

Contract No:

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Quantitative Analysis of Concrete Using Portable X-Ray Fluorescence: Method Development and Validation

William C. Narrows, Jonathan H. Christian, Leroy Msgwood, Aaron L. Washington II

Abstract

During Decommissioning and Demolition (D&D) activities at SRS, it is important that the building be screened for radionuclides and heavy metals to ensure that the proper safety and disposal metrics are in place. A major source of contamination at DOE facilities is the accumulation of mercury contamination, from nuclear material processing and Liquid Waste System (LWS). This buildup of mercury could possibly cause harm to any demolition crew or the environment should this material be released. The current standard method is to take core samples in various places in the facility and use X-ray fluorescence (XRF) to detect the contamination. This standard method comes with a high financial value due to the security levels of these sample facilities with unknown contamination levels. Here in we propose the use of portable XRF units to detect for this contamination on-site. To validate this method, the instrument has to be calibrated to detect the heavy metal contamination, be both precise with the known elemental concentrations and consistent with its actual results of a sample concrete and pristine contaminant, and be able to detect changes in the sample concrete's composition. After receiving the various concrete samples with their compositions found by a XRF wave-dispersive method, the calibration factor's linear regressions were adjusted to give the baseline concentration of the concrete with no contamination. Samples of both concrete and concrete/flyash were evaluated; their standard deviations revealed that the measurements were consistent with the known composition. Finally, the samples were contaminated with different concentrations of sodium tungsten dihydrate, allowed to air dry, and measured. When the contaminated samples were analyzed, the heavy metal contamination was seen within the spectrum of the instrument, but there was not a trend of quantification based on the concentration of the solution.

INTRODUCTION

X-Ray Fluorescence (XRF) is a quantitative analysis tool which measures secondary photon energy from an elemental species. The fluorometer shoots an incident X-ray beam at the molecule which ejects an electron from the inner shell of the molecule. Then, an outer shell electron replaces the inner electron's spot. This energy level change causes secondary photon energy to be released back into the fluorometer's detection system. Each element has unique photon energy and is

portrayed on an XRF spectrum in kiloelectron volts (keV). The fluorometer will then output the weight percent of each element found by integrating under the curve of the spectrum.

Mercury contamination has been a high priority challenge under Environmental Management (EM) in the Department of Energy (DOE) facilities. Mercury overflow has been observed from the Liquid Waste System (LWS) within the waste processing

plants of these facilities.¹ When Deactivating and Decommissioning (D&D) these infrastructures, knowledge of mercury or any heavy metal contamination is key in keeping the workers safe and not accidentally spreading the contamination to other areas of the facility.

In order to attain this knowledge, standard X-Ray Fluorescence lab techniques give a complete and accurate composition of the infrastructure to reveal contamination. What if there was a quick, on-site means of screening for heavy metal contamination using a similar XRF technique? Portable XRF units have similar X-ray sources as traditional laboratory units that can output results within a couple of minutes of a surface's composition.

EXPERIMENTAL

The two types of samples used in these experiments were standard concrete and a 70:30 mixture of concrete and fly ash. The mixture components were mixed with De-ionized (DI) water in a 1.6:1 ratio into a cylindrical mold and left to air dry in ambient lab conditions for thirty days. The samples were then cut using a water saw into three 2" x 4" cylinders (ex. Fig. 1) and left to dry again so the water would not mess up the composition of the samples.



Fig. 1. Typical Concrete Sample

In order to receive accurate concentrations to compare our new measurements by the portable XRF unit, a standard laboratory X-ray fluorometer was used to determine the elemental composition of both types of concrete samples. This Amptek unit used by the lab uses a wave dispersive technique, which uses a crystal to reflect the secondary photon energy, and a proprietary system is used to measure the energy at unique energy levels and time intervals, which creates an accurate composition of each element to compare our experimental values (See Table 1).



