SHRP2 SOLUTIONS
TOOLS FOR THE ROAD AHEAD

Techniques to Fingerprint Construction Materials (R06B) X-ray Fluorescence spectroscopy

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Tennessee Department of Transportation

Webinar
August 22, 2018

U.S. Department of Transportation
Federal Highway Administration

American Association of State Highway and Transportation Officials
AASHTO

Webinar Agenda

- AASHTO & FHWA Introduction
- R06B Overview
- Principle of X-ray Fluorescence spectroscopy
- XRF applications – Maine DOT evaluation
- XRF applications – Tennessee DOT evaluation
- Questions & Answers

Focus Areas

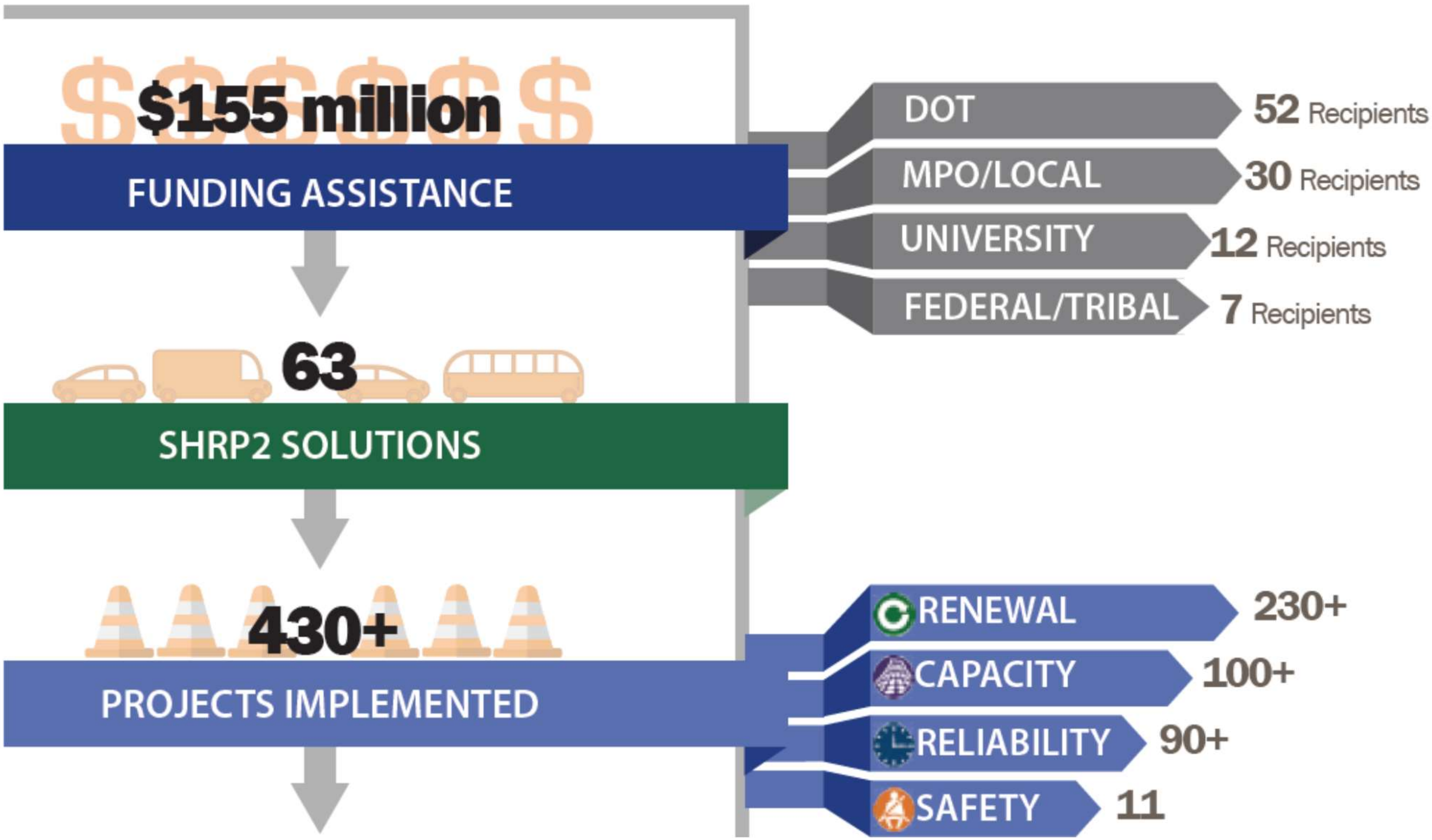
Safety: fostering safer driving through analysis of driver, roadway, and vehicle factors in crashes, near crashes, and ordinary driving

Reliability: reducing congestion and creating more predictable travel times through better operations

Capacity: planning and designing a highway system that offers minimum disruption and meets the environmental and economic needs of the community

Renewal: rapid maintenance and repair of the deteriorating infrastructure using already-available resources, innovations, and technologies

SHRP2 Implementation: INNOVATE . IMPLEMENT. IMPROVE.



SHRP2 Implementation:
INNOVATE . IMPLEMENT. IMPROVE.

304,406
PARTICIPANTS ENGAGED

12,378
OUTREACH ACTIVITIES

- TRAINING 11,435
- WORKSHOPS 710
- PEER EXCHANGES 106
- DEMOS 76
- SHOWCASES 51

16,629
HOURS TECHNICAL ASSISTANCE

RESULTS

Save lives, money, and time

- Bridges being built more quickly
- Smoother traffic flows and less congestion
- Reduced construction costs
- Safer roadways
- Smarter environmental reviews

(R06B) Techniques to Fingerprinting Construction Materials

Portable Spectroscopy Technology

RESEARCH: Explore expanded use of portable spectroscopy technologies in their ability to analyze commonly used construction materials in the field to aid in acceptance.

SOLUTION:

- Summary of Portable Methods & potential use for various materials.
- XRF – For testing pavement markings and epoxy coatings for example.
- FTIR - For evaluating Polymer in HMA, as well fingerprinting admixtures in PCC (accelerators, retarders, curing compounds)
- Generic testing procedures with sampling and data analysis guidelines, as well as proposed standards of practice.

X-Ray Florescence (XRF)

Attenuated Total Reflectance Fourier Transform Infrared (ATR FTIR) Spectroscopy

Maria Chrysochoou, Associate Professor, University of Connecticut

- Principle of X-ray Fluorescence spectroscopy

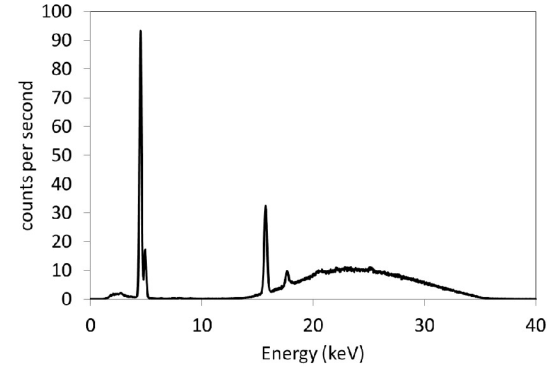
R06B Technologies

- **X-Ray Fluorescence Spectroscopy (XRF)**
  - Suited for measuring elemental composition of solids
  - Handheld equipment that can be used both in the lab and in the field

