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**Field Analytical Techniques for Mercury in Soils
Technology Evaluation**

**Topical Report
November 1994 - March 1997**

**By:
Jaroslav Solc
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RESEARCH SUMMARY

Title	Field Analytical Techniques for Mercury in Soils - Technology Evaluation
Contractor	Energy & Environmental Research Center (EERC) University of North Dakota Gas Research Institute (GRI) Contract No. 5090-253-1930 U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FC21-93MC30098
Principal Investigators	Jaroslav Šolc, John A. Harju, Ames A. Grisanti
Report Period	November 1994 - March 1997 Topical Report
Objectives	The evaluation of the four field analytical techniques for the determination of mercury concentration in soils.
Technical Perspective	Mercury detection and optimal remediation design at natural gas metering sites require fast, reliable field analytical techniques for the quantification of mercury in soils. These techniques could potentially be used in initial investigations at mercury spill sites, as guidance in site remediation activities, and during postclosure monitoring.
Results	A total of 96 discrete analyses of mercury in soil samples were performed by each of the four field and two laboratory analytical techniques. The results of analyses indicate that each of the tested field techniques is capable of providing reliable screening-level data. Because of high heterogeneity in mercury occurrence at contaminated sites, it was concluded that the sampling strategy at a specific site and sample homogenization play more critical roles in representative site characterization than does the choice of analytical technique.
Technical Approach	This report was prepared through the activities of the GRI/U.S. DOE Groundwater Research Program. Each of the evaluated field screening for mercury analyses in soils was presented with a set of 45 field samples and 3 NIST standards and their duplicates. The analyses were conducted by the developers/vendors of the respective techniques in a fixed laboratory at the EERC to ensure consistent climatic conditions and to minimize the potential for human error associated with the analyses. The performance assessment was based on the statistical comparison of accuracy and precision of each respective field method with the same parameters calculated from two laboratory techniques using standard and modified EPA Method 7471 as a common benchmark.

**Project
Implications**

This report provides quantitative data regarding the accuracy, precision, and cost of four field analytical techniques for mercury in soil. The data provide the gas industry with comprehensive information regarding the applicability and cost-effectiveness of each of these techniques at gas industry sites. The use of such techniques will expedite site assessments and remedial activities at these sites where mercury-contaminated soil exists, thereby resulting in significant cost savings.

**GRI Project Manager
James M. Evans**

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FIELD ANALYTICAL TECHNIQUES FOR MERCURY IN SOILS - TECHNOLOGY EVALUATION

EXECUTIVE SUMMARY

The issue of mercury contamination at natural gas industry metering sites has highlighted the need for analytical techniques that can both generate high-quality screening-level data and be applied in a field setting. The economic benefit of applying these techniques can be significant, when the savings resulting from minimizing the mobilization and demobilization of field crews is considered. Further, the fact that time, in and of itself, is an extremely valuable commodity, stresses the need for such techniques.

Given this need, a detailed examination of four field screening techniques for mercury in soil was undertaken. The four techniques are 1) an anodic stripping voltametry technique (ASV) developed and tested by General Electric Corporation; 2) a static headspace analysis (SHSA) technique developed and tested by Dr. Ralph Turner of Oak Ridge National Laboratory; 3) the BiMelyze® Mercury Immunoassay (Bio) developed and tested by BioNebraska, Inc.; and 4) a transportable x-ray fluorescence (XRF) instrument/technique developed and tested by Spectrace, Inc. These techniques were tested on a suite of samples consisting of 45 real-world samples collected at gas industry metering sites and three National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM). Each of the samples was presented in blind duplicate to each technique, thereby increasing the sample set to 96 samples. The same suite of samples was presented to each of two fixed laboratory techniques: EPA Method 7471 and a modified version of EPA Method 7471 developed by the Energy & Environmental Research Center (EERC) that employs larger sample sizes.

The results of the study indicate that each of the tested field techniques is capable of providing reliable screening-level data. Relatively large variation in analytical results observed in collected samples reflects the extreme heterogeneity of mercury occurrence in contaminated soils, particularly when it is primarily in the elemental form, such as at natural gas industry sites. It follows that the sampling strategy at a specific site and homogenization play more critical roles in representative site characterization than does the choice of analytical technique. As such, any technique applied, whether a field screening technique or a fixed laboratory technique, should be applied to numerous replicates of the "same" sample. The choice of a technique, for actual application, will ultimately be based on a combination of factors, including economics, precision, accuracy, detection limit, and ease of use.

FIELD ANALYTICAL TECHNIQUES FOR MERCURY IN SOILS - TECHNOLOGY EVALUATION

1.0 INTRODUCTION

1.1 Project Background

The Energy & Environmental Research Center (EERC) has been contracted by Gas Research Institute (GRI), with support from the U.S. Department of Energy (DOE) and NOVA Corporation of Alberta, to investigate gas industry sites where the soils have been contaminated in the past by elemental mercury from gas flowmeter manometers. The mercury research was an outgrowth of the Gas Industry Groundwater Research Program initiated in 1990. This long-term research program was designed to 1) identify and assess subsurface impacts related to gas industry wastes and 2) use that knowledge to provide the gas industry with the tools (for example, databases, models, characterization protocols and techniques, and remediation technologies) necessary to effectively and economically address the waste-related subsurface issues that the industry might face in the context of existing and developing regulations.

