R06B - TECHNIQUES TO FINGERPRINT CONSTRUCTION MATERIALS

FINAL REPORT

MAINE DEPARTMENT OF TRANSPORTATION
MATERIALS TESTING & EXPLORATION

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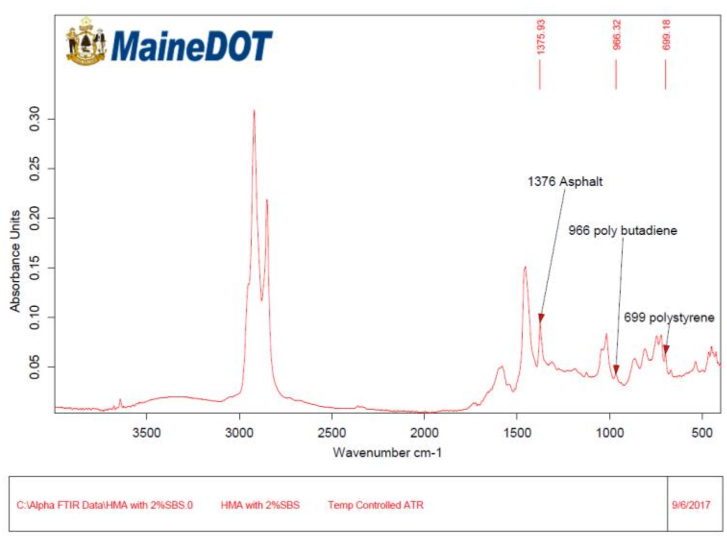
March 11, 2019



Executive Summary

The Maine Department of Transportation (MaineDOT) conducted Proof of Concept testing for the Second Strategic Highway Research program (SHRP2) Reliability project R06B, "Techniques to Fingerprint Construction Materials." The technologies evaluated were portable X-ray fluorescent (XRF) and Fourier Transform infrared (FTIR) spectroscopy. XRF measures the elemental composition of materials; FTIR identifies the molecular spectra of various materials (primarily organic compounds).

The Department conducted XRF testing on a number of materials: % chlorides in bridge deck cores; presence of recycled engine oil bottoms (REOB) in asphalt binder; arsenic and lead content of glass beads; alloy grade of reinforcing steel; titanium content of; and several other items. FTIR analysis was conducted on samples of asphalt binder to build a library of typical binders, as well as to identify the presence of polymers. Both technologies can provide quantitative data when properly calibrated. Equally important, they can provide qualitative data, identifying when a material is present that shouldn't be (such as REOB), or when the composition of a material has changed.

The test equipment was provided at no cost to the Department under the SHRP2 Implementation Assistance program. The XRF and FTIR were purchased by AASHTO and given to MaineDOT through a Memorandum of Understanding, and were delivered in the spring of 2017.

In addition to the test equipment, SHRP2 provided $250,000.00 in implementation assistance funding to be used for conducting lab and field testing, purchasing ancillary equipment and supplies, conducting data analysis, attending workshops and peer exchanges and producing a final report. In addition, technical assistance was made available at no cost, including two site visits by the R06B team, including the technical lead, technical experts from FHWA, and SHRP2 project leads from AASHTO, FHWA and Applied Research Associates.

The Department has already benefitted from this project in tangible ways. Based on an analysis of the chloride content test data, the current titration process involving hazardous chemicals can be replaced with XRF, resulting in reduced cost and testing time all while increasing technician safety. Also, inspectors will be able to verify that stainless steel rebar meets the correct grade requirements using a rapid, nondestructive test onsite. Verifying the presence of polymer and the absence of REOB in binder will help ensure pavement performance. Expanding the Department's ability to test materials such as traffic paint and glass beads with help verify specification compliance. Implementation of XRF and FTIR will have immediate benefits, and there will no doubt be additional applications discovered as the technologies are used more widely.

Introduction

The Maine Department of Transportation (MaineDOT) conducted Proof of Concept testing for the Second Strategic Highway Research program (SHRP2) Reliability project R06B, "Techniques to Fingerprint Construction Materials." The purpose of R06B was to identify and evaluate portable spectroscopic technologies that could be used to categorize and verify specific materials. The identified were X-ray fluorescent (XRF) and Fourier Transform infrared (FTIR) spectroscopy. MaineDOT's interest in the project was to investigate spectroscopy as a means to expand the range of testing available to the Department, as well as to replace current methods with nondestructive testing where possible.

The stated goals of the MaineDOT implementation project were:

- Maximize the use of real-time nondestructive testing to verify the properties of various construction materials.
- Reduce test time and cost.
- Reduce the incorporation of out-of-specification material into highway facilities.

The objectives identified when applying for implementation assistance were as follows:

- Determine which material properties can be accurately identified using portable XRF. Materials to be included in the proof-of-concept are:
  - Traffic paint – measure Titanium content and check for dilution.
  - Asphalt binder – check for presence of wear metals and lubricants (zinc, copper, molybdenum) which are indicative of recycled lubricating fluids.
  - Portland cement – rapid field chemical analysis.
  - Glass beads – measure arsenic and lead content for EPA compliance.
  - Reinforcing steel – alloy content for corrosion-resistant bars
  - Guardrail & fasteners – measure thickness of galvanized coating
  - Recycled Asphalt Shingles (RAS) – measure copper content for potential use as a means to identify presence of RAS in asphalt mixture.
  - Bridge deck core specimens – measure chloride content
- Investigate use of FTIR for testing the following material properties:
  - Hydrated lime content of asphalt mixture.
  - Polymer content of asphalt binder.

During the course of the project, it became clear that several of the applications held more promise than others, so priority was given to those applications with the highest potential for successful implementation. For example, XRF proved to be very effective in measuring the chloride content of concrete core specimens, whereas using it as an indicator of the presence of recycled asphalt shingles (RAS) in asphalt pavement proved unsuccessful.

Project Team

The following MaineDOT personnel were instrumental in completing the Proof of Concept project:

Table 1: R06B Project Team

Name	Title	Role
Mark Alley	Laboratory Testing Engineer	Overall management of XRF and FTIR testing including personnel, equipment and supplies; training, and data management
Derek Nener-Plante	Asphalt Pavement Engineer	Asphalt subject matter expert; experimental design, data analysis
Bruce Niles	Chemistry Lab Supervisor	Radiation safety; lab testing
James Robinson	Freeport Lab Supervisor	Coordinated XRF testing – Freeport
Caroline Nguembu-Tagne	Lab Technician	XRF testing – Freeport
John Clark	Lab Technician	XRF testing – Bangor
Casey Nash	Assistant Engineer	FTIR testing; data management/analysis
Ryan Vose	Independent Assurance	Onsite XRF testing
Technical assistance was provided through SHRP2:		
Name	Title	Role
Maria Chrysochoou	Dept. Head – Civil and Environmental Engineering, University of Connecticut	R06B Technical Lead; Subject matter expert (SME)
Terry Arnold	Senior Research Chemist, FHWA	Subject matter expert
Anant Shastry	Research Chemist (under contract to FHWA)	Subject matter expert

