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Project Summary

Evaluation of a Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening

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A prototype field-portable X-ray fluorescence system developed by EPA and NASA was evaluated at a site contaminated with Pb, Zn, and Cu. The objective of the field test was to evaluate the effectiveness of the instrument as a field analytical tool for locating hot spots and as a preliminary screening device where immediate data feedback aids in decision-making in the field.

By making use of an analytical method designed specifically for the XRF system, all routine field measurements for Cu, Zn, and Pb were made on site by placing the probe on the surface of the ground ("*in situ*" measurements). Subsequently, confirmatory samples were collected and analyzed in the laboratory with an Inductively Coupled Plasma spectrometer (ICP) while adhering to EPA Contract Laboratory Program (CLP) protocols.

The quality assurance consisted of measuring NBS standard reference materials to verify the data measured in the field and in the laboratory in addition to duplicates, blanks, and replicate sample analysis.

The analytical results were plotted on the sampling grid. One can immediately locate the hotspots for Cu, Zn, and Pb on site. The instrument detection limits for Cu, Zn, and Pb are 250, 200, and 70 ppm, respectively. Comparison of the XRF results with the ICP results showed an overall mean percent error (MPE, which means lack of precision and bias incorporated into one term) from NBS concentrations of only a few percent for Cu, Zn, and Pb. Precision and accuracy of the *in situ* measurements were within plus or minus 10 percent of the true value when compared to the samples analyzed in the laboratory.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas asked Lockheed Engineering and Management Services Company, Inc. (LEMSCo) to field test and evaluate the performance of a field-portable X-ray fluorescence system for making *in situ* measurements. The use of *in situ* measurements with the XRF system would allow technicians to immediately locate surface hotspots of lead, copper, and zinc on the national priority list (NPL) sites and other sites. The objective of this report is to describe the steps necessary to complete the field test, review the analytical work, and assess the instrumental performance. These steps are as follows:

- design a sound *in situ* analytical method for a field-portable X-ray fluorescence system prior to the field test,

- analyze each of the 40 samples *in situ* with the field-portable XRF system at 40 locations on a 60 foot by 150 foot grid with sample intervals at every 15 feet,
- subsequently collect confirmatory surface soil samples from the same locations,
- analyze the samples in the laboratory following the ICP CLP protocol,
- compare the XRF results with those obtained from the ICP.

The EPA has recently expressed more interest in XRF systems than in previous years because the use of microprocessors and state-of-the-art technology have made the equipment smaller and thus portable. Such field-portable XRF systems have been used to delineate hazardous waste site hotspots for priority metals in the field With immediate data feedback from the field-portable XRF system, all samples can be collected with the knowledge of their approximate concentration. This leads to a decrease in the number of unnecessary samples which would be analyzed normally. The XRF field data allows an analyst in the laboratory to calibrate his laboratory instrument to the proper concentration on the first try; thus decreasing the number of attempts at bracketing the correct one. Another use is as a laboratory analytical instrument to screen samples of unknown concentrations quickly providing the analyst with an approximate concentration. All of these applications of the XRF systems net an overall decrease in time and in money spent.

Three levels of analytical requirements are described for establishing the extent of environmental contamination. The first or highest level of analysis is used to develop data for litigation and regulatory enforcement (see Figure 1). This level demands the most rigor in sample preparation and instrument time as well as the highest degree of precision and accuracy. The seond level of analysis is used to evaluate and assess average contaminant exposures to people and animals. The data from the third level of analysis is used for screening in order to obtain a preliminary profile of sites. This data can be used for decision making while in the field. Third level data may be used also to select which samples should be sent to the laboratory for first level analysis following the Contract Laboratory Program (CLP) analytical protocols. This report discusses the results obtained by using a portable XRF system under the third level of analytical requirements.

