

The Effects of Moisture on X-Ray Fluorescence Spectrometry

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1. Abstract

The use of handheld X-ray fluorescence (XRF) in the field is beginning to gain momentum as its implications for in-situ elemental analysis are being realized, but there are still some factors that affect the instrument that need to be studied before it is a readily acceptable alternative method for the analysis of in situ soils. One such factor is the potential interference of moisture with the accuracy of the XRF result. This paper offers analysis that shows how moisture can create a systematic bias, as well as a few options for how to account for or correct this bias. A moisture study was conducted by spiking field-collected soils with known amounts of mercury and then adjusting the moisture levels of the soils to a range of 0-30% moisture. Results showed that XRF results for the 0% and 20% moisture spikes have similar slopes and R-squared values in comparison to a laboratory method (Method 7471A). A moisture correction formula was created to correct for the field sample moisture and the moisture of the samples used to calibrate the handheld XRF. The results of this correction demonstrated a slope of 1.02, which is approaching an ideal 1:1 relationship between the corrected XRF results and the laboratory method. This study found that moisture creates a systematic bias in the measurements that can be corrected for to produce results that are statistically equivalent to the results produced by laboratory method 7471A.

2. Introduction

The use of x-ray fluorescence spectrometry (XRF) has been a proven method for elemental analysis of soil samples [1-3]. The principle has been used widely for laboratory analysis, while the use of XRF for field analysis has been limited. There are several advantages to handheld XRF analysis. XRF can screen a site for any element on the periodic table to provide a rapid assessment of the contaminants on the site. Field portable devices are typically very rugged and can be used by a researcher in most environmental situations, including those that are very hard to access. This method does not require extensive sample preparation, so the results are representative of the medium being evaluated. The greatest advantage of handheld devices are the real-time results provided. Handheld devices reduce the need for laboratory analysis, which typically requires several weeks of turnaround time. If contaminants were found to be present at the site, additional sampling campaigns would be required to fully characterize the site. These additional sampling campaigns can cost extra time and money to a project that

could be eliminated with handheld, in-situ, analysis. The immediate results provided by a handheld device allow for real-time decision making regarding strategies and on-site characterization.

There are several disadvantages to handheld XRF analysis. Historically handheld units have exhibited higher detection limits and lower accuracy and precision values [4]. Several researchers have found that these complications can be minimized with site-specific or element-specific calibrations and instrument parameters [6].

Another disadvantage of handheld XRF for soil analysis is the potential interference of soil moisture with quantitative results. Kalnicky *et al.* suggested that soil samples with moisture levels above 20% should be dried prior to analysis [5]. In the field, it is not practical to dry samples prior to analysis, so samples must be analyzed at the ambient soil moisture conditions. Ambient soil moisture can vary significantly, and changes in the proportion of water molecules in the sample are reflected in changing concentrations of the elements being analyzed.

The goal of this study was to analyze the impact of soil moisture on the accuracy of handheld XRF results for mercury. This study is a continuation of ongoing remedial investigations on the South River in Waynesboro, VA. The study used a handheld XRF device that had been optimized for mercury detection with a site-specific calibration developed from on-site soil samples with known mercury concentrations. In general, the site-specific calibration yielded relatively good accuracy and precision, however, results were impacted by soil moisture. The objective of this secondary study was to quantify the impact of soil moisture on this site-specific calibration and investigate options for improving the accuracy of the handheld XRF results.

3. Materials and Methods

3.1 Instrument Parameters

The handheld XRF device used in this study was a Bruker Tracer III-SD Handheld XRF Spectrometer (#T3S2652). This device has a 4-W rhodium X-ray tube and a 25-um Cu/ 25-um Ti/ 300-um Al filter. In 2015, a site-specific empirical calibration was developed for Hg using bank soils from the South River that were analyzed for their mercury concentration using method 7471A. This site-specific calibration was developed using 10 of the samples collected from the South River with mercury concentrations ranging from 1.07 to 587 mg/kg. These samples had variable moisture levels ranging from 6.8% to 38.6%. The average moisture level for this calibration was 14.53%.