Proof-of-Concept Testing - XRF

Chlorides in Concrete

MaineDOT measures the chloride content of core specimens sampled from existing bridges as part of its bridge deck evaluation program. Cores are sliced at various depths; the slices are pulverized and tested to determine the chloride content using AASHTO T 260, “Sampling and Testing for Chloride Ion in Concrete and Concrete Raw Materials.” AASHTO T 260 is a titration test which involves digesting the pulverized concrete in a nitric acid – H_2O solution, adding methyl orange indicator and additional acid as needed, boiling the solution, filtering, and running a titration (including addition of silver nitrate), and disposal of the waste (Figures 1 - 3). The test includes numerous steps involving very precise measurements, increasing the chance for errors. It requires a greater degree of training than for typical construction material tests. A technician can complete ten to fifteen measurements in a typical work day. A chloride value exceeding 1.35 pounds/cubic yard, or 0.03%, is the threshold value above which MaineDOT’s Bridge Program has determined that rebar corrosion may occur. Replacement of the titration method with XRF would have numerous benefits in reduced test time and cost, and increased safety.

As part of the SHRP2 project, MaineDOT obtained two handheld XRF devices: an Olympus Vanta C series, and a Thermo Fisher Scientific Niton XL3t 950. During the equipment training, it was determined that chloride testing would not be possible with the Olympus device, as it uses a rhodium anode; the signal for chlorine overlaps with rhodium. The Thermo Niton has a silver anode which does not have the same limitation, so all XRF chloride tests were conducted using the Thermo device.

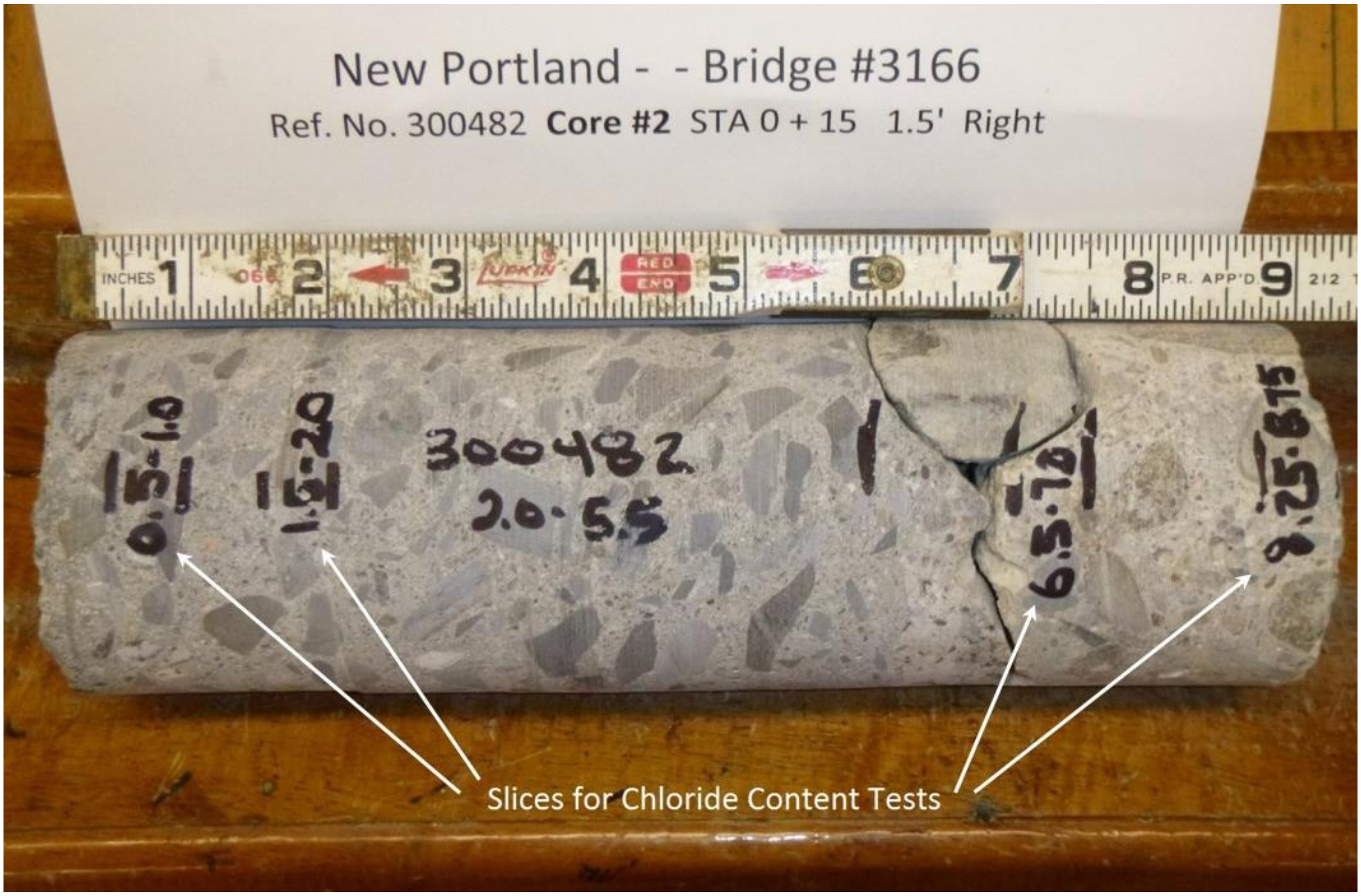


Figure 1: Typical bridge deck core

Figure 2a: Adding nitric acid

Figure 2b: Addition of indicator solution

Figure 3a: Titration

Figure 3b: Disposing of hazardous waste

During the initial onsite training session, XRF tests were conducted on specimens of pulverized concrete that remained following previous titration tests. The pulverized material was prepared by simply placing loosely into XRF specimen cups. Seven specimens were tested with the XRF, and the results compared to the previous titration measurements, resulting in a linear regression, R^2, of 0.9969, convincing the team that use of XRF to predict chloride content was feasible (Figure 4a). Additional specimens were tested using several preparation methods: placed loose in the XRF specimen cup; lightly compacted in the cup by tamping; and compacted against the Prolene film covering the inverted cup. Compacting the pulverized material resulted in the best comparison to AASHTO T 260 (Figure 4b). After further consultation with the SMEs, it was decided to purchase a pellet press to standardize the specimen compaction procedure.

