Date: October 2012

Investigations into Methods of AASHTO T 260

Nebraska Department of Roads

Research Project: Investigation into Methods of AASTHO T 260

Project Number: In-House Resaerch

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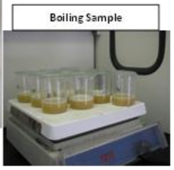
Chloride Sample

Boiling Sample



Addition of Nitric Acid


Filtration


Titration

Purpose of In-House Investigation:

The Nebraska Department of Roads analyzes and determines chloride ion content of concrete cores coming from field bridge deck structures according to AASHTO T 260. This procedure has three methods that can be used when testing by potentiometric titration.

The NDOR Materials & Research Chemistry Laboratory initiated an investigation in order to provide the best analytical accuracy results for chloride ion content of concrete field cores. These results are used by Bridge engineers to categorize bridge inventory needs. Currently the Chemistry Lab uses Method I (Potentiometric Titration).

Description of Investigation Background Tasks:

- Evaluate Florida DOT procedures for Method II.
- Evaluate AASHTO T 260 Method I by performing each sample in triplicate.
- Review, test and perform AASHTO T 260 Methods I, II, and III.

Description of Investigation Background Tasks:

The primary benefit of this investigation is to find the best analytical test method with the most accuracy and precision. In order to provide the most accurate results to Bridge engineers and increase the amount of samples that could be analyzed and reduce the man hours needed in the lab giving a cost-saving benefit to the Department.

Objective by Task of this Investigation:

1. To perform the test in triplicate using current protocol to determine intra-laboratory precision.
2. To perform the test in triplicate using current protocol using a set volume for analysis (100 mL).
3. To perform the test and analyze using Method II and compare Method I and Method II titration analysis.
4. To compare acid-soluble and water-soluble sample preparation.
5. To halve the sample volume before titration and double chloride content calculated to verify equivalence to titrating initial volume for possibility of purchasing an automatic titrator.

Conducted in the Laboratory:

Brief Description of Procedure:

Approximately three grams of sample is weighed. If the acid-soluble method is used, the material is immediately digested with nitric acid. If the water-soluble method is used, the material is allowed to digest 24 hours in water. After filtering, the final volume should be between 125 - 150 mL.

- Method I (Potentiometric Titration) for analysis is a potentiometric titration conducted by recording the millivolt reading after each 0.10 mL addition of silver nitrate before, during, and after the equivalence point.
- Method II (Gran Plot Method) for analysis is a potentiometric titration conducted by recording the millivolt reading after each 0.50 mL addition of silver nitrate after the equivalence point has been reached, which is known as a Gran Plot method.
- Method III (Automatic Titrator) for analysis is identical to Method I, but an automatic titrator is used, so the equipment monitors the millivolt readings.

Brief Discussion of Objectives:

The first objective was to simply perform the current protocol three times instead of once to check the testing precision.

The second objective was to perform the current protocol three times using a sample volume of 100 mL instead of aiming for a volume between 125 mL and 150 mL to see if this improved the precision further.

The third objective was to perform the current protocol (Method I) and the Gran Plot method (Method II) and compare the results. The benefit of using Method II was time-savings. Method II could triple the amount of samples that would be tested.

The forth objective was to compare the acid-soluble and water-soluble sample preparation. The acid-soluble preparation can be performed the same day as the analysis is conducted. The water-soluble sample preparation must begin the day before the analysis is conducted. The differences could have an impact on the final result as well as the daily sample capacity.

The final objective was to halve the sample volume to be titrated to 50 mL and then double the calculated chloride content. The prices of the automatic titrators were significantly impacted by the volume size of the sample to be analyzed.

Review of Results:

The AASHTO T 260 procedure states that when a single operator performs two properly conducted tests on the same material, the results should not differ by more than 0.0068%. The following results in Table 1 were evaluated to concur with this requirement and encompass the first four objectives. Column 2 shows the results testing Objective 1. Column 3 shows the results testing Objective 2. Column 4 shows the results testing Objective 3. Columns 5-7 show the results testing Objective 4.

Table 1

Method used for analysis	I	I	II	I	I	II
Sample preparation	Acid-soluble	Acid-soluble	Acid-soluble	Water-soluble	Water-soluble	Water-soluble
Final volume	125 – 150 mL	100 mL	100 mL	125 – 150 mL	100 mL	100 mL
Run 1	0.0182%	0.0148%	?	0.0147%	0.0150%	?
Run 2	0.0150%	0.0148%	?	0.0150%	0.0146%	?
Run 3	0.0185%	0.0148%	?	0.0150%	0.0148%	?
Maximum Difference	0.0035%	0.0000%	-----	0.0003%	0.0004%	----

The best scenario (with the lowest Maximum Difference) was using Method I for analysis of the acid-soluble preparation where the final volume was a fixed 100 mL. The Maximum Difference was also very low for the two scenarios using Method I for analysis of the water-soluble preparation; however, this preparation was discarded due to the water-soluble chloride content might not always be equivalent to total chloride.

Upon further investigation into Method II protocol, it was discovered specific paper would be required to hand plot the data before the chloride content could be calculated. The company that manufactures the brand of paper was contacted and advised that the paper is no longer produced. Therefore, Method II was unable to be tested; hence, the "?" in the table above.

Table 2 illustrates the testing of the fifth and final objective of testing the difference between titrating 50 mL vs. 100 mL. The 50 mL sample was prepared by pipetting 50 mL from the 100 mL filtered sample. The calculated chloride content was then multiplied by two.

Table 2

Date	9/27/2012	9/28/2012	10/1/2012	10/1/2012	10/1/2012
Volume Titrated	50 mL	50 mL	100 mL	50 mL	50 mL
Run 1	0.0226%	Over titrated	0.0150%	Over titrated	0.0222%
Run 2	0.0154%	0.0226%	0.0150%	0.0156%	0.0150%
Run 3	0.0224%	0.0156%	0.0150%	0.0156%	0.0222%
Max Difference	0.0072%	0.0070%	0.0000%	0.0000%	0.0072%

There were four sets prepared to titrate 50 mL samples and one set prepared to titrate 100 mL samples as a control. Three of the four sets (see columns 2, 3, and 6) had a max difference greater than the 0.0068% limit set forth in AASHTO T 260. The fourth set (see column 5) did not fail this requirement, but the first run was over titrated. It is unknown if that value would have correlated with the other two runs.

Conclusion:

This investigation concluded the modification of NDOR AASHTO T 260 as follows;

- To prepare the samples at a fixed volume of 100 mL
- To test each sample in triplicate

Due to the accuracy of results while testing according to AASHTO T 260 Method III and the amount of samples that will be tested in the future, NDOR will begin testing by a modified AASHTO T 260 Method III after the purchase of an automatic titrator, which could save more than $25,000 a year.