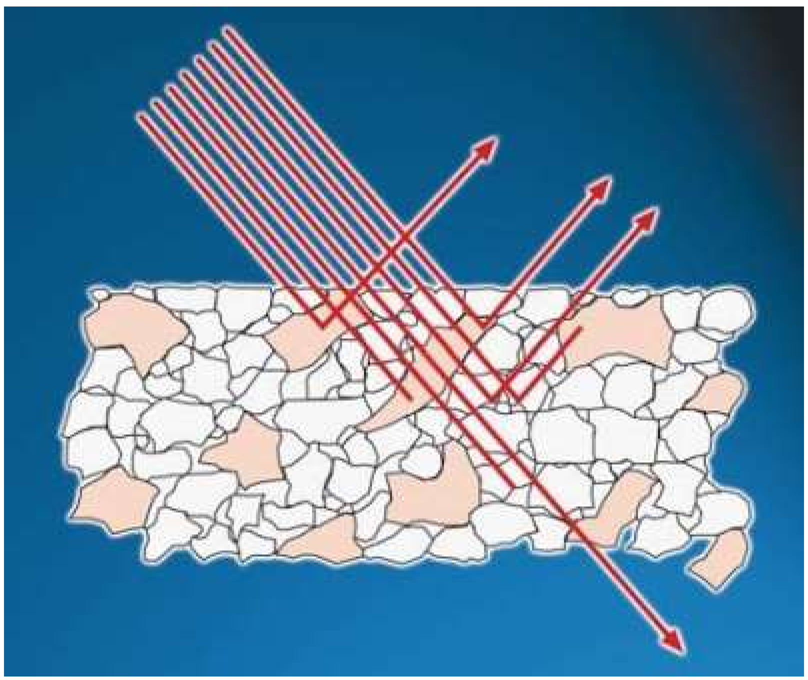
How XRF Instruments Work

X-Ray tube emits radiation of a certain energy/wavelength

Emitting X-Rays are recorded by a detector and spectrum is produced

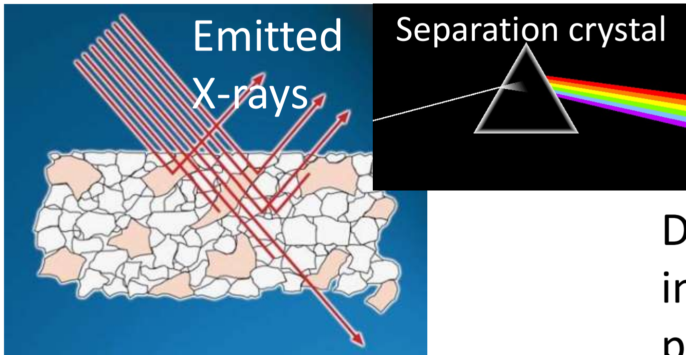


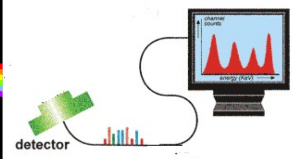
Internal calibrations are used to translate spectrum into element concentrations e.g. Ti 4,000 mg/kg



Material interacts with sample in a certain volume, i.e. there is a finite penetration depth

Types of XRF technologies

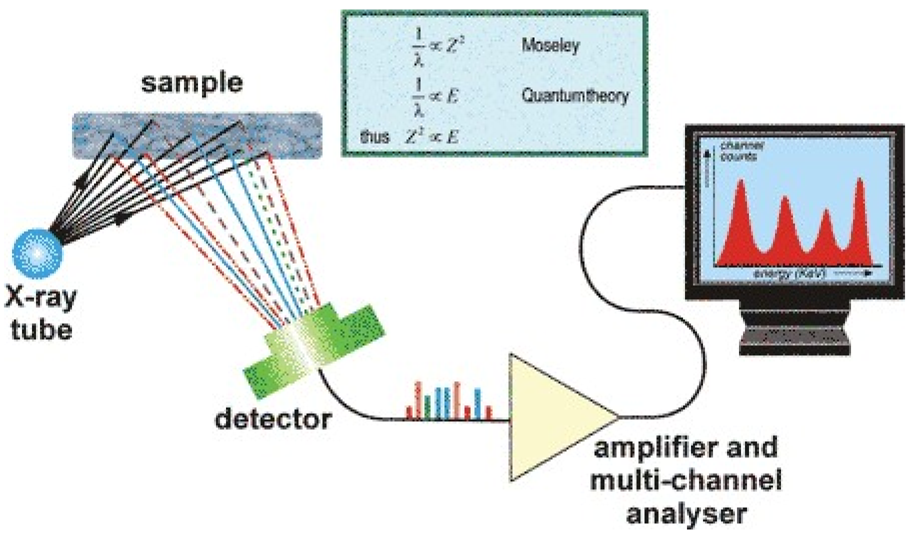




Detection of individual peaks

Wavelength dispersive XRF (WDXRF)

Detection involves a crystal that physically separates the signal into individual wavelengths which are then captured by a detector



Separation of peaks using software

Energy dispersive XRF (EDXRF)

Detection is done first of the entire signal and then it is separated into components

Types of XRF Equipment

Stationary (lab)

Requires sample preparation for granular materials)
(fusion with LiBO4, making a pellet)
Both WDXRF and EDXRF

Portable (lab or field)

No sample preparation necessary, can be deployed directly on the surface

EDXRF only

Typical Elements for Portable XRF Applications

Most portable XRF equipment comes with built in calibrations for 24-30 elements

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	**magnesium 12 Mg 24.305**											**aluminium 13 Al 26.982**	**silicon 14 Si 28.086**	**phosphorus 15 P 30.974**	**sulfur 16 S 32.065**	**chlorine 17 Cl 35.453**	argon 18 Ar 39.948
potassium 19 K 39.098	**calcium 20 Ca 40.078**	scandium 21 Sc 44.956	**titanium 22 Ti 47.867**	**vanadium 23 V 50.942**	**chromium 24 Cr 51.996**	**manganese 25 Mn 54.938**	**iron 26 Fe 55.845**	**cobalt 27 Co 58.933**	**nickel 28 Ni 58.693**	**copper 29 Cu 63.546**	**zinc 30 Zn 65.39**	**gallium 31 Ga 69.723**	**germanium 32 Ge 72.61**	**arsenic 33 As 74.922**	**selenium 34 Se 78.96**	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	**strontium 38 Sr 87.62**	**yttrium 39 Y 88.906**	**zirconium 40 Zr 91.224**	**niobium 41 Nb 92.906**	**molybdenum 42 Mo 95.94**	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	**silver 47 Ag 107.87**	**cadmium 48 Cd 112.41**	**indium 49 In 114.82**	**tin 50 Sn 118.71**	**antimony 51 Sb 121.76**	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	**barium 56 Ba 137.33**	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	**tungsten 74 W 183.84**	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	**gold 79 Au 196.97**	**mercury 80 Hg 200.59**	**thallium 81 Tl 204.38**	**lead 82 Pb 207.2**	**bismuth 83 Bi 208.98**	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]			

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	**uranium 92 U 238.03**	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

What You Do and See as XRF User

- Select a calibration
- Place the sample on the XRF window (or the XRF window on the surface)
- Push a button
- Look for the results

What You Do and See as Portable XRF User

Visual Output

Exported Results in Excel format (Concentration mg/Kg or wt.%)

Sample	Ni	Ni +/-	Ni Pass	Ti	Ti +/-	Ti Pass	Cr	Cr +/-	Cr Pass
XYZ -1	189	27	Pass	4784	248	Pass	18098	299	Pass
XYZ -2	<LOD	70		6863	215	Pass	346	18	Pass
XYZ -3	<LOD	56		5396	197	Pass	203	15	Pass
XYZ -4	85	19	Pass	4553	178	Pass	3730	65	Pass
XYZ -5	72	19	Pass	9538	231	Pass	225	14	Pass
XYZ -6	52	17	Pass	4697	146	Pass	271	13	Pass
XYZ -7	60	14	Pass	7792	170	Pass	164	10	Pass
XYZ -8	<LOD	43		9122	199	Pass	280	13	Pass
XYZ -9	78	18	Pass	10195	225	Pass	204	12	Pass
XYZ -10	74	20	Pass	5689	180	Pass	156	13	Pass

Result Error QA/QC result

Warning!!