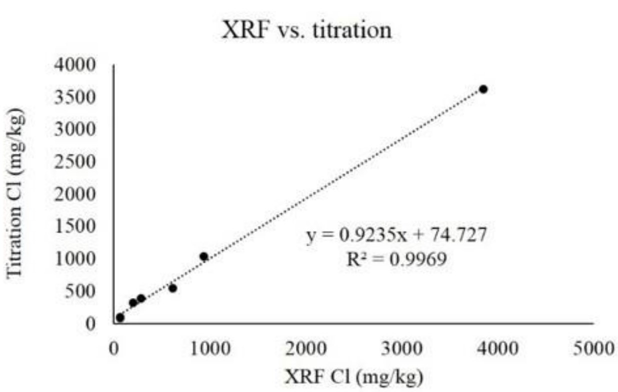


Figure 4a: Linear regression - Initial chloride trial

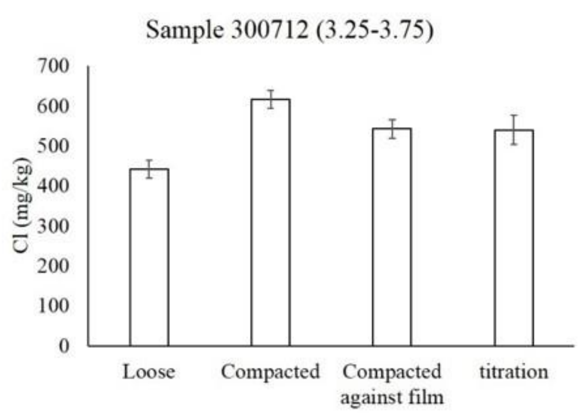


Figure 4b: Comparison of initial sample preparation

Once the press was in service, a larger correlation study was conducted using pressed pellets (Figures 5 – 7). As part of this phase, the team examined several factors, including: XRF test mode, element range @ 60 seconds, and binding agent type and percent (see Table 2). Three readings were completed on each pellet.

Table 2: XRF Test Detail Matrix

FACTOR	LEVELS	DETAILS
Analysis Mode	3	AllGeo, Mining Cu/Zn, Mining Ta/Hf
Element Range @ 60 sec	2	5/5/5/45 and 15/15/15/15 – Main, Low, High, Light
Binding Agent	6	5 recommended binding agents plus control w/no agent
Binding Agent %	2	0%, 5%, 10%
Replicates	3	3 measurements on each pellet

Figure 5a: Weighing pulverized material

Figure 5b: Mixing specimen


Figure 6: Creating pressed pellet


Figure 7: Pressed pellet ready for XRF testing

Almost all combinations of sample preparation and test parameters resulted in an excellent correlation between XRF and AASHTO T 260 (see Appendix I). Based on this, it was decided to discontinue use of binding agent when creating pellets. Further analysis of the data showed that using the “AllGeo” test mode with element range times of 5/5/5/45 seconds provided the best accuracy and precision. All further chloride testing was conducted using these parameters.

Additionally, XRF measurements were taken on the surface of the core slices to determine if pulverizing could be avoided altogether, which would dramatically reduce testing time and cost. Three readings were taken on the top, bottom, and around the perimeter of each slice (Figure 8); the nine readings were averaged to determine the chloride content. The resulting trend was very good (R2 = 0.9099), but there were several drawbacks identified. While the average chloride value compared well, the variability of individual readings was much higher than when testing pulverized material. Also, the technician needed to exercise discretion as to where to take the readings so as to avoid exposed aggregate faces. It was decided that direct testing of core slices would not provide the desired level of accuracy and precision. See test plan, Appendix II.

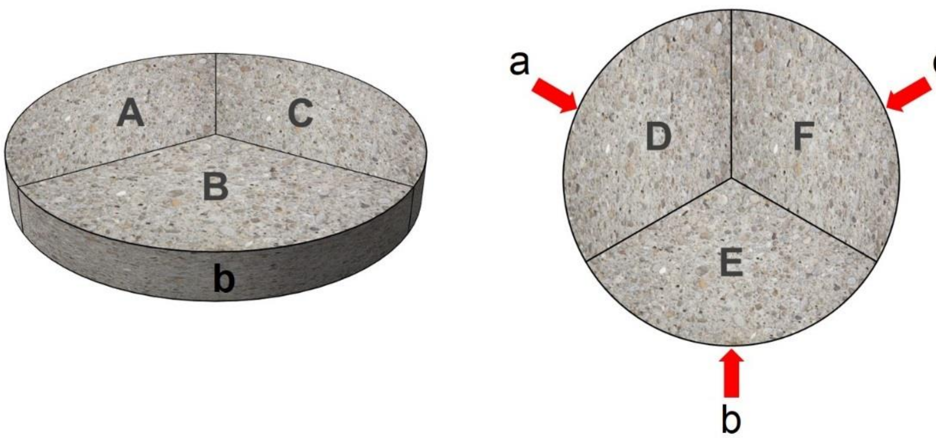


Figure 8: Core slice testing diagram

Using the findings from the initial phase, 388 specimens were tested with the XRF, and the results compared to AASHTO T 260, in order to develop a prediction model (Figure 9). This larger dataset produced a very strong correlation, with an R^2 of 0.9654.

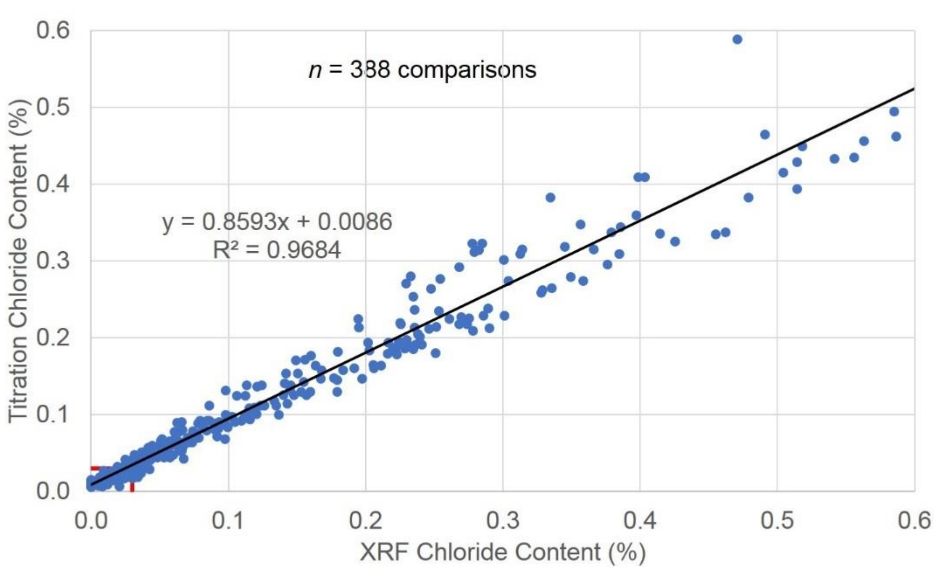


Figure 9: Linear regression - XRF v. Titration

It was noted that because the majority of test values exceeded the threshold of 0.03%, regression analysis should be conducted using only those results less than 0.10% chlorides. It is clear that the XRF limit of detection is producing values of 0.0% Cl even when the titration method detects a small amount of chlorides. It was determined that the linear relationship for values <= 0.10% was equivalent to the model using all data. The linear model for predicting titration value from XRF is:

$$\%Chlorides = 0.8593(XRF\ \%Cl) + 0.0086$$

To validate the model, 62 samples were tested with the XRF. The pressed pellets were then tested using the titration method, the results of which were compared to the XRF-predicted values. The results show excellent correlation (Figure 10); however, a paired t-test (α = 0.05) showed a significant difference (Table 3), albeit small enough to call into question whether or not it is of practical significance. It should be noted that all 62 samples were from a single bridge deck. It is possible that this introduced bias into the analysis given that the model was developed using samples from numerous decks, each having different source properties. Further validation will be conducted using samples from additional decks.

