

**FIELD-PORTABLE X-RAY FLUORESCENCE FOR CHARACTERIZATION  
OF HAZARDOUS WASTE SITES: A TWO YEAR PROGRAM SUMMARY**

by

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## NOTICE

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## ABSTRACT

The use of FPXRF provides an approach to reduce costs, increase productivity and produce data on metal contamination in soils in realtime. Although the initial instrument cost of about \$46,000 seems high, when compared to the cost of an extensive intrusive sampling program, the cost is reasonable. Using FPXRF generated data to guide the intrusive sampling program reduces the number of samples to be taken and analyzed. With each subsequent site the FPXRF analysis cost per sample goes down.

Integration of geostatistics complements the FPXRF program, by optimizing the sampling strategy, providing data quality assurance, and improving data interpretation.

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## SECTION 1.0 INTRODUCTION

### 1.1 Background Information and Milestones

Traditional determination of contaminant analytes on hazardous waste sites occurs in a laboratory under strictly controlled conditions. The Environmental Protection Agency (EPA) follows the dictates of the 1980 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the 1986 Superfund Amendment and Reauthorization Act (SARA) by providing standardized methods for analysis, quality assurance and quality control programs for the methods, and laboratory and data auditing through the Contract Laboratory Program (CLP). The central purpose governing the structure and function of the CLP is the production of legally-defensible analytical results for supporting enforcement actions.

The CLP mandates and maintains a high level of quality assurance in all aspects of program activities. Commercial laboratories must qualify on a quarterly basis. Companies contracted by the EPA to conduct on-site work are required to send their samples to laboratories within the CLP. As a result, the costs of conducting CLP analyses are generally much higher than for analyses by non-CLP laboratories. The current cost for the standard 24 inorganic analytes per sample is about \$150 with a turnaround time of 21 to 45 days.

Lockheed Engineering & Sciences Company (LESC) scientists, under contract to the EPA, identified an alternative to the CLP inorganic methods in the scrap metal industry, which has used field-portable X-ray fluorescence (FPXRF) techniques for about the last 30 years to classify the various alloys of metals in scrap piles. There were several types of portable X-ray fluorescence (XRF) units available, however, only one conformed to the EPA decontamination requirements on hazardous waste sites. This one was the X-Met 840 (later upgraded to the 880) manufactured in Finland by Outokumpu Oy and distributed in this country by Outokumpu Electronics, Inc.

The X-Met 880 is a self-contained, battery powered, microprocessor based spectrometer weighing 8.5 kg. It is hermetically sealed and can be decontaminated with soap and water. The surface analysis probe is specifically designed for field use, and contains one or two radioisotope sources, a Xe-gas tube proportional counter, a multichannel analyzer, and the associated electronics. Source protection is provided by a government approved safety shutter.

The X-Met electronic unit has 32 calibration memories called 'models'. Each model can be independently calibrated for up to six elements, ranging from potassium to uranium, with the proper isotope source. The measured intensities from unknown samples are plotted against the calibration curves to yield concentrations. The routine data are recorded by hand as this unit has no means for storing multiple analyses.

Mernitz et al., 1985, first used the X-Met 840 to detect and evaluate hazardous metals in mine and mill tailings. The authors collected intrusive samples in the field and brought them to the instrument which was housed in a condominium near the site. The samples were prepared for analysis at the condominium and analyzed with the X-Met 840. The sample results were processed with geostatistical software programs developed by Geostat Systems International, Inc. (Aulenbach and Bryan, 1985) to yield contaminant concentration isopleth maps, which display contours that are more representative than those from traditional statistical processing and hand contouring of data. This approach is not only rapid, but also allows data problems to be addressed and resolved while the instrument is still on site. Previously this was not possible due to the long turnaround time through the CLP laboratories.

In August of 1987, LESC field-tested the Martin Marietta MM1 prototype FPXRF unit which produced quantifiable in situ measurements (Raab et al., 1987). This was the first ever attempt at in situ FPXRF analysis on a hazardous waste site. The MM1 prototype was developed for a National Aeronautics and Space Administration (NASA) contract under an interagency agreement with the EPA, and is an offshoot of the instrument Martin Marietta designed and built for the Viking Martian Lander.

The MM1 has an X-ray tube, and a liquid nitrogen cooled lithium-drifted silicon solid-state detector. The accompanying Dewar flask, electronics, multi-channel analyzer, and lap-top computer are somewhat bulky, but portable nonetheless. The distinct advantage of the MM1 is the full fundamental parameter calculation capabilities of the software. This allows the field technician to conduct "standardless" calibrations without the need for site specific calibration (SSC) standards. This is a significant advantage over the X-Met, but one which we could not readily exploit because the MM1 is a fragile prototype prone to breakage. In addition, EPA Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV) did not take delivery of the MM1 until July of 1989. Since then, we have not been tasked to work with it.

