find a senior technician. They may be able to recover your results.

14. After the sample has been titrated, rinse the probes with distilled water and discard the sample properly as specified under the HAZARDOUS WASTE Disposal section.

15. Go to the next sample (repeat steps 8 - 14).

16. When finished, turn off the printer, but leave the titrator on.

17. Remove the chloride electrode (black) and lay it across the top of the probe holder. Store the reference electrode and the stirring and dispensing units in distilled water. The chloride electrode is stored dry.

CALCULATIONS:

1. If the automatic titrator (METHOD 1) fails to report the detected endpoint, you must calculate the chloride ppm as follows:

a. From the measured values, select the highest mV/mL value and its corresponding volume.

b. To calculate chloride ppm use the following formula:

$$C = \frac{A \times B}{W}$$

where:

C = ppm chloride,

A = volume of $AgNO_3$ solution used,

B = one of the following:

0.00705N $AgNO_3$ = 250 ppm,
0.0141N $AgNO_3$ = 500 ppm,
0.0282N $AgNO_3$ = 1000 ppm.

W = weight of chloride sample, in grams,

2. If the manual titrator station (METHOD 2) was used, calculate the normality of the standard silver nitrate solution as follows:

$$N = \frac{10 \times Y}{V}$$

where:

N = normality of the $AgNO_3$ solution,

V = volume in mL of $AgNO_3$ solution used, and

Y = normality of NaCl used.

REPORT:

Tear off all sheets containing that batch of completed samples. On the first and last sheets, circle the date, and sign it. For each I.D. number, write the corresponding sample number under REMARKS. Transfer the results from the computer printout to the Intra-Lab Chloride Sheet. Report results to the nearest 1 ppm.

Submit the Intra-Lab and the printout to the Lead Tester.

HAZARDOUS WASTE Disposal:

SIPHON METHOD, COLOR CODE: RED

CHLORIDE WORKSHEET

SAMPLE IDENTIFICATION	SAMPLE MASS (2.0000 g + 0.0300)
1.	
2.	
3.	
4.	
5.	
6.	
7.	
8.	
9.	
10.	
11.	
12.	
13.	
14.	
15.	
16.	
17.	
18.	

MILLIVOLT	BURETTE	METHOD
< 175	20 mL	#3
175-215	10 mL	#1
> 215	5 mL	#2

II. MANUAL POTENTIOMETRIC TITRATION OF BRIDGE DECK DRILLINGS

MATERIALS AND EQUIPMENT:

A. APPARATUS:

1. Combination solid state chloride ion selective electrode and manufacturer's recommended accessory solutions.

2. Electronic millivoltmeter (potentiometer) compatible with the ion electrode.

3. Magnetic stirrer and teflon stirring bars.

4. Burette or repipette dispenser with 0.1 mL graduations.

5. Hot plate.

6. Drying oven, capable of maintaining a temperature of 105 □3C.

7. Balance conforming to M 231, Class A.

8. 250 mL Erlenmeyer flasks and beaker.

9. Glassware; including funnels, 50 mL graduates, etc. and #54 filter paper.

B. SOLUTIONS/REAGENTS:

1. Standard sodium chloride solution, 0.0282N.

Dissolve 16.486 g sodium chloride (NaCl), dried at 105 C into a 500 mL volumetric flask and dilute to the mark with distilled water. The solution contains 1.0 mg chloride (Cl^-) per 1.0 mL (1000 ppm).

2. Standard silver nitrate solution, 0.0282 N.

a) Dissolve 4.80 g silver nitrate ($AgNO_3$), dried at 105 C, into a 1000 mL volumetric flask and dilute to the mark with distilled water.

b) Add 10.0 mL standard sodium chloride (NaCl) solution, diluted to 100 mL into a 250 mL beaker. Add 2.0 mL concentrated Nitric acid (HNO_3).

c) Place the beaker on stir plate and stir. Set the pH meter on "REL MV" and insert the electrode in the beaker. Titrate with the standard silver nitrate ($AgNO_3$) solution using a burette or a repipette dispenser to the "isoelectric endpoint". The endpoint is defined as the greatest change in the instrument reading per unit addition of titrant (the $AgNO_3$ solution).

d) Normality (N) of the solution is determined in the "CALCULATIONS" section. Adjust the normality of the standard silver nitrate solution to match that of the standard sodium chloride solution.

3. Nitric acid (HNO_3) solution.

Add 120 mL of concentrated nitric acid to 2350 mL of distilled water.

4. Standard chloride solution, preferably 100 ppm. This solution is prepared by a lab chemist.

TEST PREPARATION:

In order to confirm the accuracy and precision of the required instruments and solutions, as well as that of the technician, it is necessary to titrate a standard chloride solution (preferably 100 ppm) in duplicate before the testing of actual samples.

