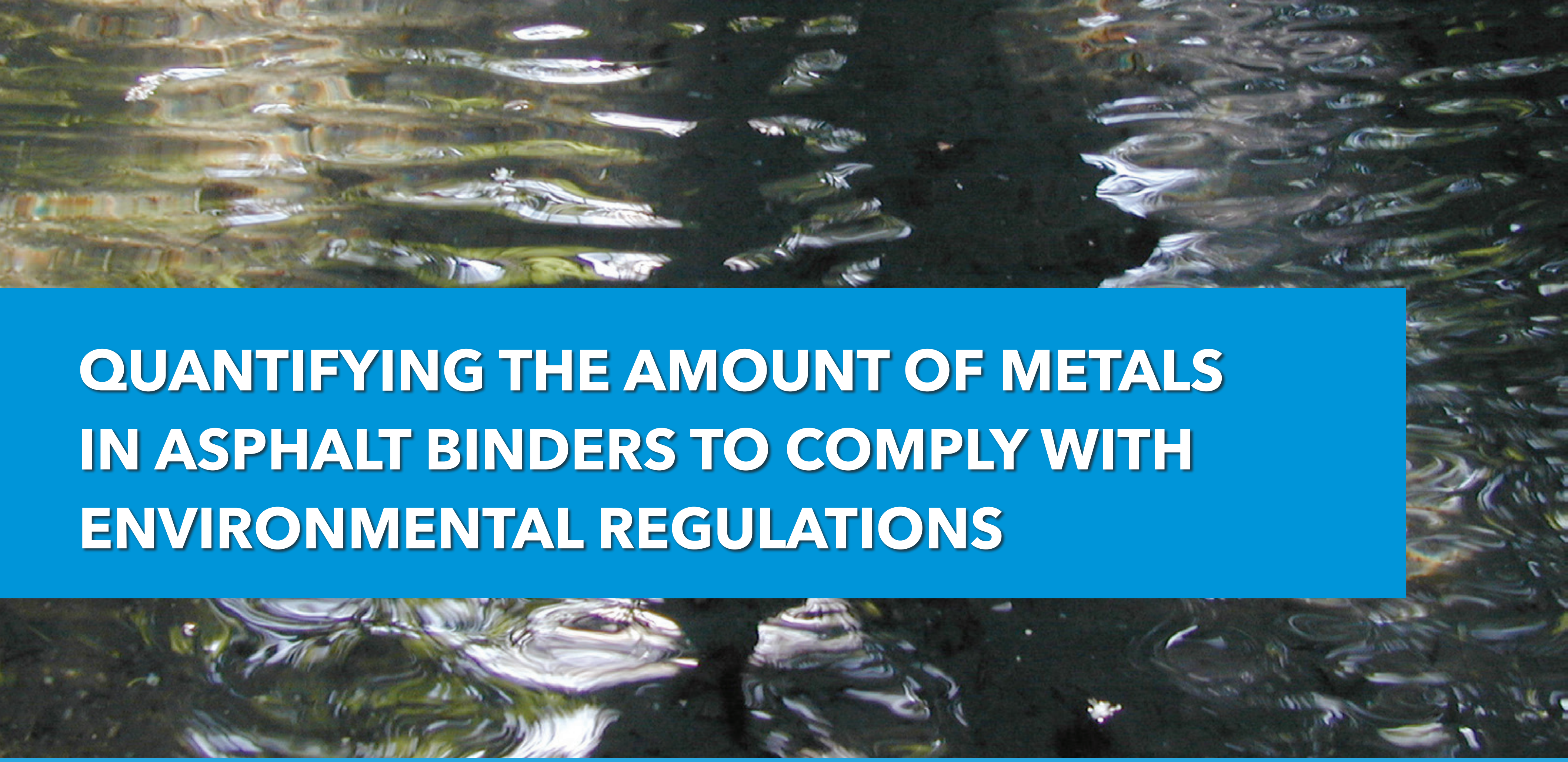


QUANTIFYING THE AMOUNT OF METALS IN ASPHALT BINDERS TO COMPLY WITH ENVIRONMENTAL REGULATIONS

The threat to safe drinking water is one of the greatest pollution problems in the world today. Less than 1% of the water on earth is clean and available for potable drinking water.
Sources of human drinking water are a mixture of groundwater aquifers and surface water reservoirs. It is vitally important for the safety of these water that the sources be protected from pollutants. A significant source of pollution to drinking water supplies comes from the discharge of untreated or under treated storm water runoff. (1) More importantly runoff from Asphalt roadways. In addition to leachable material in the Asphalt there are also surface deposits of toxic elements from road traffic. This article reviews these sources and proposes a scheme for measuring and quantifying the amounts of metals in their source materials used to bind asphalt used in making roads