While researching the applications of various XRF instruments, we had the opportunity in September, 1987 to place a laboratory grade Kevex Delta 770 XRF spectrometer in a van and analyze samples on a site. The Kevex Corporation provided the instrument and an analyst for a week. Seventy-five soil samples

were dried in a microwave oven, hand pulverized to a powder and analyzed for 15 elements. This was the first time we had field-tested a laboratory grade energy-dispersive XRF. This opportunity demonstrated that, with minimal preparation, we could attain significantly lower detection limits in the field laboratory than we get with the FPXRF (Internal Report: Raab, 1987).

In May of 1988, the Pacific Engineering & Production Company of Nevada (PEPCON) experienced a series of four explosions in their Henderson, Nevada plant. The Las Vegas Fire Department suspected that lead nitrate used in one of PEPCON's industrial processes may have been distributed over the site by the explosions. Out of concern that the lead may have posed a health hazard to their crews, the Fire Department requested support from the EPA Region 9 Emergency Response Team (ERT). The EPA requested the Lockheed X-ray team to assist the Region 9 ERT in determining the presence and extent of any potential lead contamination.

The XRF team first screened the area of concern with the X-Met 840 which was calibrated with a generic calibration curve. During the preliminary survey, we collected samples to be characterized as SSC standards. While the samples were undergoing analysis in the EMSL-LV laboratory, the XRF team used a transit and tape to establish a sampling grid over the area of concern. We completed the in situ analyses in a two day period. This was the first time that we had the mobile laboratory on site and, with a computer and plotter now immediately available, we were able to complete concentration isopleth maps in a two-day period using CPS-PC software from the Radian Corporation. Our study concluded that although there was indeed localized lead contamination, it was not a result of airborne deposition from the explosion, but from long term deposition (EPA, 1988).

In July of 1988, Region 8 requested that we assist EPA contractors at a site in Aspen, Colorado (Internal Report: Miller et al., 1988). The work entailed extensive on-site sample preparation and field laboratory analysis of the samples. The advantage to the Region was the immediate characterization of the samples being prepared and sent to the CLP laboratory. Another demonstrated advantage was the ability to go back and reanalyze certain areas which were questionable. The milestone here was the cost-effectiveness of the on-site sample preparation. Only samples whose lead results exceeded the 1000 mg/kg remediation level were sent to the CLP laboratory.

In September of 1988, the X-ray team responded to a request from Region 3 to dispatch a full team and the mobile laboratory to the C & R battery site near Richmond, Virginia (Internal Report: Cole et al, 1988). Prior to our arrival, the primary contractor had drilled 28 holes and produced 190 samples in 8 ounce sample jars to be analyzed on site by FPXRF. Given the limited time for analysis,



no sample preparation was performed and samples were merely poured onto 5x5 inch sample weighing boats. Each sample was then measured on three different spots. The mean values of the triplicate measurements corresponded well to subsequent confirmatory analyses done in a CLP laboratory.

This was the second site on which we conducted a site reconnaissance prior to the site analysis. The reconnaissance serves basically two purposes. The first purpose is to allow the LESC personnel to become familiar with the site prior to site work and to discuss the strengths and weaknesses of the XRF program with the RPM and his/her contractors. Our experience by this time had shown us that this helps to avoid future misunderstandings and clear past ones. The second is to collect samples for characterization as SSC standards if none exist. The reconnaissance team uses the X-Met calibrated with a generic curve to obtain a relative range of in situ values and then collects samples representing that relative range. The RPM sends these samples to a CLP laboratory for analysis. Using splits of the samples, we recalibrate the X-Met with the CLP results prior to the site for field work.

It was also on this site that we found a discrepancy between the CLP results and laboratory grade XRF results. We attribute this to the inability of the CLP nitric acid extraction to solubilize all of the analyte(s) of interest (in this case, elemental lead). (The CLP extraction procedure is based on the SW-846 3050 method and will heretofore be referred to as the CLP '3050' extraction.) This results in lower analyte values from the CLP '3050' extraction than from a total digestion method or XRF analysis of the same sample.

In May of 1989, Region 2 requested our services at the Nascolite site in Millville, NJ (Internal Report: XRF Team, 1989). This was the first site where we programmed the X-Met with SSC standards that had been subjected to total digestion and subsequent AA/ICP analysis. In addition, this was the first site where we fully employed our geostatistical programs. Combining the FPXRF in situ measurement technique with geostatistics allows us to optimize our sampling design and optimize data interpolation to produce more reliable and representative isopleth maps. Geostatistics shows that interpolation errors can be reduced most cost-effectively by increasing sample density, thereby justifying use of a field procedure such as FPXRF that can furnish large numbers of measurements with very little expense.

