

**NEW YORK STATE DEPARTMENT OF TRANSPORTATION**

**SPR Project # C-10-11: Correlation between Wavelength Dispersive X-Ray Fluorescence (WDXRF) Analysis of Hardened Concrete for Chlorides vs. Atomic Absorption (AA) Analysis in accordance with AASHTO T- 260; Sampling and Testing for Chloride Ion in Concrete and Concrete Raw Materials, Procedure B, Acid-Soluble Chloride Ion Content by Atomic Absorption**

---

**Final Report**

**Kristen M. Simonds  
Senior Engineering Materials Chemist**

**Office of Technical Services  
Materials Bureau Chemistry Laboratory  
Instrumental Inorganic Analysis Unit  
7 Harriman Campus Rd,  
Albany, NY 12206**



**Thermo Scientific ARL OPTIM'X  
WDXRF**

**4/1/2014**

### **DISCLAIMER**

This report was funded in part through grant(s) from the Federal Highway Administration, United States Department of Transportation, under the State Planning and Research Program, Section 505 of Title 23, U.S. Code. The contents of this report do not necessarily reflect the official views or policy of the United States Department of Transportation, the Federal Highway Administration or the New York State Department of Transportation. This report does not constitute a standard, specification, regulation, product endorsement, or an endorsement of manufacturers.



**Form DOT F 1700.7 and Instructions**  
**Technical Report Documentation Page**

into a platinum mold. The resulting bead is placed in the WDXRF for analysis. Utilizing the new methodology, a more precise and accurate chloride result is obtained and has cut the time of analysis in half. Also, the new methodology requires the use of less hazardous consumables, removing potential health and safety risks to employees. Once implemented the WDXRF method will lessen the turn around time from the cores taken from bridge decks, sent to the lab for evaluation for the total chloride measured at each depth, indicating the amount of salt present at that level. The higher the concentration of salt at greater depths indicates the potential for damage to the rebar. Recommendations for repairs are based on these results. With a faster time of analysis, results will allow the engineers to see the potential hazards before developing into a more serious issue.

17. Key Words: Chloride Analysis, WDXRF, Bridge deck,	18. Distribution Statement  No Restrictions		
19. Security Classif. (of this report)  Unclassified	20. Security Classif. (of this page)  Unclassified	21. No. of Pages 12	22. Price

## Table of Contents

Executive Summary	2
Introduction	3
Research Method	4
Findings and Conclusions	5
Implementation	5
Appendix: Data Figures	6
Appendix: Method	9

## EXECUTIVE SUMMARY

This report summarizes the results of research conducted by The New York State Department of Transportation (NYSDOT) Instrumental Inorganic Analysis Unit (IIA) of the Chemistry Laboratory. The evolution of instrumental analysis of cementitious materials utilized in state transportation projects to more precise and accurate methodologies will save both time and money for the Department.

The IIA Unit analyzes cementitious products spectrographically for conformance to state and federal guidelines for use in transportation construction projects. Presently, NYSDOT's laboratory performs the analysis of total chloride content using the Atomic Absorption Spectrophotometer for analysis (current method AASHTO T 260, Procedure B.) This AA method was developed in the NYSDOT laboratories, and samples have been analyzed for total chloride content using this method for over twenty years. Analysis begins with cores taken from bridge decks and sent to the laboratory for evaluation. The Strength of Materials Unit drills the cores at various depths and the powder is collected. It is then analyzed by the IIA Unit at each depth for total chloride concentration. The total chloride measured at each depth indicates the amount of salt present at that level. The higher the concentration of salt at greater depths indicates the potential for damage to the rebar. Recommendations for repairs are based on these results. The AA method requires the use of many potentially hazardous chemicals, numerous pieces of glassware, and is very time consuming.

Wavelength Dispersive X-ray Fluorescence (WDXRF) analysis has been shown to be more precise and accurate as well as less time consuming than Atomic Absorption (AA) analysis. There is also a reduction of consumables and hazardous chemicals with moving to a WDXRF method for the analysis of Hardened Concrete for Chlorides.

A correlation between Wavelength Dispersive X-ray Fluorescence (WDXRF) analysis of Hardened Concrete for Chlorides and Atomic Absorption (AA) analysis (current method AASHTO T- 260, Procedure B) has been found and a new method of analysis has been devised. Initially for this research, core samples from the 2011 construction season were reanalyzed using WDXRF. Sample preparation involved pressing a portion of sample with a binder to form a pellet. The pellets were then analyzed by WDXRF and a correlation of the results was found to exist. Upon further analysis it was found that the 2011 sample did not have adequate material left over to form a "good" analytical pellet and a new method of sample preparation had to be devised.