Fig. 2. Niton Xl3t Portable XRF Fluorometer

Validation of the portable X-ray fluorometer's method relies on the data points (i.e. weight percent of each element) being normally distributed, meaning there is a group of values that it trends towards with some possible outliers. The portable X-ray fluorometer used for these measurements

¹ "Technology Plan to Address the EM Mercury Challenge," (Oak Ridge National Laboratory, Oak Ridge, TN, 2016), pp. 1-32.

was the Niton Xl3t unit from Thermo Scientific (See Fig. 2) with a Geometrically Optimized Large Drift Detector (GOLDD) proprietary detector, which converts the photons to electrical current in order to detect the X-rays. The energy dispersive technique is used by the portable XRF instrument instead of the wave dispersive technique used in the standard XRF unit. This technique involves the secondary photon energy being received directly by the detector, instead of being directed by a crystal as in wave dispersive analysis. The unit measures the amount of X-ray energy quantifying the amount of ionization within the silicon photodiode detector material. The detector sends the readings to the digital signal processor which translates the data into amps. Then, these readings are processed by the CPU and stored within the unit's library and can be exported to be analyzed wirelessly or by the USB access.

Calibration of Instrument

Before the measurements of the samples were made, the instrument has to be calibrated to the baseline concentrations of the material. Measurements were taken of each sample with a linear regression slope of 1. These measurements were divided by the actual elemental compositions to find the multiplication factor between them. This factor is the calibration factor used for the particular element. Now, when the measurements are analyzed, the actual weight percent of the elements can be used as our baseline for the experimental measurements.

XRF Measurements Procedure

Many measurements of the samples have to be taken in order to analyze the statistics and the normality of the

instrument's output data. Ten measurements were taken on each side of each sample. Each full measurement was set to a time of ninety-five seconds as directed by the user manual using the mining Cu/Zn type of analysis, which was observed to have the most accurate results before the calibration factors were added to the instrument. Since we could not purge the portable XRF with helium we were not able to see the lighter elements seen with the standard XRF. We were able to see eight total elements within each composition, and the lightest of these elements was aluminum.

Statistical Analysis

After all of the measurements were taken, we needed to test the normality of each element's measurements. To confirm the normality of these elements' composition measurements, histograms were created and the Shapiro Wilke's test was calculated.

Frequency Distributions

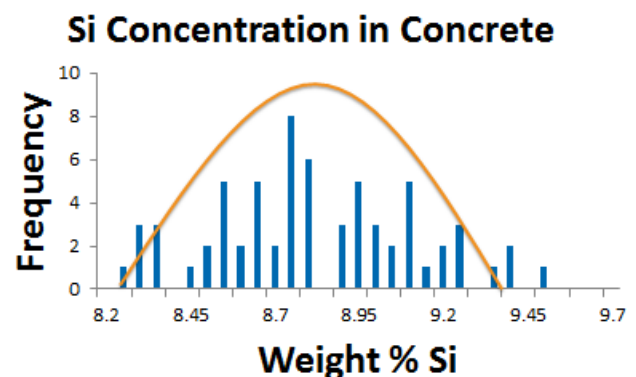


Fig. 3. Silicon Weight Percent in Concrete Histogram

Fig. 3 shows an example of the histograms created. This figure shows the frequency of the silicon compositions within all three of the concrete samples. The blue

data points represent the number of measurements within the range between the previous weight percent and its relative weight percent. The orange curve represents a normal distribution of values. The figure shows that this shape can be seen by the experimental results with some outliers from the curve. If the amount of measurements were to increase, then these data points will start to match up even more with the standard curve.

Shapiro Wilke's Test

The Shapiro Wilke's test is a numerical calculation that can confirm normality of a set of data points. By finding the appropriate values using Microsoft Excel Add-In functions, the user can confirm using defined Shapiro-Wilkes tables whether the data sets are normal or not.

Microsoft Excel T-test

The other statistical analysis needed for the data is a t-test done within Microsoft Excel. A t-test is used to check for statistical differences between sample sets. These tests were performed for each elemental composition measurement performed on each sample to check for statistical differences between both sides of the respective sample.

