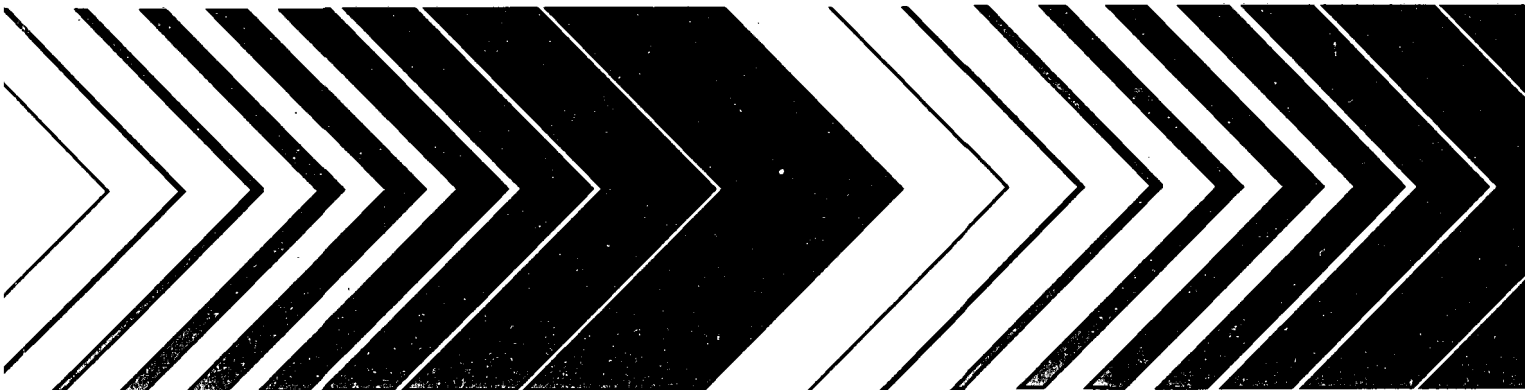




Technology Evaluation Report

Laser-Induced Breakdown Spectrometer for Metals- Contaminated Soil Characterization

MelΔok Instruments, Inc.



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Notice

The information in this document has been funded by the U.S. Environmental Protection Agency (EPA) under an Interagency Agreement (No. DW89936700-01-0) with the U.S. Department of Energy's Sandia National Laboratories. This technology evaluation was supported by the Consortium for Site Characterization Technology, a pilot program operating under the EPA Environmental Technology Verification (ETV) Program. This report has been subjected to Agency peer and administrative review, and it has been approved for publication as an EPA document. Mention of corporate names, trade names, or commercial products does not constitute endorsement or recommendation for use of specific products.

Executive Summary

Consortium for Site Characterization Technology

The U.S. Environmental Protection Agency (EPA), through the Environmental Technology Verification Program, is working to accelerate the acceptance and use of innovative technologies that improve the way the United States manages its environmental problems. As part of this program, the Consortium for Site Characterization Technology was established as a pilot program to test and verify field monitoring and site characterization technologies. The Consortium is a partnership involving the U.S. Environmental Protection Agency, the Department of Defense, and the Department of Energy.

This report describes the results of a field demonstration conducted at contaminated soil sites near Butte, Montana, in which developers of soil characterization technologies were invited to participate. The report presents soil sample analysis results from a laser-induced breakdown spectrometer (LIBS) operated by MelΔok Instruments, Inc. This laser-assisted spectroscopic technique was one of four technologies that were used to analyze soil samples for a number of target elements. Other technologies that were tested include a mobile atomic absorption spectrometer operated by Pace Environmental Laboratories, Inc.; a second laser-induced breakdown spectrometer from Los Alamos National Laboratory; and anodic stripping voltammetry systems fielded by Battelle Pacific Northwest National Laboratory. The results from these three technology demonstrations are published as separate reports.

Technology Classification

The Consortium classifies each candidate technology into one of three development levels on the basis of maturity of the technology and its expected time to commercialization. Level 1 designates the least developed and Level 3 the most developed technologies. The MelΔok laser-induced breakdown spectroscopy system falls in the Level 1 category since the system is under development. The Consortium has determined that an exhaustive verification of the relatively new and developing Level 1 technologies should not be performed. The field demonstration data sets from the MelΔok technology are compiled, organized, and presented in this report along with a validated data set from laboratories using conventional analytical methods. The degree of comparative analysis of the data is purposely limited. The results are intended for distribution to the technology developers to assist them in further development and refinement of their instruments.

Demonstration Design

A demonstration of selected Department of Energy-funded technologies was being planned by MSE-HKM, Inc., under contract to the Department of Energy. The Consortium chose to augment the planned demonstration by bringing in additional technologies and enhancing the laboratory analysis component of the project. Two sites contaminated with heavy metals were identified in the Butte, Montana, area for the demonstration. The first site, Butte/Silver Bow Creek, was contaminated by heavy metals deposited as mill tailings. The second site,

Anaconda Smelter/Mill Creek, was contaminated by dry aerosol deposition of smelter stack emissions. The surface soils at both sites contained varying concentrations of heavy metals. Soil conditions at each site were judged to be representative of typical field conditions under which the technology would be expected to operate.

Sixty samples were collected and processed using a preestablished sampling protocol. The soil samples were dried, homogenized, and split ten ways for distribution and analysis by three analytical laboratories and four technologies.

The demonstration plan incorporated the use of reference laboratories to analyze metals in the soil samples using standard EPA laboratory protocols. Laboratory data produced by inductively coupled plasma atomic emission spectroscopy and direct-aspiration, flame atomic absorption spectroscopy methods were validated to produce a reference set of target metal concentrations in the field soil samples. The reference data set was used for comparison with analytical results from the demonstration technologies. Quality control samples were also incorporated into the sample analysis plan to obtain additional performance measures for the laboratory and field tests.

Demonstration Results

Laser-induced breakdown spectroscopy is a form of atomic emission spectroscopy that uses a high-powered laser to vaporize a soil sample, causing excitation of the metal atoms in the sample. As the atoms decay back to ground state, they emit photons at specific wavelengths for each element. With appropriate calibration of photon detectors, quantitative analysis of the metal content in soil and other media is possible. The MelΔok laser-induced breakdown spectroscopy system is a relatively new technology that has successfully completed laboratory testing and is ready for initial field evaluation. This system was demonstrated alongside three other participating technologies in this study. All participants set up and operated their instruments over a 1-week period in the Butte, Montana, area in September 1995. The incorporation of conventional laboratory analysis into the demonstration plan provided a validated data set that could be used by developers to evaluate the performance of the technology.

A comparison of the field soil sample data sets from the reference laboratories showed very close agreement. This observation suggests that the soil samples distributed to the demonstration participants were homogeneous in terms of their chemical composition. A high degree of homogeneity facilitates comparison of the soil analysis results from the demonstrated technologies with those from the reference laboratories. Data from the reference laboratory and MelΔok LIBS technology data are presented in a variety of formats to assist in comparing the data sets produced during the demonstration.

The MelΔok laser-induced breakdown spectrometer system falls into a Level 1 category. Consequently, a formal assessment of the system's performance is not within the scope of this report.

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Acronyms and Abbreviations

AAS	atomic absorption spectroscopy
ac	alternating current
CAS	Columbia Analytical Services
CCV	continuing calibration verification
CLP	Contract Laboratory Program
DoD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectroscopy
K	Kelvin
kg	kilogram
kW	kilowatt
LANL	Los Alamos National Laboratory
LCL	lower 95 percent confidence limit
LIBS	laser-induced breakdown spectroscopy
MCHD	Mill Creek-high demonstration
MCLD	Mill Creek-low demonstration
MCMD	Mill Creek-medium demonstration
MPD	mean percent difference
RPD	relative percent difference
SBHD	Silver Bow-high demonstration
SBLD	Silver Bow-low demonstration
SBMD	Silver Bow-medium demonstration
SNL	Sandia National Laboratories
UCL	upper 95 percent confidence limit
μm	micrometer
V	volt
W	watt

Acknowledgments

The demonstration of contaminated soils measurement technology benefited from the contributions of numerous personnel from the U.S. Environmental Protection Agency, the Department of Energy, and the Department of Defense and their contract organizations.

Participants in the demonstration planning, execution, and analysis were:

EPA National Exposure Research Laboratory, Environmental Science Division
Stephen Billets, Eric Koglin, Gary Robertson

EPA Office of Solid Waste and Emergency Response
Oliver Fordham, Jr.; Howard Fribush

Sandia National Laboratories
Gary Brown, Wayne Einfeld, Michael Hightower, Art Verardo, Susan Bender, Robert Helgesen

MSE-HKM, Inc.
Jay McCloskey, Frank Cook

Columbia Analytical Services
Linda Huckestein

Ames Laboratory
Glenn Bastiaans, Marv Anderson

Naval Research Laboratory
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Chapter 1

Introduction

Site Characterization Technology Challenge

Rapid, reliable, and cost-effective field analysis and screening technologies are needed to assist in the complex task of characterizing and monitoring hazardous and chemical waste sites. Environmental regulators and site managers often are reluctant to use new technologies that have not been validated in an objective U.S. Environmental Protection Agency (EPA)-sanctioned testing program or through a similar process that facilitates acceptance. Until the performance of field characterization technologies can be verified through objective evaluations, users will remain skeptical of innovative technologies, despite the promise of better, less expensive, and faster environmental analyses.

The Consortium for Site Characterization Technology was established as a pilot program under the Environmental Technology Innovation, Commercialization and Enhancement Program, as outlined in 1993 by President Clinton's Environmental Technology Initiative, to specifically address many of these concerns. The Consortium is a partnership among the EPA, the Department of Energy (DOE), and the Department of Defense (DoD). The mission of the Consortium is to identify, demonstrate, and assess innovative field instruments. It also disseminates information about technology performance to developers, environmental remediation site managers, consulting engineers, and regulators. As a partnership, the Consortium offers valuable expertise to support the demonstration of new and emerging technologies. Through its organizational structure, it provides a formal mechanism for independent assessment, evaluation, and verification of emerging field analytical site characterization technologies.

Technology Demonstration Process

The Consortium provides technology developers a clearly defined performance assessment, evaluation, and verification pathway for EPA acceptance. The pathway is outlined in the four components of the Consortium's evaluation and verification process:

- Technology identification and selection
- Demonstration planning and implementation
- Performance assessment, evaluation, and verification
- Information distribution

Each component is discussed in detail in the following paragraphs.

Technology Identification and Selection

The first step of the process is a determination of technology needs. Because a wide range of field characterization and monitoring needs exists, the Consortium must prioritize a technology's suitability for demonstration. Priority is based on the environmental and fiscal impact of the technology and on the likelihood that its acceptance and use will provide cost-effective and efficient environmental solutions. Surveys of EPA, DOE, DoD, state, local, and tribal agencies and industry are carried out to identify candidate technologies that could meet the needs of the environmental characterization community.

Beyond the initial identification, a critical aspect of technology selection is an assessment of the technology's field deployment readiness. Commercialized instruments, or those ready for production, that have a history of successful laboratory or field operation are prime candidates for the demonstration process. Early prototypes, evolving technologies, or laboratory instruments requiring extensive testing and modification prior to field deployment are less desirable as demonstration candidates. The candidate technology must meet criteria for one of three levels of maturity:

Level 1 - Demonstrated in a laboratory environment and ready for initial field trials

Level 2 - Demonstrated in a laboratory environment and in limited field trials

Level 3 - Demonstrated extensively in the laboratory and in field trials and commercially available

Assessment of the readiness of candidate technologies for field demonstration is based on the following criteria:

- Field portability or transportability
- Applicability to numerous environmentally affected sites
- Potential for solving problems inherent in current analytical methods
- Per sample cost factors
- Potential improvements in data quality, sample preparation, or analysis time
- Ease of use

Demonstration Planning and Implementation

A technology demonstration plan is prepared according to guidelines provided by the Consortium. This plan includes a technology description, an experimental design, a sampling and analysis plan, a quality assurance project plan, and a health and safety plan. These plans are designed to enable an objective test of technology performance. The demonstration plan also calls for the generation of a validated reference laboratory data set with which the field technology can be compared. Following approval by the EPA and acceptance by the technology developers, the demonstration plan is implemented at appropriate field locations. The Consortium provides technical support to the technology developer during plan preparation and execution and also audits the data collection process.

Performance Assessment, Evaluation, and Verification

In this component of the demonstration process, the technology analytical results are compared with a reference laboratory data set. The principal product of this phase of the project is a technology report, prepared by an independent party known as the verification organization. The report documents demonstration results and provides an assessment of the technology's performance. The degree of data analysis in the report is determined

by the level of maturity of the technology under evaluation; the more mature technologies receive more detailed analysis.

Level 1 demonstrations are intended to provide the technology developer with access to a controlled field demonstration in which the system can be tested. A detailed evaluation of system performance is left to the developer using the validated reference data set obtained during the demonstration. Level 2 technology performance is evaluated by the Consortium on a limited basis. The most extensive evaluation is done for Level 3 technologies. In this case, the capabilities of the technology are evaluated by the Consortium, and a formal verification statement documenting the technology's performance is issued by the EPA.

Information Distribution

Innovative technology evaluation reports from these demonstrations are peer reviewed and approved for distribution by the EPA. The Consortium has developed an information distribution strategy to ensure that these documents are readily available to interested parties. This strategy includes access to information via the World Wide Web through a program supported by the Superfund Technology Innovation Office.

The Soil-Metals Characterization Demonstration

The objectives of the metals-contaminated soil characterization technology demonstration were twofold:

1. provide an opportunity for technology developers to analyze soil samples under a documented and scientifically sound experimental plan and
2. provide a validated soil analysis data set from conventional analytical laboratories using prescribed EPA laboratory analysis methods with which technology developers could compare their results

The process used for technology selection involved the publication of a notice of intent to conduct a technology demonstration, which was accompanied by solicitation of applications from interested parties. Usually, the Consortium selects applicants based on the readiness of the technology for field demonstration and on its applicability at environmentally affected sites as determined by the level of regional and national interest in the specific technology.

For this demonstration, the Consortium joined a project funded by the Department of Energy in which several technologies had already been selected for demonstration. The Consortium formalized the demonstration plan development, brought additional technologies to the demonstration, and enhanced the analytical laboratory component of the project.

Contractual arrangements were established with several chemistry laboratories to conduct soil analyses by conventional methodologies. Included in these arrangements was a plan to carry out a preliminary site assessment that involved limited sampling and analysis of soils from the area selected for the demonstrations. These preliminary data were used to further develop the site sampling and analysis plan, prior to the actual demonstration.

The following chapters of this report present the details of the demonstration project. Chapter 2 briefly describes the MelΔok laser-induced breakdown spectroscopy system (LIBS). Chapter 3 gives a description of the site selection, soil sampling, laboratory selection and analysis methodology. The technical approach taken in evaluation and validation of laboratory data is also outlined in Chapter 3. Chapter 4 gives a detailed analysis of the laboratory data validation process and describes how a reference laboratory data set was determined.

Chapter 5 gives results and a brief analysis of the MelΔok LIBS system performance. Chapter 6 contains developer's comments regarding the demonstration.

Chapter 2

Technology Description

General Description

Laser-induced breakdown spectroscopy is a form of atomic emission spectroscopy that utilizes a pulsed laser to vaporize the sample matrix. In the LIBS system, a high-powered, pulsed laser beam is focused on a soil sample. The interaction of the laser beam with the sample matrix results in the formation of a very hot (8,000 to 10,000 K) plasma in which all sample components are converted to atomic species. In this high-energy plasma, atomic species are elevated to various energy states above the ground state. As they decay back to the ground state, the atoms emit photons at discrete wavelengths for each element. A detection system counts the photons in selected spectral regions associated with each element, yielding a quantitative measure of the number of atoms of a particular element in the plasma. With appropriate calibration of the system using elemental standards, the photon count data can be directly related to mass concentration of the elements in the plasma and correspondingly, in the soil sample under analysis.

The LIBS system yields a total measure of element in the sample matrix since the entire sample volume is converted to the atomic state in the plasma. Conventional inductively coupled plasma (ICP) and atomic absorption spectroscopy (AAS) laboratory methods, on the other hand, give only a measure of acid-extractable elements in a sample. Acid-extractable content may or may not be the same as total content for a particular element. For example, if a particular element is strongly bound to an acid-insoluble component of the soil matrix, conventional laboratory methods would not detect this species. The LIBS system, on the other hand, reduces all species to their atomic state in the very high temperature plasma region it produces. Consequently, the system would detect such acid-insoluble species as well.

Technology Advantages

According to the technology developers, the LIBS analytical technique offers several advantages over conventional atomic emission or absorption spectroscopic methods. The most important advantages include the following:

- Solid, liquid, or gaseous materials may be analyzed.
- Electrically conducting and nonconducting samples may be analyzed.
- A relatively small (submicrogram) sample mass is required, making the method essentially nondestructive.
- No wet chemistry sample preparation is required.
- Sample vaporization and atomic excitation is possible in one step.
- Quasi real-time analysis may be performed.

- *In situ* analysis can be performed at a distance in hostile environments with the use of fiber optic links between the laser and the detector.

Technology Limitations

The developers indicate several limitations of the system, compared with conventional laboratory methodologies. They include the following:

- Minimum detection levels for most elements are an order of magnitude higher than laboratory methods.
- Accuracy figures are $\pm 20\%$ compared with $\pm 0\%$ for conventional laboratory methods.

Physical Characteristics

The MelΔok, Inc. (El Paso, Texas), Model MD5095 laser analyzer system has dimensions of 0.4 m (high) \times 0.22 m (wide) \times 0.48 m (deep) and weighs about 30 kg. The system draws about 60 W of 110-120 V ac power and is categorized as a field-transportable instrument. Ancillary equipment includes a computer and monitor, a laser printer, a sample pellet press (approximately 18 kg), a coffee mill/grinder, a microwave oven, and a large cylinder of laboratory-grade argon gas. Instrument setup is rapid, requiring about 5 minutes. At remote field locations, the time requirements are longer because a portable 5-kW generator has to be set up. Sample preparation and instrument operation are relatively simple. One person with technical skills and training can operate the instrument under normal conditions. Automated data processing capabilities are included in the form of proprietary spectrum analysis software.

Schematic Diagram

A schematic diagram of the MelΔok LIBS system is shown in Figure 2-1. Major components of the system include a laser, a motor-driven sample stage, collection optics, spectrograph, detector, and computer.

Operational Features

A number of operational features of the instrument as summarized by the developer are given below.

Calibration

Warm-up and calibration of the instrument takes about 15 minutes. Calibration is normally performed once per day. Two types of calibration are required, namely, laser power output calibration and spectrometer calibration. A reference thermistor is used to calibrate laser output power; the thermistor in turn requires its own independent annual calibration. A National Institutes of Standards and Technology lead metal Standard Reference Material is used for spectrometer calibration. The system software compares the spectral output from the lead metal standard with its internal spectral reference library and automatically adjusts for variations in spectral line location. Spectral line intensity, which is controlled by instrument gain settings, is also automatically adjusted using the signal output from the lead metal standard.

Sample Preparation

The accuracy and precision of the instrument depend, to a large extent, on the physical characteristics of the sample. The best results are obtained when the sample has the following characteristics:

Technology Performance Indicators

The analytical capabilities of the MelΔok LIBS system, as reported by MelΔok, Inc., are presented in Table 2-1. Minimum detection levels and accuracy and precision data are given in the table for a number of elements. These are included for informational purposes only and were not further evaluated or verified as a part of the demonstration.

Table 2-1. LIBS Analytical Capabilities as Reported by MelΔok, Inc.

Element	Analytical Parameter			
	Minimum Detection Level ^a (mg/kg)	Typical Detection Level ^b (mg/kg)	Accuracy (%)	Precision (%)
Silver (Ag)	10	100-150	±5	<1
Arsenic (As)	10	100-150	±5	<1
Barium (Ba)	10	100-150	±5	<1
Cadmium (Cd)	10	100-150	±5	<1
Chromium (Cr)	10	100-150	±5	<1
Copper (Cu)	10	100-150	±5	<1
Iron (Fe)	10	100-150	±5	<1
Manganese (Mn)	10	100-150	±5	<1
Lead (Pb)	10	100-150	±5	<1
Strontium (Sr)	10	100-150	±5	<1
Zinc (Zn)	10	100-150	±5	<1

^a Estimate based on analysis of pure material, no matrix effects.

^b Estimate based on analysis of material in a sample matrix.

Chapter 3

Demonstration Design and Description

Technology Demonstration Objectives

The primary objective of this demonstration was to prepare and execute a scientifically sound test protocol for the collection and analysis of data from metals-contaminated soil samples as determined by candidate technologies. To assist the technology developers in evaluating the data collected from their instruments, the Consortium conducted a parallel analysis of replicate soil samples by conventional laboratory methods. Table 3-1 lists the demonstration participants and their accompanying technologies.

Table 3-1. Demonstration Participants

Participant	Technology/Reference Laboratory
Los Alamos National Laboratory	Laser-induced breakdown spectrometer (LIBS) (technology)
MelΔok Instruments, Inc.	Laser-induced breakdown spectrometer (technology)
Pace Environmental Laboratories, Inc. ^a	Flame atomic absorption spectroscopy (technology)
Battelle Pacific Northwest National Laboratory	Anodic stripping voltammetry (technology)
MSE-HKM, Inc.	Inductively coupled plasma atomic emission spectroscopy (reference laboratory)
Sandia National Laboratories Environmental Restoration Program Laboratory	Inductively coupled plasma atomic emission spectroscopy (reference laboratory)
Columbia Analytical Services, Inc.	Inductively coupled plasma emission spectroscopy and flame atomic absorption spectroscopy (reference laboratory)

^aPoint of contact: Hayward Melville (915) 858-7055.

The technologies demonstrated, with one exception, were at the low end of the maturity curve. Consequently, a rigorous technology assessment was not performed on these systems. The soil analysis data from the analytical laboratories were validated and provided to the developers along with their own data for use in further development and refinement of their instruments.

Site Selection and Description

To properly assess a field screening technology, a suitable site with soil contaminated by metals was required. Early in the project, a demonstration plan was developed that presented the following criteria to assist in site selection.

- The site soils must contain a wide concentration range of the heavy metals arsenic, cadmium, chromium, copper, iron, manganese, lead, silver, and zinc.

- The site must have at least two sample collection areas with significantly different soil types.
- The heavy metal concentration levels in the soil must be reasonably well characterized and documented.
- The site must be readily accessible for conducting technology demonstrations.

The DOE Characterization Monitoring and Sensor Technology Cross-Cut Program had funded a demonstration project through the Western Environmental Technology Office in Butte, Montana, at a metals-contaminated soil site. The project had been awarded to MSE-HKM, Inc., an on-site contractor (hereafter referred to as MSE). Consortium members, including the EPA Environmental Sciences Division of the National Exposure Research Laboratory (NERL) and Sandia National Laboratories (SNL), chose to augment this demonstration by soliciting additional technologies for demonstration and by providing additional laboratory analysis of the soil samples used in the demonstration. During the preparation of the demonstration plan, two sites, Butte/Silver Bow Creek and Anaconda Smelter/Mill Creek, were selected for the study. Figure 3-1 shows the general location of the sites.