Table 3: Paired t-test results

Paired t-test, α		
Mean	0.1298	0.1336
Variance	0.0095	0.0095
Observations	62	62
Pearson correlation	0.995	
df	61	
t statistic	3.136	
P (T<=t) one-tail	0.0013	
t critical one-tail	1.670	
P(T<=t) two-tail	0.0026	
T critical two-tail	1.999	

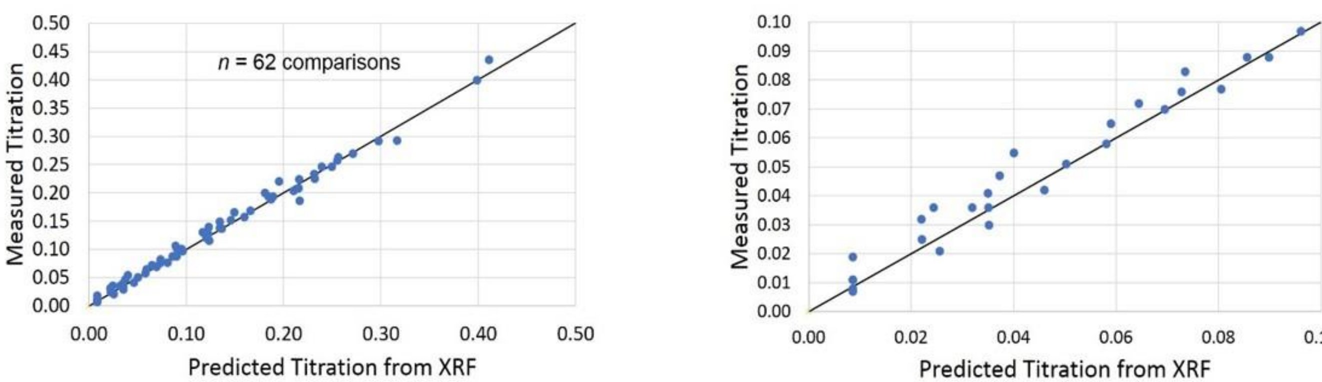


Figure 10: XRF chloride model validation

The final phase of the proof-of-concept for chloride testing is validation using known reference samples. Standard reference for this material type are not commercially available, so samples will be prepared in the laboratory using known amounts of sodium chloride.

In early 2019, a shift was noticed in the XRF chloride results. The values predicted with the linear model were not comparing as well with the titration results; the XRF values were trending lower. As part of the investigation, retained pellets that had been previously tested were retested; the retest values showed a similar reduction in percent chlorides when compared to the original XRF results. MaineDOT is working to determine the cause of this issue. One possible cause could be drift; it may be necessary to have the particular XRF recalibrated by the manufacturer. This points to the need to develop a quality control process to monitor the equipment performance.

Portland Cement

Currently, MaineDOT sends samples of Portland cement to a consultant laboratory for physical and chemical analysis, as part of our verification process for Standard Manufactured Materials. The ability to perform the chemical analysis in-house would represent a cost savings to the Department.

Ten calibration samples were purchased from the Cement and Concrete Reference Laboratory (CCRL) and tested using both the AllGeo and Mining Cu/Zn test modes. Element range @ 60 s was 5/5/5/45. Linear regression was determined for the following compounds: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3 and K_2O. The resulting linear equations were used to predict actual values when testing verification samples. To test the accuracy of the predictive models, eight verification samples were tested with the XRF. The measured value for each compound was adjusted using the applicable equation, and the results compared to the values reported by the consultant testing lab.

The linear models were reasonably accurate for Fe_2O_3, CaO, SO_3 and K_2O, but accuracy for the remaining compounds was poor. A graph displaying the results for Fe_2O_3 is shown in Figure 11. In discussing this with the project SME, it was determined that the range of elemental concentration was too narrow for several elements to provide an accurate linear model. For example, the SiO_2 contents of the CCRL samples ranged from 19.23 to 21.34 percent. In discussion with the project Technical Lead, it was determined that testing conducted at Tennessee DOT found similar results. They were able to improve the linear models by purchasing calibration standards that contained a broader range of concentration of the key elements. MaineDOT will obtain similar standards to improve the XRF calibration. Even though the initial results were mixed, the testing demonstrated that the handheld XRF has potential for use as a tool to reduce the need for MaineDOT to outsource chemical analysis of Portland cement.