3.2 Experimental Materials

The moisture analysis study was conducted using Hg-spiked soil samples with a known concentration. Spike samples were prepared from an uncontaminated soil sample collected from the banks of the North River in Bridgewater, VA. The soil samples taken

from this location had similar characteristics to the soils collected from the South River in Waynesboro, VA, but the soil from the North River was not subjected to mercury contamination. The samples were collected in the field using a hand auger from the depth of 0-2 feet. The samples were field-sorted to remove any large rocks or sticks, homogenized, and then packaged in a resealable plastic bag. Approximately 4.5 kg of soil was taken from this location back to the environment laboratory at James Madison University.

The sample was brought back to the lab where it was dried in an oven at 105 degrees Celsius for 24 hours to ensure zero-percent moisture to start. The sample was then sieved through a 2-mm screen using an automatic shaker to remove any rocks left in the sample. Once the sample was fully dried and free of rocks, the soil was divided into 100g samples to be spiked with a known mercury concentration.

3.3 Experimental Design

3.3.1 Spiked Sample Analysis

The dried and sieved soil was divided into 100-g portions to be spiked with nominal Hg concentrations of 0, 5, 10, 15, 25, 50, 75, 125, 250, 500, and 1000 ppm. Each 100-g sample was placed into a 250ml Erlenmeyer flask. A 2000 mg/L mercury stock solution was prepared from 0.6767 g HgCl₂ and 250 ml of deionized water. The stock solution was diluted to the proper concentration in 50 ml aliquots and added to obtain each of the nominal spike concentrations (Table 1). These slurries were then placed on a shaker at 21°C and 200 RPM for 24 hours. The samples were poured into plastic weigh boats and then were air dried under a fume hood for 48 hours. The samples were then crushed with a mortar and pestle and sieved through a 2-mm mesh on an automatic shaker.

All samples were analyzed with 0% moisture and 20% moisture. The 50 ppm and 250 ppm samples were analyzed with moisture levels of 0, 5, 10, 15, 20, 25, and 30 percent moisture. The different moisture levels were created by adding a 4.89g of water to the weigh boat each time. This increased the moisture level of the sample by 5%.

Table 1: Amount of deionized water added to obtain nominal samples

Nominal Value (ppm)	Concentration of 50ml spike added (mg/L)	% Moisture	Weight Before Water (g)	Water Added (g)
0	0	20	96.52	19.3
2	4	20	96.28	19.25
5	10	20	96.96	19.39
10	20	20	97.61	19.52
15	30	20	97.77	19.55
25	50	20	98.69	19.73
50	100	5	97.8	4.89
50	100	10	97.8	4.89
50	100	15	97.8	4.89
50	100	20	97.8	4.89
50	100	25	97.8	4.89
50	100	30	97.8	4.89
75	150	20	97.75	19.55
125	250	20	98.41	19.68
250	500	5	97.8	4.89
250	500	10	97.8	4.89
250	500	15	97.8	4.89
250	500	20	97.8	4.89
250	500	25	97.8	4.89
250	500	30	97.8	4.89
500	1000	20	98.09	19.61
1000	2000	20	98.37	19.67

3.3.2 Field Samples

This study also evaluated the effects of moisture in field-collected samples from a mercury-contaminated site in Waynesboro, VA. In 2016, a sampling campaign was conducted at the South River that collected 239 surficial and core samples from the site. Soil samples were collected by AECOM from marked transects perpendicular to the river. Soil cores were collected in 2-foot increments using a hand auger. Samples were homogenized by hand until the soil had a uniform consistency. These samples were analyzed in the field using the handheld XRF, sent to Lancaster Labs for analysis using method 7471A, and then analyzed again in the JMU laboratory using the handheld XRF. Lancaster Labs provided soil moisture percentages for each sample that was collected.

3.3.3 Moisture Correction

A moisture correction factor was used to adjust field measured Hg values to dry-weight Hg concentrations. Equation 1 was used to adjust Hg results for both the moisture level of field samples and the moisture level of calibration samples.