Site 1 Butte/Silver Bow Creek

Location

The Butte/Silver Bow Creek site extends from the west side of Butte, Montana, along Silver Bow Creek to the confluence of Sand Creek and Silver Bow Creek. The site is contaminated by heavy metals from historic and modern mining and mill tailings deposits. Figure 3-2 shows the Butte/Silver Bow Creek collection site.

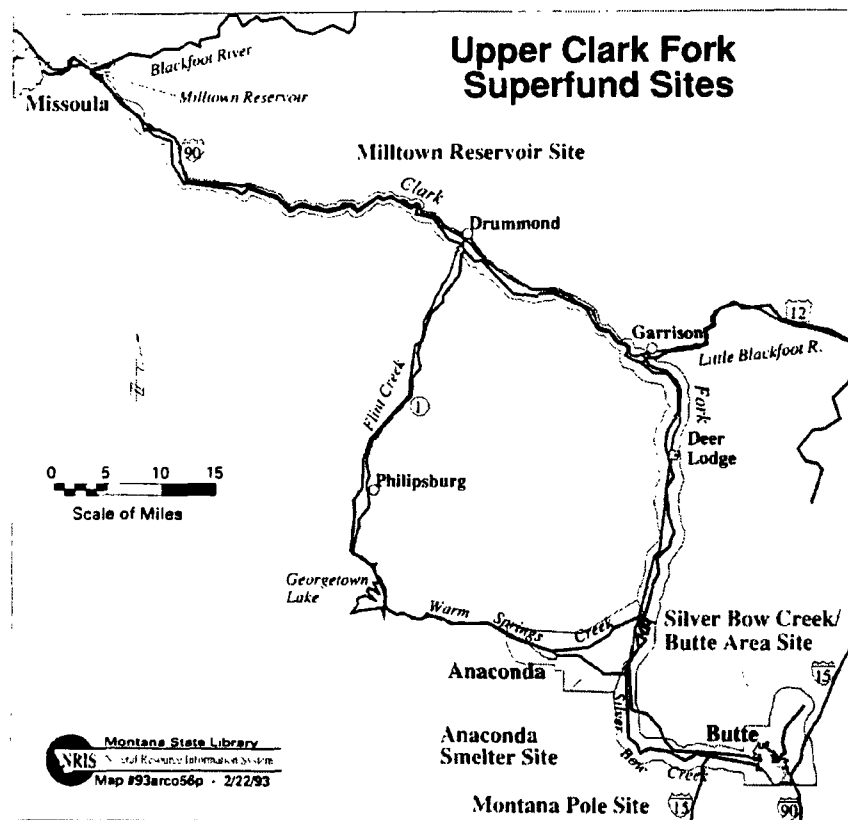


Figure 3-1. Montana regional map showing the Silver Bow and Mill Creek (Anaconda) sampling sites.

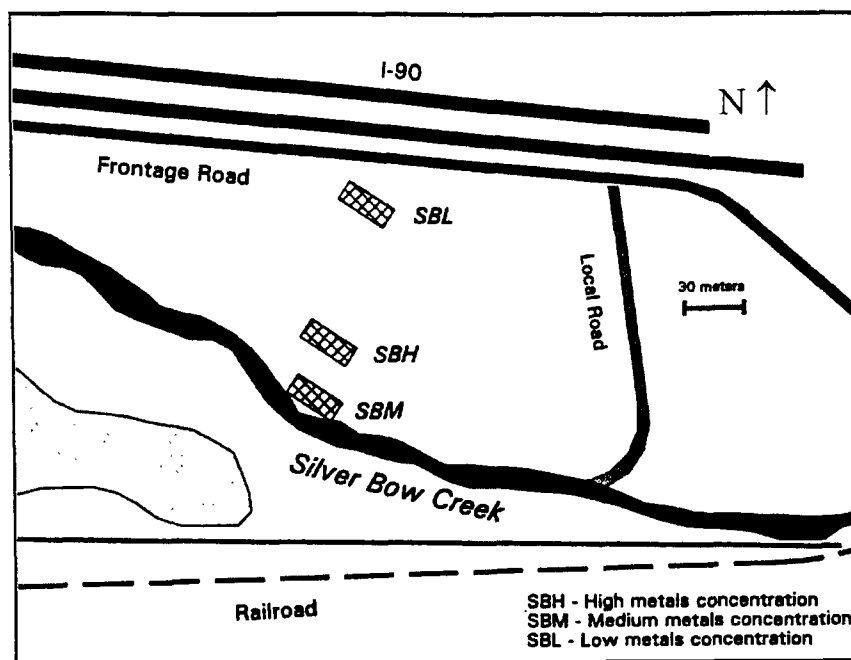


Figure 3-2. Local map of the Silver Bow sampling site.

History

Mining activities in the Butte area started with a group of small gold, silver, and copper mining operations. Butte became an important mining district in the late 1800s as the size and number of mines grew. With the growth of ore extraction activities came the need for easy access to ore processing facilities. Consequently, many mills and smelters were constructed in the region to concentrate and purify ores from the underground mines. Waste materials from the mineral extraction process, known as tailings, were impounded in ponds and were eventually discharged into Silver Bow Creek.

Approximately 230 km of stream and riparian habitat have been affected by these local operations. The region of contamination begins in Butte and extends westward along Silver Bow Creek to the Milltown Reservoir. Significant mill tailings deposits are found along the creek as well as dispersed over the Silver Bow Creek flood plain, resulting in a large area of contaminated soil.

During the 1960s and 1970s, mining activities gradually shifted from underground to open-pit mining. In 1982, the Anaconda Minerals Company discontinued underground mining in Butte. In the same year, the EPA started site contamination investigations in the area. By the early 1990s, mining operations had ceased and remediation efforts were implemented.

Characteristics

The Butte/Silver Bow Creek sample area encompasses approximately 5.5 km of Silver Bow Creek. The principal groundwater-bearing structure is a shallow alluvial aquifer composed of coarse-grained fan and floodplain deposits. Bedrock formations are found at approximately 1 to 10 m below the surface. The deposits are moderately permeable and are hydraulically connected to the perennial Silver Bow Creek surface stream. Because the Silver Bow Creek is an eroding bedrock valley, the erosion slopes are narrow and near the stream.

A relatively high surface stream gradient of 3.2 mm/m produces a high-energy stream characterized by a straight stream channel and narrow floodplain.

Mill tailings deposits at the Butte/Silver Bow Creek site have produced widespread soil contamination. The contaminated areas are continuous and confined to the narrow floodplain surrounding Silver Bow Creek. Preliminary characterization efforts, conducted during the site selection process, revealed that heavy metals deposits are most concentrated in the top 15 to 50 cm of the soil to a maximum depth of 1.2 m (MSE, 1996). A soil analysis to assess the degree of mill tailings contamination of the local soils was carried out by MSE. Surface soil analysis results for three sampling locations showing the range of contaminant metal concentrations are summarized in Table 3-2.

Table 3-2. Typical Heavy Metal Soil Contamination at the Butte/Silver Bow Creek Site

Metal	Soil Concentration (mg/kg)		
	Sample 1	Sample 2	Sample 3
Aluminum (Al)	6,780	2,990	9,480
Arsenic (As)	1,200	297	174
Cadmium (Cd)	41.1	11	0.46
Chromium (Cr)	7.23	6.25	13.5
Copper (Cu)	2,150	1,350	315
Iron (Fe)	31,800	16,500	12,200
Lead (Pb)	2,110	681	182
Manganese (Mn)	2,490	1,160	2,170
Silver (Ag)	90.4	15.9	231
Zinc (Zn)	12,300	2,710	321

Note: Data from a preliminary soil assessment by MSE-HKM, Inc. See MSE, 1996.

Sampling Location Details

The first of three sample areas was selected at a location approximately 45 m north of the Silver Bow Creek bed in the creek floodplain. The predemonstration samples from this area generally showed the highest concentrations of contaminant metals of all predemonstration samples. Consequently, this site was designated “SBHD” (Silver Bow-high demonstration).¹ A 27-m, northwest-to-southeast transect of the SBHD sample area was divided into ten 400-cm² sample plots equally spaced at 3-m intervals along the transect. Each plot was designated with the SBHD identifier followed by a plot number ranging from 1 to 10, with the number increasing from northwest to southeast.

A second sample area was located stream-side, within the Silver Bow Creek bed, and was designated area “SBMD” (Silver Bow-medium demonstration). A 27-m, northwest-to-southeast transect running along the streamside of the SBMD sample area was divided into ten 400-cm² sample plots, equally spaced at 3-m intervals. Each plot was designated with the SBMD identifier followed by a plot number ranging from 1 to 10, with the number increasing from northwest to southeast.

A third sample area was located on a hilltop overlooking the SBHD and SBMD sites approximately 120 m from the stream side and was designated area “SBLD” (Silver Bow-low demonstration). A 27-m, northwest-to-

¹ The naming convention uses high, mid, and low as a matter of convenience. These designations do not always correspond to the metal concentrations encountered in the samples.

southeast transect running along the hill top of the SBLD sample area was divided into ten 400-cm² sample plots, equally spaced at 3-m intervals. Each plot was designated with the SBLD identifier followed by a plot number ranging from 1 to 10, with the plot number increasing from northwest to southeast.

Site 2 Anaconda Smelter/Mill Creek

Location

The Anaconda Smelter/Mill Creek sample area, as shown in Figure 3-3, covers approximately 16 km² between Anaconda and Opportunity, Montana. The site is located approximately 40 km west of Butte and near the Anaconda smelter. It is bounded by state highway 1 to the north and state highway 241 to the west. Flue dust produced by 100 years of smelter operation has contaminated the site with heavy metals by the process of aerosol deposition.

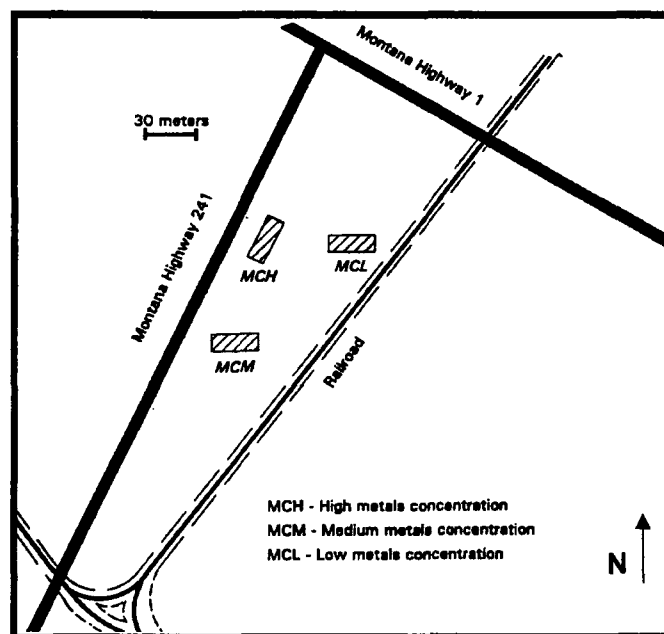


Figure 3-3. Local map of the Mill Creek sampling site.

History

The first copper smelting facilities to process ore from Butte area mining operations were in the Anaconda Smelter/Mill Creek area. The site consists of two facilities, the Upper Works, started in 1884, and the Lower Works, started in 1888. A silver ore refinery was also located between the copper smelting complexes. Smelter flue dust containing high levels of metals such as copper, arsenic, cadmium, and lead was produced as a by-product of the Anaconda smelting activities. Until 1976, flue dust generated by reverberatory furnaces was reprocessed for arsenic recovery. After 1976, the reverberatory furnaces were replaced by an electric furnace, and flue dust was collected by a pollution control system.

From 1976 through 1992, nine dust piles with a total volume of approximately 350,000 m³ were deposited on the hills around the smelter. From 1985 through 1992, wind scouring of the dust piles was controlled by surfactant

application. Since 1992, however, considerable amounts of the flue dust have been resuspended and deposited downwind from the smelter stack and dust piles.

Characteristics

The Anaconda Smelter/Mill Creek sample area is immediately adjacent to the Anaconda Smelter site. The area consists of a thick layer of moderately permeable, coarse-grained, floodplain deposits over bedrock. Mill Creek and the sample collection area lie in a structurally broad valley with an accompanying wide floodplain. Mill Creek is also a tributary of Silver Bow Creek.

Deposition of smelter flue dust at the Anaconda Smelter/Mill Creek site has produced widespread soil contamination with metals across the entire floodplain. Arsenic, cadmium, and lead are most concentrated in the top 15 cm of the soil. Cadmium and lead concentrations decrease more rapidly with depth than does arsenic concentration. Typical analysis results from three surface soil samples taken in the Mill Creek area are presented in Table 3-3, as measured during the predemonstration site assessment carried out by MSE.

Table 3-3. Typical Heavy Metal Soil Contamination at the Anaconda Smelter/Mill Creek Site

Element	Concentration (mg/kg)		
	Sample 1	Sample 2	Sample 3
Al	5,150	3,450	3,640
As	1,170	887	617
Cd	7.9	4.66	2.92
Cr	10.3	6.71	6.52
Cu	1,320	573	506
Fe	17,400	13,800	16,300
Pb	515	400	277
Mn	305	146	106
Ag	10.3	5.03	4.63
Zn	689	577	414

Note: Data from a preliminary soil assessment by MSE Inc.. See MSE, 1996.

Sampling Location Details

The first Mill Creek sampling location was approximately 115 m southwest of the highway 1 and highway 241 intersection, and was designated area "MCHD" (Mill Creek-high demonstration).² A 27-m, southwest-to-northeast transect of the MCHD sample area was divided into ten 400-cm² sample plots, equally spaced at 3-m intervals along the transect. Each plot was designated with the MCHD identifier followed by a plot number ranging from 1 to 10, with the plot number increasing from southwest to northeast.

A second sample area was located approximately 180 m southwest of the intersection of highway 1 and highway 241, and was designated area "MCMD" (Mill Creek-medium demonstration). A 27-m, west-to-east transect of the MCMD sample area was divided into ten 400-cm² sample plots, equally spaced at 3-m intervals. Each plot was designated using the MCMD identifier followed by a plot number ranging from 1 to 10, with the plot number increasing from west to east.

² The naming convention uses high, mid, and low as a matter of convenience. These designations do not always correspond to the metal concentrations encountered in the samples.

The third Mill Creek sample area was located approximately 115 m south of the intersection of highway 1 and highway 241 and was designated area "MCLD" (Mill Creek-low demonstration). A 27-m, west-to-east transect of the MCLD sample area was divided into ten 400-cm² sample plots equally spaced at 3-m intervals. Each plot was designated using the MCLD identifier followed by a plot number ranging from 1 to 10, with the number increasing from west to east.

Sample Collection, Handling, and Distribution

Sampling Methods

Ten samples were taken from each of three locations at two sites for a total sample size of 60. The soil in each 400-cm² sample plot was removed with a clean stainless steel hand trowel to a depth of 2.5 cm, passed through a No. 10 mesh sieve, homogenized by five passes through a 14-channel riffle splitter, and placed in 1,000-cm³ labeled glass containers. Each 1,000-cm³ sample contained approximately 2.5 kg of soil. Sample collection proceeded from levels of low metals concentration to high concentration. All sampling equipment was decontaminated by a detergent wash and double rinse with deionized water between use at each sampling location.

Sample Handling

All soil samples were taken to MSE, Inc., where they were dried for 12 hours at 105 °C in an oven. After drying, each soil sample was split ten ways. Each split contained an estimated 150 g of soil and was placed in a labeled container. Splits were distributed to analytical laboratories, various technology demonstrators, and archives. Soil sample collection, homogenization, drying, and splitting were carried out during the week of September 18, 1995, by SNL and MSE laboratory personnel prior to the technology demonstration. Samples were stored in locked coolers at room temperature until distribution.

Sample Distribution

The distribution of the ten sample splits is shown in Table 3-4. The sample numbering convention was in the format: AABB-NN-nnn, where

- AA = Site (SB or MC)
- BB = Transect (HD, MD or LD)
- NN = Plot No. (01-10)
- nnn = Split No. (001-010)

With the exception of Columbia Analytical Services (CAS) and Los Alamos National Laboratory (LANL), each analytical laboratory and technology demonstrator received a total of 64 samples (60 field soil samples plus 2 blank and 2 control samples). LANL received two sets of splits for a total of 124 samples and CAS received a total of 32 samples (the 30 field samples plus 1 blank and 1 control sample), because only half of the field soil samples were selected for analysis at this laboratory.

In addition to soil from the site, each laboratory and technology demonstrator received several quality control samples. Included in this set were two blank soil samples and two control soil samples prepared and analyzed by Environmental Resource Associates, Arvada, Colorado, a soils analysis quality control laboratory. These blank and control samples consisted of topsoil that was dried, ground, sieved, and spiked with various metals (in the case of the control sample). The soil was then thoroughly homogenized and split into samples that were

Table 3-4. Distribution of Field Soil Sample Splits

Soil Sample Split No.	Recipient Technology/Reference Laboratory
01	Los Alamos National Laboratory LIBS (technology)
02	Los Alamos National Laboratory LIBS (technology) ^a
03	MelΔok Instruments, Inc. LIBS (technology)
04	Battelle Pacific Northwest National Laboratory-anodic stripping voltammetry (technology)
05	Pace Environmental Laboratories, Inc.-flame atomic absorption spectroscopy (technology)
06	MSE-HKM, Inc. (reference laboratory)
07	Sandia National Laboratories (reference laboratory)
08	Columbia Analytical Services, Inc. (reference laboratory)
09	Sandia National Laboratories - archive
10	Sandia National Laboratories - archive

^a Originally, two similar laser-induced breakdown spectroscopy systems were to be fielded by Los Alamos researchers, with each requiring a sample split. As a result of logistical difficulties, only one system was actually brought to the site and used in the demonstration.

subjected to a round-robin analysis at qualified laboratories. The results from 20 or more analyses of the soil batch were used to define a mean value for each element along with a 95 percent confidence interval (mean value $\pm 2 \times$ standard deviation).

Each laboratory and developer of a demonstration technology was also instructed to produce matrix duplicates of at least two of the field soil samples so that a measure of analytical precision could be obtained. In the interest of having a diverse but manageable list of target elements, nine metals were selected for analysis by all participants: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), silver (Ag), and zinc (Zn).

Laboratory Selection and Analysis Methodology

Columbia Analytical Services

Analysis of soil samples was carried out at Columbia Analytical Services, Inc., in Kelso, Washington, along with analysis of several quality control samples. Analysis was carried out at this EPA Contract Laboratory Program (CLP) laboratory to provide a soil analysis data set that could be used as a cross check with the more comprehensive soil sample analysis carried out at the MSE laboratory. As a result of program cost constraints, analysis at the CAS laboratory was limited to half (30) of the 60 field soil samples collected during the demonstration.

Soil samples were digested using EPA SW-846 Method 3050A: *Acid Digestion of Sediments, Sludges, and Soils*. Columbia Analytical Services analyzed all 32 control and field soil samples by inductively coupled plasma atomic emission spectroscopy using the EPA SW-846 Method 6010A.

The laboratory also generated its own duplicates of the 32 soil, control, and blank soil sample digestates and conducted a second analysis by atomic absorption spectroscopy (AAS) using EPA SW-846 Method 7000A. The specific methods employed in the analysis included flame aspiration and graphite furnace. They are listed below for each of the target elements.

Ag (silver)	Method 7760A: silver (atomic absorption, direct aspiration)
As (arsenic)	Method 7060A: arsenic (atomic absorption, furnace technique)
Cd (cadmium)	Method 7131A: cadmium (atomic absorption, furnace technique)
Cr (chromium)	Method 7190: chromium (atomic absorption, direct aspiration)
Cu (copper)	Method 7210: copper (atomic absorption, direct aspiration)
Fe (iron)	Method 7380: iron (atomic absorption, direct aspiration)
Mn (manganese)	Method 7460: manganese (atomic absorption, direct aspiration)
Pb (lead)	Method 7420: lead (atomic absorption, direct aspiration)
Zn (zinc)	Method 7950: zinc (atomic absorption, direct aspiration)

A matrix duplicate sample was also made of original sample number MCLD-1-008. This duplicate was digested and analyzed by ICP and AAS methods to give a measure of overall laboratory analytical precision on matrix samples.

MSE Laboratory

The MSE laboratory, located near the sampling site in Butte, Montana, did the preassessment soil sampling and analysis. It also performed, in collaboration with SNL, the actual demonstration soil sampling, processing, and distribution. The MSE laboratory carried out a complete analysis of all demonstration soil and quality control samples. Although MSE is not a CLP laboratory, it used standard EPA SW-846 methodology in its analyses. The laboratory adheres to quality control procedures specified in the standard EPA analysis protocols used for soils analysis and operates under a written quality assurance plan.

Sixty soil samples plus 2 control soil samples and 2 blank soil samples were digested using EPA SW-846 Method 3050A: *Acid Digestion of Sediments, Sludges, and Soils*. All 64 samples were analyzed by ICP using EPA protocol SW-846 Method 6010A. Matrix duplicates were also made of 4 samples. These underwent digestion and analysis by ICP so that a measure of method precision could be obtained for this particular soil matrix.

SNL Environmental Restoration Program Laboratory

The SNL Environmental Restoration Laboratory was selected as an additional reference laboratory. This laboratory primarily provides rapid screening data which are used in conjunction with conventional CLP-type analysis for the Sandia internal environmental restoration program. A laboratory quality assurance/control plan was under development during this study. Data from this laboratory were obtained with a mobile inductively coupled atomic emission spectroscopy system. The unit is a conventional benchtop ICP system that has been adapted for field use. The instrument exhibits higher detection limits and more calibration drift than benchtop units normally used in the laboratory.

Soil samples were digested at the SNL laboratory in a slightly different manner than that used at the other two laboratories. This laboratory used a microwave-assisted acid digestion method formally designated SW-846 Method 3051: *Microwave Assisted Acid Digestion of Sediment, Sludges, Soils, and Oils*. The SNL laboratory analyzed all 64 soil and quality control samples by ICP using EPA protocol SW-846 Method 6010A.

Demonstration Narrative

Predemonstration soil samples were collected during the week of August 21, 1995. These samples were used by the participants in instrument setup and calibration. The actual demonstration soil samples were collected

September 18–22, about 1 week prior to the technology demonstration. Sample processing and packaging was completed on September 24. Participants in the demonstration were on the site during the week of September 24–29. A complete set of 60 soil samples plus quality control samples were given to each of the participants at the beginning of the week.

Because access to the actual soil sampling sites was limited and the local media were invited to observe activities on selected days during the demonstration, the demonstration area was set up on an easily accessible, paved parking lot about one-half mile from the Silver Bow sampling site. Several vans, tents and generators were installed at the site to support the various systems. Temperatures ranged from freezing in the morning to the mid-sixties during the day. Space heaters were used in some of the tents and vehicles during the cold morning hours. The actual demonstration lasted 6 days; about 2 days were used for instrument setup, checkout, and disassembly and 4 days for soil analysis. Participants worked at their own pace. A typical day during the demonstration period began at 9 a.m. and ended at 7 p.m.

Deviations from the Demonstration Plan

A comparison of the demonstration plan prepared prior to the study and the actual conduct of the study as recorded in the various field and data logbooks reveals a number of discrepancies, which are discussed below.