In August, 1989, G. A. Raab presented the invited paper in the first Environmental Section at the 38th Annual Denver X-Ray Conference (Raab et al, 1990b). The four subsequent papers presented at the conference acknowledged the work done by the LESC X-Ray team as the forerunner in the area of characterization of hazardous wastes employing XRF technology.

Table 1 displays the instrument detection limits attained while on the sites mentioned above.

Table 1: Detection Limits for three analytes on three different instruments. All values are in mg/kg.

Instrument	Site	Proposed Action Levels	Analytes of Interest		
			Pb	Cr	Zn
MM1	Test Site 1	1000	70	1000	200
KeveX (lab grade)	Test Site 2	1000	6.5	5.3	9.1
X-Met	PEPCON	1000	270	nm	nm
X-Met	Aspen	1000	24	nm	37
X-Met	C & R	500-1000	120	nm	nm
X-Met	Nascolite	500-1000	74	nm	nm

nm = not measured

## SECTION 2.0 CURRENT WORK

### 2.1 Use of the FPXRF as an Analytical Tool on Hazardous Waste Sites: Advantages and Disadvantages

In summarizing the development of the FPXRF program for site characterization, a number of advantages are manifest: (1) rapid analytical turnaround, (2) low analytical costs, and (3) ability to obtain a large number of analyses very quickly. Most importantly, high density sampling schemes can be employed because of the low costs inherent in the FPXRF method, thereby producing a more reliable model of the spatial distribution of contaminants on the site.

Considerable importance is attached to the determination of data quality in site characterization and remediation. Even more emphasis is warranted in the case of a field method such as FPXRF which typically affords lower precision and accuracy than laboratory methods. Geostatistical procedures are utilized to great advantage in the application of FPXRF, particularly for optimization of QA parameters. For example, the spatial representativeness of a set of sample concentration values depends on data variability related to sampling procedures (handling, preparation, and analysis), and on the spatial variability of the contaminant. Whereas classical statistical procedures provide no tools for assessing the latter component of variability, geostatistical procedures provide the necessary tools. Furthermore, geostatistics supplies procedures for optimal spatial estimation, thereby enabling development of the most reliable spatial model that can be obtained for a given set of FPXRF data. The reader is referred to the Appendix A for more detailed discussions of these subjects.

The initial cost of the instrument is \$46,000 or more, depending on probe and source selection. This is approximately the cost of 300 samples run through CLP at \$150 per sample. FPXRF can complete upwards of 100 sample analyses per day. Hence, the instrument can pay for itself in savings on a single site, and of course, the instrument is also available for future projects.

The X-Met has several disadvantages, the greatest of which is that the instrument lacks fundamental parameter calculation capability. This drawback requires SSC standards for each site to develop quantitative results. Also, the software utilized for generating the calibration curves is proprietary. For quality assurance (QA) purposes this is not acceptable, as the analyst can not explain exactly how the curves are generated, beyond reciting the steps followed. Finally, the instrument has no memory to retain spectra and analytical results, so all results must be recorded into logbooks to follow proper QA procedures for documentation.

## 2.2 Site Specific Calibration Standards

The X-Met 880 requires a calibration curve against which the software compares the measured analyte intensities of unknown samples to estimate concentrations. The foundation for quantitative results is established by building a calibration curve with standards from the site in question, that is, standards that have the same matrix as the soil routinely analyzed on that site. Characterization of the SSC standards employs a total digestion procedure (Buckley and Cranston, 1971) prior to analysis according to CLP instrument requirements. NIST standards are utilized as blind control samples within the batch of SSCs to provide traceability and quality control (QC) on the analyses. We have had great success in applying this technique, (Raab et al. 1989b, and Raab et al. expected 1990a).

## 2.3 Guidance Document for QAPP, SOP, and Method Development

Currently in peer review are three deliverables, "Guidance Document for Quality Assurance Project Plan", "Standard Operating Procedure" and an SW-846 Method for FPXRF.

The Guidance Document for a Quality Assurance Project Plan provides the Regional project manager (RPM) with a generic way of building an FPXRF program. It supplies all necessary information to set up the FPXRF program and maintain a level of defensible data quality.

The Standard Operating Procedure (SOP) describes the FPXRF in four phases of operation. The SOP gives an RPM a sense of the timeline that an FPXRF survey must follow to complete the individual phases. Phase 1 discusses setting up a fly-over for aerial photographs and discusses conducting the historical investigation. Phase 2 discusses the site reconnaissance. Phase 3 discusses the preparations to go onsite. Phase 4 discusses the onsite activities and the final report.

## SECTION 3.0 FUTURE WORK VITAL TO THE PROGRAM AND RECOMMENDATIONS

### 3.1 Specific Objectives

The specific objectives of the FPXRF project to this point have been:

- ▶ to investigate the applicability of XRF and FPXRF as complements and alternatives to CLP analytical methods now in use for hazardous waste site studies,
- ▶ to evaluate the performance of prototype and commercially available FPXRF systems through field and laboratory testing,
- ▶ to encourage commercial production of the federally funded prototype instrument.

