TEXAS DEPARTMENT OF TRANSPORTATION

QUANTIFYING RE-REFINED ENGINE OIL BOTTOMS (REOB) IN ASPHALT – TXDOT'S APPROACH

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TxDOT Specifications

- Special Provision 300-009
  - Re-refined Engine Oil Bottoms (REOB)
    - Beginning in the August 2015 letting, TxDOT specification limit for REOB is 5.0% by weight of the asphalt binder for Performance-Graded Binders.

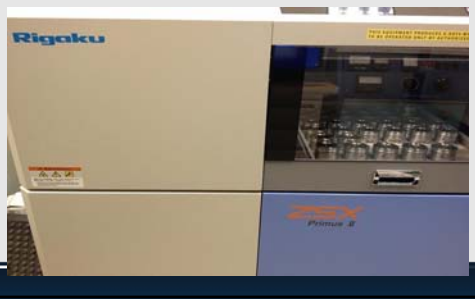
Needed a Method to Estimate REOB Content

- Researched how to develop a method for quantifying REOB in asphalt binder.

1. Determine how to analyze for REOB content (e.g. instrument, settings, sample prep, etc.)
2. Determine if instrument selected could detect the presence of REOB
3. Investigate potential correlations for quantification
4. Develop calibration standard(s)
5. Determine the accuracy of the standards
6. Develop a method to improve the accuracy

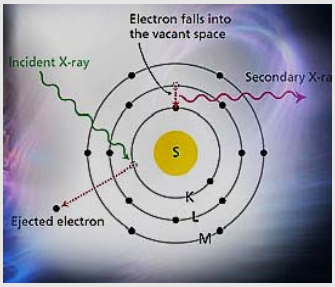
Instrumentation Chosen - WDXRF

- Wavelength Dispersive X-Ray Fluorescence (WDXRF) Spectrometer
  - Rigaku ZSX Primus II 4kW



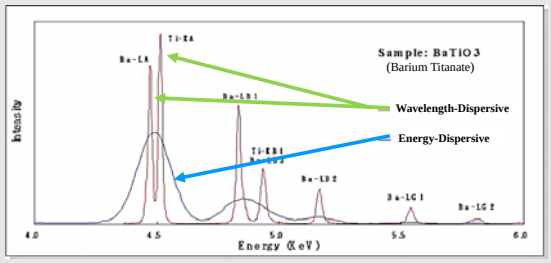
How Does XRF Work?

- Measures the intensity of secondary X-rays
  - X-ray tube emits incident X-ray and ejects inner electron creating high energy state
  - Electron from outer shell replaces electron in inner shell
  - Process releases energy in the form of secondary X-rays termed fluorescent radiation
  - Secondary X-rays are measured by XRF detector
    - **Energy = atomic number = element**
    - **Intensity = concentration**



Source: Oxford Instruments *(1)*

Wavelength Vs. Energy Dispersive XRF



Note: EDXRF cannot distinguish Barium (Ba) from Titanium (Ti). Reason – WDXRF has high resolution which results in fewer spectral overlaps and lower background intensities. The same is true for Phosphorus (P) and Sulfur (S). The ability to distinguish P from S was found to be critical in our analysis.

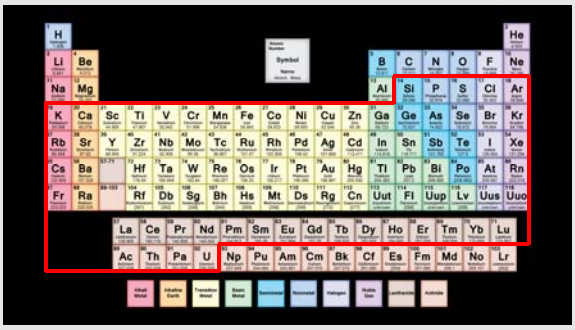
Source: Rigaku *(2)*

Detection of REOB

- Intensity is measured in kcps
- For Detection
  - Need to determine the elemental contributions of REOB
  - Analyze samples with and without REOB to determine elemental differences
    - Elemental analysis from Silicon (Si) to Uranium (U)