- The initial soil sampling effort at Silver Bow Creek had to be repeated because a temperature control circuit failed during sample drying. Soil temperatures were determined to be well in excess of the 105 °C specified in the demonstration plan. The samples were discarded and additional samples were collected and processed.
- All soil samples were dried at an oven temperature of 175 °C instead of the 105 °C specified in the demonstration plan. As noted in the previous paragraph, the primary oven failed and a backup oven had a minimum temperature control level of 175 °C. In the interest of maintaining the project schedule, the 175 °C drying temperature was used.
- Some of the soil sampling was carried out during inclement, rainy weather. Problems were encountered when sieving moist soil with a No. 10 screen. Larger (No. 6 and No. 8) sieve sizes were used to facilitate soil processing of the SBLD samples in the field. These and all other samples were homogenized following sieving so demonstrators and laboratories received comparable samples. Intercomparison of SBLD, SBMD, and SBHD samples was not done in this study, so sieve size differences among sample sets does not appear to be significant.
- The certificates of analysis that accompanied the soil control samples were distributed to participants after all analytical results were submitted to SNL. Access to control soil sample results during the demonstration was not specified in the demonstration plan, however. This procedure did not compromise the demonstration design since final analytical data were submitted prior to access to control sample results.
- Analysis of the data from the CAS laboratory revealed beyond a reasonable doubt that two blocks of five samples were mislabeled. The specific blocks in question were from the Mill Creek sampling site, series MCHD and MCMD. The switch could have occurred either as a result of mislabeling of sample containers in the field or during receipt and logging of the samples at the CAS laboratory. An investigation to determine the source of the error was carried out; however, the source could not be determined from the available chain-of-custody documentation. Despite the fact that a clear incidence of mislabeling could not be determined, the data were corrected since the switch was unmistakable in the data analysis phase of the project.

Chapter 4

Laboratory Data Results and Evaluation

Laboratory Data Validation Methodology

One of the objectives of this study was to provide the technology developers with a validated set of soil analysis results from reference laboratory methods for comparison with field results. Both qualitative and quantitative laboratory data quality indicators were used in the data validation process for all participating laboratories. These are described more fully in the following sections.

Qualitative Factors

Qualitative factors included degree of experience of the laboratory staff, experience in soils analysis, level of certification, if any, and past performance on laboratory audits. These factors were used along with additional quantitative factors in assessing laboratory data quality.

Quantitative Factors

Five specific quantitative factors were also evaluated in the soil analysis data set provided by each laboratory to assist in the data validation process. These factors were blank sample analysis, control sample analysis, analytical precision, instrument stability, and spike recovery. Each factor is described more fully in the following paragraphs.

Soil Blank Analysis

The results from the blind blank soil analyses were directly compared with the information given on the certificate of analysis accompanying the samples, which were provided by Environmental Resource Associates. These analysis data were used as a semiquantitative check on the methods used by the laboratories to detect contaminant levels, because the soil contained either low or nondetectable levels of many of the target elements.

Control Soil Sample Analysis

The results from the blind control soil sample analysis from each reference laboratory were directly compared with the certified heavy metal concentrations in the soil, as determined by interlaboratory analyses of the same lot of soil. Environmental Resource Associates prepared the soil and coordinated the interlaboratory study. An analysis certificate shipped with the control sample included a certified value and a “performance acceptance limit”¹ for each element in the sample. The results from the control samples from each of the laboratories were

¹ The certificate from Environmental Resource Associates indicates that the performance acceptance limits for each element “closely approximate the 95% confidence interval about the certified value.”

an important indicator of laboratory performance levels. Analysis results that fell within the 95 percent confidence interval were judged to indicate an acceptable level of performance.

Duplicate Analysis Precision

Laboratory analytical precision was estimated by calculating the relative percent difference (RPD) between two analyses of predigestion duplicate soil samples prepared by each laboratory. The following equation was used.

$$RPD = \frac{|Y_a - Y_b|}{\frac{(Y_a + Y_b)}{2}} (100)$$

where

RPD = relative percent difference

Y_a = sample result

Y_b = duplicate sample result

Relative differences in excess of 20 percent, as specified in EPA Methods 6010A (ICP) and 7000A (AAS), are taken to indicate questionable laboratory analytical process control.

Instrument Stability

The analytical laboratories also carried out continuing calibration procedures during their sample analyses. In this procedure, a calibration solution for each of the target elements was analyzed at the onset of the analysis. The same solutions were periodically analyzed throughout the course of the analysis, typically after every tenth sample analysis. The results of each check were reported as a percent recovery of the starting calibration value. The data give an indication of calibration drift encountered over the course of an extended analysis interval. The control limits, prescribed in EPA Methods 6010A and 7000A, are ± 10 percent of the initial calibration value. Calibration checks falling outside these limits indicate inadequate analytical process control.

Matrix Spike Recoveries

Some of the laboratories also conducted spiked sample recovery measurements on one or more soil samples. In this procedure, a measured quantity of each of the target elements was added to a laboratory replicate of a soil sample. Digestion and analysis of unspiked and spiked samples were carried out. The difference between the spiked and unspiked sample was compared with the known spiked amount and expressed as a percent sample recovery. Sample recoveries falling outside the range of 75 to 125 percent, as prescribed in EPA Methods 6010A and 7000A, are indicative of questionable analytical process control.

Laboratory-to-Laboratory Data Comparison

Summary statistical parameters and data presentation formats were used to provide a quantitative measure of the degree of comparability among the data sets from the participating laboratories. These are more fully described below.

Method Difference

The method difference or bias is a summary statistic of the difference observed for a particular method relative to a reference method. The mean percent difference (MPD) of one data set versus another reference data set was calculated using the following equation:

$$MPD = \frac{1}{n} \sum_{i=1}^n \left[\left(\frac{y_i - x_i}{x_i} \right) (100) \right]$$

where,

- MPD = mean percent difference
- n = number of measurement values
- x_i = designated reference value
- y_i = paired value from other method

Scatter Plots

Scatter plots and associated statistical parameters were also used to compare data from one laboratory with that from another. These plots enable a quick visual comparison. Related statistics include a least-squares method linear regression giving the best straight line through the data. The regression line has the following equation:

$$Y = AX + B$$

where A is the slope of the line and B is the y -intercept value.

The Pearson product-moment correlation coefficient (r) was also computed. This is a measure of the degree of linearity between the two data sets (Havlicek and Crain, 1988). A correlation coefficient of 1 suggests perfect correlation while a correlation of zero 0 indicates no correlation between two data sets.

Statistical Tests

The statistical equivalence of the analytical laboratory data sets was further evaluated with the Wilcoxon matched pair test. In essence, this nonparametric statistical test allows assessment of whether a statistically significant bias exists between two methods on a set of paired samples. The test produces a test statistic through an arithmetic scheme that ranks the differences encountered in sample pair results. The test statistic is essentially a measure of the ratio of *observed differences* in the two data sets to expected *random differences* in the same two data sets. Knowledge of the test statistic and the sample size allows one to determine whether the differences encountered in the paired data values can be attributed to the random variation that would be expected to occur between equivalent methods, or to bias in the methods or data sets. The quantitative aspect of the test is related to the p-value, which is associated with the test statistic and the number of paired samples used in the test. By convention, a p-value of 0.05 is often used as the decision point as to whether a statistically significant bias exists. For example, the determination of a test statistic with an associated p-value of 0.05 indicates that the observed differences between two methods carry a 5 percent chance of being attributable to random variation alone. Additional information on the use of this nonparametric test for paired-sample analysis can be found in Conover (1980).

The statistical test results are used in conjunction with linear regression parameters such as slope and intercept to further compare the two data sets. The statistical test provides an indication as to whether one method is

consistently biased relative to another. A second determination is made regarding the extent of that bias, if it exists. For example, consider the case where the statistical test indicates a significant bias between two sets of laboratory data. Examination of the linear regression data may reveal that the methods differ by only 5 percent. In consideration of the overall uncertainties encountered in the sampling and analytical processes, a 5 percent method bias is tolerable and is not a reason for rejecting one data set over another. This two-phase evaluation of the data is discussed further in the section dealing with laboratory-to-laboratory data comparison.

Columbia Analytical Services Data

Half of the total number of soil samples generated in this demonstration project were analyzed by CAS. A more detailed qualitative and quantitative assessment of the laboratory's performance follows.

General Indicators of CAS Data Quality

As noted earlier, CAS is a CLP laboratory and follows standard EPA analysis protocols and procedures in its soil analysis work. Since it is a part of the CLP program, the laboratory also undergoes periodic system audits and analytical process audits through the use of blind control sample analyses. The laboratory provided a quality assurance document along with the analysis results for the sample set submitted. Laboratory performance indicators, such as matrix spike recovery data, duplicate sample summary data, laboratory internal control sample analysis, and periodic instrument blank and calibration data collected throughout the analysis interval were included in the report. CAS also provided copies of sample chain-of-custody forms and all raw data generated in the analysis. No warning flags or out-of-limits quality control indicators were noted in the cover letter provided with the quality control data package. Personnel from MSE audited the CAS laboratory. The audit confirmed that CAS operations were in accordance with the standard procedures used in these analyses.

Quantitative Indicators of CAS Data Quality

The analytical results and an accompanying quality control data package were sent by CAS to the Sandia project leader. The data package contained concentration levels or nondetects reported for all nine target elements in all 32 samples. Specific quantitative data quality factors are discussed in the following paragraphs.

Blank Soil Sample Results

Analytical results from the soil blank analysis are given for CAS ICP and AAS methods as well as for other participating laboratories in Table 4-1. The "true" metal levels in the soil, as determined by round-robin analysis of the blank soil lot number at qualified laboratories, are given in the final column of the table.

The CAS analysis results on the blank soil sample track the certified levels reasonably well. Detection levels for the CAS ICP are slightly higher for As and Pb than for the other target elements. Iron, manganese, chromium, and zinc are all reported at levels very close to the certified levels. During the course of the analysis, a blank solution was periodically analyzed with the ICP instrument to check for contamination or excessive calibration drift. The results from these periodic checks showed consistent instrument detection levels in the expected concentration range for all target elements.

Control Soil Sample Results

The analytical results for the control soil samples are shown in Figure 4-1 as a percent difference from the certified value for each element. The analysis certificate supplied with the control soil sample also gives a 95

Table 4-1. Reference Laboratory Blank Soil Sample Results

Element	Metal Concentration Level (mg/kg)				
	CAS ICP	CAS AAS	MSE ICP	SNL ICP	Certified Level
As	<40	1	2.1	<98	<2
Cd	<1	<0.5	0.4	<8	<1
Cr	5	<10	6.7	<19	7
Cu	8	6	5.6	<76	<5
Fe	6,760	7,210	7,740	6,350	8,180
Pb	<20	<10	9.3	<13	9
Mn	159	167	172	<38	159
Ag	<2	<2	0.4	<6	<2
Zn	27	28	24.4	76	24

Notes: A "less than"("<") symbol indicates not detected. The number following the symbol gives the detection limit. MSE and SNL data shown are the average of two analyses.

percent confidence interval about the average value as determined by a round-robin study of the soil batch by a number of qualified analytical laboratories. The upper 95 percent confidence limit (UCL) and lower 95 percent confidence limit (LCL) are also plotted in Figure 4-1. The CAS results show that the results for all of the target elements fall within these limits. Most fall within ± 10 percent of the certified value for both ICP and AAS analysis. These data indicate acceptable laboratory performance.

Duplicate Sample Analysis Results

Duplicate results from two soil samples analyzed by both ICP and AAS are given in Figure 4-2. The relative percent difference between duplicate samples, as described earlier in this section, is plotted for each of the runs. Plotted RPD values of unity indicate a value of less than or equal to 1. With two exceptions, all RPDs fall within 20 percent. The two exceptions are Cr by AAS and Cd by ICP. No explanation is given as to why these duplicates showed poor agreement. In general, however, the data reveal acceptable analytical process control. No precision data are shown for Cr analysis by AAS on sample SBLD-1-008 since a no-detect was reported for at least one of the determinations.

Instrument Stability

An indication of instrument stability throughout the course of the analysis is given by continuing calibration verification (CCV) analysis. A known standard is repeatedly run, typically following every 10 analyses on the ICP or AAS instrument, in order to check instrument calibration drift. The time interval between successive calibration checks is on the order of 1 hour. Typical CCV results for CAS ICP analysis of four elements are given in Figure 4-3. The results are plotted in a control chart format with percent recovery relative to the starting value of the calibration solution on the y-axis and the calibration number on the x-axis. All CCV data for all target elements from both ICP and AAS analysis indicated recoveries between 90 and 110 percent, which is within the quality control criteria specified in the method.

Spike Recoveries

Spike recovery data from the CAS analyses are shown in Figure 4-4. Here the deviations from 100 percent recovery are shown for four spiked soil samples, two of which were analyzed by ICP and two by AAS methods. In accordance with the standard method, the laboratory did not report recoveries for spiked elements when the

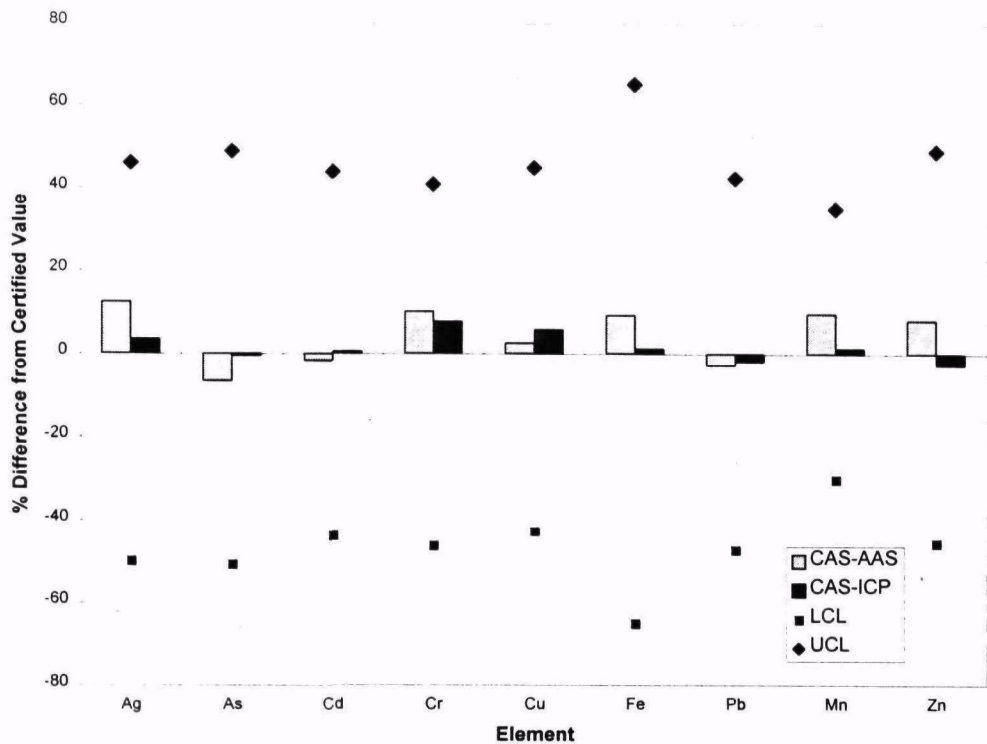


Figure 4-1. Control soil sample analysis results from CAS. The upper and lower 95 percent confidence limits with respect to the certified values are also shown.

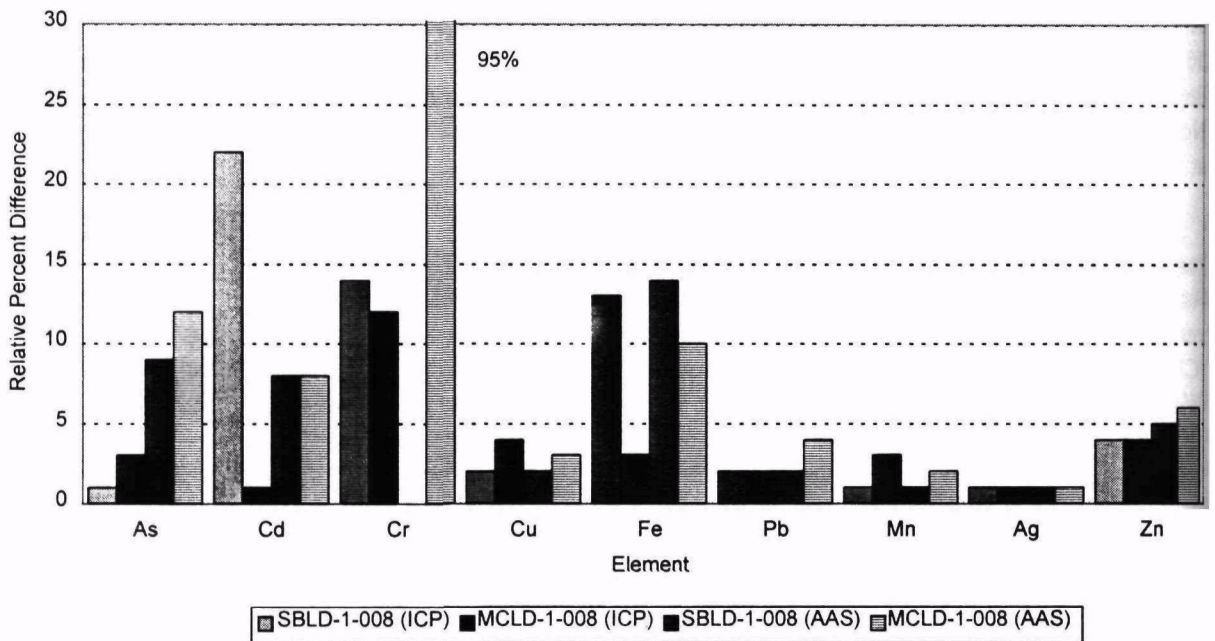


Figure 4-2. Duplicate soil sample analysis results from CAS.

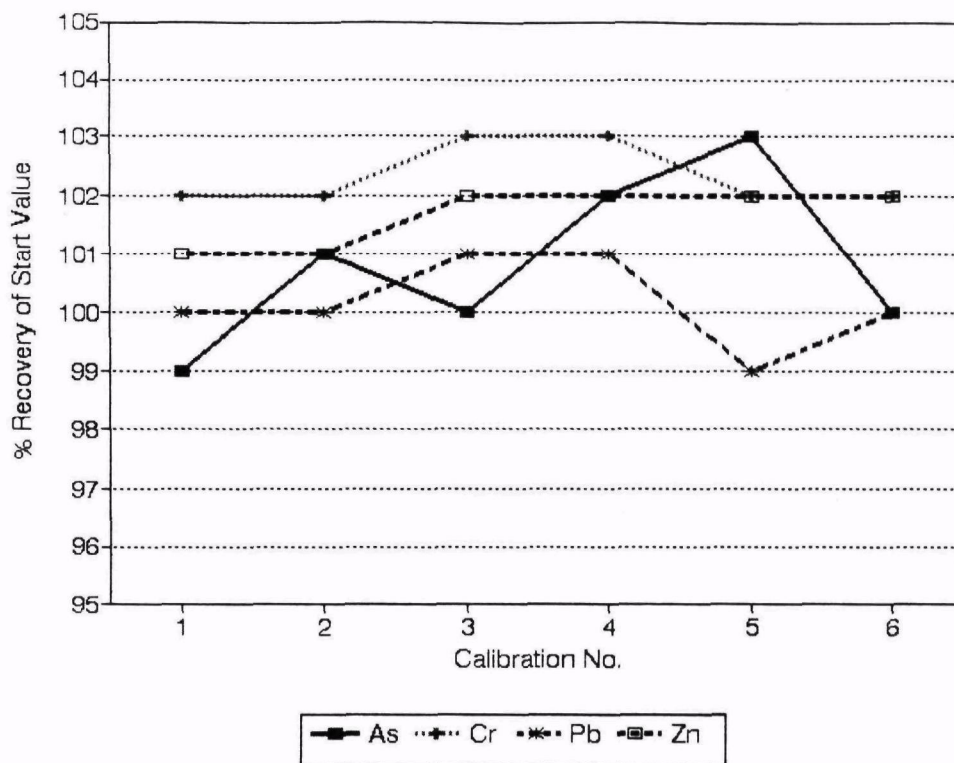


Figure 4-3. Continuing calibration verification results from CAS.

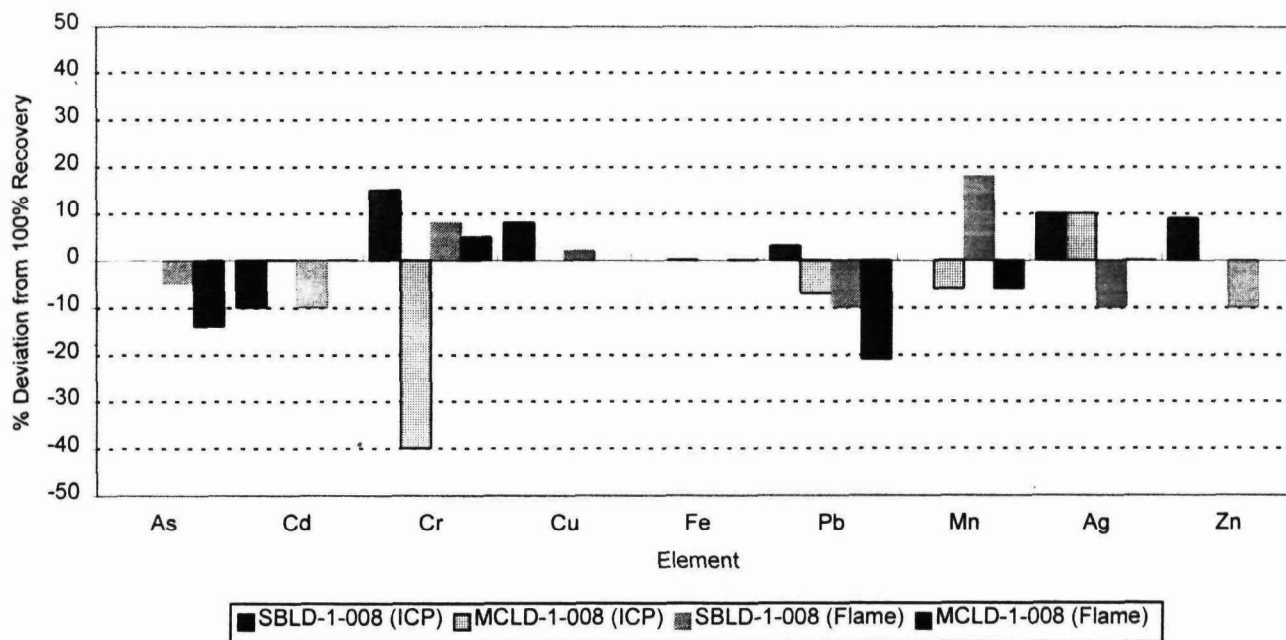


Figure 4-4. Spiked soil sample recovery results from CAS. See text for explanation of missing data.

spike amount added was less than 25 percent of the unspiked metal content of the sample. Hence, no data are seen for iron, which was present at high concentration levels in the unspiked soil samples. Spike levels were too low for As, Cu, Mn, and Zn in selected samples as well, as reflected by no data entries in the accompanying graph. Standard ICP Method 6010A specifies lower and upper recovery limits at 75 and 125 percent, respectively (corresponding to ± 25 percent difference as plotted in Figure 4-4). The data show that with the exception of Cr, none of the valid spike recovery levels fall outside this range.