Background

Heavy metals can directly harm public health by entering the body via soil and dust, dermal contact or breathing The typical elements Cd, Pb, Zn, and Cu in the roadside soils coming from traffic activity can be transported through the food chain into the human body and thus be very toxic to people. In agricultural areas, intake of heavy metals through the soil-crop system could play a predominant role in human exposure to heavy metals]. In general, heavy metals with high concentrations in the environment result in health problems adversely affecting the nervous, blood forming, cardiovascular, renal and reproductive systems. The consequences of heavy metal pollution include reduced intelligence, attention deficit and behavioral abnormality, as well as contribution to cardiovascular disease in adults . Some trace metals (such as Cu and Zn) are harmless in small amounts, but the others (mainly Pb, As, Hg and Cd), even at extremely low concentrations, are toxic and are potential cofactors, initiators or promoters in many diseases, including increased risk of cancer. However, it is not easy to remove heavy metals from the soils because of their irreversible immobilization within different soil components .

. Bitumen and mineral filler materials in asphalt road surfaces contain different heavy metal species, including Cu, Zn, Cd, and Pb . Heavy metals can be transported into the roadside soils by atmospheric precipitation or road runoff . Public health concerns of contamination of aquifers is assessed as being a severe threat. (2) Roadway runoff can include breakdown products from Asphalt emulsifiers since a significant metal concentration is found in the polar fraction of Asphalt Binders as measured on the Schieff scale. (3). This is of concern to environmental protection agencies like the Federal Highway Administration and the state DOTs, trying to balance longevity with safety concerns for road construction materials.

Table 1: Elemental analysis of asphalts from different crude sources.

Crude sources	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)	V (mg/kg)	Ni (mg/kg)
Mexican blend	83.77	9.91	0.28	5.25	0.77	180	22
Arkansas-Louisiana	85.78	10.19	0.26	3.41	0.36	7	4
Boscan	82.90	10.45	0.78	5.43	0.29	1380	109
California	86.77	10.94	1.10	0.99	0.20	4	6

Economic factors lead Asphalt makers to look for alternative material sources and to use recycled materials to deal with the waste produced by aging road surfaces and used motor and vegetable oils are natural emulsifiers for recycled asphalt paving and are readily available at low cost. The concern is the deleterious elements that are found in these materials and the need is to blend the oils correctly to minimize the concentration of metals and other organic components deemed to be public health concerns.

Typical Asphalt Compositions

`Vanadium and Nickel are naturally occurring in Crude Oil sources

And are inherently found in Asphalt as obtained from refineries

Liquid Asphalt Components

With the increasing price of petroleum-based asphalt in recent years, people have started to seek alternative binders to petroleum asphalt that can be used in pavement construction (Aziz et al. 2015; Huang et al. 2012). Some examples of asphalt alternatives include bio asphalt derived from waste cooking oil (Wen et al. 2013), waste engine oil (Jia et al. 2014Jia et al. , 2015), and biochar derived from bio-oil used as a bio modifier for asphalt cement (Zhao et al. 2014a, b

Elemental Composition Ranges Determined by Research

It stands to reason that engine oil additives would also be present in the Asphalt from waste engine oil and one would expect to see

Table 2 - Naturally occurring metal levels in Nigerian Bitumen Outcrops.

Sample	Fe	Pb	Cu	Cd	Ni	Mn	V
VAB	38.00	12.00	3.00	4.00	42.00	6.00	10.00
OI	283.00	11.00	4.00	8.00	20.00	4.001	50.00
IL	1537.00	27.00	10.00	7.00	62.00	3.00	100.001
LD	553.00	11.00	5.00	15.00	9.00	5.00	150.00

concentrations of Zinc, Phosphorus, Calcium and potentially Molybdenum metals in these Asphalt samples as well. Historical testing has shown the following metals to be present in bitumen in mg/kg. The four samples represent bitumen samples taken from Nigerian Bitumen outcrops (5) - see Table 2

The following metal levels are found in Recycled Motor Oils

Table 3 – Levels of elements of interest in REOB materials

Elements	Low Value	High Value
S	0.1%	5.00%
P	0,005%	2.00%
Ca	0.005%	2.00%
V	0.0010%	0.100%
Fe	0.005%	0.200%
Cu	0.005%	0.050%
Zn	0.005%	1.00%
Mo	0.005%	0.050%

Using XRF to Quantify the Metal Content of Asphalt Binders

The use of bench top EDXRF to characterize binders before blending them into asphalt cements is possible because the metal values are in the 10s – 1000s of ppms and are readily monitored. The characterization of Asphalt and Bitumen is also possible by using the internal ratio method available on most EDXRF systems. Sample preparation consists of transferring a constant mass to the cup to keep the mass of sample constant – the volume occupied would be a function of the density of the material.