Sample ID	Element				
	P	Mo	Zn	Cu	Ca
2599	9.776	21.08	86.32	2.307	20.32
2603	0.466	3.961	22.03	0	1.424
2629	0	0	3.258	0	0.523
2684	0.2	0	20.84	0	0.871
2695	9.028	23.06	74.82	2.191	20.25
2881	0.279	0	0	0	0.657
2601	0.462	3.497	15.15	0	1.449
2612	0.487	0	23.01	0	1.056
2615	19.6	36.86	149.2	4.127	41.57
2624	0.268	0	2.751	0	1.557
2636	0.518	0	24.86	0	1.365
2693	59.19	0	1.345	1.266	0.716

Periodic Table of Elements



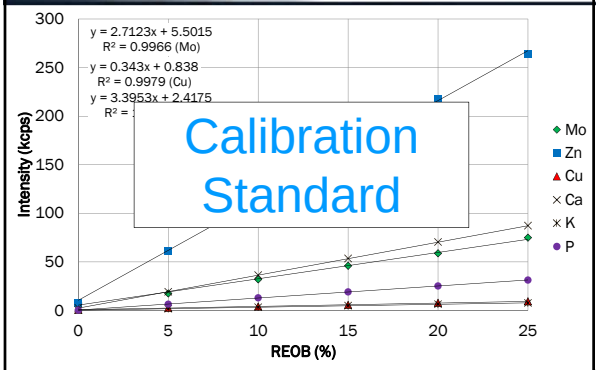
Source: Periodic Table *(3)*

Detecting REOB in Asphalt Samples

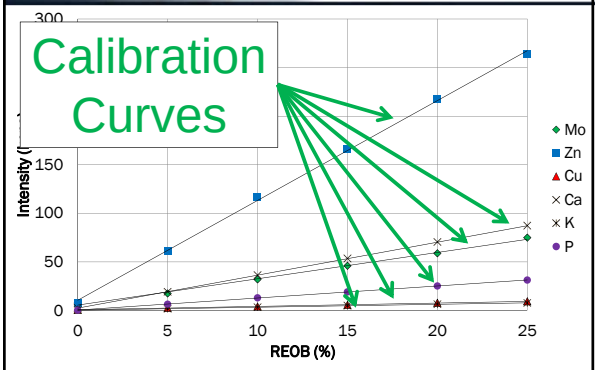
- **Asphalt Without REOB**
  - Iron (Fe)
  - Nickel (Ni)
  - Sulfur (S)
  - Vanadium (V)
- **Asphalt With REOB**
  - Iron (Fe)
  - Nickel (Ni)
  - Sulfur (S)
  - Vanadium (V)
  - Phosphorus (P)
  - Molybdenum (Mo)
  - Zinc (Zn)
  - Copper (Cu)
  - Potassium (K)
  - Calcium (Ca)

Question: Do the intensities of these elements correlate with concentration [needed for quantification]?

Correlation Between Intensity and REOB Content

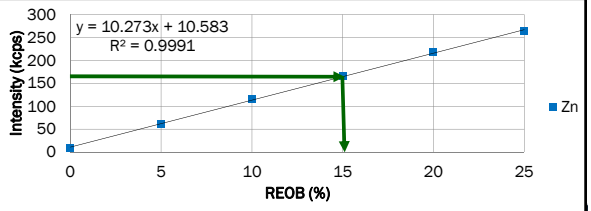


Correlation Between Intensity and REOB Content



Example of Using Calibration Curve to Estimate REOB Content

1. Measure intensity of element in unknown sample, in this case, assume Zn = 165 kcps
2. Use calibration curve to estimate the REOB content (if equation is used, the intensity measured is y-value, therefore solve for x)
   10.273x + 10.583 = 165 (= y)
   10.273x = 154.417
   x = 15.0%
3. Based on Zn intensity, REOB is estimated to be 15.0%



