Evaluation of Field-Portable X-Ray Fluorescence Spectrometry for the Determination of Lead Contamination on Small-Arms Firing Ranges

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ABSTRACT

Field analytical methods for the characterization of lead contamination in soil are being developed. In this study, the usefulness of a commercially available, field-portable energy-dispersive X-ray fluorescence spectrometer (XRF) is evaluated for determining the extent of lead contamination in soils on small-arms firing ranges at a military installation. This field screening technique provides significant time and cost savings for the study of sites with lead-contaminated soil. Data obtained with the XRF unit in the field are compared with data obtained from soil samples analyzed in an analytical laboratory by inductively coupled plasma atomic emission spectroscopy. Results indicate that the field-portable XRF unit evaluated in this study provides data that are useful in determining the extent and relative magnitude of lead contamination. For the commercial unit used in this study, improvements in the spectral resolution and in the limit of detection would be required to make the unit more than just a screening tool.

1 INTRODUCTION

High concentrations of lead and other heavy metals are commonly found on and near military small-arms firing ranges. This can pose a threat to human health and the environment.¹⁻² Concentrations of these metals are usually determined by collecting soil samples and analyzing them in an analytical laboratory by atomic-absorption (AA) spectroscopy and/or inductively coupled plasma atomic emission spectroscopy (ICP-AES).³ Sample collection and laboratory analysis require substantial expenditures of time and funds. Portable, energy-dispersive X-ray fluorescence (XRF) is an alternative method for field screening for lead and other metals at sites where levels of concern are in the 100-mg/kg range and higher.⁴⁻⁵ Portable XRF offers advantages in time and cost of analysis. Results are available immediately and can be used to determine if a problem exists. Several readings can be made in a relatively short period of time, so "hot spots" can be identified in the field. Cost per analysis is very low compared to that of sending samples to an analytical laboratory for analysis.

At Grafenwöhr Training Area, located in southern Germany, three training ranges are under investigation for lead contamination. No prior environmental studies had been performed on these historic ranges, and little information about past practices was available. The first range is a rifle range used by troops to check the accuracy of their rifle sights. No evidence of slugs is visible on this range. The second range is used for pistol practice. On the pistol range, slugs are visible on the ground around the targets and in the berm behind the targets. The third range is used to provide combat troops with experience in the use of the hand grenade. This range is pitted with craters, and pieces of shrapnel are found everywhere.

This study seeks to evaluate a commercially available field-portable XRF spectrometer to determine its utility in determining lead contamination in soil. In addition to the portable XRF data collected in the field, soil samples were collected from the ranges for laboratory analysis by ICP-AES to confirm the field XRF results.

2 EXPERIMENTAL APPROACH

The instrument used in our study was a MAP X-ray fluorescence spectrum analyzer with a cadmium-109 source, manufactured by Scitec Corp. The instrument, an energy-dispersive X-ray fluorescence spectrometer, uses a solid-state silicon detector with a resolution of 170 keV and an active area of 25 mm². The principal difference between wavelength-dispersive and energy-dispersive spectrometers is the manner of resolving the fluorescent X-ray spectrum emitted by the excited atoms in the sample.⁵ A wavelength-dispersive instrument uses an optical assembly to sort the X-rays by wavelength, while an energy-dispersive one uses an electronic detector that responds to the energy of the X-rays being detected. Radioactive elements that produce a narrow band of characteristic energies are commonly used in portable XRF instruments. Our instrument was calibrated by the manufacturer for determination of lead contamination in the soil. The calibration was done using soil spiked with known amounts of lead. A validation standard was used to ensure that the instrument was operating properly in the field. This validation standard contained a known amount of lead and was checked before, during, and after sampling. Readings varied less than five percent during this study. Field measurements were made using a 60-second sampling period to acquire the spectrum.