CAS Performance

The foregoing quantitative and qualitative indicators reveal that overall performance of the CAS laboratory was acceptable. In particular, analysis of blank soil and control soil samples by ICP and AAS reveals acceptable performance. Spiked sample analysis using the soil matrix generated in the study also gave acceptable recoveries in all cases, except Cr, in which an adequate spike of each target element was introduced into the original soil sample. Instrument stability, as evidenced by periodic calibration checks, was also within control limit guidelines. Together, the quality control parameters suggest a high level of confidence in the accompanying field soil sample data.

MSE-HKM Data

This DOE contract laboratory has not been part of the EPA CLP program; however, in practice, the laboratory follows CLP guidelines and standard EPA analysis protocols. A more detailed qualitative and quantitative assessment of the laboratory's performance follows.

General Indicators of MSE Data Quality

MSE has a complete quality assurance/control plan, which was sent to the SNL project leader as a part of the analysis results package. A member of the SNL project team also conducted an audit of the MSE laboratory prior to the demonstration to determine compliance with standard EPA methods used in this analysis. The audit report indicated acceptable laboratory procedures and conformance with standard methods used in these analyses.

MSE included quality control sample documentation in its package. Laboratory performance indicators such as matrix spike recovery data, duplicate sample summary data, results from an in-house control sample analysis, periodic instrument calibration data throughout the analysis interval, and periodic blank analysis data throughout the analysis interval were included. Several out-of-limits conditions were noted in the cover letter associated with the data package. These anomalies are discussed in detail in later sections of the data presentation.

Quantitative Indicators of MSE Data Quality

Blank Soil Sample Results

Data from the quality control blank soil sample are given in Table 4-1, along with similar data from other participating laboratories. Detectable amounts of all target elements were reported by MSE, and the agreement between MSE values and the certified blank soil levels was the best of all three laboratories. The MSE laboratory detection levels for most of the target elements were the lowest reported of all the participating laboratories. During the course of the analysis, a blank solution was periodically analyzed with the ICP instrument to check for contamination or excessive calibration drift. Results from these periodic checks showed consistent instrument detection levels in the expected concentration range for all target elements.

Control Soil Sample Results

The analytical results for control soil samples are shown in Figure 4-5 as a percent difference from the certified value for each element. The analysis certificate supplied with the control soil sample also gives a 95 percent confidence interval about the average value as determined by a round-robin study of the soil batch by qualified analytical laboratories. The upper 95 percent confidence limit and lower 95 percent confidence limit are also plotted in Figure 4-5. The MSE results, like those from CAS, fall within ± 10 percent of the certified value for nearly all of the target elements. Larger differences on the order of -30 percent are noted for Ag; however, the reported results still fall within the 95 percent confidence interval about the mean certified level. These data indicate acceptable laboratory performance.

Duplicate Analysis Results

The relative percent differences are plotted in Figure 4-6 for each laboratory analyses of the duplicate field soil sample. All RPDs, with two exceptions, fall within the 20 percent criteria. The exceptions are an Mn measurement with an RPD slightly in excess of 35 percent and a Cd measurement with an RPD of about 28 percent. Three other Mn and Cd precision determinations were within the 20 percent criteria specified in standard Method 6010A. The laboratory uses an RPD limit of 20 percent as the acceptable range of variability in duplicate analysis. Consequently, these results reveal an acceptable degree of analytical process control.

Instrument Stability

A plot of continuing calibration verification data for MSE analysis runs is given in a control chart format in Figure 4-7. The results for only four elements are given for one of the four batch analyses conducted by the laboratory. All CCV data for all analyses showed acceptable (± 10 percent of original value) recoveries, indicating acceptable instrument stability over the course of the analyses.

Spike Recoveries

Spike recovery data from the MSE analyses are shown in Figure 4-8. Element recovery values are shown for samples that were spiked prior to digestion and analysis of the sample on the ICP instrument. The laboratory reported recoveries for spiked elements even when the spike amount was less than 25 percent of the unspiked metal content of the sample. For comparability of the MSE data with CAS data, however, the same spike validation criteria specified in EPA Method 6010A were applied to the MSE data as well. If the spiked amount was less than 25 percent of the total elemental content of the sample before the spike, the spike was judged invalid and no data were reported. Consequently, no data are shown for Fe, Cu, and other elements in selected instances. The valid set of spike recovery data revealed that only Pb fell outside laboratory acceptance limits of 75 to 125 percent in one of the four batch analyses.

Additional Quantitative Laboratory Data Quality Measures

The MSE quality control data package also revealed several out-of-limits conditions for a serial dilution test that was carried out on selected field samples. In this test, the concentrations of target elements were measured by ICP in a dilution of the sample digestate. A fivefold or greater serial dilution was then made of this original sample and also analyzed by ICP. The measured amount in the diluted sample, taking dilution factors into account, is expected to agree to within ± 10 percent of the original sample amount. Large deviations suggest sample matrix effects, which may affect quantitative results. The sample matrix may introduce either positive or negative interferences for a particular element when the sample is analyzed in a relatively concentrated form. The data from these serial dilution tests are given in Table 4-2. The data show that the ± 10 percent limit of these

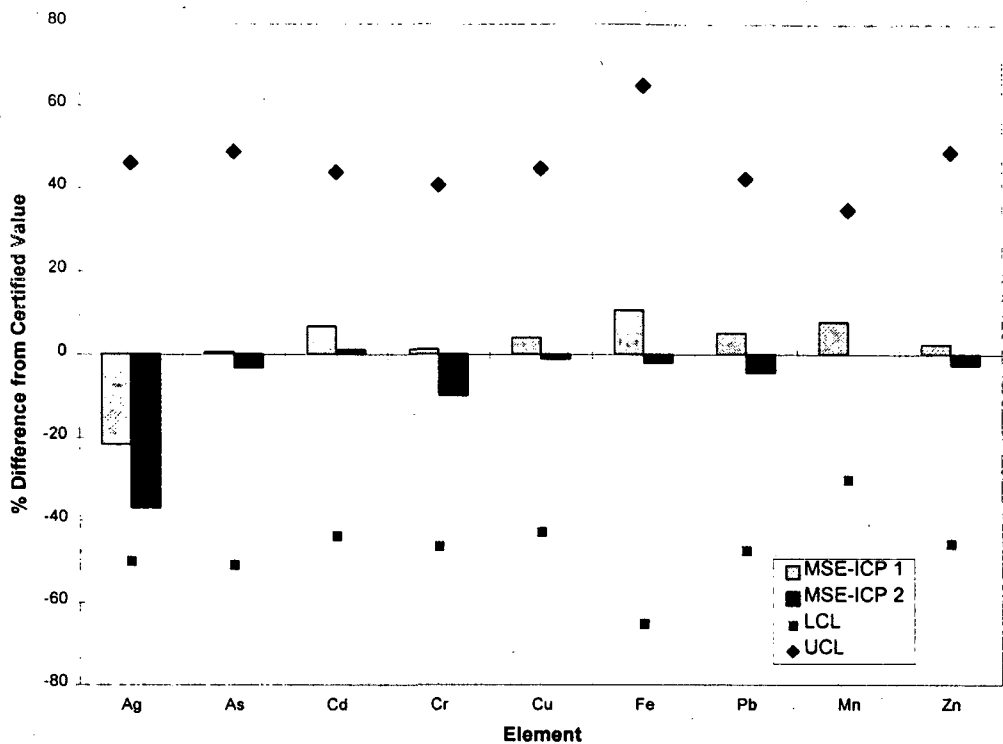


Figure 4-5. Control soil sample results from MSE. The upper and lower 95 percent confidence limits with respect to the certified values are also shown in the graph.

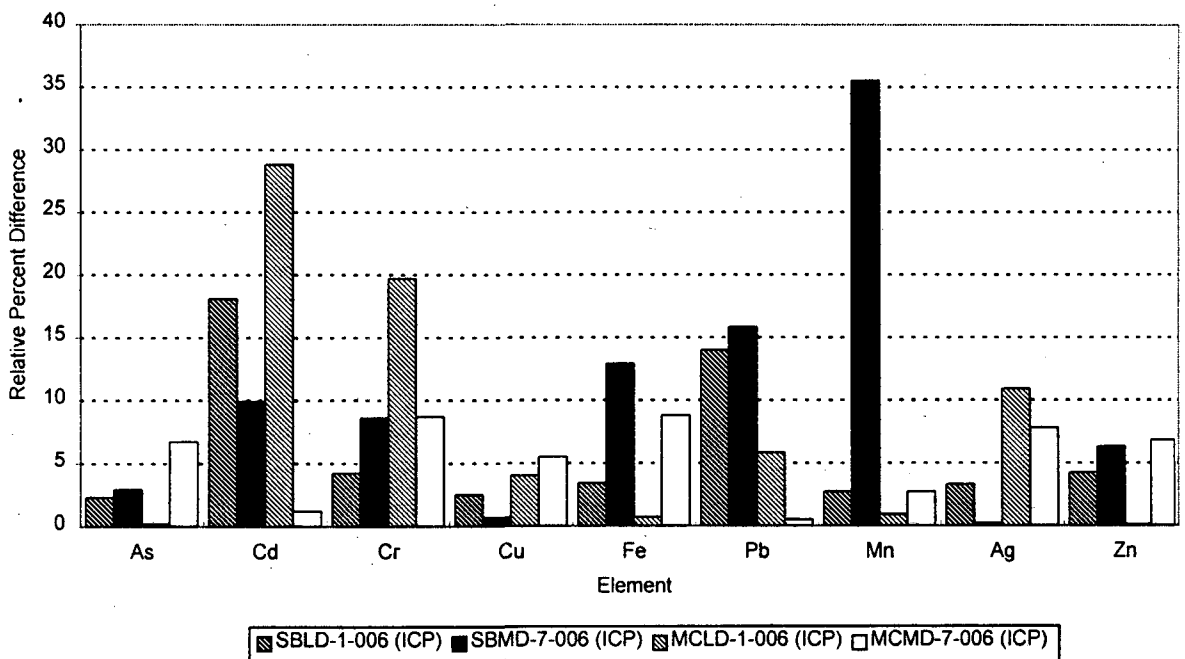


Figure 4-6. Duplicate soil sample results from MSE.

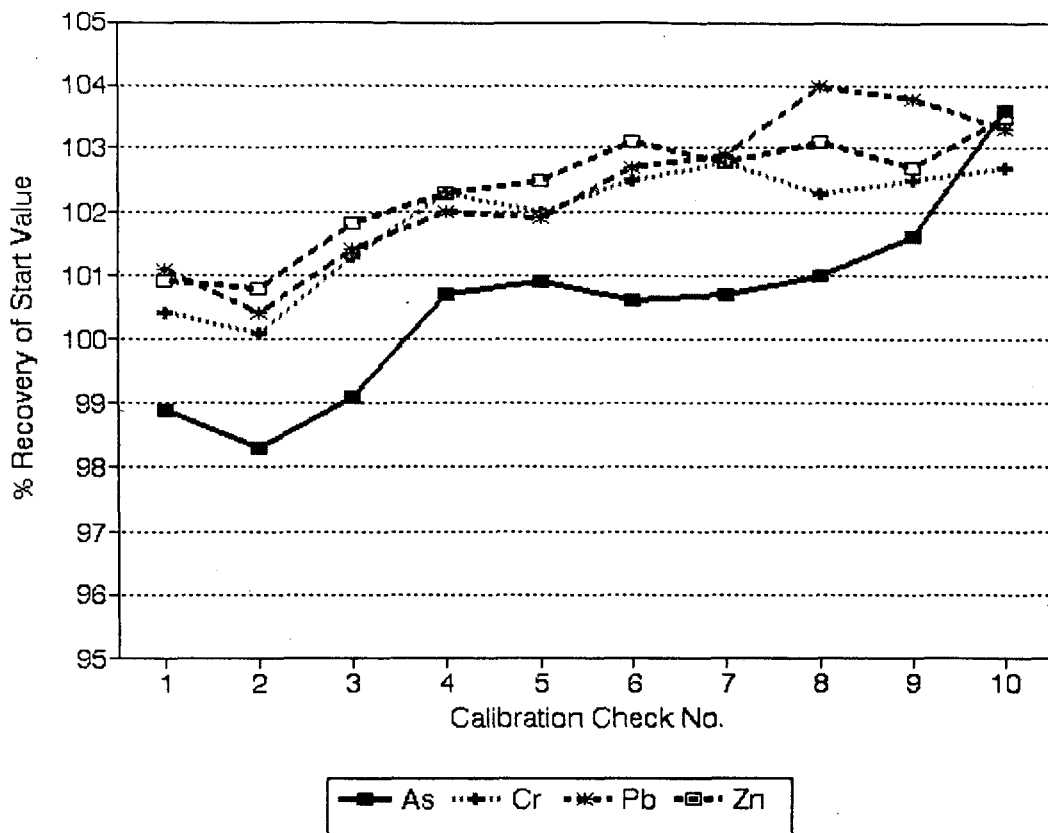


Figure 4-7. Continuing calibration verification results from MSE.

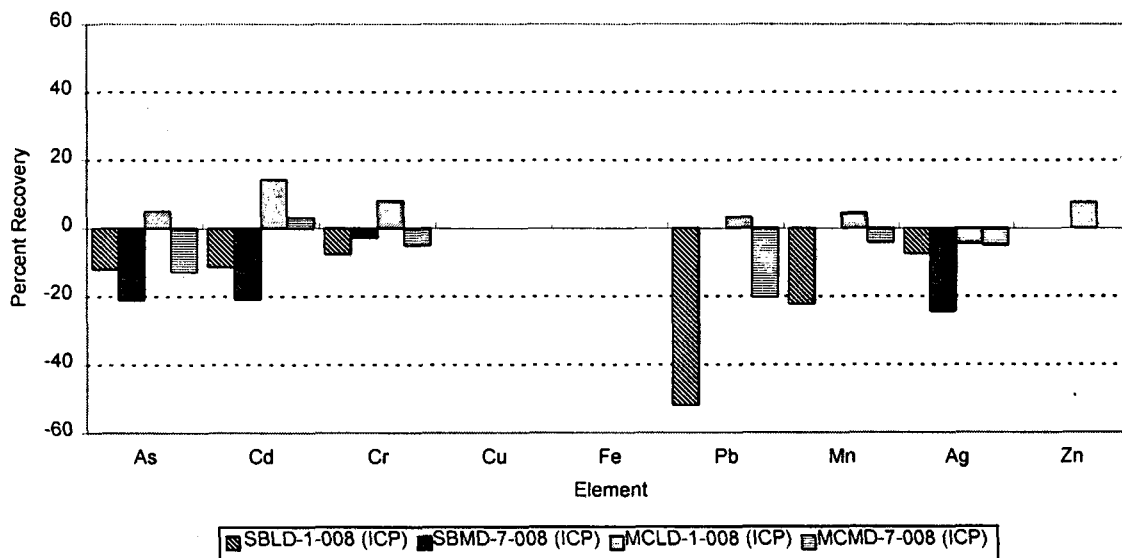


Figure 4-8. Spiked soil sample recovery results from MSE. See text for explanation of missing data.

Table 4-2. Serial Dilution Results from MSE

Element	Percent difference between measurements at two dilution levels			
	Sample No. SBLD-1	Sample No. SBMD-7	Sample No. MCLD-1	Sample No. MCMD-7
Ag	62	2.7	4.2	100
As	24	0.9	4.1	6.8
Cd	48	8.3	64	39
Cr	17	71	7.0	11
Cu	2.7	2.6	2.6	5.7
Fe	1.9	0.1	1.7	5.8
Mn	1.7	1.4	0.1	4.7
Pb	1.4	3.6	4.7	13
Zn	0.2	0.2	0.2	4.8

Note: Those values in excess of 10 percent are shown in bold type.

measurements was exceeded for Ag, As, Cd, Cr, and Pb in selected dilution tests. Although these results are not cause for exclusion of the data, they do reveal that, for at least some of the samples, sample matrix effects contribute to overall uncertainty in the analytical results.

MSE Performance

The MSE laboratory analysis results on blank and control soil samples, instrument precision and stability, and spike recovery, in general, reveal acceptable laboratory process control. Several out-of-limits warnings were encountered in the quality control reports; however, their presence does not warrant rejection of the data set. Serial dilution recoveries outside the ± 10 percent range indicate that sample matrix effects were influential in the overall quantitative recovery of the field soil samples.

Sandia National Laboratories Environmental Restoration Program Laboratory Data

The SNL Environmental Restoration Laboratory was selected as an additional laboratory. This laboratory primarily serves to provide rapid screening data which are used in conjunction with CLP-type analyses for Sandia's internal environmental restoration program.

A quality assurance/control plan was under development during this study. In this analysis the SNL laboratory followed formal laboratory procedures for soil analyses. Data from this laboratory were obtained with a mobile laboratory ICP-AES system (shortened to ICP in this report). The unit is a conventional benchtop unit that has been adapted for field use. Consequently, it exhibits higher detection limits and more calibration drift than the ICP systems commonly used in the laboratory. A more detailed qualitative and quantitative assessment of the laboratory's performance follows.

General Indicators of SNL Laboratory Data Quality

The SNL laboratory followed the SW-846 analysis protocols in the soil analysis. The demonstration project leader did not receive a copy of the laboratory quality assurance plan because the plan was under development at the time of the demonstration. The SNL laboratory did provide some quality control data such as CCV and method blank results.

Quantitative Indicators of SNL Laboratory Data Quality

Blank Soil Sample Results

Blank soil data for SNL are presented in Table 4-1, along with similar data from the other participating laboratories. Nondetectable amounts of all except two target elements were reported by SNL. Detection limits, in general, were higher for SNL than for the other laboratories owing to the characteristics of the mobile ICP instrument used in this analysis. Some of the elements, such as Cr and Pb, that were known to exist in the blank were not detected in the SNL blank analysis as a result of these high detection levels.

Control Soil Sample Results

The analytical results for control soil samples are plotted in Figure 4-9 as percent difference from certified values. The results show that, with the exception of Ag, all of the target element results fall within the lower and upper bounds of the 95 percent confidence interval established by the quality control laboratory that developed and tested the control sample. In general, the results for the target elements fall within ± 30 percent of the certified value. Silver results fall outside the lower confidence limit by a margin of nearly 20 percent. Discussions with laboratory personnel indicated that these results were most likely a result of the poor solubility of silver in the microwave digestion technique used in this analysis. The microwave method relies solely on nitric acid rather than on a mixture of nitric and hydrochloric acids used in the conventional digestion technique. With the exception of the silver analysis, the results reveal acceptable laboratory performance.

Duplicate Analysis Results

No duplicate sample analyses were conducted by the SNL Environmental Restoration Program laboratory.

Instrument Stability

A plot of CCV data for four elements in the SNL runs is given in control chart format in Figure 4-10. Calibration recoveries fell outside the ± 10 percent limits for the following elements: Cd, Cr, Cu, Pb, and Zn. Recovery data outside the normal control limits revealed stability problems attributable to the mobile ICP system.

Spike Recoveries

No spike recovery analysis was done by the SNL Environmental Restoration Program Laboratory.

SNL Laboratory Performance

Laboratory results for the control soil samples fell within the 95 percent confidence interval of the certified soil concentration value of the standard for all elements except Ag. The CCV data were outside the normal tolerance limits of ± 10 percent by as much as a factor of two for some of the target elements. Duplicate analyses were not run on any of the field samples. Consequently, no measure of instrument precision on the actual field soil sample matrix was available. Matrix spike recovery analysis also was not carried out. In light of the limited extent of laboratory quality control data, and the fact that a less stable mobile ICP system was used, the judgment was made to regard these data as informational and not include them in the validated data set from the other reference laboratories.

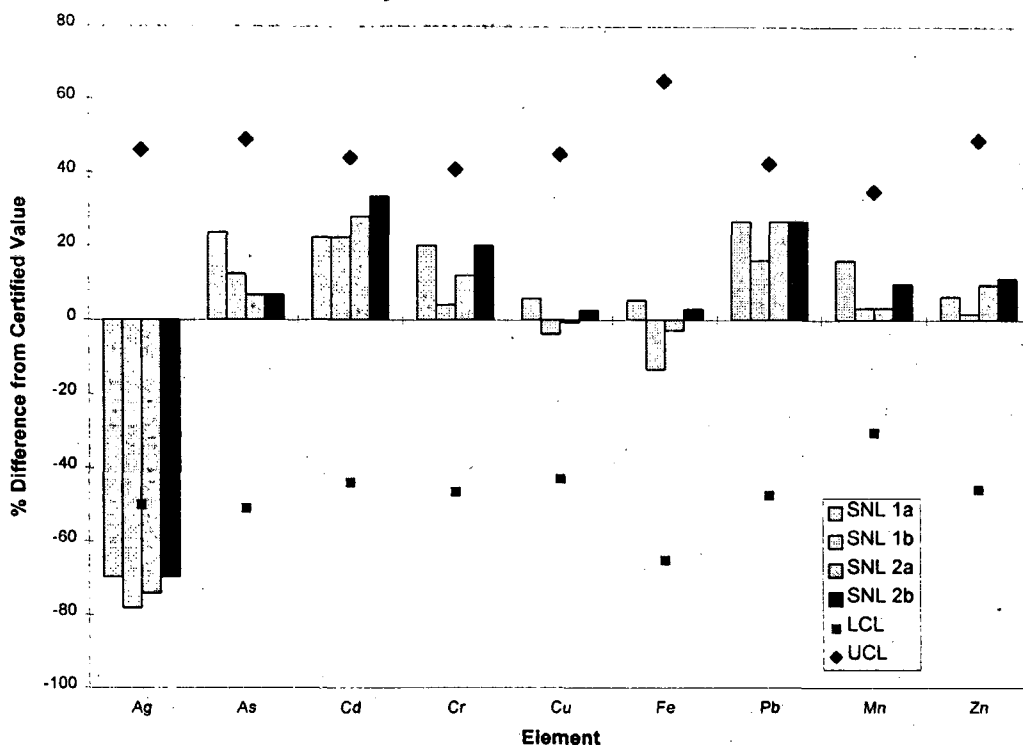


Figure 4-9. Control soil sample results from SNL. The upper and lower 95 percent confidence limits with respect to the certified values are also shown in the graph.