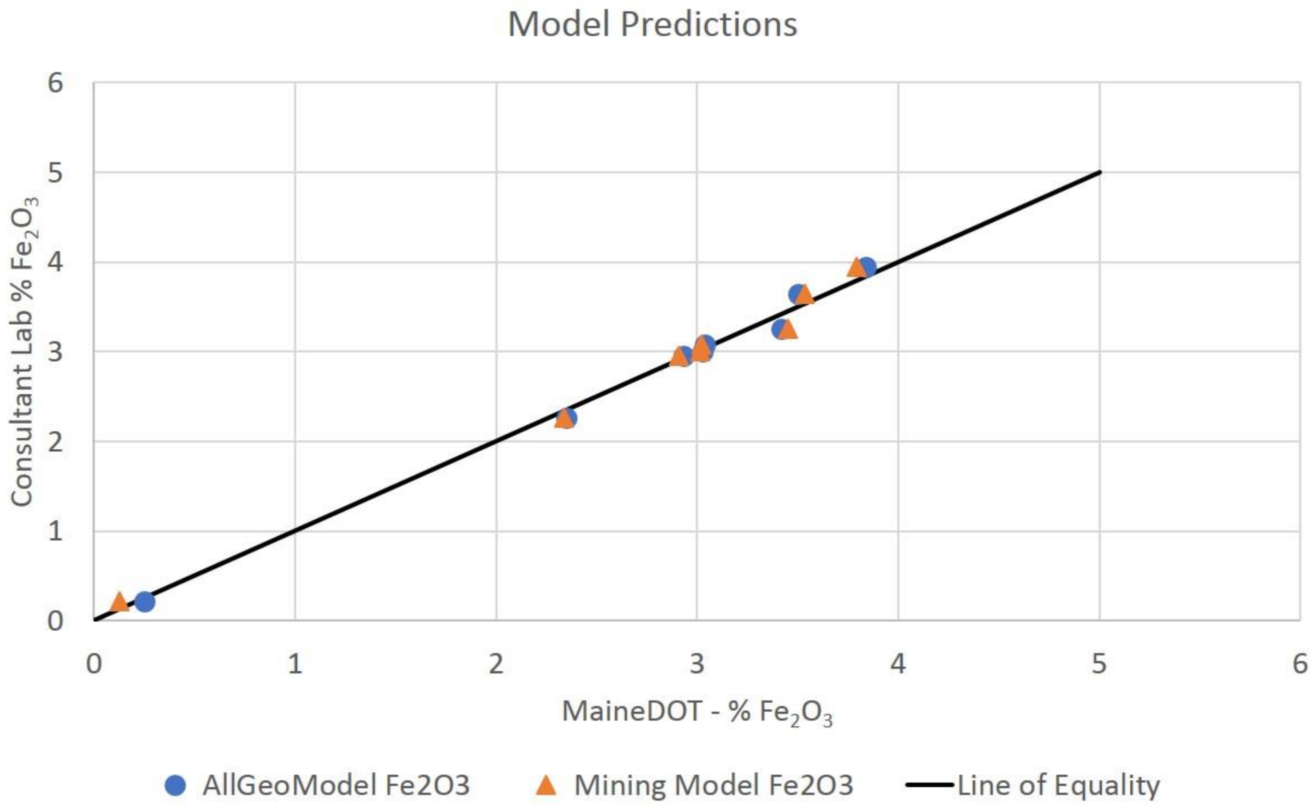


Figure 11: Linear model validation - Fe_2O_3

Reinforcing Steel

MaineDOT has increased the use of stainless steel reinforcing steel in recent years. Rebar is currently accepted based on manufacturer certification. Prior to obtaining the XRF, DOT did not possess the means to verify the certification data. Use of handheld XRF provides a tool to verify steel grade onsite, prior to rebar installation.

Measurements were taken on rebar on a bridge project in Augusta, ME. Tests were conducted using the Vanta XRF in AlloyPlus mode, by taking several readings with the XRF at different locations on the rebar surface. The results indicate that the AlloyPlus calibration provides sufficient accuracy to verify that the correct grade is being used. Additional in-situ tests will be conducted in 2019 to increase the dataset to include additional steel grades and manufacturers. See Appendix III for example data.

Table 4: Stainless steel – XRF v. Mill Report

Element (%)	Mill Report	Vanta XRF
Mn	1.74	1.82
Cr	22.73	23.49
Ni	3.57	3.76
Cu	0.34	0.35

Glass Beads

AASHTO M 247 specifies that glass beads used in pavement marking applications shall not contain more than 200 ppm of lead or arsenic, as determined using Environmental Protection Agency test methods

3052, 6010B, or 6010C. Method 3052 requires digesting specimens in nitric and hydrofluoric acids, and 6010B and 6010C utilize inductively coupled plasma-atomic emission spectrometry. As a result, MaineDOT does not currently test glass beads to verify specification compliance. XRF provides a means to conduct this testing, as it is very good at measuring heavy metals.

Several samples of glass beads were obtained from DOT projects and tested with the Thermo XRF, using both the AllGeo and the Mining Cu-Zn modes, using a test time of 60 seconds. Specimens were prepared by pouring loose beads into the XRF sample cups. Using the Mining mode, all samples were below the limit of detection (LOD); the AllGeo mode detected between 7 and 8 ppm of lead in several samples, with arsenic again being below the LOD.

Performance-Graded Asphalt Binder

In 2014, MaineDOT joined the other New England states in prohibiting the use of recycled engine oil bottoms (REOB) to modify asphalt binder. Binder suppliers are required to certify that their product does not contain REOB, but DOT did not have a way to verify this.

FHWA has developed a test method to estimate REOB content in binder using handheld XRF by measuring zinc, copper and molybdenum. It requires preparing calibration samples with known sources of binder and REOB. MaineDOT does not need to determine REOB content, only to confirm that it is not present.

Approximately 25 samples of PG binder were tested using AllGeo mode at 60 seconds. Samples were prepared by pouring heated binder into XRF sample cups. In all samples, copper was below the LOD; zinc ranged from 0 – 23 ppm and molybdenum from 0 – 16 ppm (typically 6 – 10 ppm). This data indicates that binder suppliers are not using REOB on MaineDOT projects. See Appendix IV for test plan.

Recycled Asphalt Shingles (RAS)

In an attempt to detect the presence of recycled asphalt shingles (RAS) in asphalt mix, samples of RAS were obtained from asphalt mixing plants and tested with the XRF. The goal was to determine if RAS contained metals that could be used to indicate its presence, much the way REOB is detected in binder. In addition to testing RAS, blends of RAS and RAP were tested, as this is how RAS is typically introduced at Maine asphalt plants. While all samples contained zinc and most contained copper, neither element was present in a consistent percentage, and often the zinc content in the RAS/RAP blends was < 200 ppm, making it unlikely to be detected to a significant degree when blended with virgin aggregate and binder. Therefore, no further work was done to analyze RAS. See Appendix V for test plan.

Traffic Paint

MaineDOT uses white and yellow waterborne traffic paint for pavement striping. Specifications require white paint to have a minimum of 1.0 lb/gal of titanium dioxide (TiO_2), while yellow can contain a maximum of 0.2 lb/gal. The typical density of white paint is 14.1 lb/gal, so the TiO_2 content should be at least 7.09%. For yellow paint, 13.7 lb/gal, the maximum TiO_2 would be 1.46%.

Samples of white and yellow paint were poured into XRF sample cups and tested for 60 s using AllGeo mode. The average TiO_2 content for white paint was 7.10%, for yellow paint it was 1.66%. In order to validate the XRF results, samples will be sent to an independent laboratory for TiO_2 % determination. However, the primary use of XRF for paint will be as a qualitative check to detect possible dilution. By measuring manufacturers samples for a baseline TiO_2 %, field samples can be quickly checked to determine if the paint has been diluted.

Proof-of-Concept Testing – FTIR

The primary interest in FTIR testing for MaineDOT is in the analysis of asphalt binders. Of particular interest is detecting the presence of polymer. Maine specifies polymer-modified binder with the multiple stress creep recovery (MSCR) test, and although a minimum polymer content is not specified, suppliers must add polymer to produce certain grades. FTIR can provide a rapid test to determine if a binder sample contains polymer for qualitative checks. Presence of polymer is indicated by observing peaks in the spectra (Figure 12) at wavenumbers of 966 (polybutadiene) and 699 (polystyrene). Additionally, regardless of whether or not the binder should contain polymer, FTIR can detect formulation changes which could be used to trigger further investigation.

Every verification sample of PG binder tested in 2018 was analyzed with the FTIR to build a library of MaineDOT asphalts. This database will help detect future formulation changes or contaminated product. Also, in cases where it cannot be verified through production records that a polymer-modified binder was used in a pavement when it was required, samples of binder can be extracted and recovered, and analyzed with the FTIR. See Appendix VI for test plan.