With the addition of a Katanax Fluxer, a fused glass bead is prepared using only 1 gram of sample. Combined with flux, the sample is fused in a platinum crucible and poured into a platinum mold. The resulting bead is placed in the WDXRF for analysis. In 30 minutes time, a more precise and accurate chloride result is obtained. Utilizing this new methodology has cut the sample preparation in half and total time of analysis by a third. Implementation of this methodology will save NYSDOT both time and money, as well as create a safer testing environment for laboratory staff.

## INTRODUCTION

The New York State Department of Transportation (NYSDOT) Instrumental Inorganic Analysis Unit (IIA) of the Chemistry Laboratory is conducting research to develop a correlation between Wavelength Dispersive X-ray Fluorescence (WDXRF) analysis of Hardened Concrete for Chlorides and Atomic Absorption (AA) analysis (current method AASHTO T- 260, Procedure B). This research targets the evolving nature of instrumental analysis of cementitious materials utilized in state transportation projects.

Presently, our laboratory performs the analysis of total chloride content in accordance with AASHTO T-260, method B using an Atomic Absorption Spectrophotometer. NYSDOT drills core samples from bridge decks and sends them to the lab for evaluation. The cores are then drilled at various depths by the Strength of Materials Lab Unit. The powder created in the drilling process is collected and analyzed at each depth for total chloride concentration. The total chloride concentration for each depth indicates the amount of salt present at that level. The higher the concentration of salt at greater depths indicates the potential for damage to the rebar and bridge deck. Recommendations for repairs are based on these results.

In a year's time, the Instrumental Inorganic Analysis Unit analyzes over 500 powdered concrete samples, for total chloride content, from bridge decks across the state. The current use of AASHTO T-260, Procedure B in the lab unit has proven to be very time consuming and requires many chemicals. Moving toward WDXRF analysis of cementitious materials, and phasing out the AA, would provide a more efficient and accurate analysis method and therefore be in the best interest of the IIA Unit. No method has yet been published to determine Chloride content in hardened concrete using WDXRF.

## RESEARCH METHODS

The initial chloride sample preparation method for pressed pellets was based upon NYSDOT Test Method NY 701-22c: WDXRF Method for the Chemical Analysis of Portland Cement. Changes to the weight of sample pressed had to be made due to the volume of material received for analysis. A minimum of 3 grams of sample is required for an analytical pellet; however, the chloride samples are occasionally contaminated with iron from rebar. Once the iron filings are removed it can greatly reduce the sample weight. Due to the variations in material weight a new method for sample preparation was required.

With the addition of a Katanax Fluxer to the laboratory, the fusion method was derived utilizing the 2011 concrete core samples. A flux of 49.75% Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 49.75% Li<sub>2</sub>BO<sub>2</sub>, and 0.5% LiBr was mixed with the powdered chloride sample in a platinum crucible and fused to yield a glass bead. Multiple beads were fused based upon a previous oxide fusion method. The method parameters were adjusted accordingly as to the nature of the known material(s) in the concrete. The initial resultant beads contained small bubbles on the analytical side of the bead. An increase in heating time and tilt of the crucible were made in the method parameters. These changes yielded a precise analytical bead for WDXRF analysis with a Pearson correlation coefficient going from 0.85 to 0.90.

The WDXRF method was developed using Thermo ARL Optiquant software for standardless analysis, which analyzes a sample for 93 elemental concentrations. Wavelength detection was optimized for Chloride analysis. Subsequent unnecessary elemental count times were reduced or removed to lessen analysis time. The Chloride concentration is measured based upon the wavelength of the spectral line of the desired element. The fused beads are analyzed in a vacuum environment for 30 minutes with the developed chloride WDXRF method.

The new methodology has by far shortened the sample prep and analysis time. Previously, the Atomic Absorption method would take approximately 6 hours for 9 powdered concrete samples and requires more consumable and potentially hazardous chemicals. Currently, with the new method the laboratory unit can prepare and analyze 9 samples in 4.5 hours.