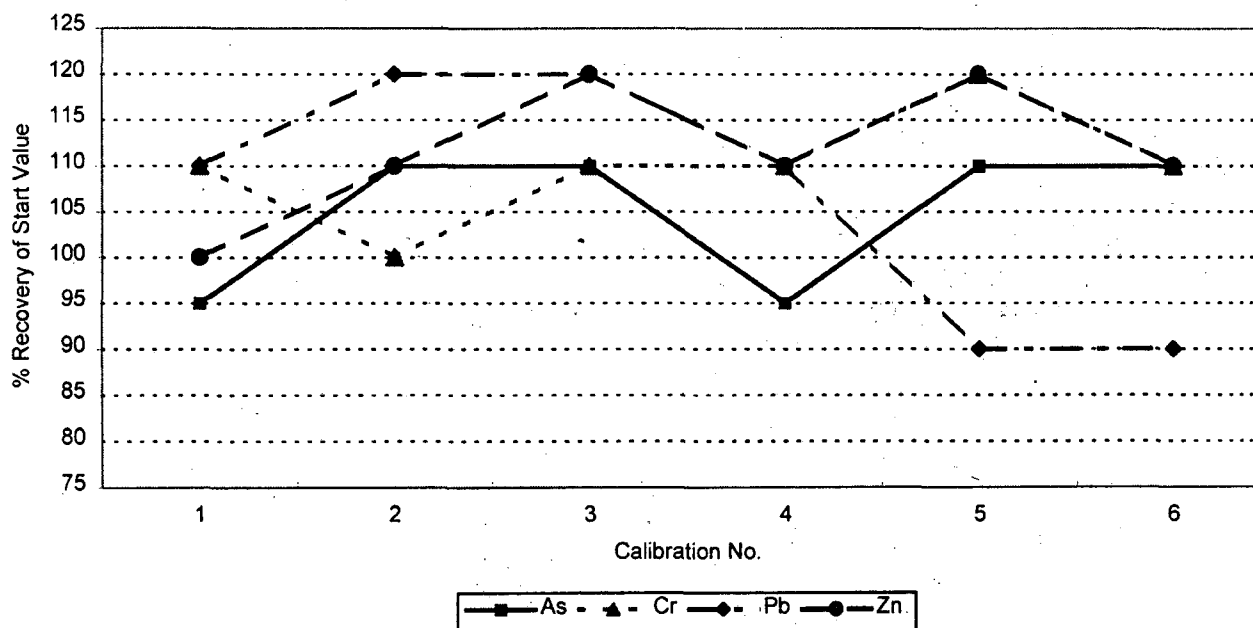


Figure 4-10. Continuing calibration verification results from SNL.

Laboratory-to-Laboratory Data Comparison

The results of several quantitative comparisons of MSE and CAS laboratory data are given in the following paragraphs. Included are the results and discussion of mean percent difference computations, scatter diagrams, statistical test results, and a semiquantitative analysis of overall sample variability.

Mean Percent Difference

An estimate of MPD for the soil samples collected at the two sites is given for each target element in Table 4-3. In this computation, CAS ICP is the designated reference data set on the basis of the laboratory's experience and acceptable performance on the quality control samples. Thirty sample pairs from each laboratory were used for comparison because CAS analyzed only half of the total number of soil samples collected. These percent difference estimates provide a measure of the overall comparability of the three data sets from the two laboratories. Low difference values reveal agreement between the analyses. The standard deviation is also given in the table and is a measure of the degree of variability encountered in the computed MPD for each element. With only a few exceptions, mean differences for nearly all elements are less than ± 10 percent in the comparisons of the CAS ICP reference data set with the CAS AAS and MSE ICP data sets. The comparison of Ag and Cd between CAS ICP and CAS AAS data sets showed differences on the order of 15 percent. Chromium by CAS AAS does not compare well at all; however, the comparison with MSE ICP Cr data is quite good. The poor figures for the CAS AAS Cr data may be attributable to the fact that most of the soil samples had Cr levels near the lower limit of detection of the AAS method.

Table 4-3. Mean Percent Differences from MSE ICP and CAS AAS Data

Element	Mean Percent Difference (ref: CAS ICP Data Set)	
	MSE Laboratory (ICP)	CAS Laboratory (AAS)
Ag	1.3 \pm 12.8	15.7 \pm 13.6
As	0.6 \pm 21.3	-10.9 \pm 7.8
Cd	10.8 \pm 25.9	-16.6 \pm 22.9
Cr	7.1 \pm 31.4	105.1 \pm 109.6
Cu	0.2 \pm 13.6	4.0 \pm 3.6
Fe	6.1 \pm 20.4	10.5 \pm 3.2
Mn	0.1 \pm 19.7	4.3 \pm 5.2
Pb	-2.1 \pm 15.3	5.4 \pm 1.9
Zn	-4.7 \pm 14.4	4.2 \pm 22.4

Notes: The mean value is followed by the standard deviation. The CAS laboratory ICP AES data set was used as the reference in this analysis.

Scatter Plots

Scatter plots showing intercomparisons of the CAS AAS and MSE ICP field soil sample data with the corresponding CAS ICP analysis data are presented in Figures 4-11 through 4-16 for selected elements to illustrate the various degrees of comparability encountered in the data. The CAS ICP data are plotted on the x-axis with either the CAS AAS or the MSE ICP data plotted on the y-axis. The comparison of the CAS AAS data with the CAS ICP data was very good with the exception of Cr data, shown in Figure 4-12, corroborating the high mean percent difference value noted for Cr in the previous section.

The MSE data show as good or better correlation with the CAS ICP data. This very close agreement is observed despite the fact that the CAS ICP and CAS AAS samples were laboratory duplicates from the same field soil

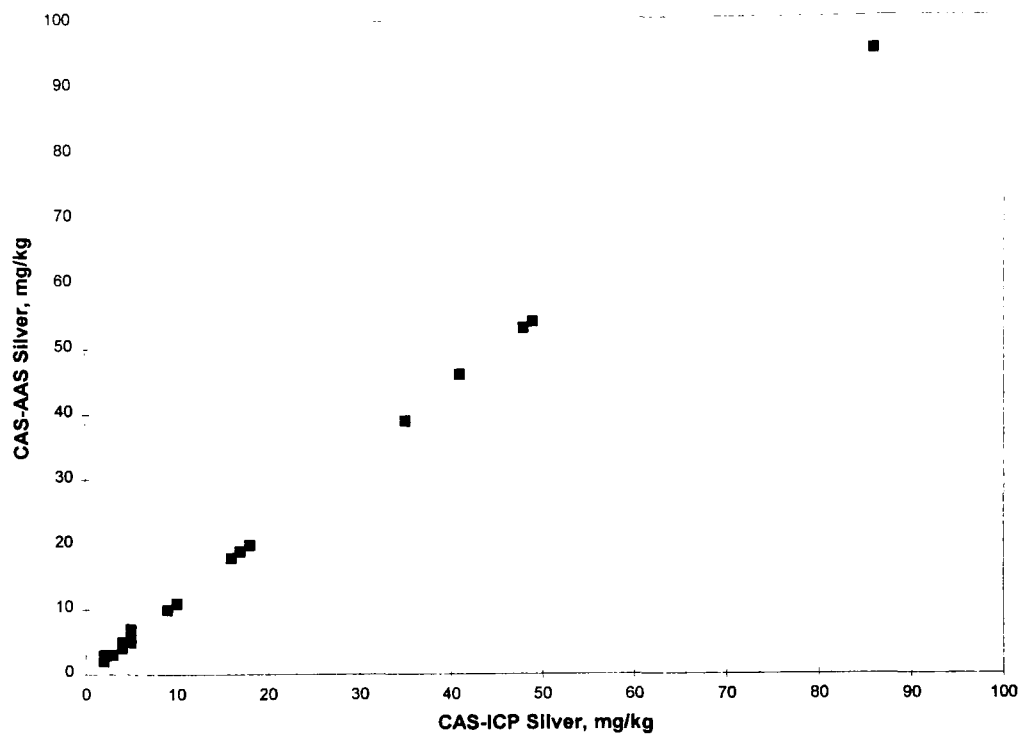


Figure 4-11. CAS AAS vs. CAS ICP silver measurements on field replicate soil samples.

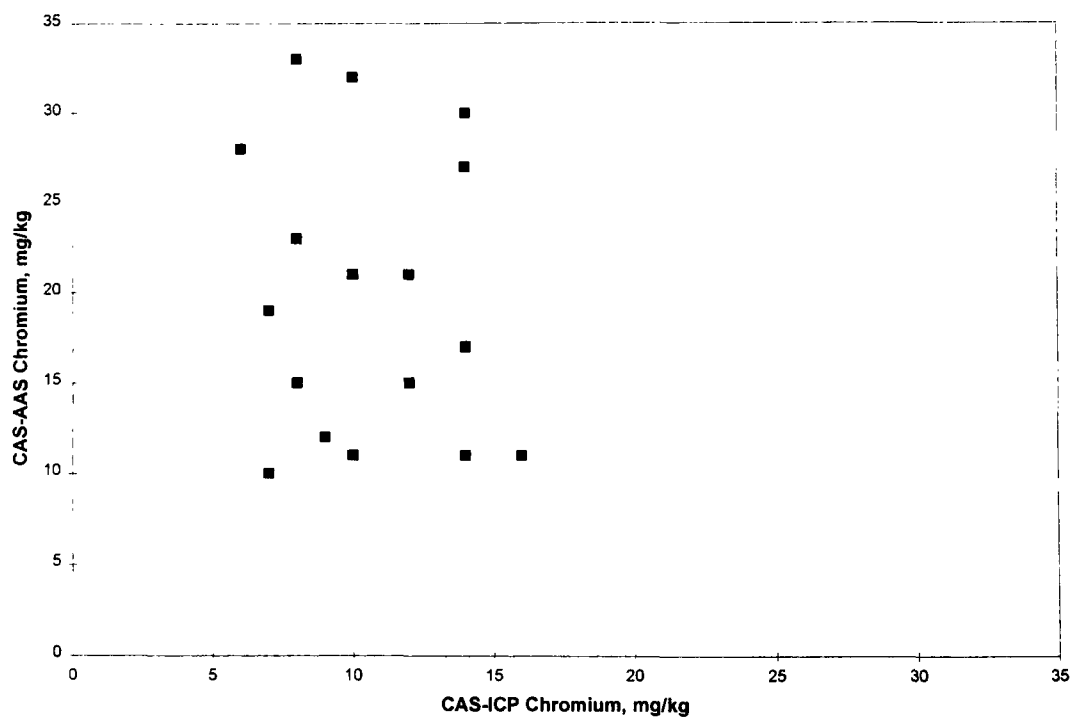


Figure 4-12. CAS AAS vs. CAS ICP chromium measurements on field replicate soil samples. Nondetectable results are not shown in the plot.

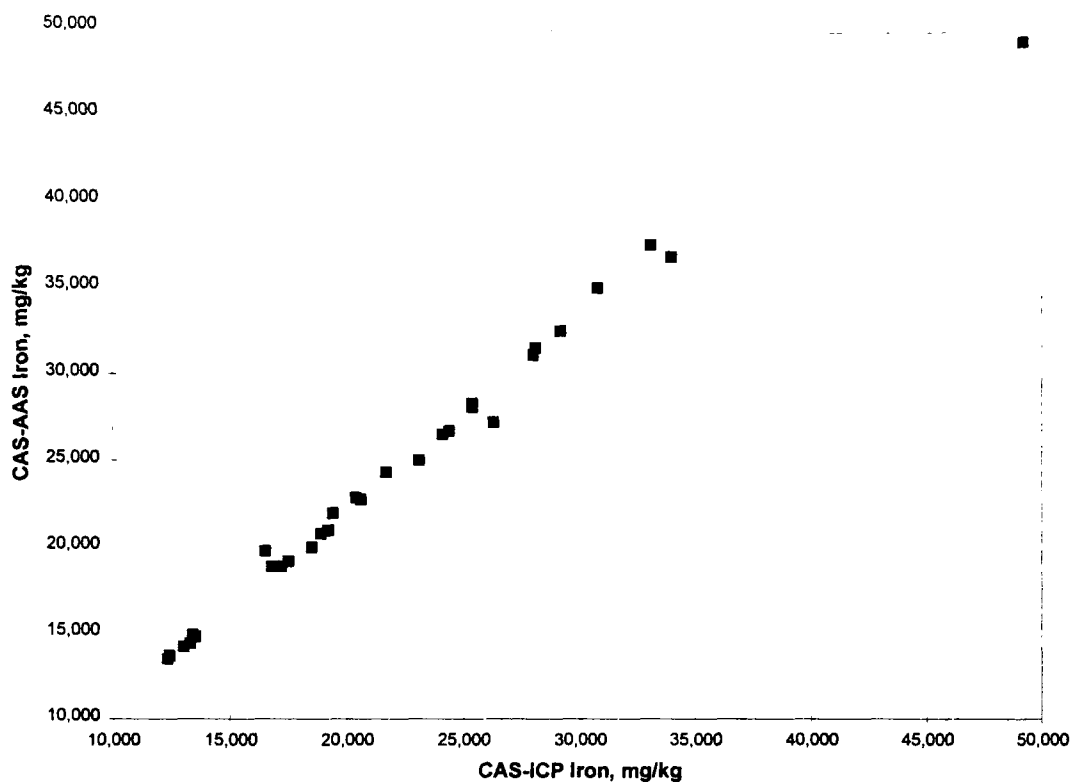


Figure 4-13. CAS AAS vs. CAS ICP iron measurements on field replicate soil samples.

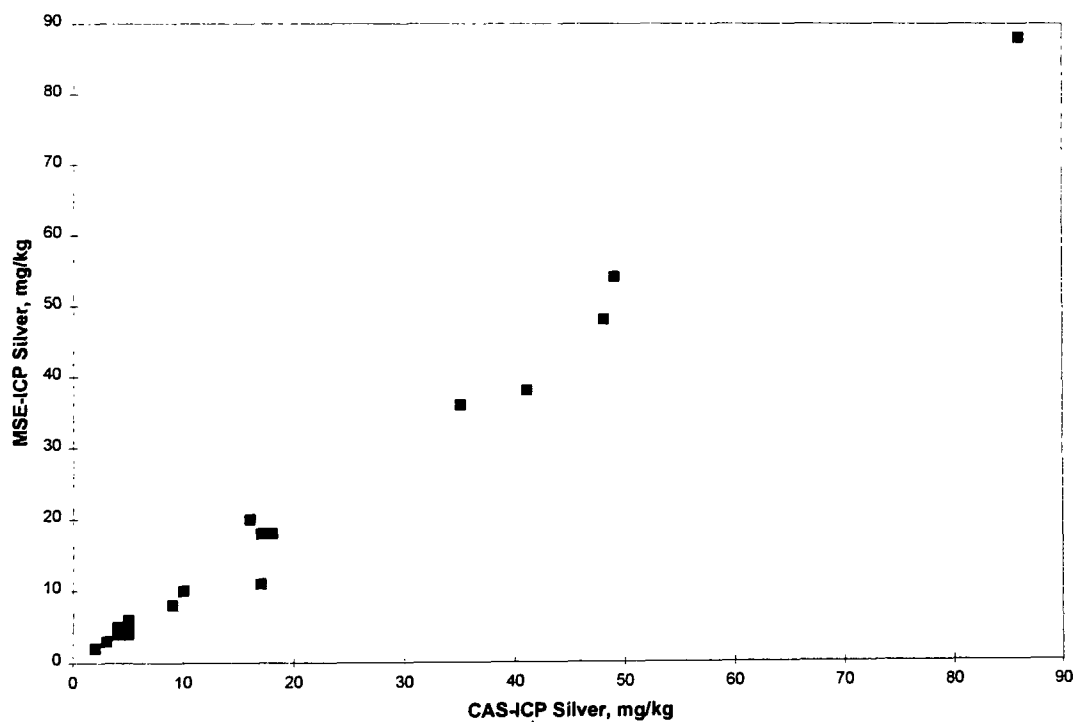


Figure 4-14. MSE ICP vs. CAS ICP silver measurements on field replicate soil samples.

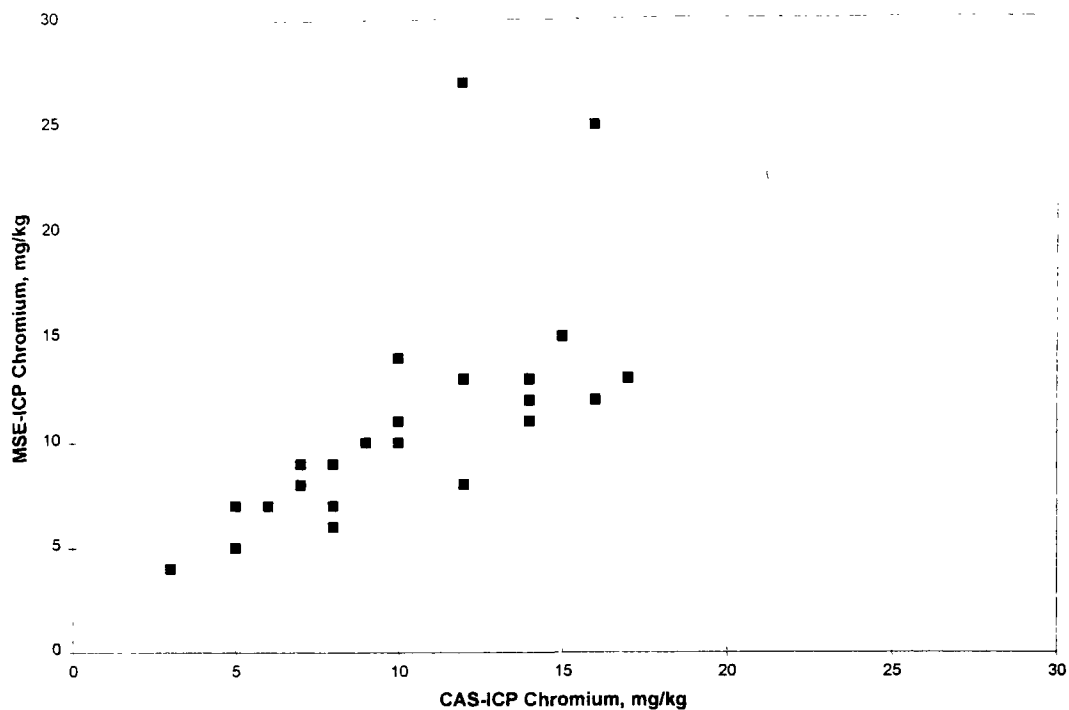


Figure 4-15. MSE ICP vs. CAS ICP chromium measurements on field replicate soil samples.

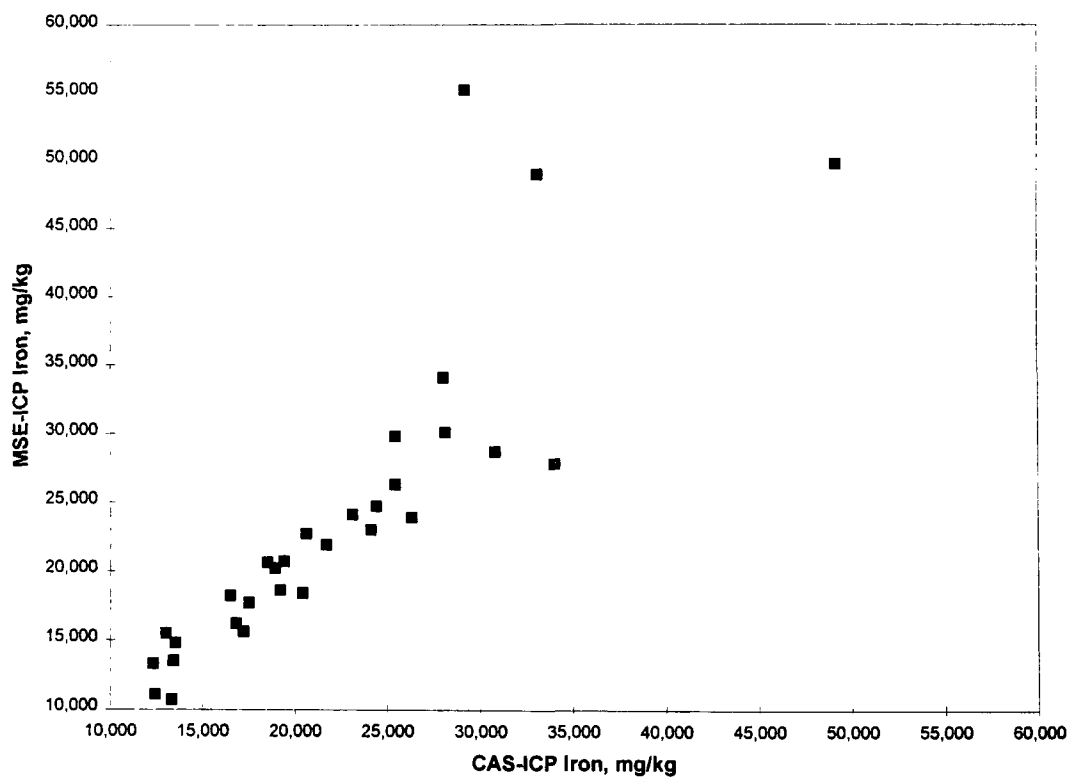


Figure 4-16. MSE ICP vs. CAS ICP iron measurements on field replicate soil samples.

sample digestate whereas the MSE samples were from a different field sample split. A good comparison between MSE ICP and CAS ICP data reveals that soil sample splits were chemically similar and that soil processing and mixing produced relatively homogeneous samples.

The slope and intercept of the best straight line through the data and the correlation coefficient, r , which is a quantitative measure of the degree of linearity in the data pairs, is given in Table 4-4 for CAS AAS and MSE ICP data set comparisons with the CAS ICP data set. Coefficients greater than about 0.8 indicate a reasonably strong linear relationship between the two data sets. Correlation coefficients less than 0.8 are encountered for Cr in both data sets. The CAS AAS Cr data were plotted against the MSE ICP Cr data and a scatter plot much like that shown in Figure 4-12 was obtained. This result further suggests that the CAS AAS Cr data may be suspect. The MSE ICP Cr data show slightly better correlation when plotted against the CAS ICP data, as shown in Figure 4-15. The slope parameters shown in Table 4-4 are a measure of the bias of one method with respect to another. With a few exceptions the regression line slopes are in the range of 0.9 to 1.10, which corresponds to a bias in the range of ± 10 percent. Exceptions are encountered for Cd and Cr in the CAS AAS data set as well as for Cr and Fe in the MSE data set.

Table 4-4. Reference Laboratory Linear Regression Results

Element	CAS AAS Data Set			MSE ICP Data Set		
	Corr. Coeff.	Slope	Intercept	Corr. Coeff.	Slope	Intercept
Ag	1.00	1.10	0.26	1.00	1.02	-0.1
As	0.99	0.96	-29	0.99	1.04	-16
Cd	0.85	0.49	2.2	0.98	0.90	1.1
Cr	-0.13	0.34	23	0.66	0.83	2.2
Cu	1.00	1.07	-16	0.99	0.99	13
Fe	0.99	1.04	1,350	0.86	1.16	-1,980
Mn	1.00	1.08	-10	0.95	0.93	36
Pb	1.00	1.06	-3.8	0.92	0.95	3.1
Zn	1.00	1.09	-28	0.99	0.91	72

Notes: The CAS ICP data set was used as the reference data set (x variable) in these regression analyses. The y variable was either the CAS AAS or MSE ICP data set. The slope and intercept values correspond to the values A and B in the linear equation $y = Ax + B$.

Statistical Bias Testing

The Wilcoxon matched pair test was used to compare the CAS AAS and MSE ICP data sets with the CAS ICP data set. The SNL laboratory data were not included in this test because they did not meet the data validation criteria. The Wilcoxon test is a nonparametric test which enables a decision to be made as to whether a statistically significant bias exists between two methods. The term “nonparametric” refers to the fact that the observations (in this case the reported metal concentrations in the soil samples) need not conform to a particular statistical distribution. The Wilcoxon test provides a quantitative measure of the likelihood or probability that observed differences between two methods are attributable to random variation only. Application of the test produces a test statistic and an accompanying p -value. The p -value represents the probability of observing a test statistic value greater than or equal to that obtained in the test from the null or “no difference” distribution—the distribution of test statistic values that would be encountered if in fact no bias is present between the two methods in question.