- Built-in calibrations are NOT always accurate

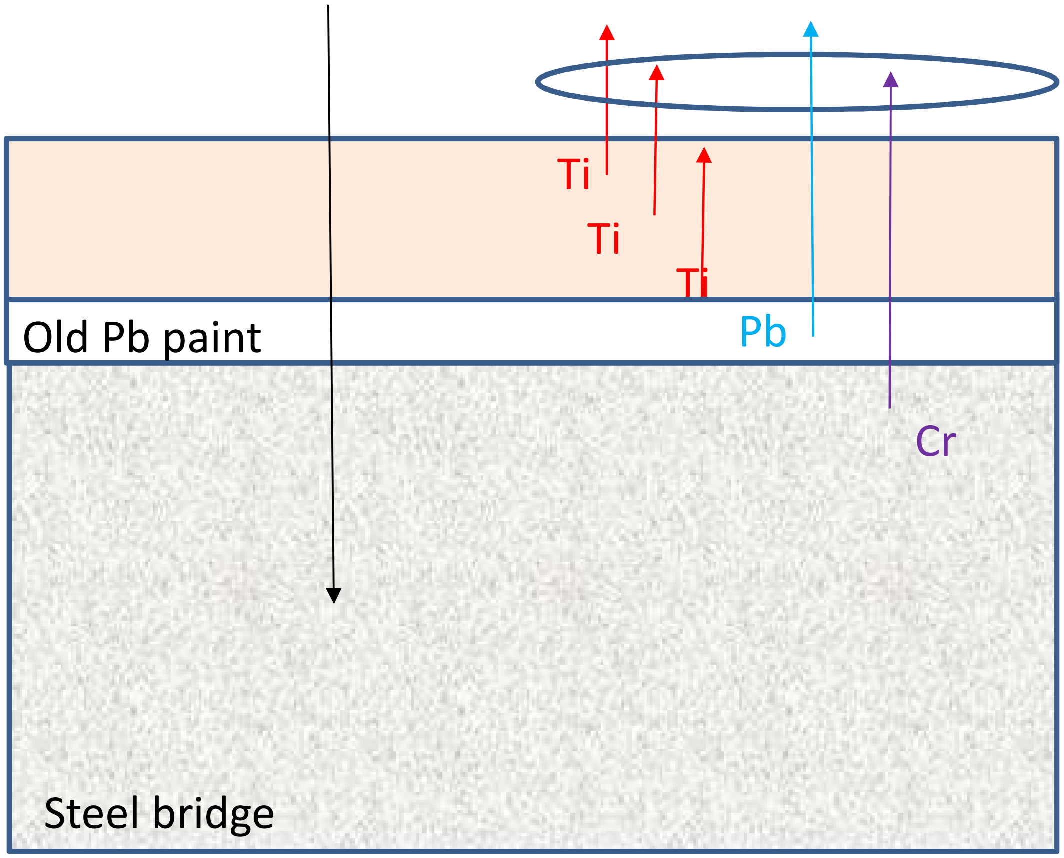
- The XRF will always produce a number, but the number may be misleading if internal calibration is not checked and developed for the specific matrix you are testing

- XRF is a very shallow measurement, you are testing only few microns of the material

Example – Paint Analysis

The energy of the incident X-Rays is enough (40-50 keV) to penetrate cm deep into the sample

Detector will pick up Ti from fresh paint, Pb from old paint and Cr from steel



Wet paint, layer thickness 130 µm

Paint: Water emulsion + TiO_2 pigment

Ti energy 4.5 keV, penetration depth ~100 µm

Pb 1770 µm

Cr 200 µm

XRF Advantages and Limitations

Advantages

- Pre-calibrated for a wide range of elements
- 1-2-minute testing time
- Little or no sample prep required, depending on the material
- No maintenance required—costs only associated with equipment acquisition ($35-$40K)
- Several applications possible (more bang for your buck)

Limitations

- Built in calibrations only work for certain material types – development of material-specific calibration often needed
- Does not work for light elements

Derek Nener-Plante, Maine Department of Transportation

- XRF applications – Maine DOT evaluation

R06B–Maine

- MaineDOT goals for R06B:
  - Maximize non-destructive testing
  - Reduce test time and cost
  - Reduce incorporation of out-of-spec material into DOT work
- XRF
  - Chlorides in bridge deck cores
  - Titanium in traffic paint
  - REOB in PG Binder
  - SS Rebar
  - Galvanized coating thickness
  - Glass Beads – lead, arsenic
  - Presence of RAS in HMA?

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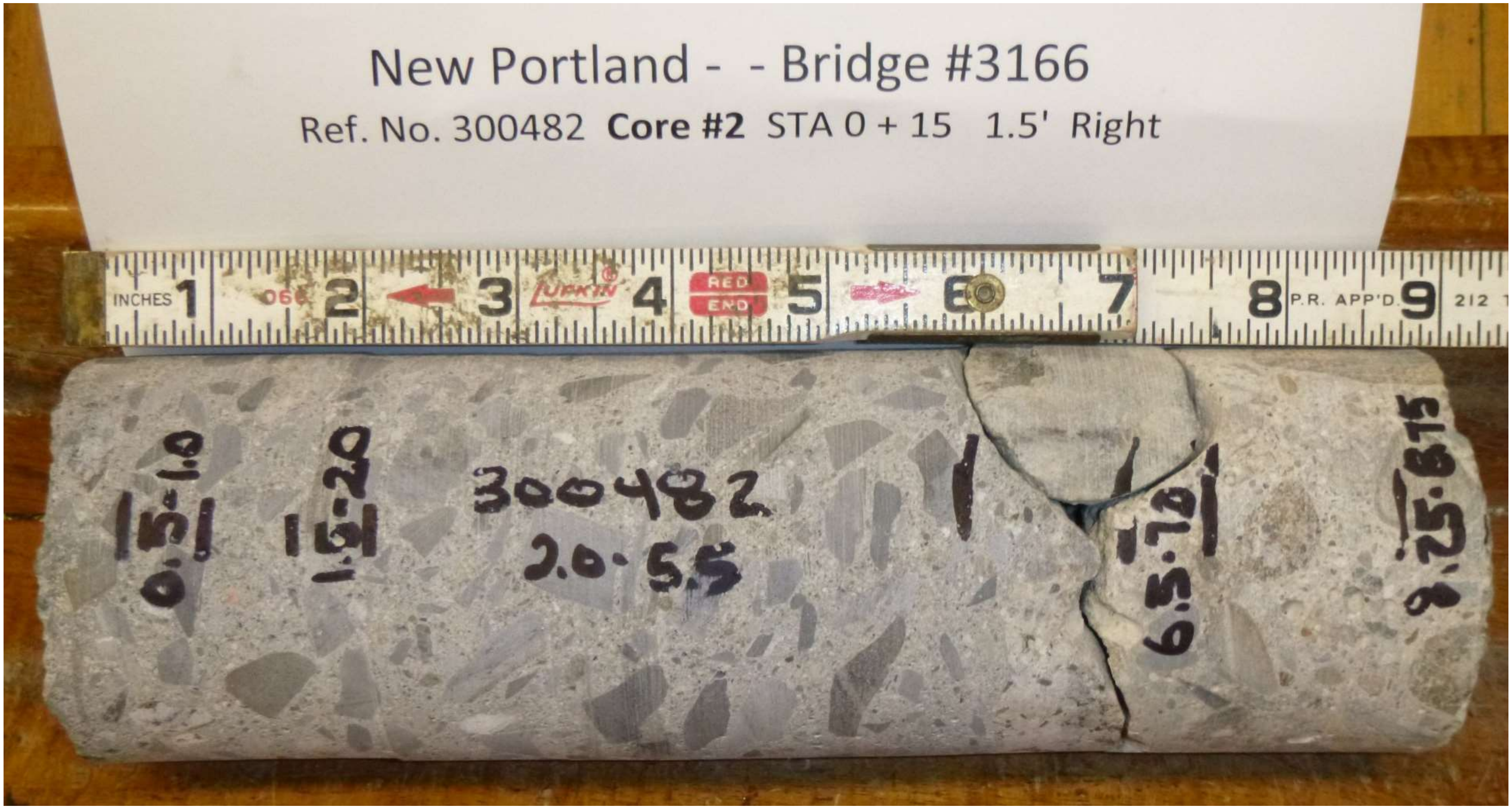
Stainless steel rebar