The mercury research has included a number of tasks resulting in products and publications that have benefitted the natural gas industry in dealing with mercury contamination at its sites (Charlton et al., 1994). These tasks have included 1) four workshops, 2) a literature review (Henke et al., 1993), 3) sampling and analysis (Bloom, 1994; Thompson and Hassett, 1995), 4) a computer model (HgSCREEN) for site prioritization (Walsh et al., 1994), 5) remediation review and database development (Stepan et al., 1993; Stepan et al., 1995b), and 6) testing of remediation technologies (Stepan et al., 1995a).

1.2 Rationale and Objectives

Because of the aforementioned problem at natural gas industry sites, there exists a need for fast, reliable field analytical techniques for the quantification of mercury in soils. These techniques could potentially be used in initial investigations at mercury spill sites, as guidance in site remediation activities, and for confirmation in postclosure monitoring. To date, no detailed comparison of available techniques to one another and to standard methods of analysis has been undertaken. The objective of the study described herein was to provide a statistically valid data set that defines the accuracy and precision of four analytical techniques for the quantification of mercury in soils.

Supplied as appendices are the following: Appendices A-D are supplemental materials, supplied by the vendors/developers of the techniques, that describe the general principles of the technique, as well as the methodology of their application. Appendix E contains all of the analytical results generated under the project. Appendix F presents the results of a real-world gas industry application of one of the field screening techniques examined in this project. Appendix G provides information on EPA Method 7471A.

2.0 SAMPLING AND SAMPLE PREPARATION

2.1 Sampling and Sample Packaging

Sampling was conducted at gas-metering sites in the province of Alberta, Canada, and in the state of Louisiana. Soil samples were collected at each site in three different areas: 1) in the immediate vicinity of the spills where visible elemental mercury was present, 2) in close proximity to the areas in which visible mercury was present, and 3) on the periphery of the respective sites. This allowed for a preliminary designation of the relative levels of mercury anticipated in the collected samples as either high, medium, or low, respectively. Samples were collected in clear polyethylene bags, labeled, and sealed. These bags were then placed in an additional clear polyethylene bag, sealed, labeled again, placed in a high-density polyethylene bucket with a securable lid, and labeled again. Thereby, each sample had three barriers to mercury transport either into or out of the respective samples. A total of 45 samples were collected: 15 each from areas with expected high-, medium-, and low-level mercury concentration.

2.2 Sample Homogenization

After all of the samples were collected, each sample was then homogenized by mixing at high speed in a large stainless steel commercial mixer and subsequently split into 12 subaliquots and repackaged in Class 100 250-mL wide-mouth glass sample containers. From each group of 12 subaliquots, three were randomly chosen and analyzed by a commercial laboratory using Environmental Protection Agency (EPA) Method 7471. This provided some information regarding the degree to which the samples had been homogenized. Table 1 displays the results of these analyses, as conducted under subcontract by Resource Technology Corporation (RTC). It was readily apparent that the analyses suggested that significant heterogeneity remained within some of the homogenized sample groups, primarily those with high mercury levels. This is likely a result of the inherent nature of elemental mercury existing as widely scattered droplets and beads, both within the initial sample as well as within the subaliquots. Furthermore, from the 250-mL sample jars, only 0.2-gram subaliquots were utilized in the analytical method itself. Therefore, the variability and poor analytical reproducibility in the samples were determined to be insurmountable in the absence of completely drying the individual samples and reducing them to a uniform grain size by grinding. It was decided that this would not be an appropriate step, since the likelihood of actually performing this in a field setting was minimal and the overall objective of this research was to evaluate the performance of field screening techniques on samples similar to those that would be encountered in the field.

After all of the collected samples were homogenized and packaged, National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) were acquired. Table 2 displays the NIST SRM samples acquired in conjunction with their certified mercury levels. These samples were subsequently repackaged into Class 100 250-mL wide-mouth glass sample containers, such that their identity would not be readily apparent.

From the collected samples and NIST SRM samples, six sets of 96 samples were created by assigning discrete sample numbers to the respective samples. These sets were made up of blind duplicate samples of the 45 original samples and the three NIST SRM samples.