The correction was calculated using Equation 1

$$Mercury\ Concen.\ (ppm) = \left[(Field\ Mercury\ Result) \left(1 + \left(\frac{\%moisture}{100} \right) \right) \right] - \left(calibration\ \frac{moisture}{100} \right) \quad Eq.\ 1$$

4. Results and Discussion

4.1 Spiked Sample Results

The first test that was performed on the spiked samples was to determine how well XRF results agreed with the nominal value. For this evaluation, XRF results of spiked samples were compared at 0% and 20% moisture. The 0% moisture had a R-

squared value of 0.99 and a slope of 1.17. The 20% moisture had an R-squared value of 0.99 and a slope of 0.92. Both of these results are demonstrated in Figure 1.

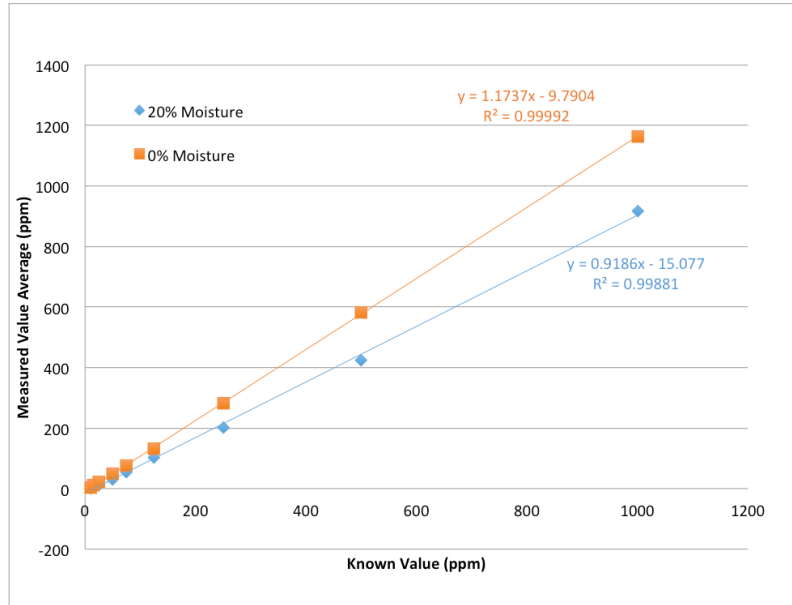


Figure 1: Comparison of XRF-measured values to nominal spiked values at 0% and 20% moisture.

The ideal slope for this comparison would be 1.0, indicating a 1:1 relationship between the XRF measured values and the true values. This 1:1 relationship would demonstrate that soil moisture is not a factor in handheld XRF analysis. The results from this comparison, however demonstrated that the handheld XRF under predicted the mercury concentration when the soil moisture was at 20%, and the device over predicted when the soil moisture was 0%. These findings are consistent in light of the moisture level of calibration samples (average = 14.53%). The XRF method under predicts Hg results, when the measured sample contains higher moisture than the calibration samples and over predicts when the measured sample contains lower moisture than the calibration samples. The R-squared value of 0.99 for both 0% and 20% moisture suggests that while moisture alters the slope of the relationship, the relationship remains linear and highly predictable.

4.2 Corrected Moisture Results

When the XRF results were compared to the nominal spike values, the slopes were within 8-17% of the ideal 1:1 relationship. The 20% spike had a slope of 0.92 and the 0% had a slope of 1.17. When the spiked samples were corrected using Equation 1, the slopes were within 3% of the ideal 1:1 relationship. When moisture corrected, the 0%

moisture results produced a slope of 1.00 and the 20% moisture results produced a slope of 0.97. These values suggest that correcting for the moisture in the spiked samples will bring the relationship between the nominal values and the XRF values to 1:1. The results of this moisture correction can be seen in Figure 2.