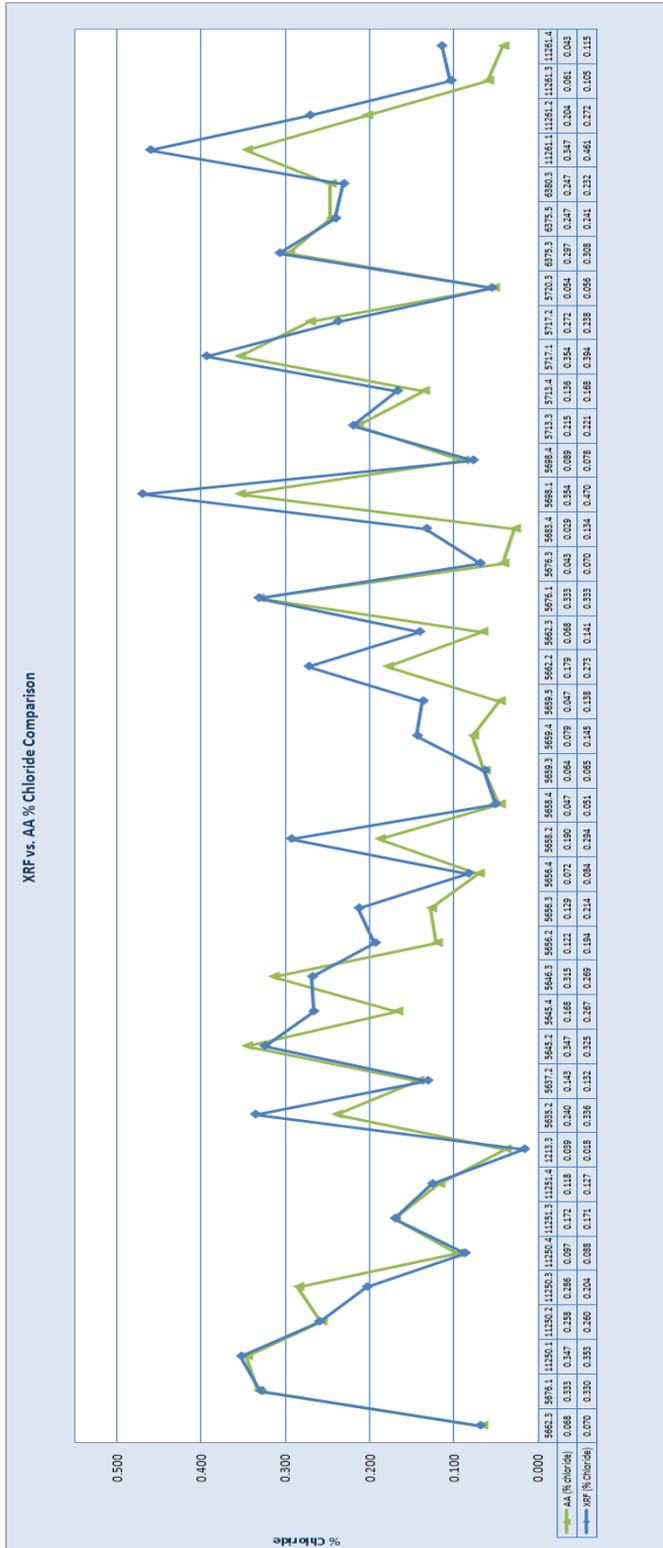
## **FINDINGS and CONCLUSIONS**

As expected, a correlation between Wavelength Dispersive X-ray Fluorescence (WDXRF) analysis of hardened concrete for chlorides and Atomic Absorption (AA) analysis (current method T- 260, Procedure B) has been found and a new method of analysis has been devised. As shown in the data, a linear relationship exists between the two methodologies. The new method has been officially implemented and has streamlined chloride analysis and provided more precise and accurate results with which to base decisions regarding bridge deck replacement.