We have investigated the applicability of XRF and FPXRF as alternatives to CLP analytical methods now in use for hazardous waste site studies, primarily through actual on-site applications of the FPXRF program. Due to program limitations we have just begun the performance evaluation (PE) of the only commercially available instrument suitable for in situ analysis. Furthermore, the technology behind this instrument is already obsolete. To date, no other commercial company has developed a new, state-of-the-art FPXRF instrument which can be used for in situ measurements in the hazardous waste industry. (HNU has developed a transportable unit which is bulky and requires two people minimum to carry it. It does not have an external probe for in situ measurements.) Although we have tried to solicit development of state-of-the-art FPXRF equipment, there has been little encouraging response from the commercial market.

Sections 1.0 and 2.0 of this report have summarized the work performed by the XRF Team on the first project objective. The remainder of Section 3.0 will deal with performance evaluation of the instruments and methods, and some field support considerations.

### 3.2 Evaluation of Prototype and Commercial Instruments

A major activity within this project framework was to evaluate prototypes and commercially available FPXRF systems as well as their applicability to hazardous waste site characterization.

We have surveyed companies that manufacture XRF equipment, and are compiling information on companies that (1) make field-portable systems, (2)

have technology for field-portable systems available or under development, or (3) are interested in commercial development of a Federally funded prototype. Early survey results for information collected to date are summarized in Raab et al. 1989a.

At present there is only one FPXRF that fulfills most of the requirements for working within the exclusion area on a hazardous waste site. These instrument requirements are:

- ▶ be man-portable, i.e. under 20 pounds in weight,
- ▶ be hermetically sealed (for decontamination),
- ▶ be ruggedly built,
- ▶ have an external probe for in situ measurements,
- ▶ have exchangeable batteries strong enough for a minimum of 4 hours of continuous use,
- ▶ if the probe contains a radioactive source, conform to NRC regulations for safety and shipping regulations,
- ▶ calculate concentrations in either mg/kg, ppm, or weight percent,
- ▶ be programmable,
- ▶ have sufficient memory to retain spectra.

The X-Met 880 meets all but the last requirement. For now, it is the best instrument available for in situ measurements on hazardous waste sites.

### 3.3 Performance Evaluation on Soils: Experimental Design for Completion of Method

The PE will be covered by first describing in Sections 3.3.1 through 3.3.4 the steps to be undertaken immediately and then by discussing in Sections 3.3.5 through 3.3.7 additional aspects that should be investigated in order to provide a complete evaluation. This division is made necessary because the program is structured in quarters and will not allow us to perform the activities described in the latter sections at this time.

### 3.3.1 Characterization of Standards by Different Methods

The demand for FPXRF applications in hazardous waste characterization has recently increased. However, there is only one commercially available set of loose soil standards for use in calibrating the X-Met. We can not use these standards for the PE because there is not a sufficient quantity available. Thus we must prepare appropriate calibration standards for the instrument evaluation and characterize them by laboratory XRF and by ICP/AAS. This will provide the EPA with an immediate source of standards which can later be certified as legitimate reference materials. It should be noted that this is only one soil matrix and can not be construed to be representative of all the soils that can be encountered on a hazardous waste site.

The sample media employed in this study will be a spiked, natural soil matrix. The spiking media will be the minerals galena (PbS), chromite (FeCr<sub>2</sub>O<sub>4</sub>) and realgar (As<sub>2</sub>S<sub>3</sub>) for the respective analytes of lead, chromium and arsenic. Spiking concentrations will be selected to simulate statistical distributions encountered for As, Cr, and Pb concentrations in field situations. We will be simulating a situation where the analytes of interest occur in a refractory form. In this situation, we will probably see the greatest discrepancy between the two extraction methods.

Fifty samples will be sent to an off-site laboratory via a Special Analytical Services (SAS) contract. Two samples will be split prior to shipment, and a blind audit pair will be included so that, effectively, there will be 46 unique samples in the study.

Due to program restrictions, we are limited to 50 sample analyses, so only one soil matrix will be employed. Originally 4 or 5 different soil matrices were to be employed but with the sample constraint, we must limit the study to one matrix to yield a statistically significant population.

The samples for the PE will be characterized using a total digestion procedure and subsequent atomic absorption/inductively coupled argon plasma spectroscopy (AA/ICP) analysis for the inorganic target analyte list (TAL) using CLP instrument and QA protocol. The samples will also be subjected to the CLP '3050' extraction procedure and subsequent AA/ICP analysis. One pressed pellet and one loose soil sample from each will be analyzed by both energy-dispersive and wave-length dispersive XRF for 22 of the inorganics on the TAL (XRF analysis cannot detect beryllium or cyanide). The FPXRF will be calibrated with 10 of the samples (separate curves with loose soil and pellets) and the rest of the samples will be run as routines. For each instrument, we will evaluate minimum detection limits, analytical range, precision and accuracy of data and the sophistication of interference corrections.