Field Test and Procedure

The objective of the field test was to assess the performance of the Martin Marietta Aerospace field-portable XRF system on an NPL site with regard to effectively identifying hotspots of lead, copper, and zinc. This was accomplished by analyzing *in situ* and by subsequently collecting surface soil samples on site at 40 locations on a 60 feet by 150 feet grid with sample intervals at every 15 feet (Figure 2). *In situ* measurements are those measurements made by the XRF probe while in direct contact to the ground surface. These measurements are conducted without any sampling and sample preparation other than clearing the ground surface to expose the soil. An *in situ* XRF measurement represents the data obtained from only the exposed ground surface and does not reflect any of the subsurface. The contaminants in a hot spot would not register a response to the X-rays if the hot spots were covered

Three Levels of Analytical Requirements for Metals

	Degree of Analytical Requirement			
	(Precision)	*(Accuracy)*	*(IDL)*	*Purpose*
Level I	*Very High*			*Litigation and Regulatory Enforcement*
	(±5%)	*(±10%)*	*(ppb)*	
Level II	*Moderately High*			*Evaluate and Assess Average Pollutant Exposure to Humans and Animals*
	(±10%)	*(±15%)*	*(ppm)*	
Level III·	*Moderate to Low*			*Screening, Preliminary Evaluation, and On-Site Decision Making*
	(±10%)	*(±50%)*	*(≤ ppm x 1000)*	

Figure 1. *Three levels of analytical requirements for metals.*

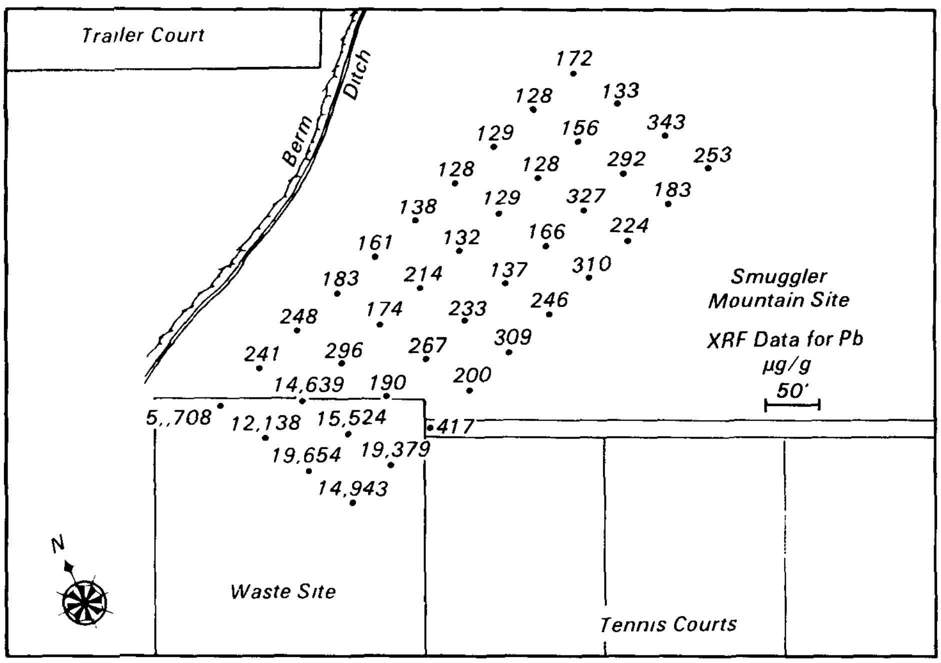

Figure 2 *XRF values for Pb plotted on sampling grid*

with as little as 1 cm of uncontaminated soil. Therefore, caution must be exercised in the use of data obtained from *in situ* measurements. Technicians analyzed each of the 40 samples *in situ* for total Pb, Cu, Zn, and Fe with the field-portable XRF system and processed the data for on site decision making.

The same samples were then collected for later confirmatory analysis in the laboratory. To further corroborate the XRF field data, we used the known and accepted CLP methods of preparation and analysis. Because the CLP method of sample preparation uses a relatively weak extraction, we also used a Parr bomb method to provide a stronger extraction method that was likely to more closely approach the NBS certified values. The Parr bomb method was performed on 13 selected samples but under CLP instrumental requirements for the ICP.