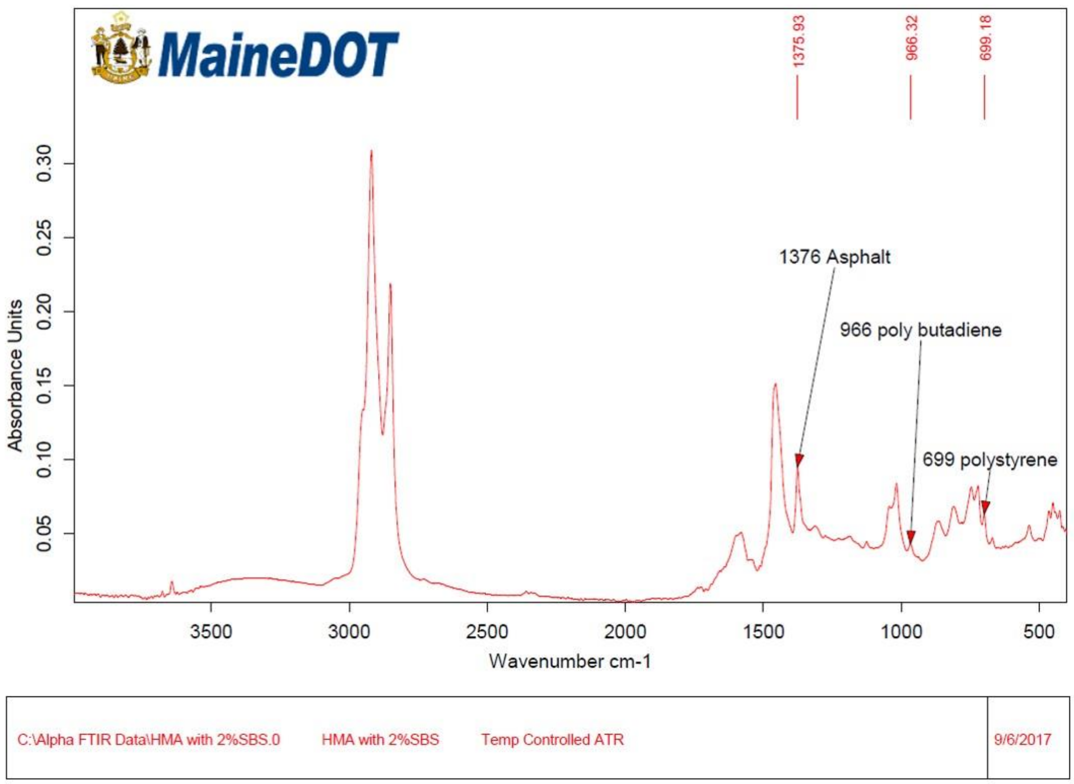


Figure 12: FTIR analysis - PG Binder w/SBS polymer

Benefits

To quantify the benefits of XRF, a comparison of relative cost of chloride content testing using AASHTO T 260 versus XRF was conducted. Assuming the XRF and pellet press last 10 years, and the laboratory runs 800 tests/year, it was estimated that the Department could save over $8.00/test. The analysis does not include additional costs associated with chemical hygiene, additional training, etc. This is in addition to the critical benefit of improving employee safety by reducing exposure to harmful chemicals.

Table 5: Cost Comparison

Cost Comparison of Chloride-in-Concrete Analysis Methods (Titration vs. XRF)

Category	Titration				XRF			
	Item	Cost	No. Tests	Cost/Test	Item	Cost	No. Tests	Cost/Test
Supplies	No. 40 Filter Paper, pkg of 100	$ 55.00	100	$ 0.55	Pellet cups, 1000ct	$ 110.00	1000	$ 0.11
	No. 41 Filter Paper, pkg of 100	$ 55.00	100	$ 0.55	Plastic vials, 100ct	$ 98.00	100	$ 0.98
	Nitric Acid, 500ml	$ 55.00	167	$ 0.33	Handheld XRF	$ 36,000.00	8000	$ 4.50
	Electrode	$ 800.00	800	$ 1.00	Pellet Press/Accessories	$ 26,000.00	8000	$ 3.25
	Silver Nitrate, 125g	$ 500.00	10000	$ 0.05				
	Filling Solution, 6-2oz. Bottles	$ 105.00	400	$ 0.26				
	Ionic Strength Adjuster, 475ml	$ 92.00	10000	$ 0.01				
	Chloride Standard, 475ml	$ 73.00	1600	$ 0.05				
	Sub-total			$ 2.80	Sub-total			$ 8.84
Waste Disposal	Truck Driver, trip	$ 250.00	250	$ 1.00				
	Truck, trip	$ 160.00	250	$ 0.64				
	Disposal, 5 gal	$ 260.00	125	$ 2.08				
	Empty containers, 1ct	$ 20.00	125	$ 0.16				
	Sub-total			$ 3.88	Sub-total			
Radiation Monitoring					Registration, per year	$ 120.00	800	$ 0.15
					Inspection, per 2 years	$ 450.00	1600	$ 0.28
					Film Badges, per year	$ 56.00	800	$ 0.07
	Sub-total				Sub-total			$ 0.50
Testing	Technician @ $23/hr.	$ 184.00	10	$ 18.40	Technician @ $23/hr.	$ 184.00	25	$ 7.36
	Sub-total			$ 18.40	Sub-total			$ 7.36
	TOTAL			**$ 25.08**	**TOTAL**			**$ 16.70**

Conclusions

The SHRP2 R06B proof-of-concept implementation project was successful in demonstrating the potential applications of portable spectroscopic devices in construction materials testing. Both XRF and FTIR will provide MaineDOT with the ability to produce qualitative and quantitative analysis of a number of materials, including the ability to verify specification compliance for several material properties that the Department did not have the ability to test prior to this project (such as presence of REOB in PG binder). The ability to verify properties such as grade of steel quickly at the project site will reduce the potential for incorporation of nonconforming material being incorporated into the work. Also, XRF has been demonstrated to be a viable replacement for the AASHTO T 260 as a means to determine chloride content of concrete in a manner that reduces test time, environmental impact and cost, while improving technician safety.

Although these spectroscopic tools have shown great promise, one of MaineDOT's lessons-learned was the importance of understanding the equipment operation and limitations. Without a clear understanding of the various calibrations, equipment settings, sample preparation techniques, etc., it is very possible to produce misleading test result. Proper training of those conducting the tests and analyzing the results is critical to successful use of these technologies.

Test standards already exist for some applications of XRF and FTIR, but additional AASHTO test methods will need to be developed.

Recommendations/Next Steps

XRF

1. Develop a quality control plan using various standard reference samples and control charts.
2. Obtain additional CCRL reference samples to improve the cement calibration.
3. Provide additional training for MaineDOT's lab technician. Note: scheduled for June 2019.
4. Identify the cause of the observed drift in chloride content results.
    a. If/when resolved, work with end users of the data to replace T 260 with XRF.
5. Incorporate XRF into the manufactured materials verification testing program for stainless steel rebar, glass beads, cement and traffic paint.
6. Identify additional uses for XRF to improve service to internal customers. Already identified: soil testing adjacent to bridge rehabilitation projects to detect contamination from lead paint.
7. Work through the AASHTO Committee on Materials and Pavements to develop test standards as needed.