A p -value of 0.05 is often chosen as the boundary point in deciding whether two methods are statistically different. A test statistic with an accompanying p -value of 0.05 or less indicates that the two methods being

compared are statistically different and that the decision to call them different carries a 95 percent chance of being correct. Alternatively, it can be stated that the decision to call the methods different has a 5 percent chance of being incorrect.

The results of the statistical test as applied to the CAS AAS and MSE ICP laboratory data sets are summarized in Table 4-5. The test results between CAS ICP and CAS AAS data sets indicate that significant differences were observed between the two methods for all elements. The p-values associated with the test statistics for all elements are less than 0.01, indicating that a clearly distinguishable bias exists between the ICP and AAS analysis. This observation is corroborated by the scatter plots shown in Figures 4-11 through 4-13. Nearly all the plotted points fall above a diagonal line extending from the lower left to the upper right corner of the figures. This line is the zero bias line. Points falling above the diagonal line reveal a positive bias of the AAS method relative to the ICP method and those falling below the line reveal a negative bias.

Table 4-5. Wilcoxon Matched Pair Statistical Test Results

Element	Statistically Significant Bias Between Two Methods?	
	CAS (AAS) vs. CAS (ICP)	MSE (ICP) vs. CAS (ICP)
Ag	Yes (<0.01)	No (0.67)
As	Yes (<0.01)	No (0.91)
Cd	Yes (<0.01)	No (0.39)
Cr	Yes (<0.01)	No (0.94)
Cu	Yes (<0.01)	No (0.68)
Fe	Yes (<0.01)	No (0.31)
Mn	Yes (<0.01)	No (0.99)
Pb	Yes (<0.01)	No (0.98)
Zn	Yes (<0.01)	No (0.68)

Note: The p-value associated with the test statistic is given in parentheses.

A statistical comparison of the MSE ICP data with the CAS ICP data reveals that the two data sets are statistically equivalent; thus no statistically significant method bias exists in one data set with respect to the other. In this case all p-values associated with the computed test statistic are significantly greater than 0.05. For example, the p-value associated with the test statistic for Cu was 0.68. This indicates that the observed differences between the MSE ICP data and the CAS ICP data carry a 68 percent likelihood of being attributable to random variation between two equivalent methods. These results are corroborated by the scatter plots shown in Figures 4-14 through 4-16. The plotted points fall above and below the diagonal “zero bias” line with approximately equal frequency, indicating no consistent bias in the results.

Intra- and Interlaboratory Variability

Each laboratory conducted a duplicate analysis of a digestate from a soil sample split made from a homogenized bulk field soil sample. The intralaboratory ICP instrument variability was estimated by computing the RPD for each target element from the duplicate analysis results of sample number MCLD-1 from the CAS and MSE laboratories. The average of these RPD values is shown in column 2 of Table 4-6 for each target element. The interlaboratory variability was estimated by computing four RPD values between the four measurement results from both laboratories and averaging the results. These data are shown in column 3 of Table 4-6. A comparison of the two columns of data (intra- and interlaboratory RPDs) suggests that in most cases instrument variability is

Table 4-6. Estimates of Intra- and Interlaboratory Sample Variation

Element	Average Intralab RPD	Average Interlab RPD
Ag	5.1	5.1
As	1.5	8.1
Cd	14.3	14.3
Cr	15.6	9.8
Cu	3.9	7.4
Fe	1.9	1.7
Mn	2.1	2.9
Pb	3.9	4.6
Zn	2.2	4.7

of the same order of magnitude as the variability arising from heterogeneity in the sample splits going to the different laboratories and technologies.

Reference Laboratory Data Set

Based on the foregoing analyses, a reference data set was compiled by averaging the MSE ICP, CAS ICP, and CAS AAS data sets. This reference data set was then further used for comparison with the soil analysis data sets provided for the various demonstration technologies. A summary of the reasons for including or excluding the laboratory data sets in the reference data set is given below.

- The CAS ICP data are judged to be valid, based on the laboratory's acceptable performance on the various control, duplicate, and soil recovery analyses. The 30-sample CAS ICP data set is used as one component in the reference data set.
- The 30-sample CAS AAS data set is also included in the reference data set despite the fact that the data set was shown to be biased with respect to the CAS ICP data set. The decision to include these data in the reference set was founded upon the linear regression results. Linear regression and correlation analysis show a high degree of correlation and small bias between the CAS ICP and CAS AAS data. The CAS AAS biases relative to the CAS ICP method are typically less than 10 percent for most target elements. A bias of ± 10 percent is relatively small and acceptable in light of the ± 20 percent tolerance in laboratory precision that was deemed acceptable in the laboratory data validation process. The AAS Cr data, although not well correlated with the ICP data, were also included in the reference data set. No substantive reasons to exclude one set of measurements over another were apparent in this particular case. Consequently, both were included.
- The MSE data are similarly accepted as valid in light of their very good correlation with the CAS ICP data for all elements and their demonstrated statistical equivalence with the CAS ICP data set.
- The SNL laboratory data are not used in the reference data set. The data package could not be validated because some key quality control parameters were not provided in the analysis results package. Furthermore, a less sensitive, lower precision, mobile ICP instrument was used, which contributed to greater uncertainty in this data set.

In summary, the reference data set is made up of an average of the MSE ICP, CAS ICP, and CAS AAS data sets for the 30 field soil samples that were analyzed by all three methods. Single values from the MSE ICP data set are used for the other 30 field samples not analyzed by CAS.

The interlaboratory comparisons revealed that all validated data had either a tolerable bias or were statistically equivalent. Consequently, no elements were excluded in compilation of the reference data set. Although all of the target elements were included in this set, it should be noted that interlaboratory comparisons revealed that the results from some elements should be regarded with a lower level of confidence than others. In particular, Cr results were variable among all three methods and should be treated with appropriate caution when they are used for comparison with field technology results.

Chapter 5

Demonstration Results

Technology-Laboratory Data Comparison Methods

For Level 1 technologies such as the MelΔok LIBS system, a formal comparison of field technology and laboratory results is left to the instrument developer. To assist the developer in the interpretation of the data, data formats and simple comparative analyses are included with the raw data. The MelΔok LIBS results from the quality control samples (blank soil, control soil, and duplicates) are presented in the same manner as described earlier for the laboratory data, but with little interpretation or assessment. In addition, the field soil sample analysis data are presented in tabular format in Appendix A with the validated results from each laboratory shown alongside the MelΔok LIBS results for each target element. Scatter plots are included in this chapter in which the MelΔok LIBS data are plotted against the laboratory reference data set. To further assist the technology developer in understanding the data, possible analytical approaches are suggested that might be taken in comparing the technology data with reference laboratory data.

Field Observations

Periodically during the demonstration, an observer checked in with the MelΔok LIBS demonstration team to monitor progress. No instrument breakdowns were noted, and the soil analyses proceeded smoothly. Two MelΔok personnel were at the site and operated the instrument. The MelΔok LIBS team began soil analysis on Monday, September 25, and completed their work on Thursday, September 28, averaging about 15 soil samples per 10-hour work day. Although the weather during the demonstration interval was occasionally rainy, windy, and cold, it did not appear to adversely affect the performance of the MelΔok LIBS instrument.

General Description of MelΔok LIBS Results

A total of 60 field soil samples plus 2 control soil samples and 2 blank soil samples were analyzed with the MelΔok LIBS system for 9 target elements. The MelΔok LIBS analysts produced a complete report in which an analytical result (either a reported level or an indication of nondetectable) was included for each sample that was submitted to them. Although duplicate analyses of several field soil samples were requested, no duplicate analyses were reported.

Quality Control Sample Results

The results of various MelΔok LIBS analyses of quality control samples are presented in the following sections. The results are presented in a format that facilitates comparison of LIBS and laboratory data. Since the MelΔok LIBS technology is Level 1, a limited analysis of the data is presented.

Blank Soil Sample Analysis

Table 5-1 shows a comparison of the MelΔok LIBS and certified levels for blank soil samples. The MSE laboratory results are also shown since their results tracked the certified values most closely of all the participating laboratories. Three of the nine target elements—Fe, Pb, and Cr—were detected by the MelΔok LIBS system in the blank samples. No detection limits were given by the MelΔok team for the other six elements for which a “no detect” was reported; however, a generic detection limit of 100-150 mg/kg has been reported by the developers for all elements.

Table 5-1. MelΔok LIBS Blank Soil Sample Results

Element	Metal Concentration Level (mg/kg)		
	MelΔok LIBS	MSE by ICP	Certified Level
Ag	<?	0.4	<2
As	<?	2.1	<2
Cd	<?	0.4	<1
Cr	28	6.7	7
Cu	<?	5.6	<5
Fe	12,160	7,740	8,180
Pb	450	9.3	9
Mn	<?	172	159
Zn	<140	24.4	24

Notes: A “less than” (<) symbol indicates not detected; no detection limits are given for these elements in the analysis report. MelΔok reported a general detection limit of 100-150 mg/kg for all elements.

Control Soil Sample Analysis

Control soil samples, with well-characterized target element concentrations, were analyzed by all participants in the demonstration, including MelΔok. The results for each control sample analysis from the MelΔok LIBS system are shown in Figure 5-1. They are expressed in terms of a percentage difference from a certified concentration level for each element in this particular soil lot as determined through a multilaboratory, round-robin study. The plotted data show LIBS analysis results outside of the 95 percent upper and lower confidence limits about the mean certified value for all target elements except Zn. Arsenic, Cu, Fe, Pb, and Mn were all reported high—in the range of 200 to 1,000 percent, whereas Ag, Cd, and Cr were reported low—in the range of –50 to –100 percent.

Duplicate Sample Analysis

No duplicate sample analyses were reported by MelΔok, hence no precision analysis was carried out.

Recovery Analysis

None of the soil and control samples analyzed with the MelΔok LIBS system were spiked prior to analysis. Consequently there are no recovery data to present.

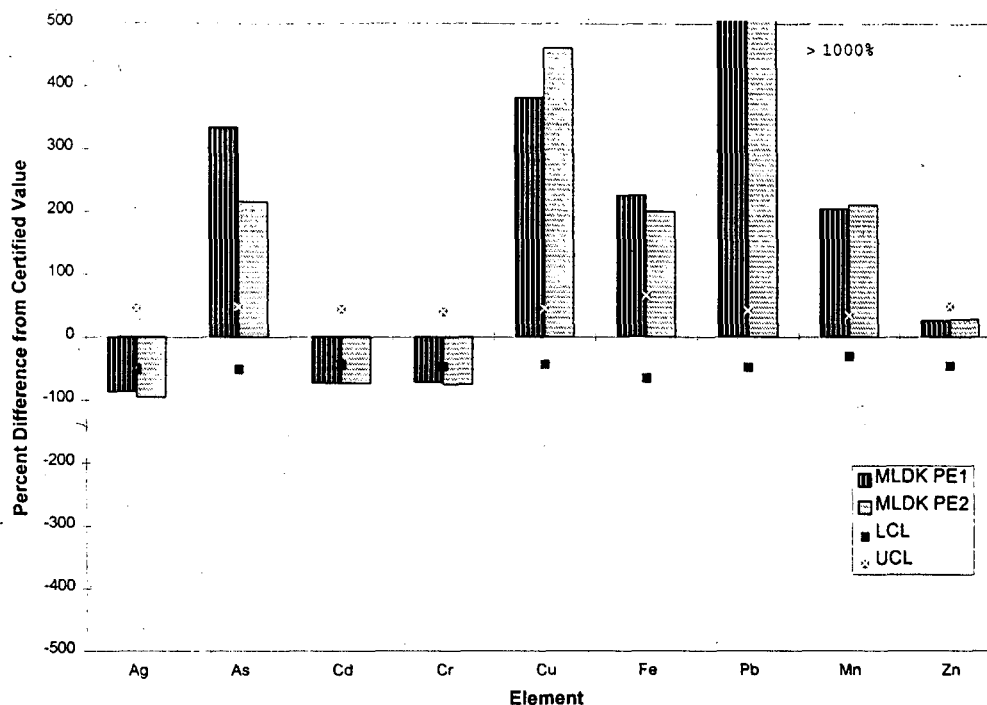


Figure 5-1. Control soil sample analysis results from the MelΔok LIBS system. The upper and lower confidence intervals about the certified level are also shown on the graph. The percent difference of the lead determination was >1,000 percent and is off the graph scale.

Field Soil Sample Analysis Results

Analysis results were returned for all 60 field soil samples submitted to the MelΔok analysis team during the demonstration. In nearly all cases, measured values above instrument detection limits were reported. The field sample analysis data are presented in both graphical and tabular formats to assist the developers in comparing their data against the reference data set from the analytical laboratories. A series of nine scatter plots (Figures 5-2 through 5-10) are presented in which the MelΔok LIBS data are plotted against the reference laboratory data. As a part of the laboratory data validation process, laboratory data from the CAS ICP, CAS AAS, and MSE ICP analyses were averaged together to yield a reference laboratory value. (See Chapter 4 for a discussion of the makeup of the reference laboratory data set.) Normally, 60 data points are plotted in the scatter plots; however, in many cases the points on the scatter plots are overlaid and are thus indistinguishable from each other. The zero bias line extends from the lower left to the upper right of each plot. Plotted points falling on or close to this line reveal close agreement between MelΔok LIBS and reference laboratory data.

The MelΔok LIBS data are also presented in tabular form in Appendix A to facilitate their comparison with individual reference laboratory results. In the appendix, a series of tables are given in which the 60 sample analysis results are given for CAS ICP, CAS AAS, MSE ICP, reference laboratory, and MelΔok LIBS analysis for the nine target elements.

Care must be taken in comparing the MelΔok LIBS and laboratory results since differences in measurement technique are likely to influence the results. For example, it was noted in Chapter 2 that the LIBS method gives a measure of total elemental content in a sample whereas the conventional laboratory method yields a measure of

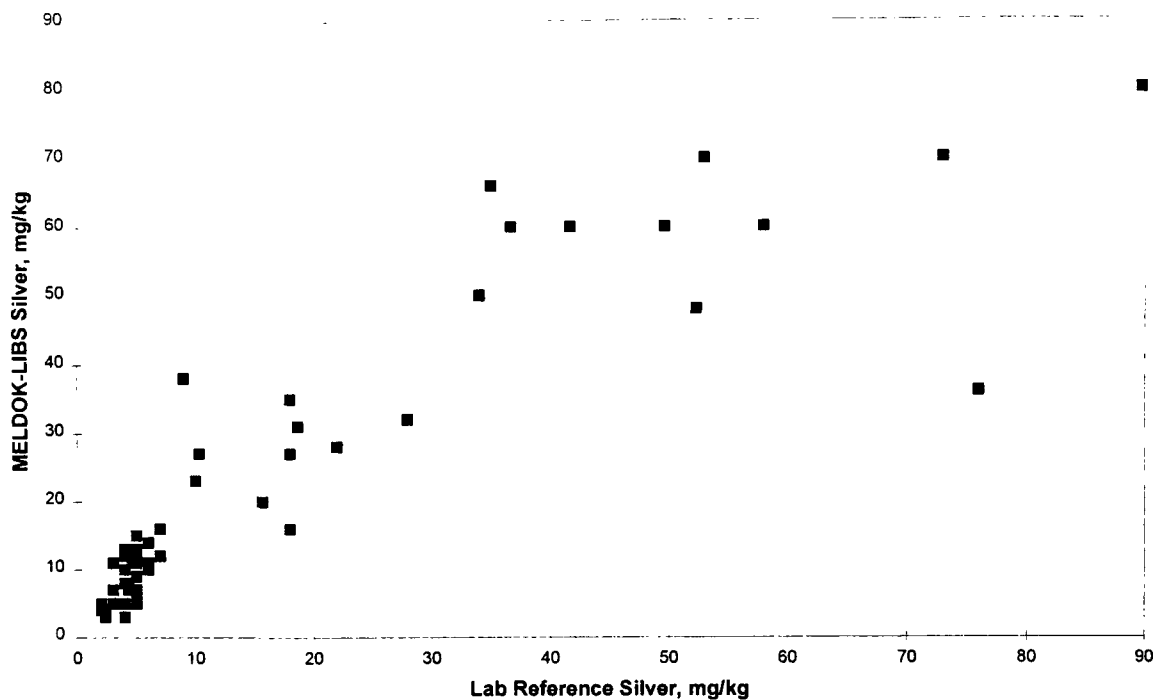


Figure 5-2. MelΔok LIBS vs. reference laboratory silver.

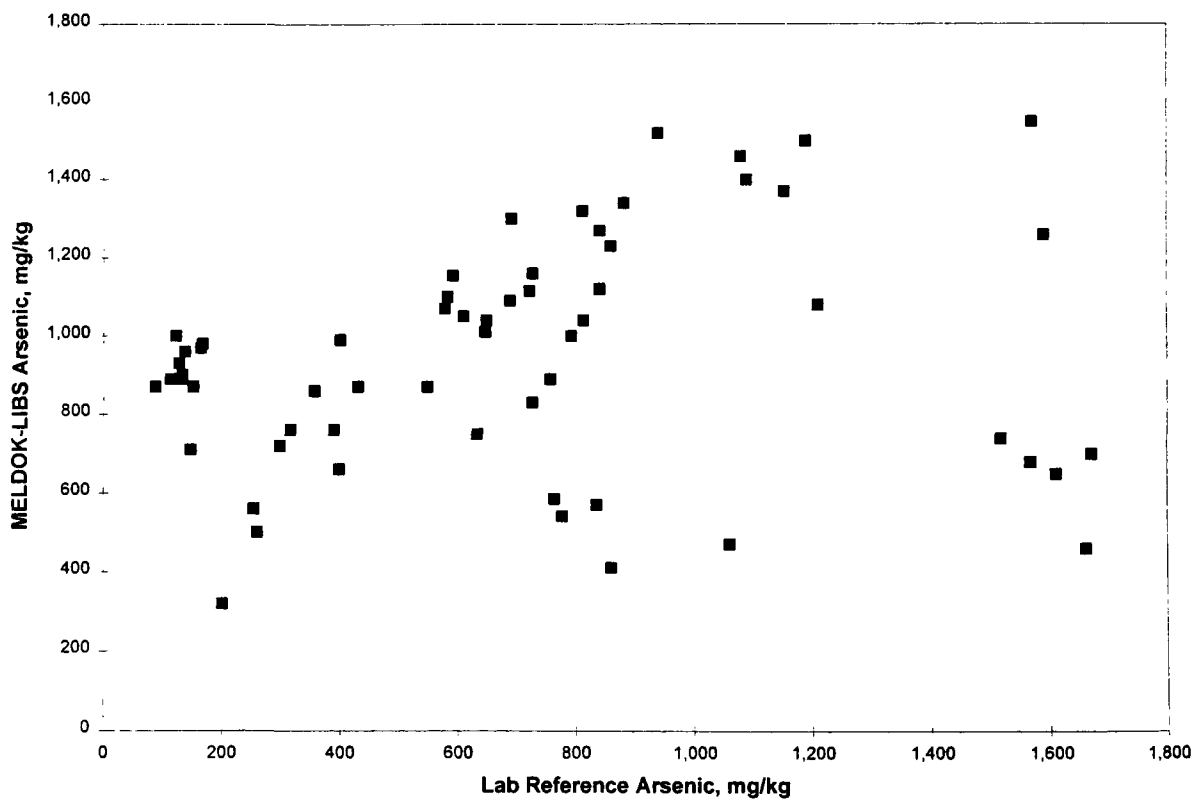


Figure 5-3. MelΔok LIBS vs. reference laboratory arsenic.

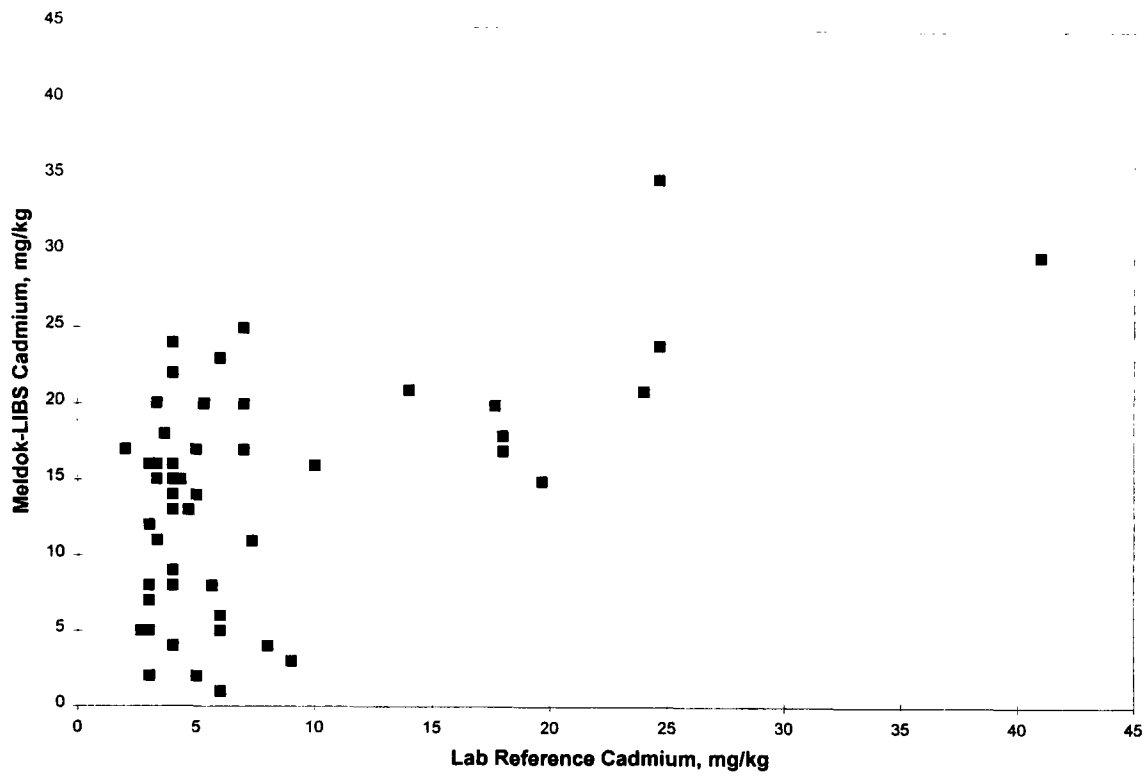


Figure 5-4. MelΔok LIBS vs. reference laboratory cadmium.