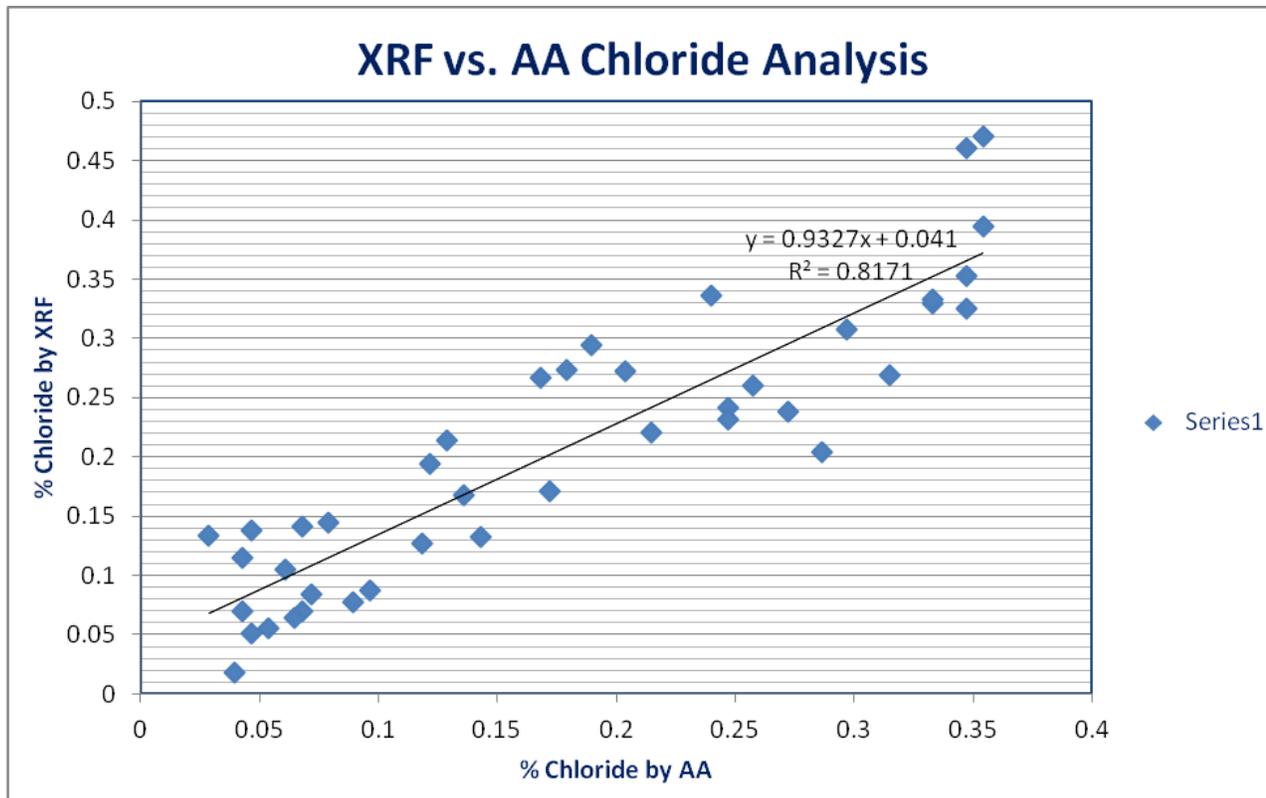
## **STATEMENT ON IMPLEMENTATION**

NYS DOT has implemented the test method WDXRF method for the Chemical Analysis of Hardened Concrete for Chlorides after it was formally reviewed and approved by the Materials Bureau as an acceptable test method. Proper training of laboratory staff has commenced subsequently and the method will be utilized for all future chloride analysis.

# XRF vs. AA % Chloride Comparison



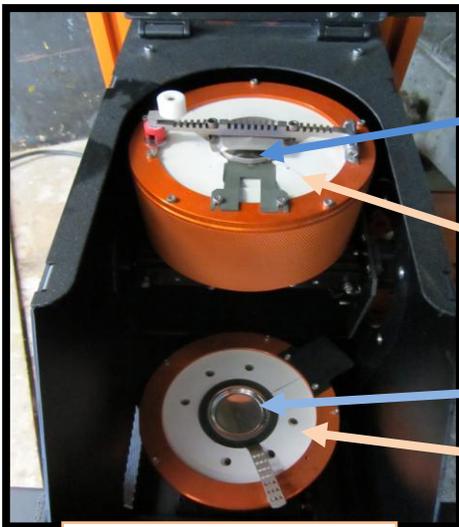
# Final Data Analysis of Random 2010-2012 Chloride Samples



Pearson Correlation Coefficient      0.9039  
Coefficient of Determination ( $R^2$ )      0.8171



Katanax K1 Prime Fusion Instrument



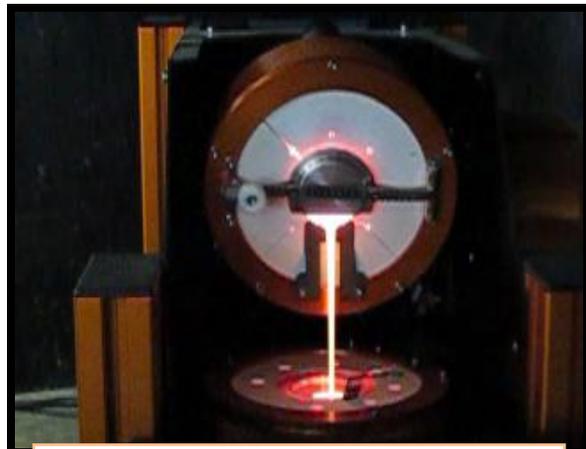
Interior view

Platinum Crucible

Platinum Crucible  
Heater

Platinum Mold

Mold heater



Katanax pouring a sample into the mold.