The MAP X-ray fluorescence spectrum analyzer measures the spectrum of energies of X-rays emitted from the sample (Figures 1-3). The spectrum of energies detected during a measurement is recorded, evaluated, and saved in the memory of the instrument. The spectrum can be copied to a portable computer and analyzed in detail later to determine the concentration of metals not targeted at the

time of analysis. This spectrum reveals much information about the sample and gives the analyst data with which to determine the nature of the soil matrix, whether the XRF is operating properly, and if interferences are affecting the reading for the targeted element. The large peak on the right side of the spectrum (channels 150 - 160) is due to Compton backscatter of radiation from the source and corresponds to approximately 20 keV. The Compton backscatter peak can be used to determine the relative density of the soil matrix. The lead L-shell emission peaks are located in channels 80 - 100, which correspond to approximately 10.5 - 12.5 keV. The resolution is low compared with laboratory-type XRF units. An algorithm that uses the L-emission peaks and the Compton backscatter peak is used to identify and quantitate lead.

Soil samples were collected to confirm the XRF measurements collected in the field. The samples were analyzed at Argonne National Laboratory (ANL) by using ICP-AES. Samples were digested using U.S. Environmental Protection Agency (EPA) Method 3050A (Acid Digestion of Sediments, Sludges, and Soils), followed by measurement using U.S. EPA Method 6010 for ICP-AES.³

The digestion method involved taking one to two grams of soil and heating to 95°C in nitric acid and hydrogen peroxide. The samples were then refluxed in hydrochloric acid, filtered, and diluted to 200 mL. The ICP-AES procedure used a two-point calibration with standards prepared by dilution of certified solutions. Measurements were made with an Instruments S.A., Inc., JY-86 ICP-AES. This instrument consists of a 1-m JY-48 polychromator and a JY-38 scanning-monochromator sequential analysis system.

Quality control (QC) samples were run in accordance with the U.S. EPA methods. These included sample duplicates, laboratory control samples, spikes, spike duplicates, post-digestion spikes, serial dilutions, and calibration verifications. All QC results were within acceptable ranges.

3 RESULTS AND DISCUSSION

The portable XRF unit is relatively lightweight (4.8 kg) and easily carried by one person. The battery held sufficient charge to remain operational throughout an eight-hour day; the battery was recharged overnight. More than 100 measurements were made each day.

Readings taken on the rifle range indicated high levels of lead in the surface soil (1,000 mg/kg and higher). Readings were highest near the target areas and near the stations where the rifles are fired. However, at increasing depths of only a few centimeters below the surface, levels of lead decreased to less than detection limits. On Range 124, for example, several surface readings in the range of 2,000 to 7,000 mg/kg were recorded. In all cases, (1) the readings decreased dramatically with subsurface measurement increments, and (2) lead readings of zero were obtained at depths of 15 to 60 cm. This was valuable information because it indicated that the lead contamination was confined to the surface. The XRF data made it possible to identify the "hot spots" and determine that the contamination was limited to the surface soil. This information was available immediately after the readings were made in the field.

Readings obtained on the pistol range indicated much lower levels of lead in the surface soil. This seemed to be inconsistent with the observation that several more slugs were visible on and in the soil on this range than in the rifle range, which had higher readings. In discussions with ballistics experts, it was learned that the rifle slugs are designed to disintegrate into small particles on impact, while the pistol slugs remain intact upon impact. This is consistent with our data: lead from the intact slugs did not readily leach into the soil on the pistol range, whereas the

minute particles produced on the rifle range were more easily incorporated into the soil.

Readings on the hand grenade range indicated low levels of lead, which was confirmed by laboratory analysis. This was consistent with the recorded use of this range for hand grenade practice.

Accuracy and precision are two measures of the quality of analytical data produced by a given method. Table I shows a comparison of field XRF data vs. analytical laboratory ICP data for two samples taken from a rifle range and homogenized and dried in the field. Eight replicate measurements were made on each sample in the field. Four replicates were run in the laboratory. The percent relative standard deviation for the field measurements was in the 8-10% range, which is very acceptable precision for a field method. For sample 1, field XRF results (1,200 ppm) and laboratory ICP results (1,400) agree fairly well if one ICP outlier data point is ignored. The outlier result in the laboratory data may indicate a problem with the homogeneity of the sample. For sample 2, the field XRF results (5,050 ppm) indicate substantially less lead than do the laboratory data (8,930 ppm). These samples contain relatively high levels of lead. The XRF unit is expected to be biased toward low values on samples with high concentrations. This bias is due to matrix effects; as the absorption of fluoresced X-rays increases with concentration, the low bias increases.