TABLE 1

RTC Analytical Data

Sample ID	Beginning, $\mu\text{g/g}$	Middle, $\mu\text{g/g}$	End, $\mu\text{g/g}$	Mean, $\mu\text{g/g}$	Sample ID	Beginning, $\mu\text{g/g}$	Middle, $\mu\text{g/g}$	End, $\mu\text{g/g}$	Mean, $\mu\text{g/g}$
Louisiana Soils					Alberta Soils				
LL - 1	9600	12000	9000	10200	CLM 1	4100	4400	5300	4600
GL - 1	5100	3800	2600	3833	E. Cross 1	590	2700	1300	1530
MLG - 4	4400	12000	4400	6933	WD 2	590	410	280	427
DARB - 1	1000	1000	1600	1200	WR 1	550	360	560	490
OL - 1	820	1500	740	1020	BN 1	180	140	160	160
MLG - 1	740	920	540	733	WR 2	110	820	310	413
GL - 4	230	130	380	247	CLM 2	110	110	110	110
MLG - 7	170	130	210	170	CM 1	32	82	33	49
DARB - 2	47	44	55	49	AN 1	28	30	25	28
LL - 2	33	210	160	134	E. Cross 2	13	12	14	13
OL - 2	25	33	30	29	TB 1	9.00	7.70	9.20	8.60
MLG - 5	19	15	15	16	WD 1	7.1	7.1	7.2	7.1
MLG - 2	11	11	11	11	PW 1	2.20	2.00	2.20	2.10
GL - 2	1.4	1.5	0.78	1.2	CM 2	0.69	0.64	0.60	0.64
MLG - 8	0.72	0.58	0.99	0.76	WR 3	0.46	0.13	0.18	0.26
MLG - 6	0.66	0.66	0.94	0.75	CLM 3	0.26	0.27	0.19	0.24
OL - 3	0.42	0.41	0.28	0.37	AN 2	<0.11	<0.10	<0.10	<0.10
LL - 3	0.39	0.39	0.44	0.41	PW 2	<0.11	<0.098	<0.10	<0.10
DARB - 3	0.12	<0.17	1	0.43	BN 2	<0.10	<0.10	<0.098	<0.10
GL - 5	<0.11	0.24	<0.11	0.15	CM 3	<0.10	<0.10	<0.10	<0.10
MLG - 9	<0.10	0.13	<0.098	0.11	WD 3	<0.099	<0.10	<0.10	<0.10
MLG - 3	<0.099	<0.10	<0.098	<0.10					
GL - 3	<0.097	<0.10	0.13	0.11					
GL - 6	<0.097	<0.10	<0.096	<0.098					

TABLE 2

Analyzed NIST Standards	
NIST Sample	Certified Mercury Level, (mg/kg), ppm
SRM 2709	1.40 $\pm$ 0.08
SRM 2710	32.6 $\pm$ 1.8
SRM 2711	6.25 $\pm$ 0.19

3.0 FIELD SCREENING TECHNIQUES

Each of the field screening techniques was presented with a set of 96 samples as described previously. The analyses were conducted by the developers/vendors of the respective techniques in a fixed laboratory at the EERC. This ensured that climatic conditions were consistent for each respective technique and that the potential for human error associated with the analyses would be minimized, since the technique developers ran the analyses. The laboratory was equipped with an electronic analytical balance for weighing sample aliquots and a fume hood for safety. Electrical outlets were also provided. Since battery-powered electronic balances are commercially available, as well as generators for electricity, this was seen as irrelevant with regard to the demonstration of field portability. Given the aforementioned conditions, it is safe to assume that the results obtained from the respective techniques represent a best-case scenario.

The following subsections describe the general principles of the analytical techniques as tested. Detailed descriptions of the respective techniques, as received from the developers/vendors, can be found in Appendices A to D.

3.1 Static Headspace Analysis - Summary of Method

3.1.1 Method's General Principles

Static headspace analysis (SHSA) for mercury, developed at Oak Ridge National Laboratory (ORNL), is a field screening method for the rapid determination of mercury in soils. Mercury in soils is first digested (oxidized and extracted) with aqua regia, and then an aliquot of the digest is transferred to another container for chemical reduction and analysis of the mercury vapor in the sample headspace. While this method has a detection limit comparable to typical laboratory methods employing cold-vapor atomic absorption, this method is not intended to be an alternative to formal laboratory methods. However, when the method is carefully applied, it is fully capable of producing results comparable to laboratory methods. The method requires a portable mercury vapor analyzer, and the description given here assumes use of a Jerome Model 431-X mercury vapor analyzer. The Jerome Model 431-X is manufactured by Arizona Instrument Inc., Phoenix, AZ, and is widely available in the HAZMAT equipment rental market. Other portable detectors may also function satisfactorily, but this method has not been tested nor optimized for any other detector. Applications include field selection of soil/sediment samples for formal laboratory analysis, rapid field definition of the areal and depth boundaries of mercury contamination in soil, and rapid field guidance of cleanup activities, including verification sampling.