The CLP '3050' extraction method employs aggressive acid leaching in the sample preparation which only extracts those analytes soluble in nitric acid. Often these data are considered to be total elemental analyses, when, in fact, they may represent only partial concentrations for some analytes found in the samples. In these cases a discrepancy results when compared to any XRF analysis, which is a true total elemental analysis.

This PE will deviate from the CLP protocols only in sample preparation and will include a comparison of CLP '3050' extraction and total digestion methods prior to AA/ICP analysis. This will validate the necessity for the total digestion procedure that we specify for the characterization of the standards used to calibrate the FPXRF instrument.

### 3.3.2 Loose Soils, Pellets, Fusion

There are three ways to handle an intrusive (i.e., one that has been removed from the ground) soil sample prior to XRF analysis. The first is with minimal preparation: dry, sieve, and homogenize then place a 5 g subset into a 31 mm diameter X-ray cell (this is the loose soil sample). The second is to dry, sieve, homogenize, pulverize, and press a 6 to 7 g sample into a pellet. The third preparation method for XRF analysis is to dry, sieve, homogenize, pulverize, and fuse into a glass disk. The majority of our work is in situ measurement, so we analyze loose soils to simulate the in situ soil matrix with regard to particle size heterogeneity and mineralogy. To fully characterize the samples by laboratory XRF, we pelletize the samples to reduce interferences to the elemental level (i.e., particle size and mineralogical interferences are negligible when the particle size is less than 0.053 mm [270 mesh]). Even though fusion is in some cases the best of the three because it dilutes the elemental interferences, the necessary equipment is not at hand to include this preparation method.

### 3.3.3 Moisture Study

The soils encountered on most sites contain some percentage of moisture. Moisture effects have been studied in the laboratory, but not relative to an in situ measurement. The effects of soil moisture on XRF analysis of loose soils must be determined to establish precedence for, or against, moisture correction on in situ analytical results. Increasing soil moisture should attenuate the impinging X-ray energy which would result in underestimation of concentration for the analytes of interest. However, the degree to which this affects in situ measurements is unknown. We need to know whether to develop a correction factor or if the effect is negligible. In this study, we will examine soils in the X-ray cells in two end-point states: oven dried and fully saturated to determine if a more intensive study on soil moisture effects is warranted.



### 3.3.4 Spiking into Soils

Spiked soils were chosen in preference to samples from a hazardous waste site for two reasons. First is the lack of availability of the soils with various analytes in the necessary concentration ranges. By spiking the soils we can better represent a typical statistical distribution. Secondly, we will be simulating a situation where the analytes of interest occur in a refractory form. In this situation, we will probably see the greatest discrepancy between the two extraction methods.

Liquid or slurry spikes were considered, but the liquid mixed into the soil will destroy any remnant soil structure which is what we try to retain for the loose soil samples to emulate in situ conditions. The effects of liquid spikes on a soil is an entirely separate study that we are not prepared to address at this time.

An issue we do need to resolve is whether site personnel can accurately spike background soils to augment calibration curves. This study will determine our degree of accuracy in spiking soil.

### 3.3.5 Mineralogy verses Particle Size

Soils, with the exception of organic soils, are composed of various minerals, and their mineralogy has a strong effect on the particle size and thus the FPXRF analyses. Each mineral has a specific hardness and resistance to weathering, and these relate directly to particle size distribution.

The effect of particle size distributions on XRF are well known. The coarser the material, the more attenuation of the fluorescent yield, thus a lower response. Because there is virtually no sample preparation involved with an in situ measurement, we need to understand and account for these effects, therefore, we recommend that a study be funded to ascertain the effects due to mineralogy verses particle size distributions relative to the FPXRF in situ measurement.

### 3.3.6 Matrix Matching

The scrap metal industry uses XRF spectral matching to specifically identify or classify groups of alloys. Therefore, most XRF instruments have software programs which pattern match the spectra from unknown samples to known spectra. In the future, we hope to study this application in the spectral classification of soils from hazardous waste sites. This may allow us to use standards from one hazardous waste site to calibrate the FPXRF instrument for another provided there is a high degree of confidence on the spectral match.

### 3.3.7 Water Analysis

Water samples are quickly and easily analyzed directly with both field portable and laboratory grade XRF instruments. Standards are relatively easy to make up because liquid spiking into a liquid medium is much less difficult than spiking soils.

For trace metals analysis, there are preconcentration methods which, in effect, enable the analyst to substantially lower XRF detection limits to the parts per billion range. The preconcentration method is a chemical precipitation onto a media which is then analyzed by XRF thin film methods. The larger the starting volume of water, the more accurately trace analytes can be quantified and the lower the effective detection limits.