Contamination Tests

Following the statistical analysis tests, all six of the concrete samples were contaminated with sodium tungstate dehydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) to simulate a lab-safe contamination of a heavy metal instead of mercury. Three solutions of sodium tungstate dehydrate and 100 mL of DI water were created: 2.0M, 1.0M, and 0.5M. The samples were placed into the solutions and left to soak for about sixteen

hours. Then, they were left to air dry in ambient lab conditions for 4 days. Fig. 4 shows an example of how the salt crystallized on the surface of one of the samples. Five measurements were taken of each sample in various places across the sample to receive an average reading of the concentration of tungsten on the surface of the sample.



Fig. 4. Sodium Tungstate Dihydrate Contaminated Sample

RESULTS

Table 2 and Table 3 show the average weight percent of each element, the propagated error, and the average standard deviation of all the sample measurements. Fig. 5 and Fig. 6 show an example of the spectrum of both the concrete and the concrete/ fly ash mixture. Comparing our values in Table 2 and Table 3 to the wave dispersive technique values in Table 1 shows that the experimental measurements reveal a maximum deviation of about 3.5 % from each other. The normality tests performed on the data show that over 90 % of the elemental concentration data sets are normally distributed. The t-tests showed mostly that each side of a particular sample was the same as the opposite side. However, there was some variance showing that some opposite sides of samples were statistically different within the 95 % confidence.

Analysis of the tungsten contamination measurements reveal that the portable XRF unit is capable of identifying heavy metals similar to mercury. However, the concentration of the solution the sample was placed in did not create a trend with the weight percent measurements (i.e. increasing the concentration will increase the average weight percent).

CONCLUSIONS

The portable XRF unit produced accurate results within 3.5 % of the given accurate compositions. The normal distribution of values for the data sets represents the conclusion of being statistically confident in the measurements outputted by the unit. The variance that is observed with some of the t-test results is being tentatively ascribed to the inhomogeneity of the concrete samples, because some of the elements might have settled in different places within the sample.

Since a trend was not observed with the tungsten contamination data, the conclusions were that the portable XRF would have a hard time quantifying the amount of tungsten within a sample because of the pinpoint detection area used by the unit. However, since the unit was able to detect the tungsten on the surface of the sample up to 14 % of the weight, the portable XRF could be used for screening the infrastructure of a DOE facility for the mercury contamination. If an accurate quantification of the amount of

contamination is needed, the standard wave dispersive method would need to be utilized because of its proprietary detecting using a crystal to reflect the secondary photon energy.

FUTURE WORK

The portable XRF unit's wave dispersive method has been systemized and validated using statistical tests for the two different concrete compositions. The next phase of the project would include using different compositions of concrete and other mixtures to further test and calibrate the unit. Then, the concrete samples can be contaminated with mercury and measured using the portable XRF unit within a traditional lab setting. If the unit can positively within the 95 % confidence range identify mercury, the XRF can then be applied to an actual DOE facility to test its applied ability of screening for mercury contamination within D&D infrastructures.

ACKNOWLEDGEMENTS

This research project was funded by the DOE through the SULI program in which Natalie Ferguson organizes at SRNL. The undergraduate student intern was mentored by Aaron Washington, Jonathan Christian and Leroy Magwood.



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ENERGY

Office of
Science

SRNL-STI-2017-00493

APPENDIX A

Table 1 Baseline X-Ray Fluorescence Elemental Compositions

Material	Ca	Si	Al	Fe	S	Mg	K	Ti	Na	Sr	P	Mn	Balance
Concrete	45.712	9.388	2.598	2.322	1.246	0.531	0.274	0.168	0.214	0.101	0.0262	0.0349	2.59
Concrete/Fly Ash	34.794	13.360	4.667	2.993	0.949	1.348	0.620	0.312	0.944	0.157	0.0589	0.0467	2.05