Applying a Calibration Standard

- Using the calibration curves of P, Mo, Zn, Cu, Ca, and K, the intensities of these elements measured in an unknown binder could be correlated to a REOB content
  - Allows us to estimate the REOB content based on each element
  - All values are averaged to determine REOB Content

Estimate REOB Content Based on Element (%)						Average REOB (%)
P	Mo	Zn	Cu	Ca	K	
15.1	14.5	15.2	14.8	15.2	14.9	**15.0**

Applying a Calibration Standard

- In a perfect world, only 1 calibration standard is needed to estimate the REOB content and to do so accurately. However, this doesn't work…Why?
  - Influences of the asphalt binder
    - Different elements in binders (elemental interferences)
    - More elements in some binders than others
  - Different stock used to produce REOB
    - Engine oil from cars versus trucks
    - Hydraulic fluid (other lubricating oils)
    - Time of year
  - Different REOB sources and processes
    - Processing may be different (different production temperatures)
    - Different sources of oil (or combinations of lubricating oils)
  - Other causes
    - We may not know

Same REOB Different Asphalt

Sample ID	Calibration Standard Used	Estimated Average (%)	Actual REOB Content (%)	Error (%)
A2R1	A1R1	3.8	5.0	-24.0
		7.7	10.0	-23.0
		11.9	15.0	-20.7
		15.8	20.0	-21.0
		19.9	25.0	-20.4
A3R1	A1R1	5.3	5.0	6.0
		10.1	10.0	1.0
		15.2	15.0	1.3
		20.1	20.0	0.5
		24.4	25.0	-2.4

Different REOB Different Asphalt

Sample ID	Calibration Standard Used	Estimated Average (%)	Actual REOB Content (%)	Error (%)
A4R4	A1R1	6.3	5.0	26.0
		20.8	15.0	38.7
		35.0	25.0	40.0
A5R4	A1R1	5.7	5.0	14.0
		18.7	15.0	24.7
		28.6	25.0	14.4
A6R4	A1R1	6.9	5.0	38.0
		22.1	15.0	47.3
		36.6	25.0	46.4

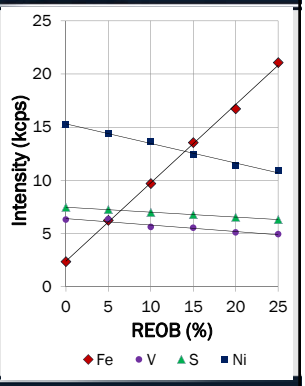
Initial Observations

- Same REOB with same asphalt
  - Maximum error of 2.0%
- Same REOB with different asphalt
  - Maximum error of 49.3% (at REOB dosage of 7.5%)
  - Suggests asphalt binder influences the estimated REOB content
- Different REOB with different asphalt
  - Maximum error of 92.0% (at REOB dosage of 5.0%)
  - Suggests not all REOB are the same

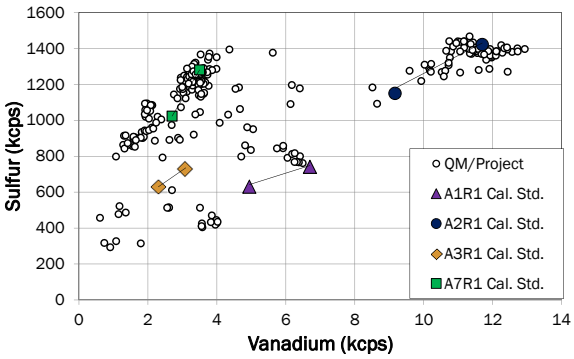
NEED TO REDUCE THE ERROR!