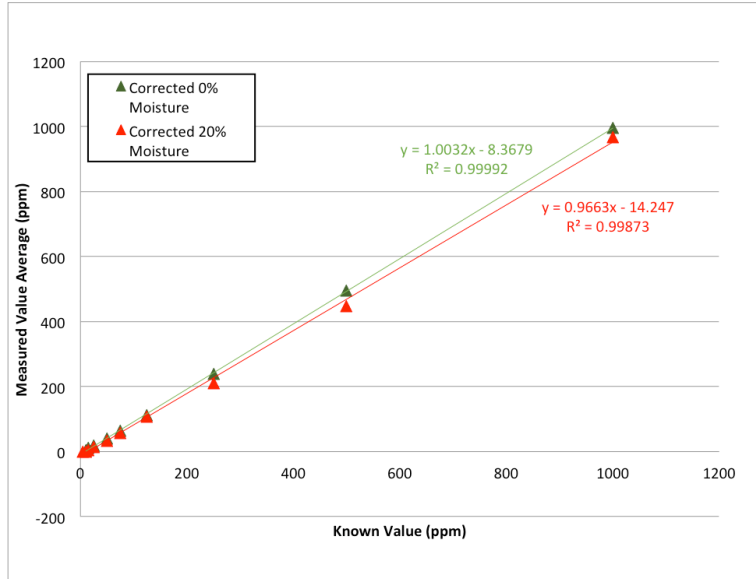


Figure 2: Comparison of moisture corrected XRF measured values to nominal spiked values at 0% and 20% moisture

The XRF results from the 239 field samples without moisture correction were compared to the results from method 7471A. This comparison demonstrated a slope of 0.8731. When XRF results from the 239 field samples were corrected for moisture, the results showed a slope of 1.0187. An ideal slope would be 1.0, so the slope for the corrected values would almost demonstrate a 1:1 relationship. These comparisons can be seen in Figures 4 and 5 respectively.

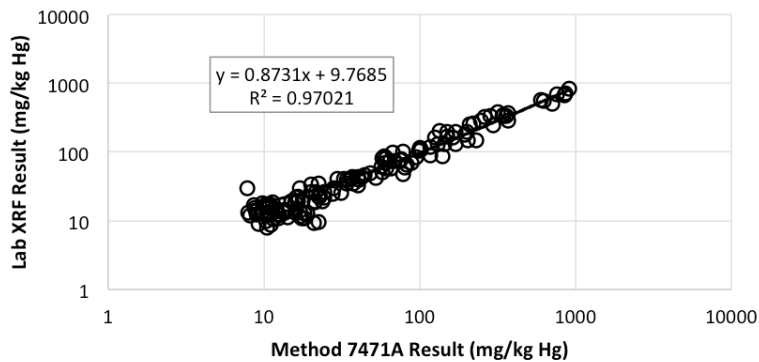


Figure 4: Relationship between the uncorrected handheld XRF results from field analysis versus the results from method 7471A.

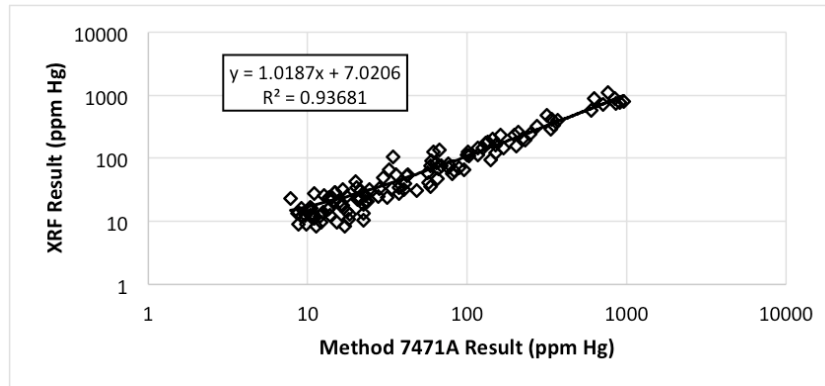


Figure 5: Relationship between the corrected handheld XRF results from field analysis versus the results from method 7471A.

5. Conclusion

5.1 Systematic Bias

A systematic bias is present in analytical measurements when results have high precision, but low accuracy that is shifted in one particular direction. The findings of this study demonstrate that sample moisture produces systematic bias in the results of handheld XRF field measurements of soils. The moisture of the field-collected soil and the moisture of the samples used to calibrate the handheld XRF will ultimately determine how closely these values align with true values as determined by spiking or correlation from laboratory analysis.

The cause of the systematic bias is the physical interference of soil moisture with the XRF signal. If there is an excess of water present in a given soil sample, then the handheld XRF results would be lower compared to a minimal amount of water, which would provide a higher XRF result. This could be attributed to the fact that a more saturated sample would have more water particles for the x-rays to diffract off of. This diffraction could result in less mercury being detected. If the sample is not very saturated, then the x-rays have much more soil to measure without any interference from the water particles.