1. Using a graduated cylinder, pour 50 mL of the standard chloride solution into a 250 mL beaker.

2. Still using the graduated cylinder, add 50 mL distilled H_2O to the beaker, then titrate.

3. Having successfully titrated the duplicate samples, their results are given to an experienced lab technician who will evaluate the data and decide whether or not to proceed with the regularly scheduled testing.

TEST PROCEDURE:

1. Dry the chloride samples overnight in an oven set at 105 C.

2. Remove samples, allow cooling, and then weigh 2.0000 to 2.0010 g into 250 mL Erlenmeyer flasks. Record the data in workbook.

3. Add 50 mL of Nitric Acid Solution to each flask and heat at a temperature just below boiling for 30 minutes.

CAUTION: DO NOT ALLOW SAMPLES TO BOIL!!!

4. Filter through #54 filter paper into a 250 mL beakers. Rinse each flask twice with distilled water. Dilute to 100 mL.

5. Titrate each sample with the standard silver nitrate solution using the potentiometric titration method.

CALCULATIONS:

1. Calculate the normality of the standard silver nitrate solution as follows:

$$N = \frac{10 \times 0.0282}{V}$$

where:

N = normality of the $AgNO_3$ solution, and

V = volume in mL of $AgNO_3$ solution used.

2. Calculate the chloride content of the Portland Cement Concrete as follows:

$$C = \frac{A \times 1000}{W}$$

where:

C = total chloride content in ppm,

A = mL of titrant ($AgNO_3$) used to reach the endpoint, and

W = weight of sample.

REPORT:

1. Report the total chloride content to the nearest 1 ppm.

2. Report the results in the chloride workbook.

HAZARDOUS WASTE DISPOSAL:

SIPHON METHOD, COLOR CODE: RED

System for identifying the endpoint and determining the endpoint values:

CASE 1
Previous no. is closer to endpoint

INCREMENT MILLIVOLTS	mL $AgNO_3$ ADDED	
19	0.5	← Use this
20	0.6	no. then add
13	0.7	0.09

0.50
+ 0.09
Final vol. = 0.59

CASE 2
Following no. is closer to endpoint

INCREMENT MILLIVOLTS	mL $AgNO_3$ ADDED	
18	0.6	
20	0.7	← Use this
19	0.8	no. then add 0.04

0.70
+ 0.04
Final vol. = 0.74

CASE 3
Previous and following nos. equally apart

INCREMENT MILLIVOLTS	mL $AgNO_3$ ADDED	
17	0.3	
20	0.4	← Use this no.
17	0.5	

Final vol. = 0.4

CASE 4
Duplicate endpoint nos.

INCREMENT MILLIVOLTS	mL $AgNO_3$ ADDED	
19	1.1	
22	1.2	← Use avg.
22	1.3	←

Final vol. = 1.25

III. CONCRETE ADMIXTURE

MATERIALS AND EQUIPMENT:

A. APPARATUS:

1. Combination solid state chloride ion selective electrode and manufacturer's recommended accessory solutions.

2. Electronic millivoltmeter (potentiometer) compatible with the ion electrode.

3. Magnetic stirrer and teflon stirring bars.

4. Burette or repipette dispenser with 0.1 mL graduations.

5. Hot plate.

6. Glassware including 50 mL graduates, 250 mL beakers, and Erlenmeyer flasks.

7. Gooch crucibles and glass microfiber filters or glass funnel and #54 filter paper.

B. SOLUTIONS/REAGENTS:

1. Cobalt nitrate, $Co(NO_3)_2$.

2. Diluted acetic acid solution.

Dilute 11.5 mL glacial acetic acid to 50 mL using a 50 mL graduate.

3. Standard silver nitrate solution, 0.100N.

Dissolve 0.1700 g silver nitrate ($AgNO_3$), dried at 105 C, into a 1000 mL volumetric flask and dilute to the mark with distilled water.

TEST PROCEDURE:

1. Weigh 5 g of admixture into a 250 mL beaker.

2. Add 50 mL of distilled water.

3. Filter the sample solution through either a gooch crucible or #54 filter paper into a 250 mL beaker.

4. Acidify the filtered sample solution with diluted acetic acid solution to a pH of about 4.

5. Add 3.0 g cobalt nitrate $Co(NO_3)_2$.

6. Boil the solution for ten minutes.

7. Filter through either a gooch crucible or #54 filter paper into a 250 mL beaker.

8. Titrate each sample with the standard silver nitrate solution using the potentiometric titration method.

CALCULATIONS:

1. Calculate the normality of the standard silver nitrate solution as follows:

$$N = \frac{10 \times 0.0282}{V}$$

where:

N = normality of the $AgNO_3$ solution, and

V = volume in mL of $AgNO_3$ solution used.

2. Calculate the chloride content of the concrete admixture as follows:

$$C = \frac{A \times 1000}{W}$$

where:

C = total chloride content in ppm,

A = mL of titrant ($AgNO_3$) used to reach the endpoint, and

W = weight of sample.

REPORT:

1. Report the total chloride content to the nearest 1 ppm.

2. Record the results in the Chloride Workbook.