FTIR

1. Continue to build a library of PG binder results.
2. Identify additional uses for FTIR to improve service to internal customers.

Technical Assistance

MaineDOT personnel received training from several sources, including:

- Participation by Mark Alley, Bruce Niles and Rick Bradbury in the SHRP2 R06B Technology showcase hosted by UConn on November 1 & 2, 2016.
- X-Ray safety and equipment operational training provided the vendors (Olympus and Thermo Fisher Scientific).
- Onsite training and technical support workshop at the MaineDOT Freeport Lab provided by the SHRP2 support team (Maria Chrysochoou, Terry Arnold and Anant Shastry) on October 10 & 11, 2017.
- Onsite training and technical support workshop at the MaineDOT Bangor Lab provided by the SHRP2 support team (Maria Chrysochoou and Terry Arnold) on June 27 & 28, 2018.
- Participation by Mark Alley, Derek Nener-Plante, Caroline Nguembu-Tagne, John Clark and Rick Bradbury at SHRP2 R06B Peer Exchange hosted by Tennessee DOT on September 26 & 27, 2018.

Technical Presentations

MaineDOT presented their preliminary findings in the following ways:

- SHRP2 XRF webinar, August 22, 2018 – presentation by Derek Nener-Plante.
- AASHTO Committee on Materials and Pavements annual meeting, August 9, 2018 - presentation by Rick Bradbury.
- NorthEastern States Materials Engineers Association annual meeting, October 16, 2018. presentation by Rick Bradbury.
- SHRP2 FTIR webinar, March 27, 2019 – presentation by Derek Nener-Plante.

APPENDIX I – XRF CHLORIDE TEST MODE & BINDING AGENT TRIAL

Mode/Range @ 60 Sec.	Binding Agent	% Binding Agent	R^2
Mining Ta/Hf 5/5/5/45	A	5	0.996445
AllGeo 5/5/5/45	B	5	0.996009
Mining Cu/Zn 5/5/5/45	A	5	0.995589
AllGeo 5/5/5/45	None	---	0.99518
Mining Ta/Hf 5/5/5/45	B	5	0.994987
AllGeo 5/5/5/45	A	5	0.99459
AllGeo 5/5/5/45	C	10	0.994295
Mining Ta/Hf 5/5/5/45	A	10	0.994101
Mining Cu/Zn 5/5/5/45	None	---	0.993977
AllGeo 5/5/5/45	A	10	0.993585
Mining Cu/Zn 5/5/5/45	A	10	0.993433
AllGeo 5/5/5/45	C	5	0.993298
Mining Ta/Hf 5/5/5/45	D	10	0.992926
Mining Cu/Zn 15/15/15/15	A	5	0.992883
Mining Cu/Zn 5/5/5/45	B	5	0.992812
Mining Cu/Zn 15/15/15/15	E	5	0.992806
Mining Cu/Zn 5/5/5/45	E	5	0.992745
Mining Ta/Hf 5/5/5/45	None	---	0.992719
Mining Cu/Zn 15/15/15/15	C	10	0.992453
Mining Ta/Hf 5/5/5/45	C	10	0.992397
Mining Cu/Zn 15/15/15/15	A	10	0.992358

APPENDIX II – BRIDGE DECK CORE TEST PLAN – XRF % CHLORIDES

Measurement of Chloride Content Through XRF Study
January 26th, 2018

Testing Plan Goals

The goals of the testing plan are as follows:

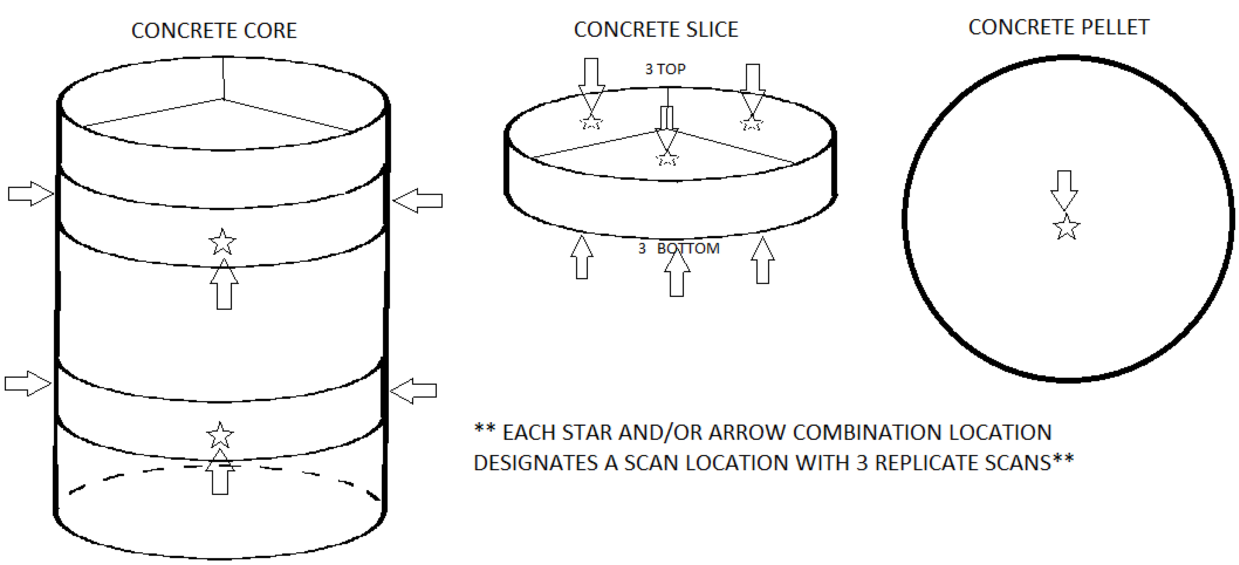
- Evaluate the feasibility of using the Niton ThermoScientific XRF to measure chloride content in bridge deck cores.

Methodology

Multiple bridge deck cores will be tested as part of this study. There will be three phases to this study: intact concrete cores, slices of concrete cores, and pulverized concrete cores. XRF analysis on the surface of the intact concrete core will be performed prior to slicing. The core will be sliced at the marked locations and measurements will be taken on the top and bottom of the concrete slice. The slice will be pulverized and two pellets will be made from the pulverized material. Intact Concrete Core: Each intact concrete core will have 9 XRF measurements/slice location: 3 replicate scans in 3 separate sections on the surface of the core. Each concrete slice will have a total of 18 XRF measurements: 3 replicate scans in 3 separate sections on the top of the slice and 3 replicate scans in 3 separate sections on the bottom of the slice. Each pulverized concrete slice will have a total of 6 XRF measurements: 3 replicate scans of the 2 pelletized specimens. An attempt will be made to not scan directly on large pieces of aggregate. The tables below summarize the experimental plan if there were 2 slices/core.