NBS standard reference materials (SRM) were used as quality assurance/quality control standards. The NBS standards were incorporated to give us reference data of known quality. Those used were SRM 1633a, coal fly ash, SRM 1645, river sediment, and SRM 1648, urban air particulate. The NBS standards were analyzed in the field with the XRF system. These values were compared against the SRM-certified values.

The quality assurance (QA) procedures developed for the XRF field analysis allowed for the proper verification of the data. The verification establishes the quality of the data. To evaluate the reproducibility of measurements offers many advantages. The data from the initial screening allows field crews to:

(1) identify the hotspots,
(2) restrict the investigation to the contaminated area,
(3) either go to the next level of investigation or stop at the screening level, and
(4) make decisions based on the data base which is generated from the analyses.

The next level of investigation above screening requires confirmatory samples be taken and analyzed. These can be analyzed in the field. If this were in an area being investigated for the first time, the hotspot would be identified and the locations registering as "background" (non-contaminated) by *in situ* XRF analysis need not be sampled for confirmation. In our case, the intensified effort would be restricted to the area marked "waste site" in Figure 2. This would decrease the number of samples, which might otherwise be analyzed, and thereby reduce overall analytical costs.

As more samples are analyzed, the data base for the area grows. The initial screening provides the foundation from which the investigation proceeds. The subsequent measurements then provide data of higher quality from which plots can be generated. Field crews can make decisions based on these plots and this data base.

Conclusions

- The XRF system produced data of known quality from 229 *in situ* measurements (defined as measurements made by placing the probe on the ground surface and by analyzing the same surface without moving the probe). The XRF field results on the NBS standards compared relatively well with the certified NBS values of the same standards.
- Field personnel can greatly decrease the time spent on site by making *in situ* measurements. If necessary, the technician can collect a confirmatory sample after each XRF analysis.
- The detection limits are low enough for obtaining data when third level requirements are necessary for analytical work on hazardous waste site investigations.
- The NBS standards were adequate for quality control and quality assurance. These standards were SRM 1633a, coal fly ash; SRM 1645, river sediment; and SRM 1648, urban particulate.
- The instrument uses cryogenics to cool the silicon-lithium detector which requires a Dewar container filled with liquid nitrogen. Even though the Dewar container will last 8 hours before a refill is necessary, maintaining a continuous supply of liquid nitrogen in the field can be difficult in some locations.
- The overall advantages of all X-ray fluorescent systems include: minimal sample preparation time, rapid turnaround time for analyses, multi-element analytical capability, nondestructive analyses, and sample size required for analysis is small or possibility of surface analysis without the need for sampling at all. These advantages make the XRF system very cost effective.

Recommendations

- A field methods manual should be written for field XRF measurements and should incorporate field sampling, sample preparation techniques, and analysis.
- Characterized spiked soils should be prepared for the XRF systems as reference standards. These would be spiked at concentrations ranging from 5 to 10 times the IDL, to the highest likely to be encountered; or at levels considered to be a public health hazard.
- A procedure for primary calibration, field update of calibration and of QA/QC checks of the instrument accuracy and precision should be worked out.
- The investigation of a sample preparation method for non *in situ* measurements should be tested. This should include examination of both the pelletizing and fusing techniques, and the use of loose soil. Indications are that one would obtain different levels of precision.
- The Martin Marietta XRF system should be compared with other commercially available field XRF systems. The detection limits, precision, and accuracy of each instrument could be determined side by side in the laboratory with the ICP or AAS by using rigorous QA/QC protocols, characterized samples, and certified spiked standards.
- Once the instrument detection limits are established for XRF field-portable systems, the initial steps may be implemented in developing these instruments for characterization of uncontrolled hazardous waste sites with respect to specific toxic metals.

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The complete report, entitled "Evaluation of a Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening," (Order No. PB 87-227 633/AS; Cost: $11.95, subject to change) will be available only from:
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