A Method to Reduce Error

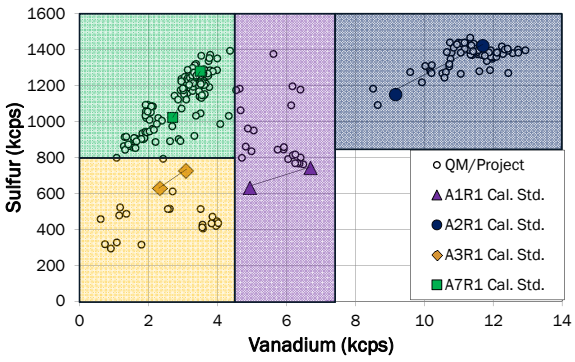
- How?
  1) Look for similar elements in all asphalt samples
     - Iron, Sulfur, Nickel, and Vanadium
  2) Look for elements that do not increase the intensity as REOB increases
     - Increase in intensity means REOB is contributing more of the element than is present in the asphalt
     - Iron was abandoned
  3) Sulfur and Vanadium met criteria and gave the best correlation to reduce the error
  4) Increase the number of standards
     - Four standards proposed
     - Use standards with varying amounts of Sulfur and Vanadium



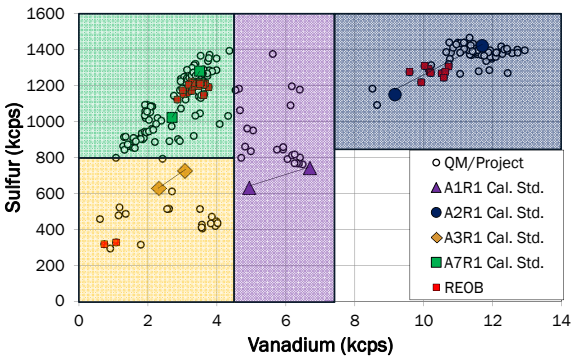
Sulfur Vs. Vanadium



Sulfur Vs. Vanadium Method



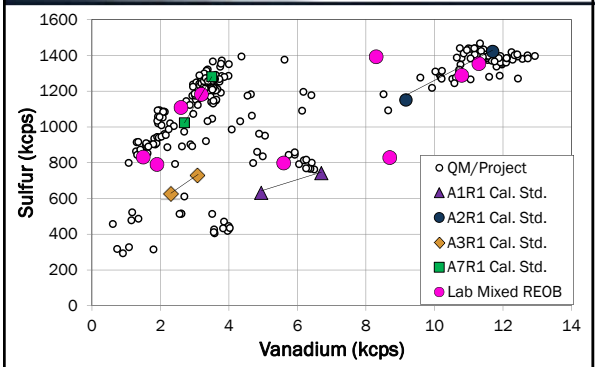
Sulfur Vs. Vanadium Method



Let's Test It

- Same REOB with 9 different binders

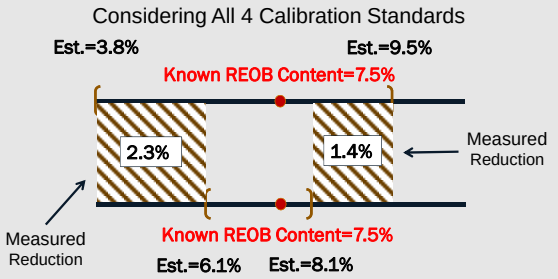
Sulfur Vs. Vanadium



Same REOB Different Asphalt- 21 Samples with 9 Asphalts

Sample ID	Actual Dosage (%)	Intensity		Relative Error (%)			
		S (kcps)	V (kcps)	A1R1	A2R1	A3R1	A7R1
A4R1†	5	828	8.7	**-2.0**	28.0	-14.0	4.0
A4R1†	15	764	7.9	**-2.0**	24.0	-4.0	9.3
A4R1†	25	708	6.7	2.8	24.4	**-0.4**	11.2
A5R1†	5	1392	8.3	-36.0	**-2.0**	-42.0	-18.0
A5R1†	15	1276	7.6	-20.7	**0.7**	-23.3	-12.7
A5R1†	25	1167	6.9	-17.6	**-3.2**	-18.0	-8.4
A6R1†	5	790	1.9	**-12.0**	24.0	-14.0	14.0
A6R1†	15	729	1.5	1.3	28.7	**0.0**	14.0
A6R1†	25	674	1.5	4.4	27.2	**2.0**	14.0
A8R1†	7.5	1353	11.3	-38.7	**-18.7**	-49.3	-36.0
A8R1†	12.5	1294	10.7	-27.2	**-9.6**	-35.2	-20.0
A9R1†	7.5	798	5.6	-9.3	26.7	-14.7	**0.0**
A9R1†	12.5	769	4.9	**-4.0**	26.4	-6.4	8.0
A10R1†	7.5	1108	2.6	-16.0	9.3	-28.0	**-8.0**
A10R1†	12.5	1068	2.6	-12.8	8.0	-20.8	**-6.4**
A11R1†	7.5	1288	10.8	-17.3	**8.0**	-21.3	-9.3
A11R1†	12.5	1238	10.4	-14.4	9.6	-21.6	**-4.8**
A12R1†	7.5	831	1.5	-9.3	20.0	-16.0	**4.0**
A12R1†	12.5	795	1.4	-10.4	21.6	-11.2	**3.2**