XRF Testing for Each Concrete Core

Intact Core	Core Slice	Pulverized Slice
Concrete Core 1	Concrete Slice 1	Pellet 1
		Pellet 2
	Concrete Slice 2	Pellet 1
		Pellet 2
9 scans/slice location	18 scans (9/side)	6 scans (3/pellet)



Sample Preparation

Each sample will be prepared in the same manner. The coring crew will core the bridge decks and mark the sections for chloride content analysis. The XRF will be used to analyze the intact core and then the core will be cut at the marked locations. The sample tracker will be filled out as each slice is produced by entering the bridge number into the "Material Source" field, the sample reference number into the "TIMS REF #" field, and the depth range in the "DESCRIPTION" field. The XRF will be used to analyze the top and bottom of the slices and then the slices will be pulverized. The pulverized material will be sent to the chemistry lab for T260 analysis and the remaining material will be used to produce 2 pellets. Each pellet will be immediately labelled with the sample tracker specimen number.

Testing Items

The following settings/procedures will be used on Chloride Content XRF testing:

Mode: The detection mode for the Thermo XRF will be **AllGeo** with all four element range filters turned on.

Time: A total detection time of 60 seconds will be used for all XRF Chloride Content testing. The time breakdown per element range filter will be 5 seconds each for Main/Low/High and 45 seconds for Light. **Element Range Filter: 5/5/5/45**

Replicates: Testing of replicates will be accomplished by repositioning the specimen over the detection window and scanning the same location.

Sample Identification: The abbreviation at the beginning of the XRF specimen number will be CC for Concrete Core, CS for Concrete Slice, and CP for Concrete Pellet. Type the XRF specimen number into the "NOTE" field on the Thermo XRF for each measurement.

APPENDIX III – XRF STAINLESS STEEL REBAR TEST REPORT

OLYMPUS

Method : **AlloyPlus**
Daily ID : **1**
Time : **2018-01-30 00:33:44**

Chemistry

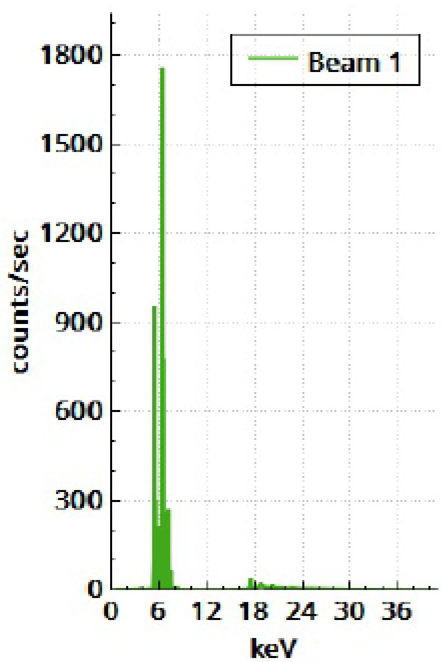
1_4362 2304 1_4062

1_4362

Exact - X2CrNiN 23-4 |r|n Duplex

El	%	+/- 2σ	1_4362
V	0.110	0.010	Resid. 0.2
Cr	23.490	0.073	
Mn	1.818	0.045	
Fe	70.056	0.093	
Co	0.123	0.045	Resid. 0.6
Ni	3.758	0.044	
Cu	0.347	0.014	
Zr	0.004	0.001	Resid. 0.1
Nb	0.018	0.001	Resid. 0.1
Mo	0.253	0.004	
W	0.017	0.005	Resid. 0.3
Pb	0.007	0.002	Resid. 0.1

Spectrum



Notes

Inspector: CNT
Location: Reading 3
N:
Note: AB024
Sample Descript: PG 58-28
Sample ID: 301529

Signature: ____________________ **Date:** ____________________

APPENDIX IV – XRF TEST PLAN – PG BINDER

Identification of Recycled Lubricating Fluids Through XRF Study

January 17th, 2017

Testing Plan Goals

The goals of the testing plan are as follows:

- Evaluate the feasibility of using XRF to measure zinc, copper and molybdenum content for potential use to identify presence of recycled lubricating fluids in asphalt mixture.

Methodology

Multiple sources of asphalt binder will be tested as part of this study. A partial table of the samples to be tested is attached. One specimen will be fabricated by the asphalt binder lab for each asphalt binder sample. Each asphalt binder sample will have a total of 6 XRF measurements: 3 for each piece of equipment. The table below summarizes the experimental plan.

XRF Testing for Each Asphalt Binder Source

Specimen / XRF Equipment	Thermo	Olympus
Specimen 1	3 replicates	3 replicates

Sample Preparation

Each sample will be prepared in the same manner. As the asphalt binder lab performs their standard testing they will fill a specimen cup approximately half way with binder. Each specimen will be immediately labelled with the TIMS reference number as well as the base binder grade on the sample cup.

Testing Items

The following settings/procedures will be used on Asphalt Binder XRF testing:

Mode: The detection mode for the Thermo XRF will be **TestAllGeo**. The detection mode for the Olympus XRF will be **geoChem-Extra**.

Time: A detection time of 60 seconds will be used for all XRF Asphalt Binder testing.

Replicates: Testing of replicates will be accomplished by repositioning the sample cup over the detection window.

Sample Identification: Type the XRF reference number into the “NOTE” field on both the Thermo XRF and the Olympus XRF for each measurement.

APPENDIX V – XRF TEST PLAN – RECYCLED ASPHALT SHINGLES

Identification of RAS / RAP Through XRF Study
November 7th, 2017

Testing Plan Goals

The goals of the testing plan are as follows:

- Evaluate the feasibility of using XRF to measure copper or zinc content for potential use to identify presence of RAS in asphalt mixture.

Methodology

Multiple sources of RAS and or RAP will be tested as part of this study. A full table of the samples to be tested are attached. Five specimens will be fabricated for each RAS/RAP source from material in the bucket. Each RAS/RAP source will have a total of 30 XRF measurements: 15 for each piece of equipment. The table below summarizes the experimental plan.

XRF Testing for Each RAS/RAP Source

Specimen / XRF Equipment	Thermo	Olympus
Specimen 1	3 replicates	3 replicates
Specimen 2	3 replicates	3 replicates
Specimen 3	3 replicates	3 replicates
Specimen 4	3 replicates	3 replicates
Specimen 5	3 replicates	3 replicates

Sample Preparation

Each sample will be prepared in the same manner. RAS and RAP are heterogenous materials so multiple specimens will be fabricated from the same bucket of material. The material shall be scooped out of the bucket into the sample cup. An effort shall be made to compact the material into the sample cup to reduce the air voids in the sample. The prolene film will then be installed. Each specimen will be immediately labelled with the Specimen ID number on the sample cup.

Testing Items

The following settings/procedures will be used on RAS XRF testing:

Mode: The detection mode for the Thermo XRF will be **TestAllGeo**. The detection mode for the Olympus is unknown at this time.

Time: A detection time of 60 seconds will be used for all XRF RAS testing.

Replicates: Testing of replicates will be accomplished by repositioning the sample cup over the detection window.

Sample Identification: Type the XRF reference number into the “SAMPLE” field on the Thermo XRF for each measurement. The input field for the Olympus is not yet known.