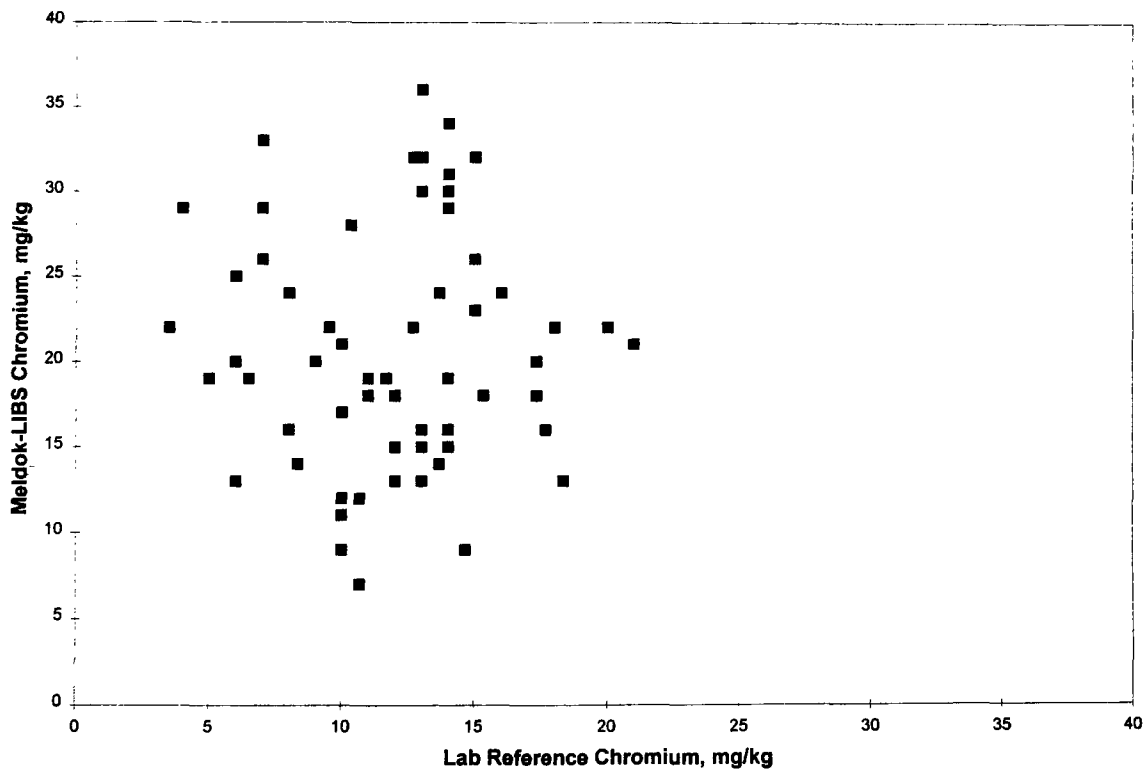


Figure 5-5. MelΔok LIBS vs. reference laboratory chromium.

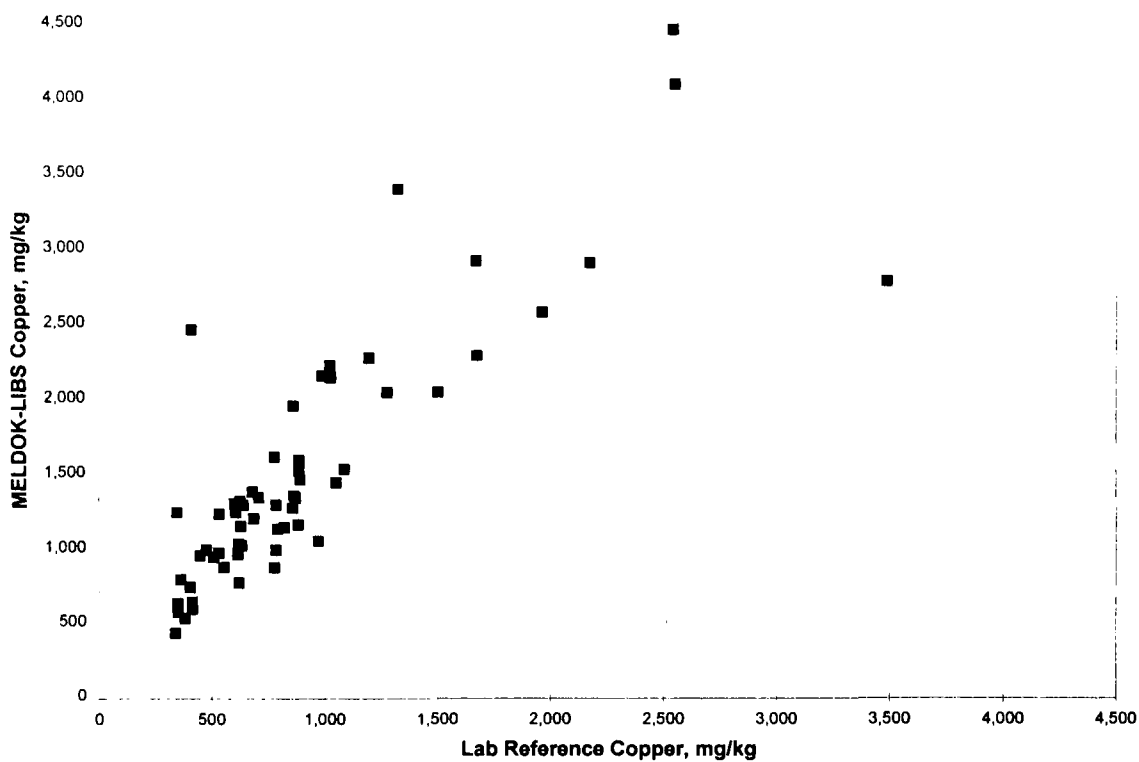


Figure 5-6. MelΔok LIBS vs. reference laboratory copper.

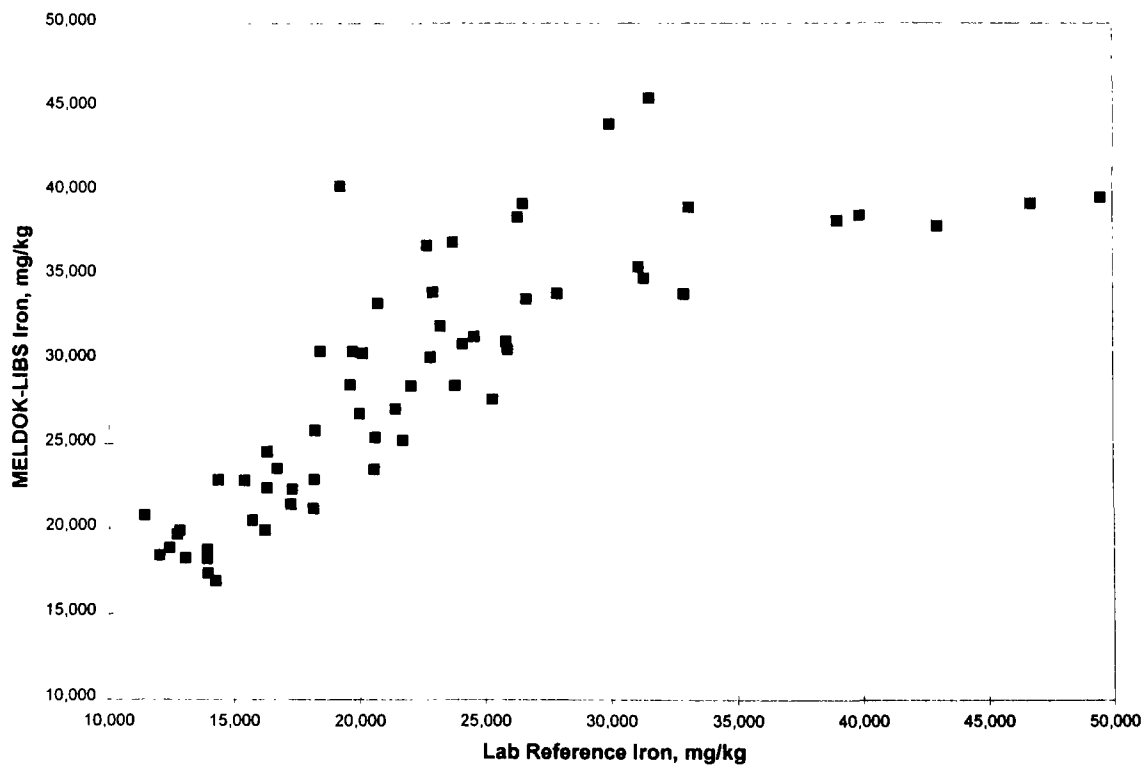


Figure 5-7. MelΔok LIBS vs. reference laboratory iron.

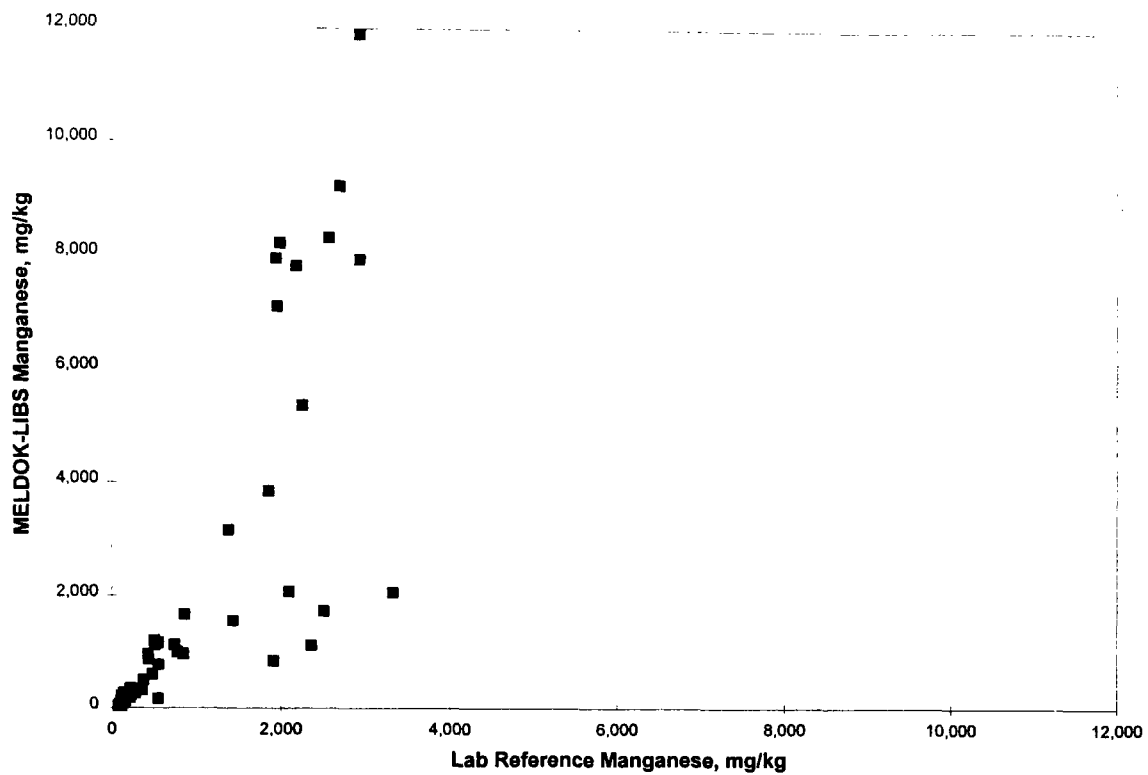


Figure 5-8. MelΔok LIBS vs. reference laboratory manganese.

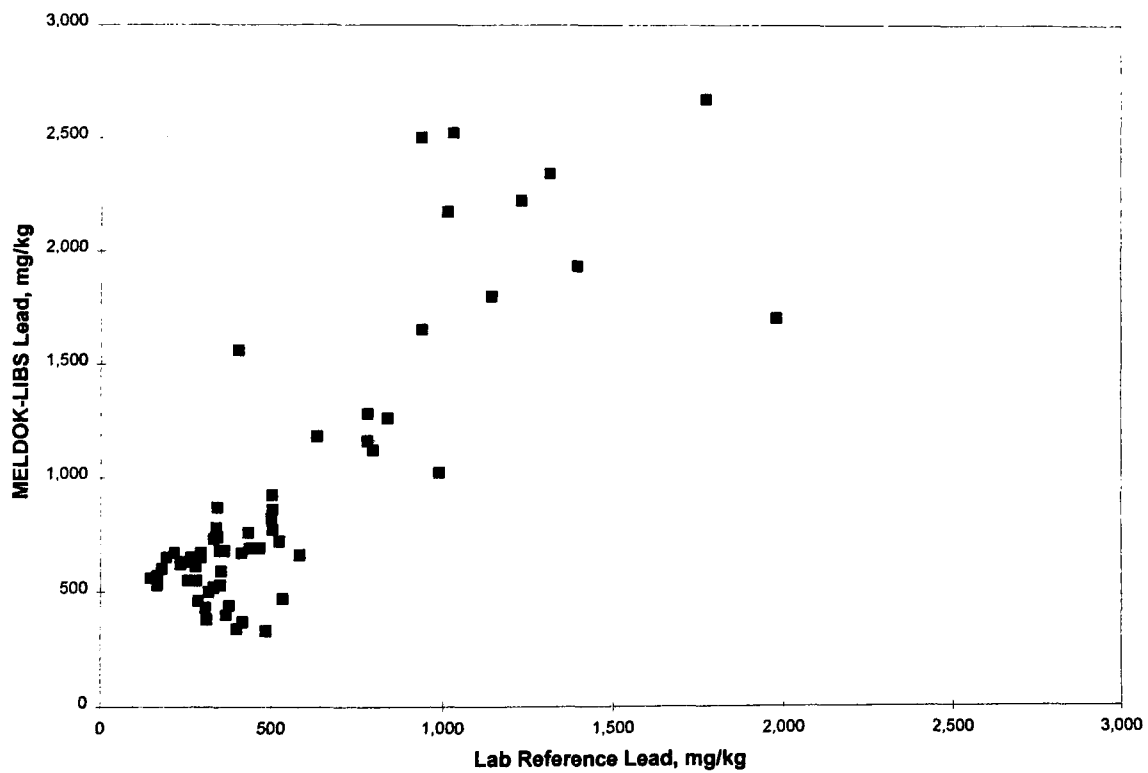


Figure 5-9. MelΔok LIBS vs. reference laboratory lead.

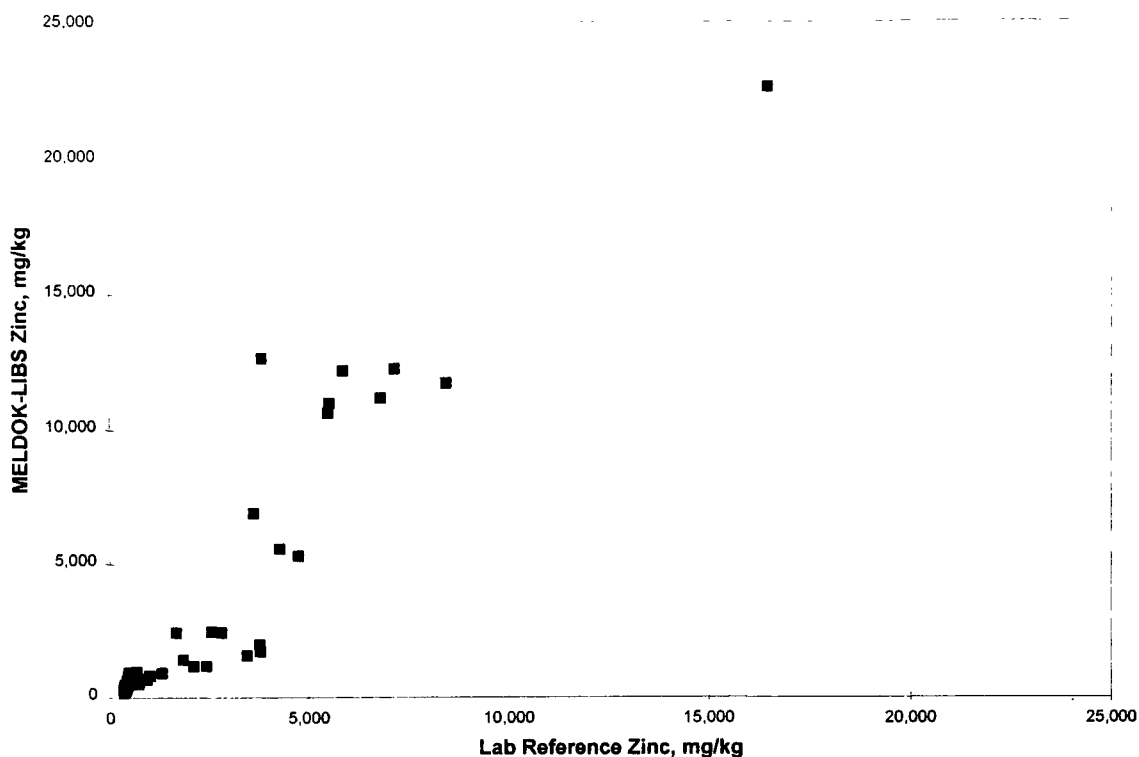


Figure 5-10. MelΔok LIBS vs. reference laboratory zinc.

acid-extractable elemental content. The LIBS technique, as noted in the MelΔok informational literature, works best for finely ground, well-mixed soil samples. Large heterogeneous soil particles can skew the analysis results since the laser spot diameter is on the order of 50 μm and may be influenced by single large particles of metal-contaminated soil.

Comparison of LIBS Results with Reference Laboratory Data

The following analytical approaches are offered as illustrations of how an evaluation of LIBS performance relative to a laboratory data set might be carried out.

Mean Percent Difference

The mean percent differences, as defined in Chapter 4, for the MelΔok LIBS data set relative to the reference laboratory data set are given in Table 5-2. A small number for mean percent difference and for the accompanying standard deviation is an indicator of good comparability between methods. Mean percent differences between MelΔok and reference laboratory data range from a low of 20 percent for zinc to a high of 143 percent for Cd. In all cases the mean percent differences are greater than zero. The accompanying standard deviations are generally greater than the mean percent difference values shown.

Correlation Coefficients

The slope, y-intercept, and correlation coefficient from linear regression analysis between the MelΔok and reference laboratory data are given in Table 5-3. The slope yields a measure of the linear association of two data

Table 5-2. Mean Percent Differences for MelΔok LIBS and Reference Laboratory Data

Element	Mean Percent Difference Reference Laboratory Data Set
Ag	74 ± 72
As	139 ± 227
Cd	143 ± 179
Cr	107 ± 124
Cu	81 ± 69
Fe	33 ± 23
Mn	57 ± 98
Pb	91 ± 73
Zn	20 ± 49

Note: The mean value is followed by the standard deviation.

Table 5-3. Linear Regression Parameters for MelΔok LIBS and Reference Laboratory Data

Element	Slope	Intercept (mg/kg)	Correlation Coefficient
Ag	0.90	7	0.89
As	0.13	850	0.20
Cd	0.44	10	0.40
Cr	-0.04	20	-0.02
Cu	1.15	480	0.83
Fe	0.72	13,000	0.81
Mn	2.43	-270	0.80
Pb	1.31	220	0.84
Zn	1.51	-280	0.94

sets. A slope of 2 indicates that MelΔok reports a value two times that of the reference laboratory, whereas a slope of 0.5 indicates a MelΔok value half of the laboratory value. The slope should always be examined alongside the correlation coefficient. A regression analysis will always yield a slope value, even when the data are poorly correlated. The correlation coefficient is an indication of the strength of linear association between two variables. Values near unity suggest good correlation between the data sets. Values near zero suggest no correlation of the data. With three exceptions, the correlation coefficients shown in Table 5-3 are greater than 0.8, indicating relatively good correlation of the MelΔok LIBS data with the reference laboratory data.

Statistical Bias Testing

A statistical test such as the Wilcoxon matched pair test can be used to investigate whether a statistically significant bias exists between the MelΔok LIBS data set and the reference laboratory data set. The results from such a test should be used in conjunction with the linear regression data such as that presented in Table 5-3. Although the statistical test may indicate that a significant bias exists between the two methods, the magnitude of that bias must also be taken into account in the overall assessment of method comparability. In light of the fact

that the MelΔok LIBS is designated a Level 1 technology, statistical testing is left to the discretion of the technology developer.

Conclusions

Since the MelΔok LIBS system is a developing technology that has not undergone extensive field testing, a comprehensive assessment of its performance was not undertaken in this demonstration. Conclusions as to the system's overall performance are left to the technology developer. Comments from the developers concerning their own performance assessment, if any, may be found in Chapter 6.

Chapter 6

Developer's Comments

A copy of this report in draft form was sent to MelΔok, Inc. for review and comment. Despite repeated attempts to contact personnel at MelΔok to obtain review comments, no response was obtained.

References

Conover, W. J., 1980. *Practical Nonparametric Statistics*, 2nd ed, Wiley, New York.

Havlicek, L., and R. D. Crain, 1988. *Practical Statistics for the Physical Sciences*, American Chemical Society, Washington DC, pp. 84–93.

MSE, 1996. “Final Report for RCRA and Other Heavy Metals in Soils Demonstration,” MSE Technology Applications, Inc., Butte, Montana.