Scientists at Martin Marietta Aerospace, Inc. in Denver, CO, developed a preconcentration method and equipment for the MM1 prototype (Clark and Thornton, in review). This laboratory method may be usable in the field laboratory. EMSL-LV has recently taken delivery of this equipment from Martin Marietta. We will conduct a PE on this instrument in the near future.

### 3.4 Field laboratory support for FPXRF with laboratory grade EDXRF

EMSL-LV has recently placed a laboratory grade EDXRF in the FPXRF mobile laboratory for support in field programs. We have shown that with the FPXRF instrument we can match laboratory analyses in concentrations greater than the level of quantitation (Raab 1989b), but those levels are generally a few hundred mg/kg for most heavy metals. However, a laboratory grade XRF in the mobile laboratory will yield lower detection limits than the FPXRF, by an order of magnitude or more, and avoid the long delay of CLP analyses. Therefore, we can prepare and analyze the SSC standards immediately after collecting them on site. On site laboratory grade XRF analyses will further reduce the number of samples requiring CLP laboratory analysis. The RPM need send only those samples necessary for confirmation of the XRF procedure and enforcement or litigatory samples.

### 3.5 Incorporation of Locator/Telemetry System

Martin Marietta Energy Systems Inc., under contract to the Oak Ridge National Laboratory, has built a locator/telemetry system which allows the field analyst on a hazardous waste site to locate all sample points on a two dimensional grid. These coordinates, along with the concentrations of the elements identified, are transmitted to a PC at a nearby field station. Field station personnel can then use geostatistical software to evaluate the data and plot concentration isopleth maps.

The locating of each prospective sample point using standard surveying techniques is the most time-consuming portion of the FPXRF field work (Berven et al., 1987). The time savings achievable by implementing the locator/telemetry system are substantial. Acquisition of this technology is being actively pursued.

### 3.6 A Case Study

It is paramount for the acceptance of this program to complete at least one case study. We have worked on numerous sites in the past but, always being subject to the mandates of the RPM, have never really been able to demonstrate the full capabilities of the program. Also, with the recent addition of a new, bigger mobile laboratory equipped with a laboratory grade XRF instrument, our capabilities have substantially increased.

We recommend two case studies. The first is a single analyte, non-contaminant situation, at Red Rock Canyon, near Las Vegas, NV, where there are concentrations of iron as high as several percent. This would provide us with a 'clean' training site for Regional people, new employees, etc. The second case study would be a multiple analyte Superfund site, such as Kellogg, ID. The multiple analyte site would provide the EPA with the reference the Regions need to justify employing the FPXRF and geostatistics program.

## SECTION 4.0 CONCLUSIONS

### 4.1 Proven Advantages with FPXRF and Geostatistics

The FPXRF program has demonstrated that:

- ▶ the combination of FPXRF with geostatistics can optimize field sampling programs, (Raab et al., 1989b; Raab et al., expected 1990a & b),
- ▶ we can effectively use in situ measurements to characterize hazardous or mining waste sites in real-time with defensible quality assurance procedures,
- ▶ field crews can examine the real-time data before physically collecting any samples,
- ▶ we can accurately measure concentrations above our quantitation limits without corroboratory analyses,
- ▶ we can measure several hundred sample locations within a relatively short period of time,
- ▶ the quality of the acquired data is expressed quantitatively by the parameters of semivariograms and by the spatial estimation error,
- ▶ we can quickly provide a document to the project manager complete with calibration curves, routine and quality control data, aerial photographs, and optimized concentration isopleth maps whose reliability is quantitatively expressed as kriging errors.

## SECTION 5.0 REFERENCES

### Published Documents:

ACS Committee on Environmental Quality, "Principles of Environmental Analysis" Anal. Chem. 1983, 55, 2210-2218.

Aulenbach, S. M., and R. C. Bryan, 1985. Final Report of Geostatistical Use, Methods, and Results, Smuggler Mountain Site, Pitkin, CO. Geostat Systems International, Inc. Golden, CO. 70pp.

Berven, B. A., M. S. Blair, and C. A. Little, 1987. Automation of the Radiological Survey Process: USRADS Ultrasonic Ranging and Data System. In: Proceedings of the 1987 International Decommissioning Symposium. Conf-871018-Vol.2. Richland, Washington.

Buckley, D.E. and Cranston, R.E., 1971. Atomic Adsorption of 18 Elements from a Single Decomposition. Chem. Geol. 7:273-284.

Clark, B.C. and Thornton, M.G. (in peer review). Study for Development of a Portable X-ray Fluorescence Spectrometer for Water Quality Monitoring. National Aeronautics and Space Administration, Langley Research Center, Hampton, VA.