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

Chloride Content – Bridge Deck Cores



- Concrete cores pulverized and analyzed for chloride content ~ rebar corrosion begins at 1.35lb/cy or 0.03%

Chloride Content – Bridge Deck Cores

- Current method: AASHTO T 260 (Gran Plot Method)
  - Requires nitric acid and silver nitrate
  - Numerous steps
  - 10 tests/day

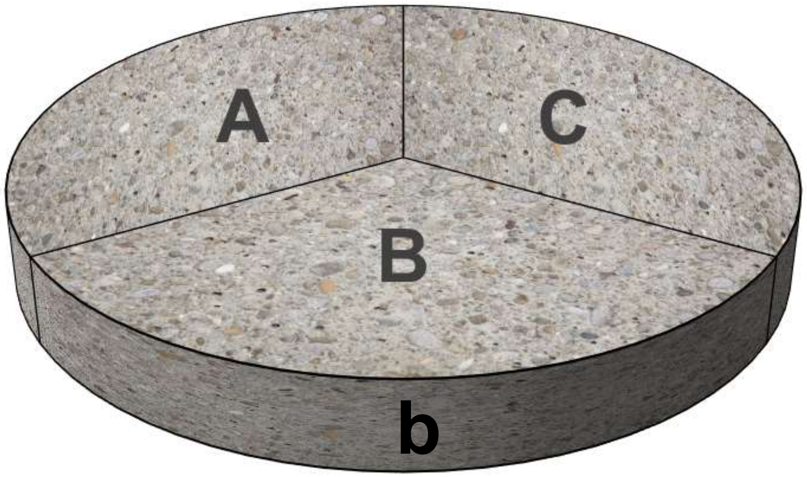
- XRF method
  - No chemicals
  - 25+ tests/day
  - Less training required

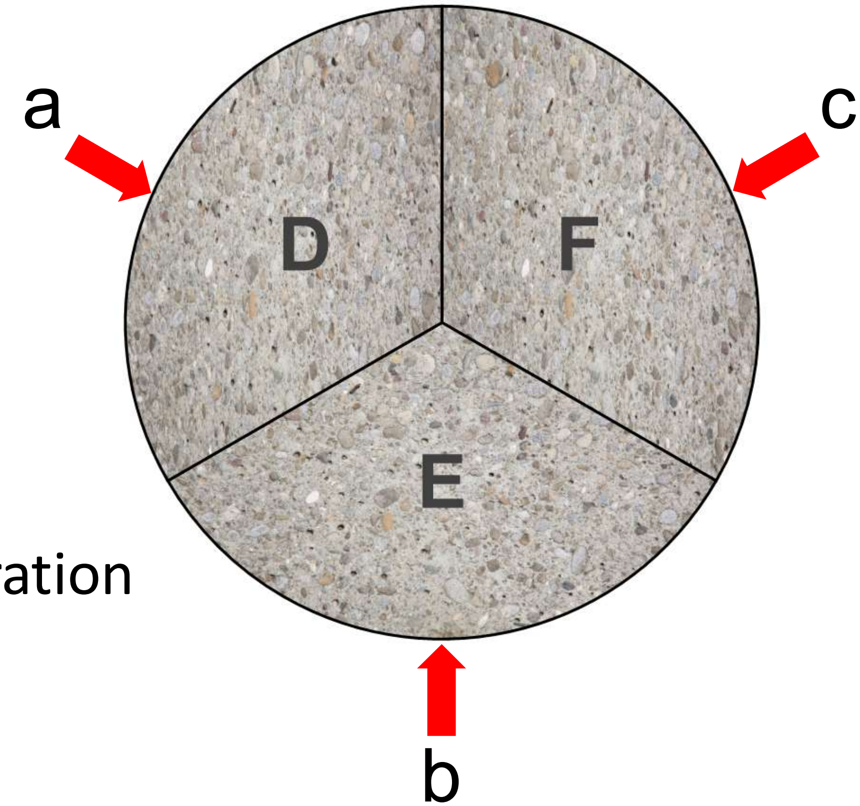
Chloride Content – Bridge Deck Cores

- Split-sample comparison on two types of samples:
  - Concrete Cores
  - Pellets from Pulverized Cores
    - Evaluated numerous binding agents for pelletized samples, XRF settings, direct measurement of concrete
    - Selected the settings that provided the best correlation on a limited amount of measurements vs. titration values
    - Expanded population of comparison

Item	Levels	Details
Analysis Mode	3	AllGeo and Two Mining Modes
Time Breakdown	2	5/5/5/45 & 15/15/15/15
Binding Agent	6	None and 5 recommended agents
Binding %	2	5% & 10%
Replicates	3	Three measurements on each pellet