The direction and magnitude of the bias is determined by the difference between the moisture of the measured sample and the moisture of calibration samples. In this study, results were low when samples contained more moisture than the 14.53% present in the calibration samples, and the results were high when samples contained less moisture than the moisture present in calibration samples. The 20% moisture spikes were reporting lower values because of this difference in the moisture of the calibration. The 0% moisture spikes were reporting higher than expected because of this difference compared to the calibration samples. If calibration samples were created with 0% moisture, and samples were dried out, we would expect 1:1 relationships from the nominal and laboratory values compared to the handheld XRF values. This would not be easily done in a field setting, but an alternative is available in the post-processing stage of the data analysis.

5.2 Options for Addressing Soil Moisture

5.2.1 Heterogeneity of Soil

The first option for addressing soil moisture is to ignore the bias. It is important to note that the systematic bias here has similar error percentages as the sample heterogeneity itself. The heterogeneity of the soil in nature introduces the same possibility of error as moisture would. Figure 6 demonstrates the relative standard deviation versus cumulative probability for the handheld XRF results before and after moisture correction. Before moisture correction the median relative standard deviation (RSD) is 15.4%. After the moisture is corrected for, the median RSD is 16.5%. The similarity of these values shows that whether moisture is corrected for or not, there will still be error between field and laboratory results on the order of ~16%.

These results suggest that while the systematic bias associated with soil moisture can be measured across a large number of samples, the effect of this bias on the results of an individual sample at this particular site may be small compared to the random variability associated with sample heterogeneity. At sites with more homogeneous soils and more homogeneous distribution of elements within a soil sample, the systematic bias associated with soil moisture would be more important to correct.

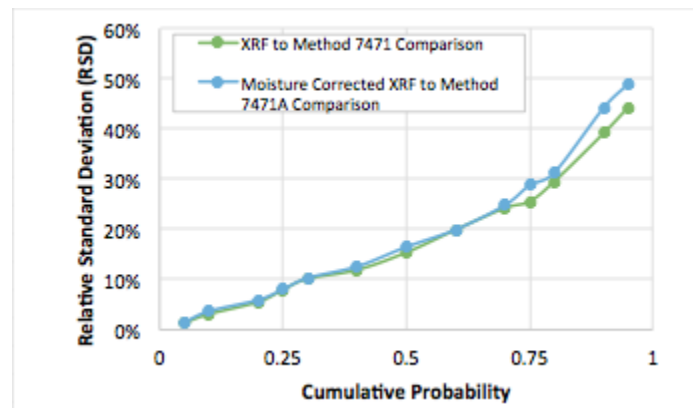


Figure 6: Comparison of the XRF uncorrected method to the corrected method.

5.2.2 Mathematical Correction

Results indicate that moisture does affect the accuracy of the handheld XRF device, but this discrepancy can be addressed. A mathematical correction for the moisture will correct for the systematic bias so that the relationship between the field samples and the laboratory samples are almost 1:1. The correction addresses the field moisture percentage of the sample, and the moisture percentage of the samples used to create the calibration. By correcting for these two types of moisture in the analysis, parameters most accurately reflect the conditions used in the laboratory. When the calibration moisture and sample moisture are both corrected to be 0%, the relationship between the handheld XRF values and the Lancaster Labs values demonstrate a slope of 1.02, which is close to the ideal 1:1 relationship. A mathematical correction for moisture addresses the

systematic bias in these results and should be considered in future investigations using the handheld XRF device, particularly at sites where soil heterogeneity is low.

5.2.3 Calibrate Using a Moist Sample

To address the systematic bias associated with moisture in soils a calibration could be created using known moisture content. For example, this study used a moisture content of 14.53% in calibration samples, and the results produced a good fit with true values without any correction. This moist sample calibration will provide results that are more reflective of the natural environment in which the contaminants are located. Without drying out the samples or adjusting for the moisture content in the sample, results may actually better represent true environmental exposures of organisms under natural conditions. From a remediation standpoint, determining the exposure levels for species in their natural habitat may be more beneficial than measuring a dried laboratory concentration, or a corrected concentration to match the dried laboratory values.

6. References

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