3.1.2 Procedure Summary

A 0.20-g sample of homogenized soil is extracted with 8 mL of an acid mixture, aqua regia (three parts concentrated hydrochloric acid and one part concentrated nitric acid), in a 40-mL glass bottle with a Teflon-lined silicone septum cap. The glass bottles are left loosely capped to vent any gas pressure created during digestion, which requires a minimum of 15 minutes. After dilution with deionized water, a 0.01–1.0-mL aliquot of the well-mixed extract is transferred to a 1-L polyethylene bottle containing 100 mL of deionized water. A 5-mL aliquot of a saturated (20%) stannous chloride (SnCl_2) solution is added to the sample. A square of parafilm is placed on the bottle, and the cap is pressed gently over the parafilm. The bottle is vigorously shaken manually for 1 minute. The cap is removed, and the parafilm seal is punctured using a special probe tip fitted to a portable mercury vapor analyzer (Note: after this project, the method was modified such that the parafilm was only used after shaking). As tested, two or more successive samples of the headspace gas were taken with the analyzer and the results recorded, although currently the method has been modified such that only one sample is drawn.

Quantitative results can be obtained in the range of 0.1–14 $\mu\text{g/L}$ in the diluted extract. The method detection limit for soil depends largely on the extract aliquot size transferred for reduction and analysis. For example, the method detection limit for a 0.2-gram soil sample, with a total extract volume of 23 mL (acid and diluent) and a transferred extract volume of 1.0 mL, would be approximately 1 $\mu\text{g/g}$. Lower detection limits for soil can obviously be achieved by digesting larger samples and/or by increasing the extract aliquot volume transferred for analysis. Use of the smallest aliquot size transferred (e.g., 0.01 mL) or additional extract dilution can bring even very high mercury concentrations in soil extracts within the operating range of the method. See Kriger and Turner (1995) for additional information about method development.

3.2 Anodic Stripping Voltametry – Summary of Method

3.2.1 Method's General Principles

The method developed and performed by Corporate Research and Development of the General Electric Company is based on the selective removal of mercury species from solid substrates into a KI/I_2 extracting solution followed by anodic stripping electroanalysis. The stripping current and charge have been found to be linear with Hg concentration. Oxygen present in solution has essentially no influence on the electroanalysis, which thus eliminates the time-consuming solution deoxygenation procedure and the need for carrying an inert gas cylinder to the field. Small variation in iodine and iodide concentrations due to various degrees of KI/I_2 consumption by different substrates has practically no effect on the stripping results. The method possesses a great selectivity to Hg, and no interference from other heavy metals such as Cd, Pb, Fe, and Cu has been observed. The method's sensitivity increases with increasing electrodeposition time. A detection limit of 20 ppt has been achieved with a 10-minute deposition time. Application of this method has also been extended to simultaneous detection of other metals. The electroanalytical results for real-world samples contaminated with a wide range of Hg concentration in a variety of substrates agree well with the analytical results based on a modified EPA atomic absorption method. Furthermore, this electroanalytical probe is not only very useful for rapid field screening and on-site remediation analysis, but also for manufacturing process on-line monitoring and medical diagnosis for numerous heavy metals.

3.2.2 Procedure Summary

The method is based on computer-controlled anodic stripping voltametry (ASV) assisted by KI/I₂ oxidative extraction. Different mercury species existing in an aqueous solution or a solid substrate are first converted into a mercuric iodide complex (HgI₄²⁻) by reacting with the KI/I₂ extraction solution. The HgI₄²⁻ complex is subsequently electrochemically reduced and accumulated at the electrode surface as elemental Hg, which is finally oxidized off the electrode surface by ASV. The electroanalysis takes place in a diluted KI/I₂ extraction solution; thus no solution medium exchange is needed. Furthermore, the strong adsorption of iodide and iodine at the Au electrode surface guarantees a reproducible electrode surface for Hg analysis in the solutions extracted from various substrates. Detecting sub-ppb levels of Hg in an aqueous medium requires essentially no sample preparation and takes about 1 minute. Detection of Hg in solid matrices takes about 15 minutes and requires only one-step extraction before electroanalysis. A 1.0-gram soil sample was used in the extraction and analysis chain of this study. No interference from other heavy metals such as Cd, Pb, Fe, and Cu has been observed. The method's sensitivity increases with increasing electrodeposition time. A detection limit of 20 ppt in aqueous media has been achieved with a 10-minute deposition time.

3.3 BiMelyze® Mercury Immunoassay Analysis – Summary of Method

3.3.1 Method's General Principles

The BiMelyze® mercury immunoassay (Bio) is manufactured by BioNebraska, Inc. Enzyme-linked immunosorbent assays (ELISA) are based on highly specific interactions of antibodies with specific analytes. ELISA technology has been adapted in the last 10 years to detect contaminants in environmental matrices, with current environmental immunoassays on the market detecting numerous analytes (e.g., heavy metals, such as mercury, and organics such as polychlorinated biphenyls [PCBs]). The BiMelyze® mercury immunoassay is an ELISA-based test for mercury in environmental matrices using mercuric ion monoclonal antibodies (patent pending). The field-portable tube assay format allows analysis of up to 13 samples and three controls in approximately 1.25 hours. BioNebraska also markets the same assay in a 96-well plate assay for quantitative measurements of numerous samples in a laboratory setting. Two positive controls, generally at 5 and 15 ppm mercury, and a negative control are supplied with the extraction kit. Standards at other concentrations can be supplied to meet the end user's requirements or action levels. The standards and unknowns are extracted and analyzed at the same time for semiquantitative mercury determination. The lower limit of quantitation for the assay is 0.5 ppm in soils and 0.25 ppb for aqueous samples.