Mernitz, S., R. Olsen, and T. Staible. 1985. Use of a Portable X-Ray Analyzer and Geostatistical Methods to Detect and Evaluate Hazardous Metals in Mine/Mill Tailings. Proceedings from the 6th National Conference on Management of Uncontrolled Hazardous Waste Sites. Hazardous Materials Control Research Institute, Washington, D.C.

Raab, G. A., D. Cardenas, and S. J. Simon, 1987. Evaluation of a Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening. EPA/600/4-87/021. U.S. Environmental Protection Agency, Las Vegas, Nevada.

Raab, G. A., M. L. Faber, and S. J. Simon, 1989a. Development of a Field-Portable X-Ray Fluorescence System for On-Site Hazardous Waste Screening. Proceedings of the Thirteenth Annual British Columbia Mine Reclamation Symposium, June 7, 8 and 9, 1989. Mining Association of B.C., Technical and Research Committee on Reclamation. British Columbia, Canada.

Raab, G.A., R.E. Enwall, W.H. Cole III, C.A. Kuharic, and J.S. Duggan, 1989b. Fast Analysis of Heavy Metals in Contaminated Soils Using Field-Portable X-Ray Fluorescence Technology and Geostatistics. Presented at the 95th Northwest Mining Association Convention, Spokane, Washington. December 6 - 8, 1989.

Raab, G.A., R.E. Enwall, W.H. Cole III, M. L. Faber and L. A. Eccles, expected 1990a. X-Ray Fluorescence Field Method for Screening of Inorganic Contaminants at Hazardous Waste Sites. In: Hazardous Waste Measurements, ed. M. Simmons. Lewis Publishers, Chelsea, MI.

Raab, G.A., C.A. Kuharic, W.H. Cole III, R.E. Enwall, and J.S. Duggan, expected 1990b. The Use of Field-Portable X-Ray Fluorescence Technology in the Hazardous Waste Industry. In: Advances in X-Ray Analysis, Volume 33, Proceedings of the Thirty-eighth Annual Conference on Applications of X-Ray Analysis, held July 31 - August 4, 1989 in Denver, Colorado. Plenum Press.

U.S. EPA, 1987. Data Quality Objectives for Remedial Response Activities: Development Process. EPA/540/G-87/003, U.S. Environmental Protection Agency, Washington, D.C., 137pp.

U.S. EPA. 1987. Data Quality Objectives for Remedial Response Activities: Development Process. EPA/540/G-87/004. U.S. Environmental Protection Agency, Washington, D.C., 154pp.

U.S. EPA. 1988. Special Report on the Distribution of Lead at the PEPCON Site Using X-Ray Fluorescence for On-site Screening, Henderson, Nevada. EPA /600/X-88/336. U.S. Environmental Protection Agency, Washington, D.C., 81pp.

Unpublished, Internal Reports:

Cole, W.H., G.A. Raab, T. Hunt, R. McClafflin, and T. Nail. 1988. Site Screening Report, C & R Battery Site, Chesterfield County, Virginia. Lockheed Engineering & Sciences Company. Las Vegas, NV.

Miller, G.A., J. Miyagishima, M. Fillinger, E. Oswald, N. Bingert, G.A. Raab, R.E. Enwall, W.H. Cole, R.K. Grant, and T.W. Nail. 1988. Site Screening Report, City of Aspen, Colorado. Lockheed Engineering & Sciences Company. Las Vegas, NV.

Raab, G.A. 1987. Site Evaluation Employing Laboratory-Grade EDXRF: Western Processing. Report awaiting completion of research.

X-Ray Fluorescence Team, LESC. 1989. Site Screening Report, Nascolite Site, Millville, New Jersey. Lockheed Engineering & Sciences Company. Las Vegas, NV.

SECTION 6.0  
APPENDIX A

6.1 Quantification of Spatial Variability

The spatial variability of a regionalized (spatially autocorrelated) variable, such as contaminant concentration, can be expressed quantitatively by the semivariogram in which the averages of squared differences between pairs of sample values are plotted against intersample distances for a given direction (cf. Figure 1). In essence, the semivariogram expresses the error incurred when extending a sample value to estimate concentration at an unsampled location at a specific distance in a given direction. Uncorrelated errors relating to sampling and analysis appear in the nugget variance component of the semivariogram, so that the relative contributions of sampling errors and spatial extension errors can be directly assessed (see Figure 1). Because the latter errors are usually the largest, spatial representativeness is most sensitive to intersample distances and can usually be improved most cost-effectively by increasing sample density rather than by employing more costly sample preparation or analytical procedures. Assessment of the spatial limits of representativeness of an average sample, in terms of area or volume, is afforded directly by the range of the semivariogram.