A13R1†	7.5	1182	3.2	-18.7	**6.7**	-24.0	-9.3
A13R1†	12.5	1136	3.2	-18.4	**4.8**	-26.4	-9.6

Same REOB Different Asphalt– 9 Asphalts



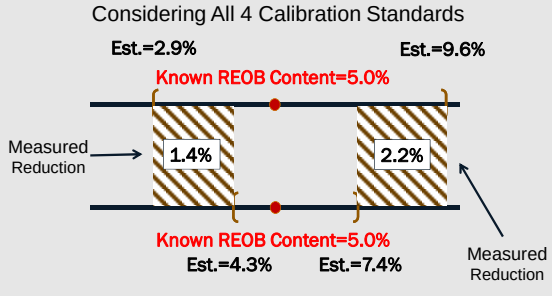
Let's Test It

- 4 different REOB sources with 3 different binders

Different REOB Different Asphalt- 36 Samples with 3 Asphalts/4 REOB

Sample ID	Actual Dosage (%)	Intensity		Relative Error (%)			
		S (kcps)	V (kcps)	A1R1	A2R1	A3R1	A7R1
A4R1†	5	828	8.7	**-2.0**	28.0	-14.0	4.0
A4R1†	15	764	7.9	**-2.0**	24.0	-4.0	9.3
A4R1†	25	708	6.7	2.8	24.4	**-0.4**	11.2
A5R1†	5	1392	8.3	-34.0	**-2.0**	-42.0	-18.0
A5R1†	15	1276	7.6	-20.7	**0.7**	-23.3	-12.7
A5R1†	25	1167	6.9	-17.6	**-3.2**	-18.0	-8.4
A6R1†	5	790	1.9	**-12.0**	24.0	-14.0	14.0
A6R1†	15	729	1.5	1.3	28.7	**0.0**	14.0
A6R1†	25	674	1.5	4.2	27.2	**2.0**	14.0
A4R2	5	829	8.6	-10.0	18.0	-24.0	**-4.0**
A4R2	15	767	8.0	-8.0	8.0	-10.0	**2.7**
A4R2	25	694	6.5	-3.2	20.4	-2.4	**2.0**
A5R2	5	1393	8.6	-28.0	**-4.0**	-32.0	-24.0
A5R2	15	1273	7.5	-25.3	**-6.0**	-28.0	-18.0
A5R2	25	1160	6.7	-21.6	**-2.8**	-22.0	-12.4
A6R2	5	788	1.8	10.0	36.0	**8.0**	12.0
A6R2	15	728	1.6	**-4.0**	20.0	-6.0	7.3
A6R2	25	667	1.3	-4.4	18.8	**-3.6**	8.4
A4R3	5	830	8.8	**6.0**	38.0	**6.0**	16.0
A4R3	15	770	7.5	8.0	44.0	**6.7**	22.0
A4R3	25	713	6.5	**4.4**	37.6	5.2	18.8
A5R3	5	1372	8.5	-14.0	14.0	-20.0	**-8.0**
A5R3	15	1282	7.9	-16.0	12.0	-16.0	**0.0**
A5R3	25	1170	7.0	-14.0	12.8	-14.0	**2.8**
A6R3	5	788	1.8	**18.0**	52.0	24.0	50.0
A6R3	15	737	1.5	10.0	37.3	**8.7**	24.7
A6R3	25	677	1.5	**12.4**	39.6	14.0	28.8
A4R4	5	827	8.5	**26.0**	78.0	**26.0**	40.0
A4R4	15	769	7.6	**38.7**	83.3	**44.0**	56.7
A4R4	25	712	6.7	**40.0**	82.0	42.4	58.8
A5R4	5	1398	8.3	14.0	40.0	**-10.0**	20.0
A5R4	15	1269	7.5	24.7	56.0	**24.0**	39.3
A5R4	25	1165	6.6	**14.4**	48.0	15.2	35.2
A6R4	5	786	1.8	**38.0**	92.0	48.0	64.0
A6R4	15	730	1.8	**47.3**	86.0	48.0	67.3
A6R4	25	678	1.3	**46.4**	89.2	48.8	66.0