3.3.2 Procedure Summary

The operator/analyst labels the soil sample bottles with identification numbers and places 5 g of soil into the corresponding bottles. Hydrochloric acid and nitric acid are added to the water in the supplied acid mixture bottle (final dilution of 2:1:1). The contents are mixed, and 4 mL of the acid solution are added to each of the samples and controls. The soil samples and controls are vigorously swirled at least 15 seconds of each minute during the 10-minute extraction. Glass beads enclosed in the bottles aid in sample dispersion and extraction.

After extraction, 7 mL of sample buffer are added to each of the acidic soil sample bottles; the samples are swirled to mix the contents and then filtered using supplied filter tips. Three drops (0.105 mL if using pipettes) of the filtered extract solution are added to the supplied dilution bottles containing the 35-mL dilution buffer. The large dilution is necessary to adjust the extract solution to pH 7 and to dilute the mercury concentration into the assay working range.

Samples and standards are added to tubes labeled with identification numbers. Quantitative additions are accomplished by dropper bottles up to a fill line or, alternatively, using pipettes capable of measuring 0.5 mL. The samples are incubated at ambient temperature for 5 min, then emptied, and the tubes rinsed three times with distilled water. Next is the addition of 0.5 mL of monoclonal antibody solution to the tubes. The antibody is supplied as a lyophilized powder and dissolved into antibody diluent prior to use. After the 5-minute antibody incubation, the tubes are emptied and washed three times with a detergent solution, then rinsed three times with distilled water. The third 5-minute step is the addition of Conjugate, a secondary, horseradish peroxidase complexed antibody that binds to the mercury antibodies. The tubes are emptied, detergent-washed three times, and distilled-water-rinsed three times. The final step is the addition of substrate which is oxidized by the horseradish peroxidase complexed antibody, turning the liquid from colorless to a blue-green. The resulting color intensity is dependent on the mercury concentration in the original sample. After the 5-minute incubation, color development is terminated by three drops of stop solution added to each tube. The tubes are swirled at least once during each of the incubations and after the addition of the stop solution to facilitate thorough mixing.

3.4 Transportable Energy-Dispersive X-Ray Fluorescence Spectrometry – Summary of Method

3.4.1 Method's General Principles

The Spectrace 6000 was used by TN Spectrace Company in a study to determine the effectiveness of energy-dispersive x-ray fluorescence spectrometry for the analysis of mercury in soil. The Spectrace 6000 uses an x-ray tube for sample excitation. The x-ray tube is an evacuated glass envelope containing a filament and a pure metal anode which is typically rhodium. The tube voltage and current are automatically controlled through the software to produce the necessary x-rays to excite elements in a sample. The x-rays produced in the tube radiate towards the sample through a window that is sealed with beryllium. These x-ray photons from the tube are passed through a primary radiation filter for the purpose of optimizing the incident x-ray beam. The x-rays then strike the sample and excite elements by photoejecting an inner orbital electron. Once an element has a vacancy in an inner orbital electron shell, this element is in an excited state. In order to return to the ground state, an electron from an outer orbital shell undergoes electron shell transfer to fill the vacancy. This transition will emit an x-ray photon that is characteristic of the element. Common emission lines are termed K_{α} , K_{β} , L_{α} , and L_{β} . For the analysis of mercury, the spectrometer will detect the L_{α} and L_{β} of mercury at 9.987 and 11.823 keV, respectively. Upon excitation, these x-rays are emitted in all directions from the sample.

The detector sits at 45° from the sample (90° from the x-ray tube) to detect the elemental fluorescence from the sample. The x-ray detector is an electrically cooled semiconductor made of lithium-drifted silicon or Si(Li). When an x-ray photon enters the detector region, its energy is dissipated into the semiconductor region by creating electron hole pairs. The number of the electron

hole pairs is proportional to the energy of that x-ray photon. This charge is swept off of the detector region by a voltage bias across the detector region. This signal is amplified and converted to a digital energy value which is then assigned to a channel on a 2048-channel multichannel analyzer. That x-ray photon is now considered one count in the assigned energy channel.

Spectral data are transferred to the interfaced personal computer (PC) for spectrum acquisition. A spectrum of x-ray photon counts is acquired which results in a histogram containing element peaks. Once the spectrum has been acquired from a sample, the PC software is responsible for data processing. The element peaks are integrated by the software to obtain counts-per-second data for each element of interest in the sample. Element intensities (counts/sec) are compared to those of known standards to calculate results for the unknown sample. A Fundamental Parameters algorithm was used to calculate mercury results on the Spectrace 6000.