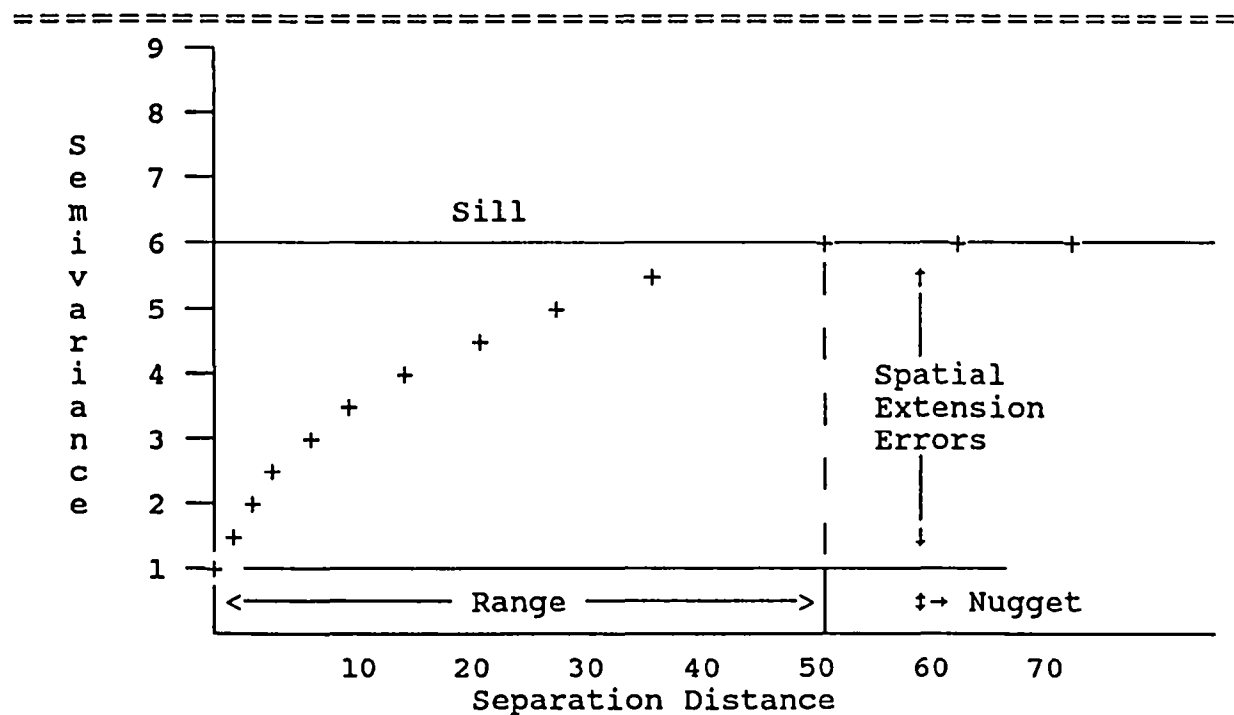


Figure 1. The semivariogram

Geostatistical principles show that the estimation error incurred by a set of samples is simply a linear combination of the errors relating to individual samples<sup>1</sup>. Since the latter depend on the semivariogram, and thereby only on the relative proximities and geometry of sample locations, the estimation error for any given sampling configuration can be calculated and utilized for a priori optimization of sampling design. The estimation error also serves as a quantitative data quality indicator for the spatial representativeness of the sampling configuration.

## 6.2 Optimal Spatial Estimation

One of the principal objectives of site characterization is to determine the spatial distribution of concentrations of the contaminants. Exhaustive sampling is precluded for obvious physical and economic reasons; hence, it is necessary to obtain a limited number of concentration measurements which are then used to estimate concentrations at unsampled locations. The process of spatial estimation is the most important single step in site characterization because it establishes the inferential link between samples and the spatial population they are supposed to represent. This link is typically expressed in the form of a spatial model that gives quantitative description of concentration throughout a site. It is upon this model that subsequent decisions regarding the site are made, and it provides the basis for such graphical decision-making tools as isopleth maps and isometric plots.

Many procedures currently exist for spatial estimation. They employ different parameters and assumptions regarding spatial variability, and lead to widely varying results. It is literally true that an infinite number of spatial models can be generated for a single set of data. Regrettably, most data users are unaware of these facts, and usually accept any result produced by their software as a unique, accurate representation of the spatial distribution of their data. Therefore, procedures employed for spatial modeling and isopleth mapping should be subject to QA review.

Geostatistics provides the necessary procedures for optimal spatial estimation and for QA assessment of the results. Optimal estimation is afforded by kriging which, under appropriate conditions, represents an unbiased, minimum error estimator. Utilizing semivariograms, kriging automatically compensates for the spatial variability of the data and for the spatial distribution of the sampling locations. Kriging errors, equivalent to estimation errors, are calculated for each estimation point and serve as data quality indicators for the spatial model.

<sup>1</sup> Journel, A.G. and Huijbregts, C.J. (1978). Mining Geostatistics. Academic Press, NY. 600p.