The data generated in this study was collected on a Xenemetrix X-Cite Benchtop using the Analytix software package which has both empirical and fundamental parameter processes for evaluating data. Matrix effects were compensated for using the de Jongh algorithm and the data acquisition was accomplished in three segments providing optimal excitation conditions for the metals measured. Synthetic crude oil standards with multi-element compositions that varied independently were used to establish calibration curves and NIST reference standards were used to validate the method.

Validation Results on NIST Standards - See Table 5

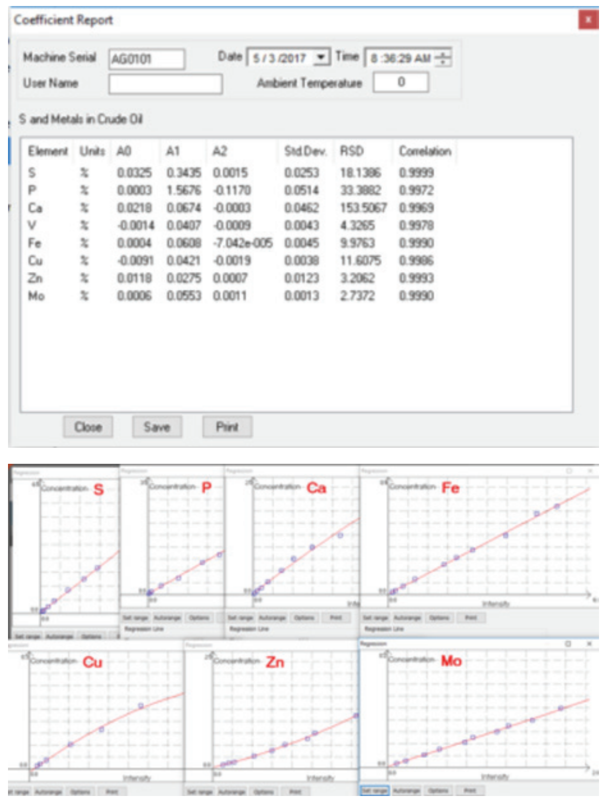
Two NIST standards were used to validate the method

Summary

The monitoring of metals in asphalt additives and ultimately in roadway runoff is able to be monitored using a very simple technique that is both robust and precise if calibrated correctly

Table 4 – Typical ranges of elements of interest to Asphalt producers

Elements	Low Value	High Value
S	0.1%	5.00%
P	0,005%	2.00%
Ca	0.005%	2.00%
V	0.0010%	0.100%
Fe	0.005%	0.200%
Cu	0.005%	0.050%
Zn	0.005%	1.00%
Mo	0.005%	0.050%



Element	Units	A0	A1	A2	Std.Dev.	RSD	Correlation
S	%	0.0325	0.3435	0.0015	0.0253	18.1386	0.9999
P	%	0.0003	1.5676	-0.1170	0.0514	33.3882	0.9972
Ca	%	0.0218	0.0674	-0.0003	0.0462	153.5067	0.9969
V	%	-0.0014	0.0407	-0.0009	0.0043	4.3265	0.9978
Fe	%	0.0004	0.0608	-7.042e-005	0.0045	9.9763	0.9990
Cu	%	-0.0091	0.0421	-0.0019	0.0038	11.6075	0.9986
Zn	%	0.0118	0.0275	0.0007	0.0123	3.2062	0.9993
Mo	%	0.0006	0.0553	0.0011	0.0013	2.7372	0.9990

Figure 2 - Calibration Coefficients and Resultant Calibration Lines

and the interelement effects are correctly assessed and compensated for. Multi element capability as well as very precise excitation conditions characterize EDXRF and make it the ideal instrument for routine laboratory measurements with the higher end EDXRF systems having the capability to quantify the carbon content of solid asphalt aggregate compacted into a briquette under substantial hydraulic pressure. In central laboratory facilities where the price of a 4kW WDXRF can be justified, the use of these instruments can be to measure secondary standards to be used for in-type material validation in solid form and disseminated to satellite instruments for real time in situ measurements.

Conclusion

XRF is a very cost effective method for characterizing the metal content in asphalt and asphalt related materials. Relatively simple sample preparation steps and sophisticated matrix correction methods can lead to highly accurate and precise results. Cross checking by ICP would be a good practice for any large scale XRF monitoring program but essentially well characterized samples that are products of round robin analysis as run through the Federal Highways Department can serve as check standards in XRF protocols.

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Table 5 - Comparison of values for NIST certified reference materials 1085-c and 1848

	SRM 1085-c Metals in Lubricating Oil	Measured on X-cite	SRM1848 Lube Oil Addidtives	Measured on the X-cite
Element	mg/kg		mg/kg except * m/m%	
Calcium	299	298	0.359*	0.355
Phosphorus	304	299	0.788*	0.783
Sulfur			2.3270*	2.345
Zinc	285	286	0.873*	0.860

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