3.4.2 Procedure Summary

The following steps were taken to perform the procedure:

1. Prior to analysis, approximately 10 grams of each moist sample was placed into a dish and set in a fume hood for a few hours to air-dry. This method of drying was chosen to prevent or minimize the volatilization of Hg.
2. The dried sample was then placed into a grinding vessel and pulverized in a shattermill for 1 minute. This reduced the particle size of the soil to around 100 mesh.
3. The sample was then put into a standard 32-mm x-ray fluorescence sample cup ($\frac{1}{2}$ to $\frac{3}{4}$ full) and sealed on the open end with Mylar (6.0 mm) x-ray transparent material.
4. The sample cup was then placed into the sample chamber of the Spectrace 6000 for a 10-minute measurement.
5. While the previous sample was running, the grinding vessel was washed, and Steps 3, 4, and 5 were repeated until all samples were analyzed.

3.5 Nonquantitative Screening Technique Summary

A commonly employed screening technique, capable of providing a quick indication of the presence of elemental mercury, can be used to guide initial on-site activities. The method, which employs the Jerome 431-X mercury vapor analyzer, is not capable of generating quantitative data on mercury soil concentrations but is nonetheless valuable in certain applications and sees widespread industry use. In this approach, a soil sample is collected in a jar or plastic bag and heated to a minimum of 85°F for 5 minutes. The mercury vapor analyzer is then inserted into the heated container. If the result is above a certain value (typically between 0.01 and 0.015 mg/m³), the sample is considered contaminated with elemental mercury above regulatory guidelines. Conversely, if the result is below the chosen value, the sample is considered clean, and a more detailed analytical technique, such as those described previously, or a fixed laboratory technique is employed to provide confirmation of that conclusion.

This type of screening process results in a simple pass/fail determination, with the vapor analyzer trigger value chosen based on a consideration of the cleanup level and the instrument's response to mercury concentrations at or near that level. Experience suggests that this technique may provide screening level data that is very useful, provided that all, or nearly all, of the mercury present in the sample is in the elemental form. This is typically the case at gas industry sites.

4.0 LABORATORY TECHNIQUES

4.1 Sample Analysis by Fixed Laboratory Techniques

Two fixed laboratory techniques were utilized for the analyses of equivalent sample sets as previously described: EPA Method 7471 performed by GP Environmental, Inc., and an internal EERC Analytical Research Laboratory method. EPA Method 7471 was utilized since it provides a common benchmark for the comparison of each of the field screening techniques, as well as the other fixed laboratory technique. The internal EERC Analytical Research Laboratory method was utilized since it employs larger sample sizes than EPA Method 7471, which could theoretically overcome some of the analytical variability associated with subsample heterogeneity.

4.2 EPA Method 7471

The complete methodology of EPA Method 7471 can be found in Appendix G.

4.3 EERC Analytical Research Laboratory Method (Modified EPA Method 7471)

Two representative aliquots (1 g each) are extracted with 10 mL of hot (95°C) aqua regia (hydrochloric and nitric acids in a 3:1 ratio) for 3 hours. Following the extraction, a known amount of the liquid is filtered and diluted with a known amount of distilled, deionized water and analyzed using the cold-vapor atomic absorption spectrometry technique, as in EPA Method 7471. If a significant discrepancy appears between the duplicate samples, the extraction is repeated with a 5-g sample and 50 mL of aqua regia. In cases where duplicate discrepancy persists, an extraction from a 10-g sample in 100 mL of aqua regia is deemed necessary.

5.0 RESULTS AND DISCUSSION

5.1 Concept of Data Processing

The project database consists of 576 mercury analyses in soils performed using each of the four targeted field screening methods, two fixed laboratory techniques, plus 75 control analyses during sample homogenization performed under subcontract by RTC Laboratory (Table 1). Forty-five samples and their duplicates from soils and three duplicate samples of SRMs from NIST made up the total of 96 samples analyzed using each method. The originally designated sample groups based on expected high-, medium-, and low-level mercury concentrations prior to analytical work were revised, and the resulting values were regrouped into three concentration subgroups to assess both overall performance of respective techniques and their sensitivity within specific concentration ranges. The selected arbitrary limits are 20 and 260 mg/kg. The lower limit reflects a

U.S. EPA proposed action level (55 FR 30798 from July 26, 1990) for total mercury in soil above which a material would have to be treated before disposal and a commonly applied state cleanup standard. The 260-mg/kg total mercury limit reflects the U.S. EPA Land Disposal Restrictions (LDR) limit for hazardous waste. Under the LDR, D009 and U151 hazardous wastes below this limit must be treated to reduce leachability before disposal. If the grab sample contains more than 260 mg/kg total mercury, the soil or sediment must be treated by the best demonstrated available technology (BDAT) (Henke et al., 1993). Thereby, the three concentration groups are as follows: less than 20 mg/kg, 20–260 mg/kg, and greater than 260 mg/kg. The SRMs from NIST form a separate (fourth) group.