Different Binder Different REOB



S and V Method Observations

- Same REOB with same asphalt
  - Maximum error of 4.4%
- Same REOB with different asphalt
  - Maximum error of 49.3% (at REOB dosage of 7.5%)
  - **Reduced to 18.7%** (at REOB dosage of 7.5%)
  - Suggests asphalt binder influences the estimated REOB content
- Different REOB with different asphalt
  - Maximum error of 92.0% (at REOB dosage of 5.0%)
  - **Reduced to 56.0%** (at REOB dosage of 7.5%)
  - **Reduced to 48.0%** (at REOB dosage of 5.0%)
  - Suggests not all REOB are the same
- **Also important, a method has been established**
  - **S and V Method – Method of matching the S and V intensities of the binder being analyzed with the calibration standard**

Future Direction

- Monitor REOB composition over time
  - Determine how consistent REOB is from same source
- Test additional sources of REOB
  - Compare them to the four tested
- Determine if REOB source can be determined
  - Significant reduction in error is REOB source is known
    - Same REOB different binder maximum error = 18.7%
    - 81% of binders tested had 10% error or less when same REOB was used
  - Manganese (Mn) and Potassium (K) may be key elements
  - Ratio of intensities (e.g. Zinc/Copper)
  - **Work with asphalt producer to identify REOB source used**

Future Direction

- Address Other Asphalt Additives
  - Polyphosphoric Acid (PPA)
    - High amounts of Phosphorous (P)
    - Much higher than in REOB
  - Ground Tire Rubber (GTR)
    - Contain similar elements as REOB and PPA
      - No Molybdenum (Mo) which is key
      - Silicon (Si) is a key element
      - Zinc (Zn) and Silicon (Si) are much higher than in REOB
  - H_2S Scavengers
    - Reduces hydrogen sulfide in asphalt
    - Contain zinc and possibly other elements of interest
  - ASTM E 178 T_n Test for outliers

Future Direction

- Ultimately we need a binder performance based test method to determine REOB dosage
  - S and V method using WDXRF is a stop gap until a better method is available
- Research Projects
  - Center for Transportation Research (CTR) is investigating non-standard binder tests
  - Texas Transportation Institute is investigating binder and mixture properties to define the maximum REOB content in HMA and seal coats

Acknowledgements

- Special thanks to Carmen Iglehart, Andre Demings, and Clifton Coward for their assistance.

QUESTIONS?

References

- (1) Oxford Instruments http://www.oxford-instruments.com/businesses/industrial-products/industrial-analysis/xrf
- (2) Rigaku http://www.rigaku.com/en/products/xrf/primini/app004
- (3) Periodic Table http://sciencenotes.org/hd-periodic-table-wallpaper-muted-colors-2015/