Surface Testing of Core Slices

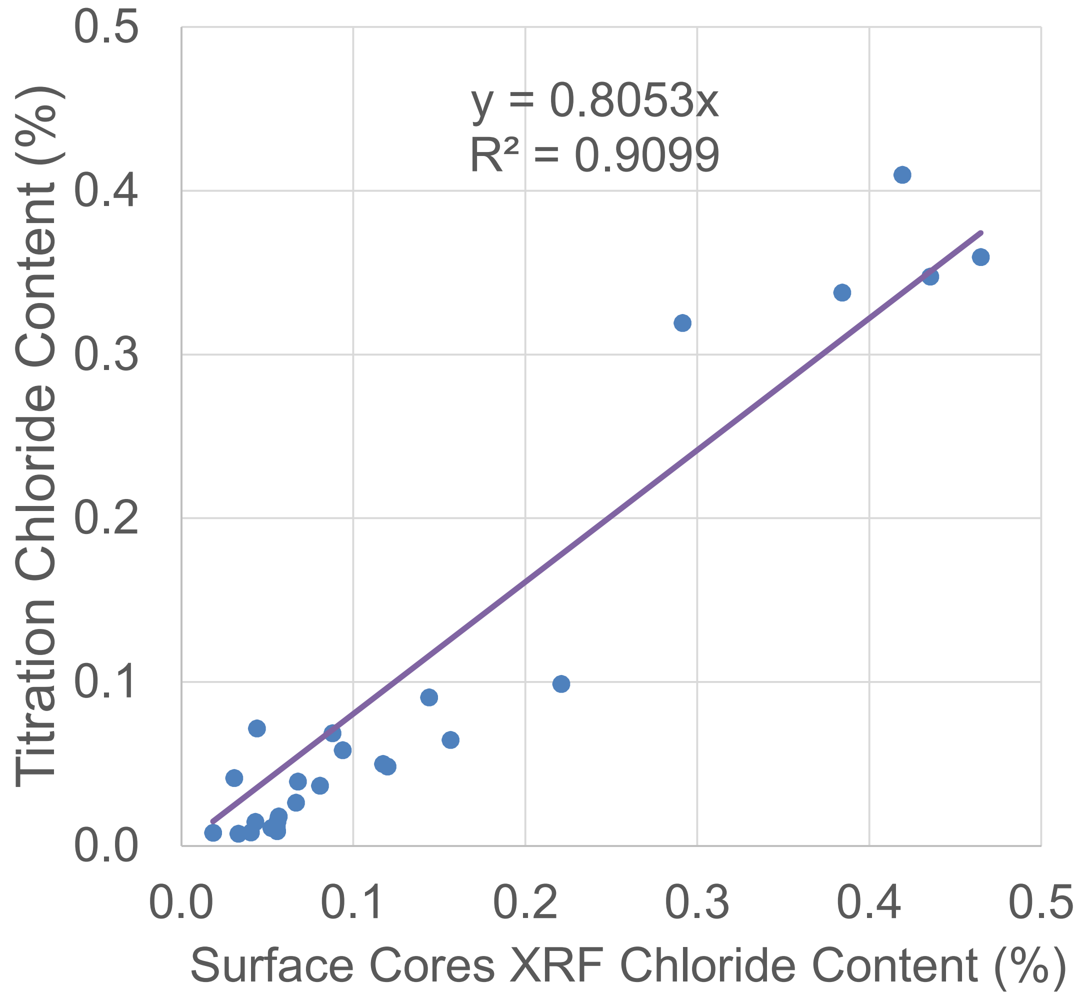




- Top, bottom, edge of slice
- Average of all readings v. Titration

Surface Testing of Core Slices

- General trend exists but significant drawbacks
- Technician discretion to avoid exposed aggregate
- Higher variability in measurements



Chloride Content – Pellets from Cores

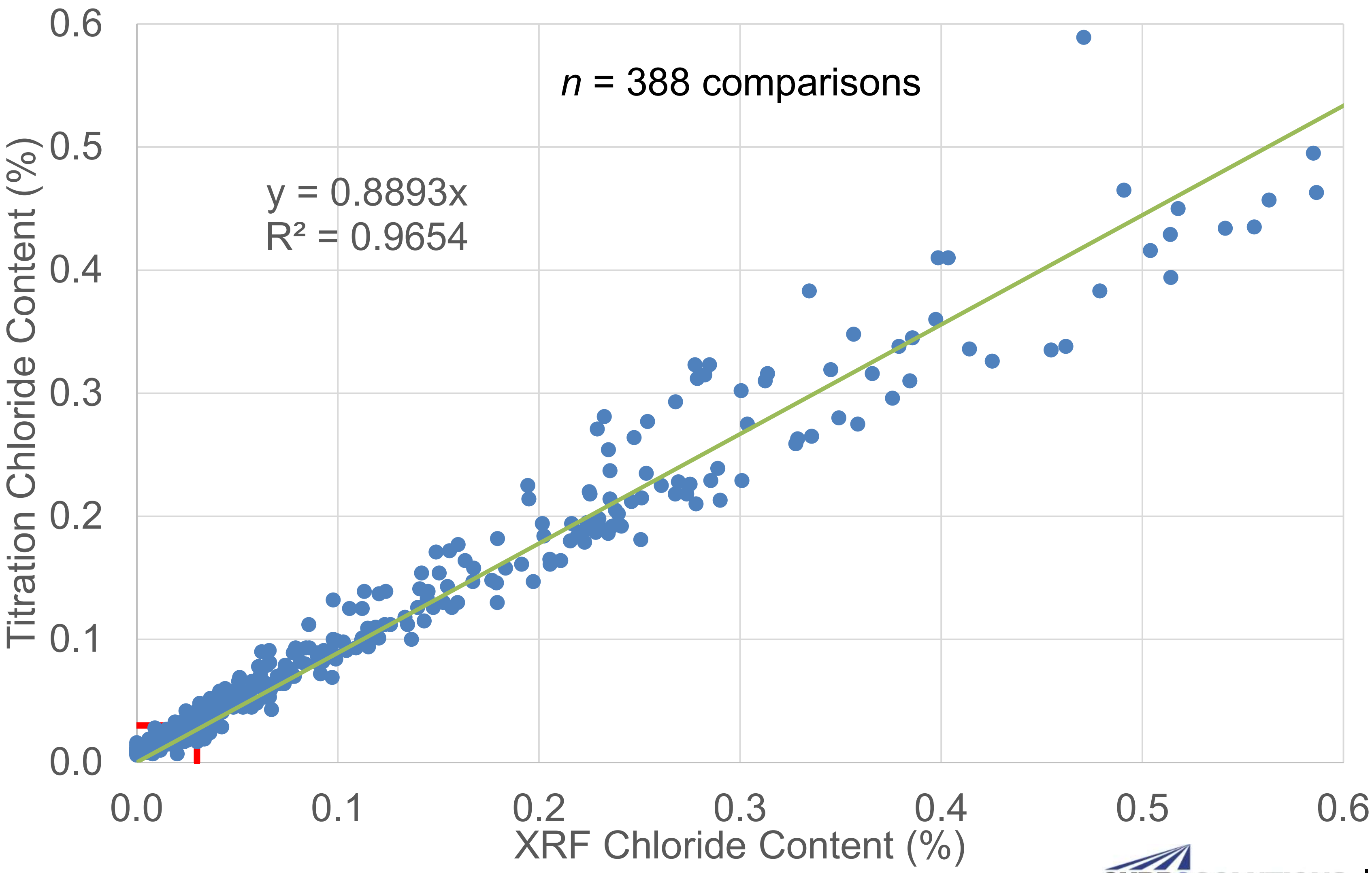
Mode/Range @ 60 Sec.	Binding Agent	% Binding Agent	R^2	Coefficient
Mining Ta/Hf 5/5/5/45	A	5	0.996445	1.091516
AllGeo 5/5/5/45	B	5	0.996009	1.142771
Mining Cu/Zn 5/5/5/45	A	5	0.995589	1.078925
AllGeo 5/5/5/45	None	---	0.99518	0.993099
Mining Ta/Hf 5/5/5/45	B	5	0.994987	1.145006
AllGeo 5/5/5/45	A	5	0.99459	1.084792
AllGeo 5/5/5/45	C	10	0.994295	1.082809
Mining Ta/Hf 5/5/5/45	A	10	0.994101	1.065355
Mining Cu/Zn 5/5/5/45	None	---	0.993977	0.985461
AllGeo 5/5/5/45	A	10	0.993585	1.061301
Mining Cu/Zn 5/5/5/45	A	10	0.993433	1.06045
AllGeo 5/5/5/45	C	5	0.993298	1.031429
Mining Ta/Hf 5/5/5/45	D	10	0.992926	1.008566
Mining Cu/Zn 15/15/15/15	A	5	0.992883	1.129886
Mining Cu/Zn 5/5/5/45	B	5	0.992812	1.144496
Mining Cu/Zn 15/15/15/15	E	5	0.992806	1.053816
Mining Cu/Zn 5/5/5/45	E	5	0.992745	1.045713
Mining Ta/Hf 5/5/5/45	None	---	0.992719	0.973055
Mining Cu/Zn 15/15/15/15	C	10	0.992453	1.051661
Mining Ta/Hf 5/5/5/45	C	10	0.992397	1.102904
Mining Cu/Zn 15/15/15/15	A	10	0.992358	1.034796

- Nearly all combinations showed excellent correlation
- Selected the simplest configuration with no binding agent