Figure 4 shows a comparison of field XRF data vs. laboratory ICP data for samples measured once in the field by XRF in the "routine" mode and then brought to the laboratory for analysis. All XRF measurements were made directly on the soil surface, with no preparation. After a measurement was made, a sample was taken

from the same spot for laboratory analysis. If three poor data points are omitted out of 51 total data points, a correlation coefficient of 0.903 is obtained.

Twenty-seven samples with XRF readings of 0 mg/kg lead were found to contain a mean concentration of 93.7 mg/kg of lead by ICP. The highest ICP value for an XRF reading of 0 mg/kg was 366 mg/kg. This indicates that for the conditions encountered, the limit of detection for the portable XRF unit used in this study was approximately in the range of 50 to 400 mg/kg of lead, depending on the soil matrix. This limit was acceptable for screening purposes, because our level of concern for lead contamination was 500 mg/kg. However, a lower limit of detection would be highly desirable.

For samples with XRF readings in the range 0 to 500 mg/kg (see Table II), variations in the degree of agreement between portable XRF and lab ICP results may be due to the nature of the contamination. Lead contamination on small-arms ranges is usually in the form of fine metallic particles, which are very heterogeneous. This is probably the reason that two of the samples gave readings of less than 500 mg/kg in the field but greater than 500 mg/kg by lab ICP. Table II also contains data from samples with XRF readings greater than 500 mg/kg of lead. Of the 24 samples indicated in Table II, the ICP result agreed with the XRF result within 50% for only eight. Better correlation would be required for field XRF to be useful as more than just a screening tool. All field readings that indicated lead contamination were confirmed by the laboratory results.

4 CONCLUSION

The portable XRF unit used in this study proved to be of value for screening contaminated small-arms sites. Field measurements cannot be expected to agree exactly with the analytical laboratory results on soil samples. The limit of detection and the spectral resolution of the commercial unit used limited the use of the XRF data. However, the XRF data were useful for deciding in the field whether a problem existed and for determining the dimensions of contaminated areas. The ability to make hundreds of measurements quickly and inexpensively made the portable XRF unit a useful tool for field work.

Field-portable XRF is being used to screen for lead and other heavy metal contamination in the field. Improvements in spectral resolution and in the limit of detection will make XRF more than just a screening tool.

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TABLE I - Comparison of Field-Portable X-Ray Fluorescence Measurement of Lead Contamination vs. Laboratory Determination by Inductively Coupled Plasma Emission Spectroscopy (ppm)

Sample	Field XRF ¹		Lab ICP ²
Sample 1	1,270	1,274	1,310
	1,050	1,167	1,420
	1,165	1,158	2,570
	1,316	1,203	1,470
Mean	1,200 +/- 100 ppm		1,690 +/- 510 ppm (1,400 +/- 70 ppm) ³
Sample 2	5,099	5,159	9,260
	5,276	5,303	8,900
	4,086	4,707	15,100
	5,532	5,211	8,620
Mean	5,050 +/- 500 ppm		10,470 +/- 2,680 ppm (8,930 +/- 270 ppm) ³

¹ Mean and standard deviation of eight readings.

² Mean and standard deviation of four replicates.

³ Questionable data point ignored.

TABLE II - Comparison of Field-Portable X-Ray Fluorescence Measurement vs. Laboratory Determinations by ICP (mg/kg)

For Field Values between 0 and 500mg/kg		For Field Values Greater than 500 mg/kg	
Field XRF	Lab ICP	Field XRF	Lab ICP
11	138	646	1270
25	418	685	1250
35	132	1796	1310
51	143	2528	3000
80	108	3312	47200
80	142	3764	8540
128	384	3987	2830
145	161	4192	8900
213	5080	4741	31800
349	123	6822	14800
351	650	7732	7570
489	50	10853	1040

Figure 1

Figure 2

Figure 3

Sample 2 5,211 mg/kg Lead

Figure 4

Field XRF vs. Lab ICP