Table 2 Concrete Portable X-Ray Fluorescence Experimental Results

Composition	Average Weight Percent	Standard Deviation
Ca	46.735 \pm 4.6152	0.7724
Si	8.689 \pm 0.8933	0.3035
Al	2.233 \pm 0.4101	0.1599
Fe	2.392 \pm 2.3920	0.0494
S	0.909 \pm 0.1515	0.0828
K	0.125 \pm 0.06161	0.0118
Ti	0.0403 \pm 0.05799	0.0028
Sr	0.103 \pm 0.01730	0.0023

Table 3 Concrete / 30% Fly Ash Portable X-Ray Fluorescence Experimental Results

Composition	Average Weight Percent	Standard Deviation
Ca	38.297 \pm 3.8820	0.9653
Si	13.321 \pm 1.1155	0.4702
Al	5.319 \pm 0.5354	0.2804
Fe	3.303 \pm 0.4269	0.0719
S	1.0448 \pm 0.1588	0.1912
K	0.709 \pm 0.07940	0.1239
Ti	0.376 \pm 0.08310	0.0203
Sr	0.165 \pm 0.02530	0.0039

APPENDIX B

Concrete XRF Spectrum

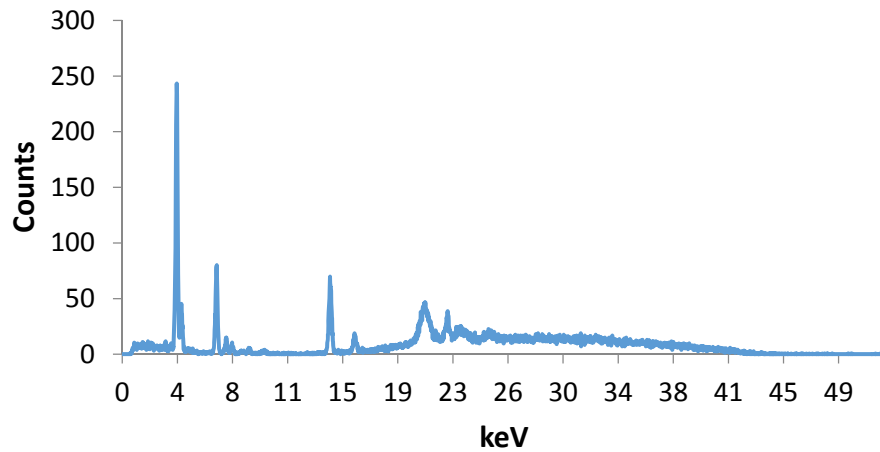


Fig. 5. Concrete X-Ray Fluorescence Experimental Spectrum

Concrete/Flyash XRF Spectra

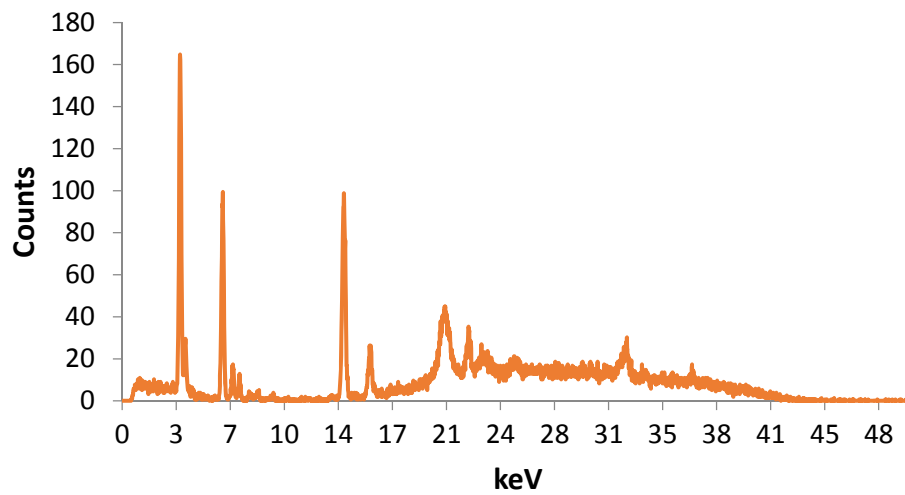


Fig. 6. Concrete/ 30% Fly Ash X-Ray Fluorescence Experimental Spectrum