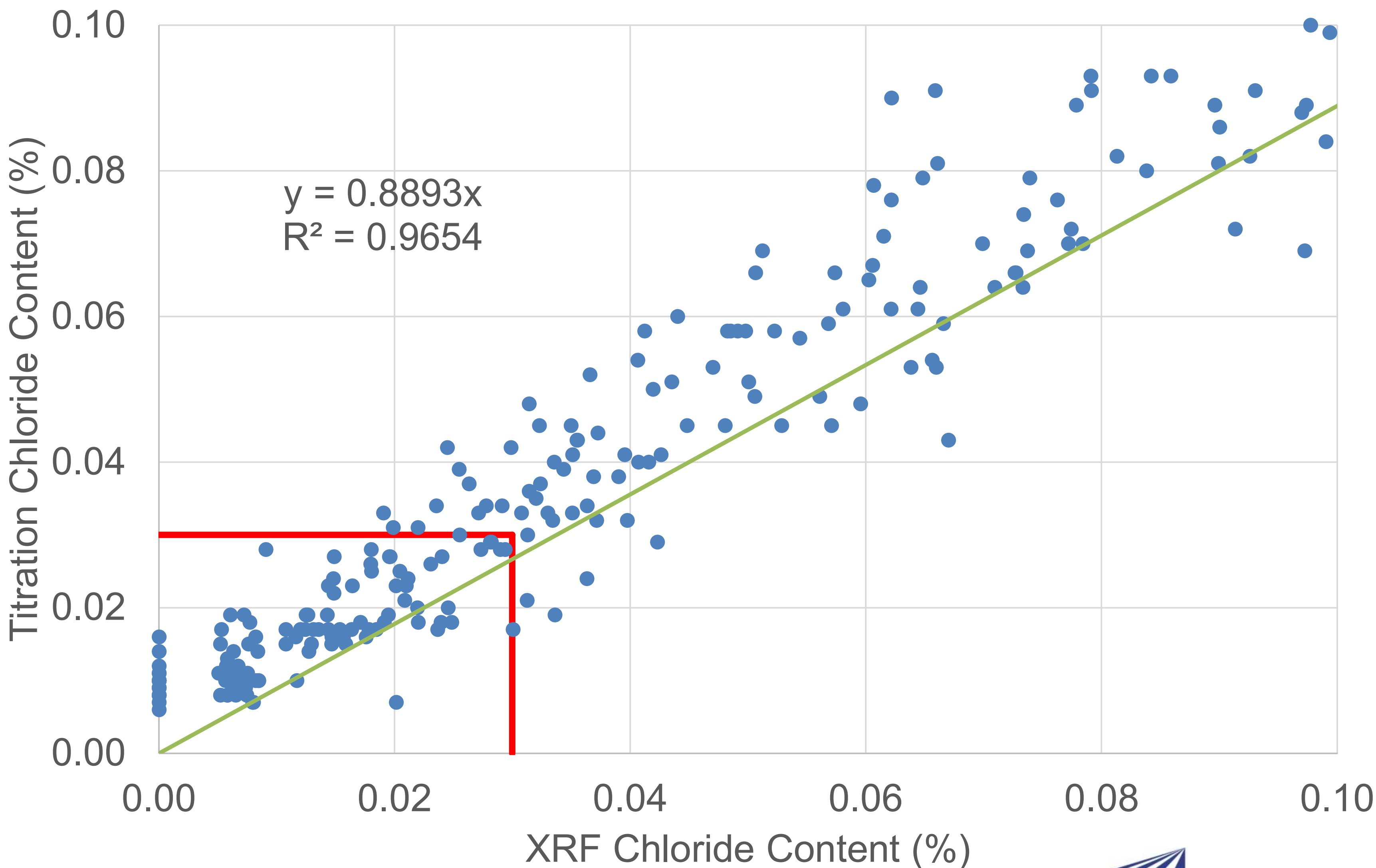
Pulverized & Pelletized Specimens

Pulverized & Pelletized Specimens

Split Sample Comparison



Split Sample Comparison



Chloride Content – Bridge Deck Cores

- Conclusions from study
  - Pellets of pulverized material superior to surface readings of slices
  - No binding agent required
  - In process of testing lab-prepared reference samples
  - In process of validating correlation with independent split-sample comparisons

Joe Kerstetter, Tennessee Department of Transportation

- XRF applications – Tennessee DOT évaluation

R06B—Tennessee

- XRF
  - Silica and Calcium Carbonate in Limestone
  - Titanium in Thermoplastic
  - Glass Beads – lead, arsenic
  - REOB & PPA in Binder?
  - Galvanized coating thickness?

Heavy Metals in Glass Beads

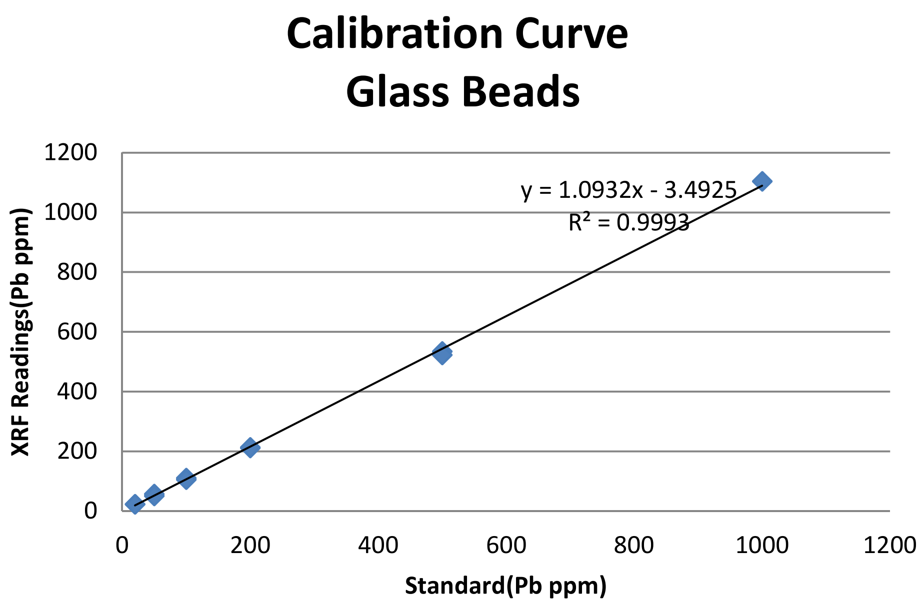
- Current Practice:
  - Tennessee requires every lot to be tested with EPA tests 3052, 6010B, or 6010C.

- Future Method:
  - Perform XRF testing on every lot. Allow manufacturer to Certify lots to Federal Aid Standard.

Heavy Metals in Glass Beads

ID	Sample	Reading(ppm)	Assay(ppm)
NCS73330	W1BSNCSZPO	23	20
	W2BSNCSZPO	23	20
NCS73331	W1BSNCSZPO	57	50
	W2BSNCSZPO	51	50
NCS73332	W1BSNCSZPO	111	100
	W2BSNCSZPO	105	100
NCS73333	W1BSNCSZPO	211	200
	W2BSNCSZPO	214	200
NCS73334	W1BSNCSZPO	535	500
	W2BSNCSZPO	523	500
NCS73335	W1BSNCSZPO	1104	1000

- Measured the Standards and compared them to their Assays.



- Used this data to create a calibration curve for each machine, but found that at the low end it was not needed.