The performance assessment of each respective analytical technique was based on an evaluation of accuracy and precision as relative comparative criteria. The results described in Sections 5.2 and 5.3 tend to rank some evaluated methods as being superior to the others. It is important, however, to realize that even though an effort was made to achieve the most objective interpretations, the results have to be understood in the context of relevant factors such as 1) the nature of elemental mercury resulting in residual heterogeneity even after the best effort has been made to homogenize samples, 2) variability of analytical sensitivity within the specific concentration ranges resulting in some methods yielding better results in low-concentration samples and vice versa, and 3) sensitivity of statistical computation and probability distribution parameters to the number of samples in groups.

To minimize possible errors, three computational procedures have been used. The first method employs common statistical formulas and probability distribution parameter t to obtain results within a 90% confidence interval; the second method is basically common sense calculations of plus and minus differences from either an NIST standard (accuracy) or a duplicate mean (precision). Regression analysis has been used to confirm general trends and interrelationships within data sets. It is important to note that the totals used in the tables do not represent the average of values given in the tables, but always represent the value of the total that has been calculated from the originally reported sets of data.

The results of immunoassay analysis performed by BioNebraska, Inc., are reported in semiquantitative form and, as such, cannot be processed by traditional computational methods. Semiquantitative data are compared with standards for accuracy and with each other for precision on a yes or no basis—if the compared value is within the correct interval (accuracy) or the intervals are the same (precision) indicating correct analysis, then the answer is yes and vice versa. Simple counts of correct and incorrect analyses then translate to a quantitative representation expressed in percent. Any comparison with quantitative analysis, however, has only informative character.

Finally, a third means employed in evaluating the data was to group the soils into concentration ranges and then to simply categorize the frequency with which each technique reported the concentration to be in that respective interval.

Quantification of mercury in soils is also sensitive to the moisture content of the soils. In EPA Method 7471, it is stated that moisture may be driven off in a drying oven at 60°C. The results of EPA Method 7471 are reported on a dry weight basis. The field screening methods did not employ this method. The SHSA technique was performed on undried samples, but gravimetric moisture analyses were undertaken by weighing an aliquot of each sample, air-drying these

samples, weighing again, calculating a percent moisture based on those measurements, and subsequently correcting the analysis for reporting on a dry weight basis. The transportable x-ray fluorescence technique air-dried samples prior to analysis. The ASV technique was performed on undried samples, as was the BioNebraska technique. Simple logic dictates that significant error in these analyses may be associated with variations in the moisture content of the samples. However, the application and utility of field screening techniques dictate that they may often be conducted on samples that have not been previously dried for analysis.

The ASV technique was unable to quantify the concentration of mercury in seven of the 96 samples provided for analysis. This was likely due to an unspecified analytical interference. In all computational approaches to data analysis, these data points were not considered, with the exception of those approaches examining the percent correctly reported in discrete concentration groups, where a not-reported value was considered as a failure. All of the other techniques reported values for all of the 96 samples. However, many resultant data from analyses from each of the techniques were reported as being less than a particular concentration or sometimes as nondetects. These data were not considered in computations of accuracy and precision but were considered in the more qualitative approach examining percent samples correctly reported.

Each of the tested techniques has its own respective detection limit, which ultimately skews any direct comparison of the individual results. The approximate detection limit for each technique can be found in Table 3.

TABLE 3

Technique	Approximate Detection Limits
	Approximate Detection Limit, mg/kg
SHSA	0.05
ASV	0.5
Bio	0.5
XRF	5.0

5.2 Accuracy

Accuracy is a quantitative and qualitative measure of the ability of the laboratory/field analytical technique to correctly report the actual concentration of the sample. The performance of each method was evaluated versus NIST SRM, summarized in Table 2, followed by accuracy calculations for collected field samples using the results of EPA Method 7471 as provided by the GP Environmental laboratory as an internal arbitrary standard because of its designation by EPA as the standard method.

The analytical performance versus three duplicate NIST standards was evaluated using the ASTM D5314 formula and calculated at the 90% confidence level. The results summarized in Table 4 and Figure 1 can be interpreted as relative comparable criteria. The low number of analyzed NIST standards and, consequently, the applied high probability distribution parameter

result in a relatively high range of uncertainty (accuracy, $\pm R$). This factor, however, is equally valid for each analytical method and, unlike missing or incorrect analysis, does not represent an inherent disadvantage for any respective method. Lines three and four of Table 4 summarize the simply computed average of $\pm$ differences as an absolute (mg/kg) or relative (%) error from NIST standards. The error expressed in percents, however, has to be always interpreted in the context of other reported values, because even minimal absolute errors in mg/kg can translate into large relative errors when expressed in percent, if calculated from values in the low mercury concentration group. The same is valid for the data in Table 5. The values representing the range of uncertainty for analyses performed by BioNebraska, Inc. (Table 4), have in all tables and graphs only informative character, as discussed in Section 5.1. It also deserves mention that the NIST SRM samples contain relatively low Hg concentrations, thus limiting the overall range of accuracy assessment.