Appendix A

Tabular Data for MelΔok LIBS and Reference Laboratory Field Soil Samples

Table Description

The results are organized by element with two tables for each element. The first table gives results from the Silver Bow site and the second gives results from the Mill Creek site. The data are further described as follows:

Column 1	Sample Number
Column 2	MSE Laboratory ICP AES Results
Column 3	CAS Laboratory ICP AES Results
Column 4	CAS Laboratory Flame AAS Results
Column 5	Reference Laboratory Data Set (Average of Columns 2-4)
Column 6	Field Technology Results

Table A-1. Silver Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Ag (mg/kg)	C_IC_Ag (mg/kg)	C_AA_Ag (mg/kg)	Ref_Ag (mg/kg)	MDK_Ag (mg/kg)
SBHD1	38	41	46	42	60
SBHD2	53			53	70
SBHD3	36	35	39	37	60
SBHD4	34			34	50
SBHD5	88	86	95	90	80
SBHD6	58			58	60
SBHD7	48	48	53	50	60
SBHD8	73			73	70
SBHD9	54	49	54	52	48
SBHD10	35			35	66
SBMD1	10	10	11	10	27
SBMD2	22			22	28
SBMD3	11	17	19	16	20
SBMD4	76			76	36
SBMD5	18	18	20	19	31
SBMD6	28			28	32
SBMD7	18	17	19	18	35
SBMD8	18			18	16
SBMD9	20	16	18	18	27
SBMD10	10			10	23
SBLD1	2	2	2	2	4
SBLD2	2			2	5
SBLD3	2	2	3	2	3
SBLD4	3			3	5
SBLD5	2	2	3	3	4
SBLD6	3			3	7
SBLD7	4	5	6	5	5
SBLD8	3			3	5
SBLD9	4	5	6	5	7
SBLD10	5			5	9

Table A-2. Silver Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Ag (mg/kg)	C_IC_Ag (mg/kg)	C_AA_Ag (mg/kg)	Ref_Ag (mg/kg)	MDK_Ag (mg/kg)
MCHD1	3	3	3	3	11
MCHD2	5			5	12
MCHD3	4	4	4	4	13
MCHD4	4			4	12
MCHD5	6	5	7	6	11
MCHD6	6			6	11
MCHD7	5	4	5	5	11
MCHD8	5			5	13
MCHD9	8	9	10	9	38
MCHD10	5			5	15
MCMD1	4	4	5	4	7
MCMD2	4			4	8
MCMD3	4	4	4	4	5
MCMD4	4			4	5
MCMD5	4	4	4	4	10
MCMD6	5			5	13
MCMD7	5	5	5	5	11
MCMD8	5			5	12
MCMD9	6	5	7	6	14
MCMD10	7			7	12
MCLD1	4	4	5	4	8
MCLD2	4			4	10
MCLD3	4	4	4	4	12
MCLD4	4			4	10
MCLD5	4	4	4	4	3
MCLD6	5			5	11
MCLD7	5	5	5	5	12
MCLD8	5			5	6
MCLD9	6	5	7	6	10
MCLD10	7			7	16

Table A-3. Arsenic Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_As (mg/kg)	C_IC_As (mg/kg)	C_AA_As (mg/kg)	Ref_As (mg/kg)	MDK_As (mg/kg)
SBHD1	1060	1110	1010	1060	470
SBHD2	1660			1660	460
SBHD3	874	866	765	835	570
SBHD4	764			764	585
SBHD5	947	866	766	860	410
SBHD6	1670			1670	700
SBHD7	1510	1470	1570	1517	740
SBHD8	1610			1610	650
SBHD9	1680	1490	1530	1567	680
SBHD10	777			777	541
SBMD1	145	162	137	148	710
SBMD2	254			254	560
SBMD3	315	155	132	201	320
SBMD4	549			549	870
SBMD5	290	316	291	299	720
SBMD6	357			357	860
SBMD7	414	408	380	401	990
SBMD8	399			399	660
SBMD9	423	405	342	390	760
SBMD10	260			260	500
SBLD1	136	144	120	133	900
SBLD2	152			152	870
SBLD3	130	156	129	138	960
SBLD4	165			165	970
SBLD5	165	181	157	168	980
SBLD6	132			132	890
SBLD7	113	148	106	122	1000
SBLD8	128			128	930
SBLD9	101	137	102	113	890
SBLD10	88			88	870

Table A-4. Arsenic Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_As (mg/kg)	C_IC_As (mg/kg)	C_AA_As (mg/kg)	Ref_As (mg/kg)	MDK_As (mg/kg)
MCHD1	637	629	565	610	1050
MCHD2	1,570			1,570	1550
MCHD3	326	347	275	316	760
MCHD4	583			583	1100
MCHD5	1,260	1,240	1,130	1,210	1080
MCHD6	813			813	1040
MCHD7	466	461	366	431	870
MCHD8	812			812	1320
MCHD9	697	716	663	692	1300
MCHD10	882			882	1340
MCMD1	586	604	587	592	1155
MCMD2	860			860	1230
MCMD3	717	757	708	727	1160
MCMD4	689			689	1090
MCMD5	1,240	1,190	1,030	1,153	1370
MCMD6	940			940	1520
MCMD7	907	828	789	841	1270
MCMD8	1,090			1,090	1400
MCMD9	1,650	1,680	1,440	1,590	1260
MCMD10	1,080			1,080	1460
MCLD1	640	704	604	649	1040
MCLD2	647			647	1010
MCLD3	576	580	581	579	1070
MCLD4	757			757	890
MCLD5	619	668	612	633	750
MCLD6	726			726	830
MCLD7	814	811	753	793	1000
MCLD8	722			722	1115
MCLD9	877	837	808	841	1120
MCLD10	1190			1,190	1500

Table A-5. Cadmium Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Cd (mg/kg)	C_IC_Cd (mg/kg)	C_AA_Cd (mg/kg)	Ref_Cd (mg/kg)	MDK_Cd (mg/kg)
SBHD1	22.6	27	23.7	24.4	24
SBHD2	12.5			12.5	
SBHD3	21.6	22	14.9	19.5	15
SBHD4	9.9			9.9	16
SBHD5	48.5	54	20.1	40.9	30
SBHD6	18.3			18.3	18
SBHD7	19.0	18	15.7	17.6	20
SBHD8	18.0			18.0	17
SBHD9	15.5	14	11.5	13.7	21
SBHD10	24.3			24.3	21
SBMD1	5.8	6	2.7	4.8	0
SBMD2	11.8			11.8	0
SBMD3	7.8	15	3.4	8.7	0
SBMD4	16.5			16.5	0
SBMD5	14.6	11	7.1	10.9	0
SBMD6	7.8			7.8	4
SBMD7	9.8	7	9.7	8.8	3
SBMD8	4.6			4.6	2
SBMD9	6.6	6	5	5.9	1
SBMD10	5.7			5.7	5
SBLD1	4.9	5	3.7	4.5	13
SBLD2	3.5			3.5	4
SBLD3	3.8	3	2.8	3.2	11
SBLD4	2.7			2.7	8
SBLD5	3.1	3	2.7	2.9	2
SBLD6	4.9			4.9	14
SBLD7	7.3	8	6.6	7.3	11
SBLD8	3.1			3.1	12
SBLD9	2.4	4	2.6	3.0	16
SBLD10	3.7			3.7	14

Table A-6. Cadmium Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Cd (mg/kg)	C_IC_Cd (mg/kg)	C_AA_Cd (mg/kg)	Ref_Cd (mg/kg)	MDK_Cd (mg/kg)
MCHD1	4	3	3	3	15
MCHD2	4			4	15
MCHD3	3	3	2	3	5
MCHD4	4			4	9
MCHD5	5	4	3	4	8
MCHD6	3			3	5
MCHD7	4	3	2	3	7
MCHD8	6			6	6
MCHD9	27	25	22	25	35
MCHD10	4			4	24
MCMD1	3	4	3	4	20
MCMD2	4			4	13
MCMD3	4	3	3	3	16
MCMD4	4			4	16
MCMD5	6	5	5	5	20
MCMD6	5			5	17
MCMD7	7	5	5	5	8
MCMD8	7			7	17
MCMD9	8	7	6	7	25
MCMD10	6			6	23
MCLD1	2	2	2	2	17
MCLD2	4			4	13
MCLD3	4	3	3	3	15
MCLD4	4			4	9
MCLD5	4	4	3	4	18
MCLD6	4			4	15
MCLD7	5	4	4	4	15
MCLD8	4			4	22
MCLD9	5	3	3	4	18
MCLD10	7			7	20

Table A-7. Chromium Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Cr (mg/kg)	C_IC_Cr (mg/kg)	C_AA_Cr (mg/kg)	Ref_Cr (mg/kg)	MDK_Cr (mg/kg)
SBHD1	6	8	<10	6.8	29
SBHD2	4			4.4	29
SBHD3	5	5	<10	5.0	19
SBHD4	6			5.7	25
SBHD5	7	8	23	12.7	22
SBHD6	7			6.8	26
SBHD7	7	5	<10	6.2	25
SBHD8	6			5.7	20
SBHD9	7	6	<10	6.6	19
SBHD10	9			9.2	20
SBMD1	13	17	<10	15.0	23
SBMD2	20			20.0	22
SBMD3	27	12	15	18.1	22
SBMD4	21			21.2	21
SBMD5	25	16	11	17.3	20
SBMD6	14			13.7	19
SBMD7	14	10	<10	12.0	18
SBMD8	14			13.8	16
SBMD9	10	9	<10	9.4	22
SBMD10	8			7.8	24
SBLD1	15	15	<10	15.2	32
SBLD2	14			14.0	34
SBLD3	13	14	11	12.5	32
SBLD4	13			12.7	32
SBLD5	12	14	<10	12.8	36
SBLD6	14			13.5	31
SBLD7	13	17	<10	14.9	26
SBLD8	13			12.6	30
SBLD9	12	16	<10	13.9	29
SBLD10	14			13.5	30

Table A-8. Chromium Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Cr (mg/kg)	C_IC_Cr (mg/kg)	C_AA_Cr (mg/kg)	Ref_Cr (mg/kg)	MDK_Cr (mg/kg)
MCHD1	8	7	10	8	14
MCHD2	10			10	9
MCHD3	4	3		4	22
MCHD4	6			6	13
MCHD5	11	10	11	11	12
MCHD6	10			10	11
MCHD7	7	6	28	14	14
MCHD8	10			10	17
MCHD9	10	9	12	10	28
MCHD10	13			13	16
MCMD1	11	10	21	14	15
MCMD2	10			10	12
MCMD3	11	14	30	18	13
MCMD4	13			13	13
MCMD5	13	14	17	15	9
MCMD6	10			10	21
MCMD7	13	12	21	15	18
MCMD8	12			12	15
MCMD9	12	14	27	18	16
MCMD10	13			13	15
MCLD1	7	8	33	16	24
MCLD2	8			8	16
MCLD3	9	7	19	12	19
MCLD4	12			12	13
MCLD5	8	12	21	14	24
MCLD6	11			11	18
MCLD7	10	10	32	17	18
MCLD8	7			7	33
MCLD9	9	8	15	11	7
MCLD10	11			11	19

Table A-9. Copper Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Cu (mg/kg)	C_IC_Cu (mg/kg)	C_AA_Cu (mg/kg)	Ref_Cu (mg/kg)	MDK_Cu (mg/kg)
SBHD1	1,570	1,670	1,790	1,677	2920
SBHD2	1,330			1,330	3400
SBHD3	2,460	2,510	2,700	2,557	4080
SBHD4	991			991	2160
SBHD5	2,620	2,410	2,620	2,550	4440
SBHD6	1,680			1,680	2290
SBHD7	1,010	1,010	1,060	1,027	2230
SBHD8	1,030			1,030	2150
SBHD9	1,620	1,400	1,500	1,507	2050
SBHD10	1,970			1,970	2575
SBMD1	281	385	371	346	1250
SBMD2	864			864	1960
SBMD3	788	512	522	607	1250
SBMD4	2,180			2,180	2900
SBMD5	1,090	1,240	1,270	1,200	2280
SBMD6	780			780	1620
SBMD7	1,270	1,290	1,280	1,280	2050
SBMD8	449			449	960
SBMD9	608	644	635	629	1326
SBMD10	710			710	1350
SBLD1	394	374	376	381	540
SBLD2	351			351	610
SBLD3	339	357	359	352	580
SBLD4	414			414	600
SBLD5	347	332	338	339	440
SBLD6	404			404	750
SBLD7	566	647	648	620	780
SBLD8	414			414	650
SBLD9	305	376	370	350	640
SBLD10	363			363	800

Table A-10. Copper Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Cu (mg/kg)	C_IC_Cu (mg/kg)	C_AA_Cu (mg/kg)	Ref_Cu (mg/kg)	MDK_Cu (mg/kg)
MCHD1	682	663	701	682	1390
MCHD2	792			792	1140
MCHD3	419	400	420	413	2470
MCHD4	687			687	1210
MCHD5	956	828	880	888	1530
MCHD6	533			533	1240
MCHD7	589	626	668	628	1160
MCHD8	859			859	1280
MCHD9	3,340	3,490	3,640	3,490	2770
MCHD10	889			889	1600
MCMD1	631	631	657	640	1300
MCMD2	532			532	980
MCMD3	585	621	651	619	1040
MCMD4	632			632	1030
MCMD5	825	795	845	822	1150
MCMD6	893			893	1470
MCMD7	890	821	885	865	1360
MCMD8	871			871	1350
MCMD9	1,020	1,010	1,130	1,053	1450
MCMD10	784			784	1300
MCLD1	476	513	535	508	950
MCLD2	477			477	1000
MCLD3	595	598	610	601	1310
MCLD4	554			554	880
MCLD5	721	775	837	778	880
MCLD6	971			971	1060
MCLD7	853	878	916	882	1170
MCLD8	784			784	1000
MCLD9	624	598	622	615	970
MCLD10	1,090			1,090	1540

Table A-11. Iron Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Fe (mg/kg)	C_IC_Fe (mg/kg)	C_AA_Fe (mg/kg)	Ref_Fe (mg/kg)	MDK_Fe (mg/kg)
SBHD1	28,700	30,800	35,100	31,533	45510
SBHD2	19,200			19,200	40290
SBHD3	21,900	21,700	24,400	22,667	36760
SBHD4	26,300			26,300	38440
SBHD5	30,100	28,100	31,600	29,933	43980
SBHD6	26,500			26,500	39230
SBHD7	20,700	19,400	22,000	20,700	33310
SBHD8	22,900			22,900	33970
SBHD9	29,800	25,400	28,400	27,867	33910
SBHD10	23,700			23,700	36948
SBMD1	27,800	34,000	36,900	32,900	33880
SBMD2	43,000			43,000	37930
SBMD3	55,200	29,200	32,600	39,000	38250
SBMD4	46,700			46,700	39280
SBMD5	49,000	33,100	37,600	39,900	38560
SBMD6	31,300			31,300	34810
SBMD7	34,100	28,000	31,200	31,100	35500
SBMD8	33,100			33,100	39050
SBMD9	26,300	25,400	28,200	26,633	33570
SBMD10	23,200			23,200	31950
SBLD1	15,500	13,000	14,200	14,233	16910
SBLD2	13,900			13,900	18760
SBLD3	13,300	12,300	13,500	13,033	18270
SBLD4	13,900			13,900	18230
SBLD5	13,500	13,400	14,900	13,933	17380
SBLD6	12,700			12,700	19670
SBLD7	11,100	12,400	13,700	12,400	18890
SBLD8	12,000			12,000	18440
SBLD9	10,700	13,300	14,400	12,800	19890
SBLD10	11,400			11,400	20800

Table A-12. Iron Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Fe (mg/kg)	C_IC_Fe (mg/kg)	C_AA_Fe (mg/kg)	Ref_Fe (mg/kg)	MDK_Fe (mg/kg)
MCHD1	24,100	23,100	25,100	24,100	30,890
MCHD2	21,400			21,400	27,070
MCHD3	23,900	26,300	27,300	25,833	31,030
MCHD4	25,900			25,900	30,550
MCHD5	24,700	24,400	26,800	25,300	27,620
MCHD6	23,800			23,800	28,440
MCHD7	23,000	24,100	26,600	24,567	31,340
MCHD8	22,800			22,800	30,130
MCHD9	49,800	49,200	49,500	49,500	39,630
MCHD10	15,400			15,400	22,840
MCMD1	14,800	13,500	14,800	14,367	22,870
MCMD2	16,700			16,700	23,540
MCMD3	15,600	17,200	18,900	17,233	21,440
MCMD4	16,200			16,200	19,900
MCMD5	17,700	17,500	19,200	18,133	21,170
MCMD6	15,700			15,700	20,490
MCMD7	18,200	16,500	19,800	18,167	22,890
MCMD8	16,300			16,300	22,390
MCMD9	16,200	16,800	18,900	17,300	22,320
MCMD10	16,300			16,300	24,510
MCLD1	18,600	19,200	21,000	19,600	28,490
MCLD2	20,100			20,100	30,350
MCLD3	20,600	18,500	20,000	19,700	30,470
MCLD4	21,700			21,700	25,210
MCLD5	18,400	20,400	22,900	20,567	23,490
MCLD6	20,600			20,600	25,380
MCLD7	20,200	18,900	20,800	19,967	26,790
MCLD8	18,400			18,400	30,460
MCLD9	22,700	20,600	22,800	22,033	28,440
MCLD10	18,200			18,200	25,790

Table A-13. Manganese Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_MN (mg/kg)	C_IC_MN (mg/kg)	C_AA_MN (mg/kg)	Ref_Mn (mg/kg)	MDK_Mn (mg/kg)
SBHD1	2,460	2,520	2,720	2,567	8300
SBHD2	2,940			2,940	11890
SBHD3	2,100	2,130	2,320	2,183	7800
SBHD4	1,380			1,380	3160
SBHD5	2,000	1,900	2,070	1,990	8200
SBHD6	2,700			2,700	9210
SBHD7	1,920	1,870	2,040	1,943	7930
SBHD8	2,930			2,930	7920
SBHD9	1,800	1,780	1,970	1,850	3850
SBHD10	1,960			1,960	7093
SBMD1	935	794	847	859	1660
SBMD2	2,500			2,500	1730
SBMD3	1,150	2,270	2,320	1,913	840
SBMD4	3,320			3,320	2060
SBMD5	2,560	2,130	2,380	2,357	1120
SBMD6	2,090			2,090	2070
SBMD7	1,070	1,530	1,680	1,427	1550
SBMD8	549			549	160
SBMD9	1,080	608	652	780	996
SBMD10	850			850	960
SBLD1	708	730	794	744	1120
SBLD2	478			478	600
SBLD3	409	458	456	441	860
SBLD4	379			379	500
SBLD5	563	532	564	553	770
SBLD6	556			556	1160
SBLD7	391	448	456	432	960
SBLD8	505			505	1200
SBLD9	434	540	593	522	1150
SBLD10	513			513	1120

Table A-14. Manganese Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Mn (mg/kg)	C_IC_Mn (mg/kg)	C_AA_Mn (mg/kg)	Ref_Mn (mg/kg)	MDK_Mn (mg/kg)
MCHD1	113	115	115	114	90
MCHD2	122			122	90
MCHD3	71	78	82	77	37
MCHD4	94			94	70
MCHD5	121	124	105	117	37
MCHD6	75			75	0
MCHD7	88	96	98	94	70
MCHD8	161			161	120
MCHD9	2,180	2,230	2,350	2,253	5360
MCHD10	222			222	350
MCMD1	284	267	280	277	340
MCMD2	202			202	220
MCMD3	263	266	271	267	300
MCMD4	210			210	250
MCMD5	222	206	210	213	190
MCMD6	170			170	240
MCMD7	288	270	277	278	270
MCMD8	235			235	250
MCMD9	219	225	236	227	240
MCMD10	188			188	210
MCLD1	119	124	125	123	150
MCLD2	102			102	110
MCLD3	120	113	113	115	220
MCLD4	139			139	160
MCLD5	132	138	143	138	270
MCLD6	146			146	250
MCLD7	163	155	158	159	240
MCLD8	139			139	220
MCLD9	115	108	108	110	130
MCLD10	357			357	320

Table A-15. Lead Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_PB (mg/kg)	C_IC_PB (mg/kg)	C_AA_PB (mg/kg)	Ref_Pb (mg/kg)	MDK_Pb (mg/kg)
SBHD1	1,170	1,220	1,290	1,227	2220
SBHD2	1,010			1,010	2170
SBHD3	946	902	955	934	2500
SBHD4	936			936	1650
SBHD5	2,080	1,850	2,000	1,977	1700
SBHD6	1,310			1,310	2340
SBHD7	1,030	992	1,060	1,027	2520
SBHD8	1,770			1,770	2670
SBHD9	1,500	1,310	1,370	1,393	1930
SBHD10	1,140			1,140	1797
SBMD1	410	1,260	1,290	987	1020
SBMD2	631			631	1180
SBMD3	456	513	539	503	770
SBMD4	779			779	1280
SBMD5	677	823	883	794	1120
SBMD6	836			836	1260
SBMD7	696	798	840	778	1160
SBMD8	466			466	690
SBMD9	537	471	494	501	923
SBMD10	342			342	870
SBLD1	200	166	171	179	600
SBLD2	166			166	530
SBLD3	139	147	154	147	560
SBLD4	245			245	630
SBLD5	173	161	165	166	570
SBLD6	217			217	670
SBLD7	324	374	393	364	680
SBLD8	193			193	650
SBLD9	264	302	315	294	670
SBLD10	294			294	650

Table A-16. Lead Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Pb (mg/kg)	C_IC_Pb (mg/kg)	C_AA_Pb (mg/kg)	Ref_Pb (mg/kg)	MDK_Pb (mg/kg)
MCHD1	391	391	417	400	340
MCHD2	582			582	660
MCHD3	384	415	452	417	370
MCHD4	312			312	380
MCHD5	520	521	556	532	470
MCHD6	484			484	330
MCHD7	355	361	388	368	400
MCHD8	376			376	440
MCHD9	388	396	423	402	1560
MCHD10	332			332	730
MCMD1	229	235	240	235	620
MCMD2	350			350	530
MCMD3	267	283	294	281	550
MCMD4	256			256	550
MCMD5	442	424	441	436	690
MCMD6	265			265	650
MCMD7	362	336	362	353	590
MCMD8	349			349	680
MCMD9	484	495	529	503	860
MCMD10	413			413	670
MCLD1	298	306	319	308	430
MCLD2	316			316	500
MCLD3	291	279	288	286	460
MCLD4	331			331	520
MCLD5	264	275	297	279	610
MCLD6	342			342	740
MCLD7	350	330	340	340	780
MCLD8	432			432	760
MCLD9	540	497	530	522	720
MCLD10	499			499	820

Table A-17. Zinc Analysis Results for MelΔok LIBS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_ZN (mg/kg)	C_IC_ZN (mg/kg)	C_AA_ZN (mg/kg)	Ref_Zn (mg/kg)	MDK_Zn (mg/kg)
SBHD1	7,410	8,590	9,340	8,447	11710
SBHD2	3,830			3,830	12640
SBHD3	6,750	6,540	7,130	6,807	11150
SBHD4	3,620			3,620	6880
SBHD5	14,800	16,600	18,000	16,467	22600
SBHD6	5,530			5,530	10970
SBHD7	5,440	5,240	5,810	5,497	10610
SBHD8	5,870			5,870	12170
SBHD9	4,710	4,510	5,000	4,740	5300
SBHD10	7,160			7,160	12230
SBMD1	1,270	2,040	2,190	1,833	1420
SBMD2	3,440			3,440	1580
SBMD3	1,410	2,810	3,040	2,420	1190
SBMD4	3,760			3,760	1980
SBMD5	4,080	3,390	3,860	3,777	1730
SBMD6	2,550			2,550	2480
SBMD7	2,810	2,640	2,950	2,800	2440
SBMD8	1,300			1,300	930
SBMD9	2,020	2,040	2,230	2,097	1175
SBMD10	1,660			1,660	2440
SBLD1	426	396	442	421	400
SBLD2	327			327	290
SBLD3	310	343	381	345	390
SBLD4	404			404	260
SBLD5	343	341	375	353	180
SBLD6	413			413	560
SBLD7	543	700	773	672	540
SBLD8	363			363	490
SBLD9	325	429	473	409	550
SBLD10	420			420	630

Table A-18. Zinc Analysis Results for MelΔok LIBS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Zn (mg/kg)	C_IC_Zn (mg/kg)	C_AA_Zn (mg/kg)	Ref_Zn (mg/kg)	MDK_Zn (mg/kg)
MCHD1	609	640	141	463	940
MCHD2	525			525	730
MCHD3	577	623	137	446	800
MCHD4	662			662	970
MCHD5	640	611	673	641	800
MCHD6	474			474	770
MCHD7	538	588	657	594	890
MCHD8	669			669	930
MCHD9	4,080	4,130	4,600	4,270	5570
MCHD10	430			430	650
MCMD1	388	417	462	422	540
MCMD2	447			447	550
MCMD3	406	441	483	443	460
MCMD4	387			387	380
MCMD5	722	686	739	716	520
MCMD6	596			596	520
MCMD7	746	671	741	719	580
MCMD8	657			657	550
MCMD9	858	887	1,000	915	680
MCMD10	698			698	670
MCLD1	437	468	517	474	670
MCLD2	543			543	740
MCLD3	587	541	586	571	660
MCLD4	529			529	540
MCLD5	591	651	727	656	660
MCLD6	687			687	710
MCLD7	755	751	805	770	700
MCLD8	642			642	850
MCLD9	654	610	668	644	740
MCLD10	994			994	830