Heavy Metals in Glass Beads

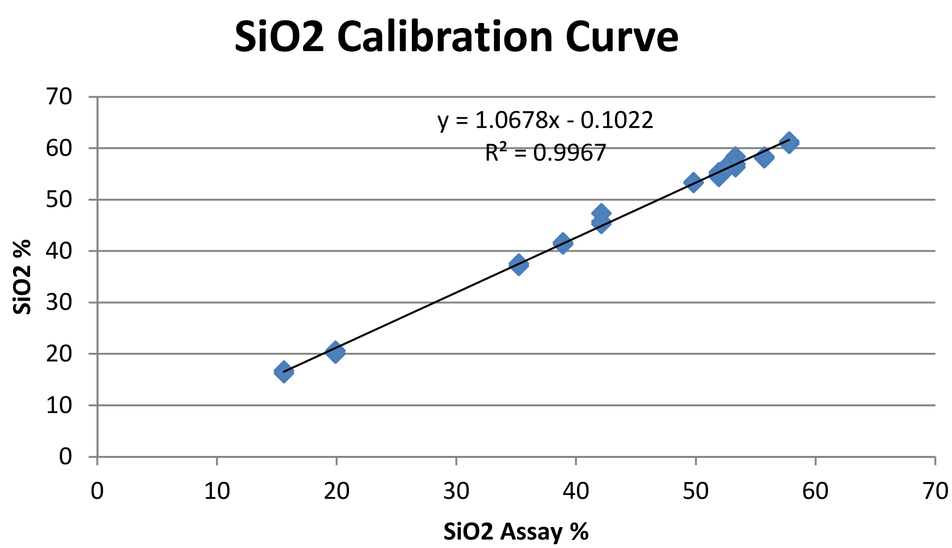
Sample ID	Notes	Pb Concentration (ppm)	As Concentration (ppm)
17C1358P	W1BPENF1IS	10	26
	W2BPENF1IS	9	17
17C1519P	W1BPENF1IS	68	23
	W2BPENF1IS	29	27
17C1566P	W1BPENF1IS	12	10
	W2BPENF1IS	14	13
17C158P	W1BPENF1IS	24	19
	W2BPENF1IS	27	20
17C913P	W1BPENF1IS	9	7
	W2BPENF1IS	8	10
17C914P	W1BPENF1IS	35	11
	W2BPENF1IS	32	13
17C915P	W1BPENF1IS	9	5
	W2BPENF1IS	10	3

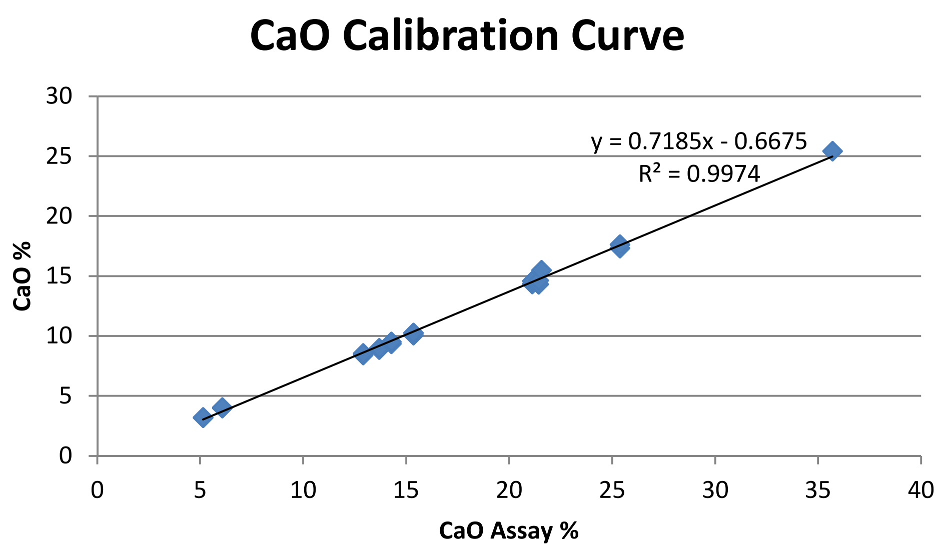
- In-Situ Testing with the handheld XRF showed good results.

Silica in Limestone

- Currently tested by standard-less program on WDXRF in Lab.
- Handheld XRF can perform same testing but still requires a lot of sample prep to be accurate.

Silica in Limestone





- Standards consisted of ICRM, NCS, and CCRL samples.
- Calibration Curves show very little matrix effects.

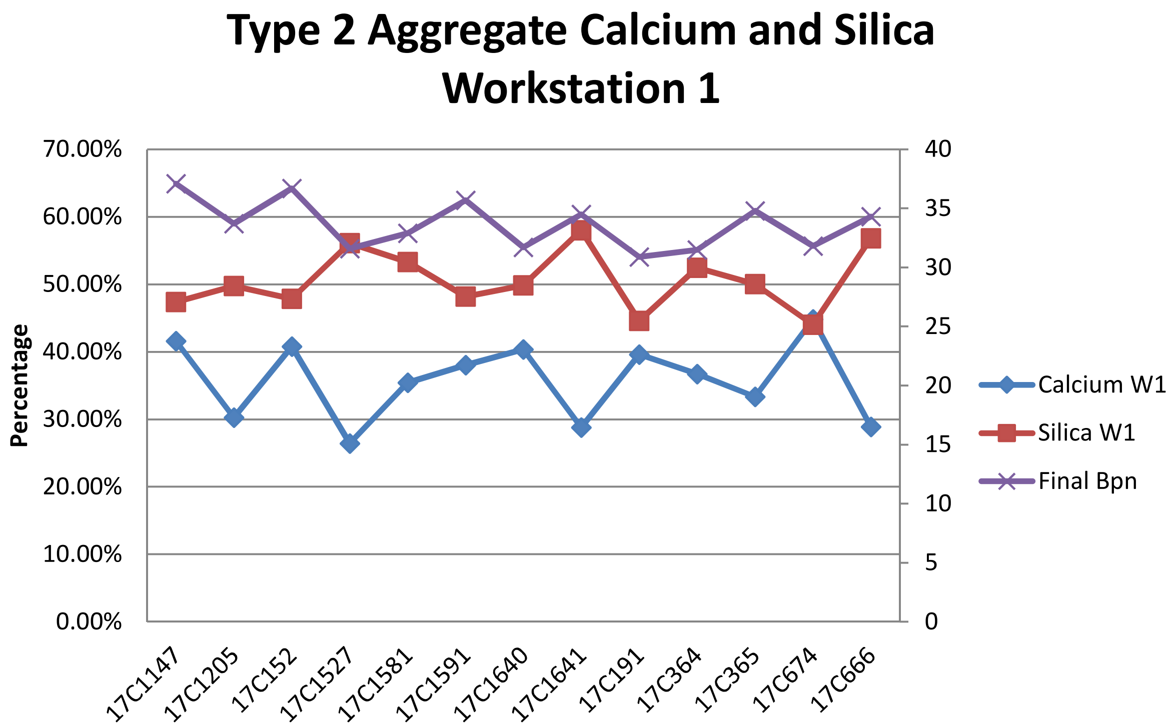
Silica in Limestone

Silica Sample Preperation Study						
Sample	Silica (IS) W1	Silica (IS) W2	Silica (PO) W1	Silica (PO) W2	Silica (PP) W1	Silica (PP) W2
17C1147	29.91%	30.89%	32.75%	31.47%	47.37%	46.23%
17C1205	28.46%	33.35%	43.36%	43.56%	49.76%	49.32%
17C152	24.40%	21.95%	30.27%	29.87%	47.84%	47.35%
17C1527	39.23%	43.63%	48.22%	48.18%	56.08%	56.92%
17C1581	42.11%	43.20%	44.85%	43.31%	53.29%	53.00%
17C1591	41.68%	41.46%	39.60%	38.32%	48.17%	46.79%
17C1640	20.62%	21.25%	39.13%	38.59%	49.86%	48.80%
17C1641	40.20%	37.19%	50.30%	50.09%	57.98%	56.81%
17C191	26.31%	25.63%	36.42%	36.45%	44.57%	44.48%
17C364	38.57%	37.50%	43.85%	44.80%	52.44%	51.03%
17C365	35.84%	37.31%	41.31%	41.13%	50.04%	49.45%
17C674	50.44%	50.32%	35.98%	37.47%	44.00%	45.56%
17C666	49.94%	48.92%	50.38%	51.64%	56.82%	56.76%
	9.0%		6.27%		4.27%	

- Three Specimen Preparation Techniques were compared.