 <p>NEW YORK STATE DEPARTMENT OF TRANSPORTATION MATERIALS BUREAU ALBANY, NY 12232-0861</p> <p><b>TEST METHOD</b></p>	<p>Test Method No. 555-1c</p> <p>Issue Date: April 2014 Subject Code: 7.42-5</p>
	<p><b>SUBJECT: WDXRF METHOD FOR CHEMICAL ANALYSIS OF HARDENED CONCRETE FOR CHLORIDES</b></p>
<p>APPROVED: <u><i>John Rondinaro</i></u> FOR John Rondinaro, Director, Materials Bureau</p>	<p>Supercedes: n/a</p> <p>Dated:</p>

**1. SCOPE**

1.1 This test method covers the chemical analysis of Hardened Concrete for Chlorides by Wave Dispersive X-ray Fluorescence.

The methods were developed by New York State Department of Transportation, Instrumental Analysis-Inorganic Unit of the Chemistry Laboratory.

A powdered concrete sample is blended with a Lithium Borate flux and fused to form a bead. The beads are analyzed by WDXRF in a vacuum environment, and the concentration is measured based upon the wavelength of the spectral line of the desired element.

**2. REFERENCED DOCUMENTS**

- 2.1 Katanax K1 Prime User's Manual
- 2.2 ARL OPTIM'X Users Manual
- 2.3 UniQuant<sup>®</sup> 5 User Manual, chapters 6-7.

**3. METHODS**

3.1 The methods appear in the order shown in Table 2.

**Table 2 – Order of Methods**

METHOD	SECTION
Sample Preparation	7
Cl <sup>-</sup>	8

#### 4. INTERFERENCES AND LIMITATIONS

- 4.1 These procedures were developed primarily for the analysis of Hardened Concrete. Limitations are noted in the procedure for specific constituents.

#### 5. APPARATUS AND MATERIALS

- 5.1 Wave Dispersive X-ray Fluorescence Spectrometer: Power supply 50 watts (50 kV max. or 2 mA max), Goniometer with: Fixed collimator (medium angular admittance), Crystal changer with 3 crystals fitted: PET, AX06, and LiF200 and 2 detectors fitted: Flow Proportional Counter and Scintillation Counter.
- 5.2 Gas cylinders of P10 gas: 90% Ar (48), 10% ( $\pm 5\%$ ) of CH<sub>4</sub>(35) and Helium (46) with a two-gauge, two stage pressure reducing regulators compatible with the gas required.
- 5.3 Analytical Balance meeting requirements of AASHTO T-105, Section 4.2.
- 5.4 Weighing dish.
- 5.6 Automatic Fluxer with platinum crucible and bead mold

#### 6. REAGENTS

- 6.1 A suitable Lithium Borate Flux containing 49.75% Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 49.75% LiBO<sub>2</sub>, 0.5% LiBr

**NOTE 1:** The text of this method is most applicable to the use of an ARL OPTIM'X with UniQuant<sup>®</sup> and Katanax K1 Prime Automatic Fluxer. Laboratories using instruments other than ARL and Katanax should utilize the method to the fullest extent possible.

#### 7. PREPARATION OF SAMPLE

- 7.1 Preparation of Beads— Weigh 10.000 grams of Flux into tared weighing dish and record weight. Pour flux into platinum crucible. Weigh 1.000 gram of powdered concrete onto weighing paper and record weight. Pour powdered concrete sample into platinum crucible containing flux. Blend flux and powdered concrete together using a glass stirring rod until well mixed. Carefully place platinum crucible in to Automatic Fluxer. Fuse sample utilizing desired method.
- 7.2 Analyze for Cl<sup>-</sup> on WDXRF using OptiQuant method. Report in SM/LIMS

#### 8. PROCEDURE FOR Cl<sup>-</sup>

- 8.1 Samples are prepared in accordance with ARL OPTIM'X User Manual AA83612, Chapter 4 Samples, Thermo Scientific, 2002 and UniQuant<sup>®</sup> User Manual, chapters 6-7.

#### 9. PROBLEMS ENCOUNTERED

- 9.2 Interferences may arise due to scatter, absorption or other elements; therefore standardization is based upon internal calibration and standards for the WDXRF Instrument. Calibration discrepancies can be resolved with drift correction which is performed utilizing Setting-Up Samples provided by the manufacturer.

## **10. CALCULATIONS**

10.1 The WDXRF's software program gives a direct reading of the concentrations in percent.