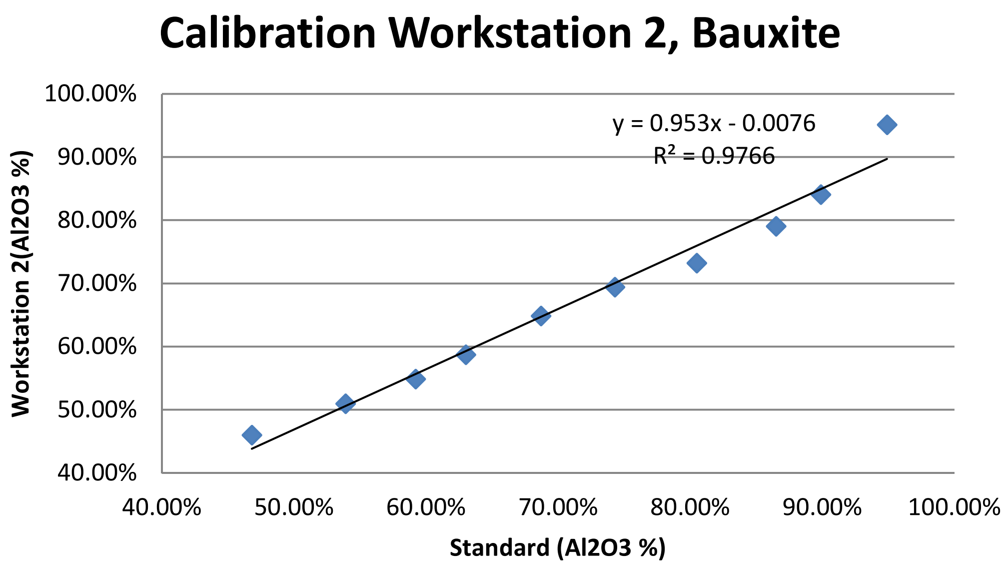
- Pressed Pellet had the least diviation.

Silica in Limestone



- The handheld XRF coupled with pressed pellet sample preparation, was able to produce suitable results.
- However the pressed pellet method would prohibit field testing.

Al2O3 in Calcined Bauxite



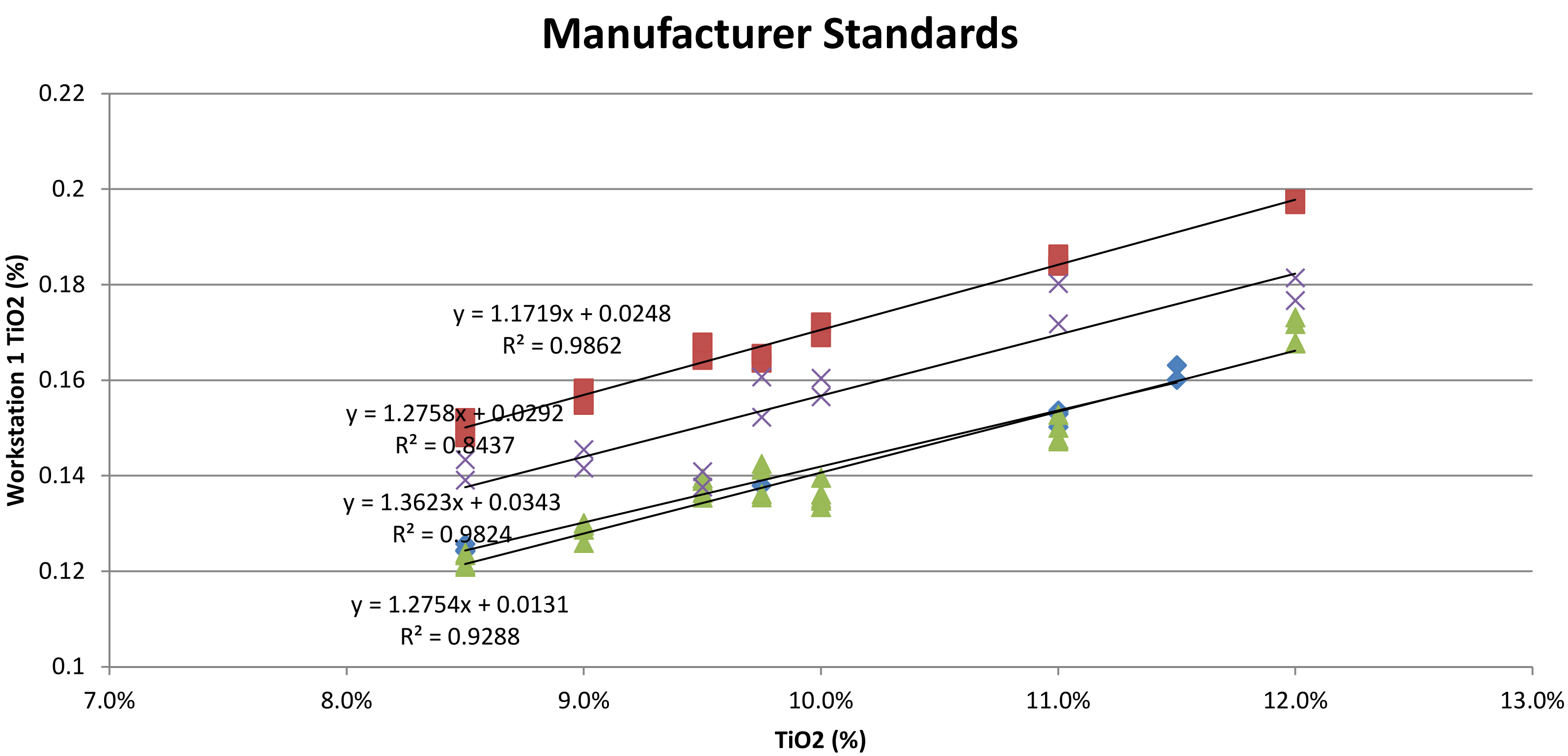
Sample ID	Vanta	ARL-X
2016-002	75.31%	86.07%
2016-003	84.77%	85.80%
2016-008	82.94%	88.96%
2016-010	79.32%	84.65%
2016-012	79.45%	85.17%

- JRRM calcined bauxite standards were used.
- Handheld XRF used pressed pellet, and WDXRF used fused bead with Lithium Tetraborate flux.
- Significant differences suggest matrix effects may be involved.

Titanium in Thermoplastic

- Current Practice:
  - Tennessee currently accepts thermoplastic on certification.
- Future Practice:
  - The handheld can perform verification testing in the field/lab on Thermoplastic.
  - There may be some issues with some fillers in the Thermoplastic.

Titanium in Thermoplastic



- Standards were supplied by manufacturers and made to 7 different concentrations.
- Standards are being tested by a third party Lab to verify percentages

Future for this Product in TN

- Looking into other materials
  - Following Maine and using XRF as a rapid test for Chloride Content of Bridge Decks.
  - Using the XRF and FTIR to detect REOB's and PPA's in our Binders.
  - Will look at Sulphur content of Acid producing rock and soil, and try to minimize costly third party testing.

TN TDOT Department of Transportation

What's Next for R06B?

The Future

- SHPR2 R06B Peer Exchange September 26 - 27, 2018 Tennessee Department of Transportation Region Three Office Nashville, TN
- Peer Exchange Web site: https://fs6.formsite.com/Mrussell/form204/index.html
- Final reports from Maine, Tennessee and Alabama will be made available on the R06B product page: http://shrp2.transportation.org/Pages/R06B.aspx

Questions? For More Information on R06B use these contacts.

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Additional Resources:

GoSHRP2 Website:	fhwa.dot.gov/GoSHRP2
AASHTO SHRP2 Website:	http://shrp2.transportation.org
R06B Product Page	http://shrp2.transportation.org/Pages/R06B.aspx