TABLE 4

	Accuracy Versus NIST Standards					
	SHSA	ASV	XRF	Modified 7471	Method 7471	Bio
SD from NIST	0.94	7.27	5.73	0.87	0.37	
$\pm R$	1.3	11.1	6.8	1.6	0.6	
Average Absolute Difference, mg/kg	1.33	10.36	8.11	1.24	0.53	
Average Absolute Difference, %	28.61	71.49	73.29	15.54	4.29	66.66

Figure 1. Accuracy versus NIST standards.

TABLE 5

Accuracy Versus GP Analyses ($\pm$ percent) - EPA 7471					
	SHSA	ASV	XRF	Mod. 7471	Bio
> 260	74.9	72.2	38.7	39.4	43.0
20-260	48.4	81.6	53.4	60.6	62.0
< 20	206.7	99.0	145.1	50.9	28.0
Total Mean	145.1	75.3	89.4	44.9	
Absolute Total	147.4	89.4	103.2	49.6	38.0

EPA Method 7471 analyses, as performed by GP Environmental Laboratory, were used as an internal standard for the evaluation of the accuracy of field analytical techniques and the modified version of EPA Method 7471, as performed by the EERC. The resulting values representing average $\pm$ difference (range of uncertainty), in percent, are summarized in Table 5 and Figure 2. The values for concentration ranges represent the average of differences between EPA Method 7471 duplicate (blind) mean and the mean of blind duplicate analyses of each respective method. Similarly, total mean represents the average of compared means from all duplicate analyses performed by each respective method, including the analyses of NIST standards. Absolute total represents the average $\pm$ difference in percent between absolute values reported by the respective field method and absolute values reported by EPA Method 7471. Extremely high values in the range of <20 mg/kg result from the disproportionately high contribution of values from the low concentration end (<20 mg/kg) to overall error when expressed in percent, even though their absolute differences expressed in mg/kg are relatively negligible. For example, a 0.25-mg/kg absolute difference from a 0.5-mg/kg concentration in a measured standard value

Figure 2. Accuracy versus GP analyses (EPA 7471).

yields 50% error, while an absolute difference of 100 mg/kg yields only 20% error compared to a 500-mg/kg concentration in an analyzed standard.

Extremely high values of uncertainty (accuracy, $\pm R$) for field analytical techniques and even the EERC's modified 7471 method likely reflect high residual heterogeneity within the soil samples. It is extremely important to refer to the precision achieved by EPA Method 7471 itself and calculated by the analogous mathematical method reported in Table 8. The EPA Method 7471 precision expressed as an average error in Table 8 ranges from 3.5% for NIST standards up to 33.5% in the concentration group > 260 mg/kg, with an average error of 21.7%. It is obvious that even under laboratory conditions utilizing a standard EPA method, the precision interval for mercury in soils is extremely wide, and as such, the standard method does not necessarily represent the most accurate value.

Even though regression analysis cannot provide information on accuracy per se (due to the impossibility of reporting the absolute error of the measurements), the values of correlation coefficients in Table 6 can represent a relationship of both compared duplicate means and absolute analytical values versus EPA Method 7471 results. It follows from Table 6 and Figure 3 that values of correlation coefficient are independent of accuracy values calculated in Table 5 and could be possibly used to track problems, such as calibration, resulting in a systematic error of measurements.

TABLE 6

Regression Analysis as a Parameter of Accuracy				
	SHSA	ASV	XRF	Mod. 7471
EPA 7471 (GP) r-means	0.5120	0.9219	0.8224	0.9429
EPA 7471 (GP) all	0.6941	0.8782	0.7632	0.8363

5.3 Precision

Precision, as the ability of the laboratory/field technique to reproduce results, is determined by submitting blind duplicate samples from the same source. Precision, as a criteria of the performance of respective field and laboratory analytical techniques, is reported as $\pm$ range in percent using ASTM D5314 formulas at the 90% confidence level and as an average error in percent, represents the oscillation of reported duplicates around their mean. The results are summarized in Tables 7 and 8 and Figures 4 and 5.

TABLE 7

	Precision, %				Total
	> 260	20-260	< 20	NIST	
EPA 7471	28.0	19.7	4.0	15.3	7.7
SHSA	30.8	23.7	3.9	17.5	7.9
ASV	12.3	20.4	5.8	438.0	9.8
XRF	6.1	9.6	7.9	*	8.3
Mod. 7471	11.2	12.4	3.3	52.6	5.0

Figure 3. Regression analysis as a parameter of accuracy.

TABLE 8

	Average Error (%) as a Measure of Precision			NIST	Total
	> 260	20-260	< 20		
EPA 7471	33.5	17.0	19.8	3.5	21.7
SHSA	34.5	20.5	19.2	4.0	22.0
ASV	20.8	17.6	36.0	100.0	33.1
XRF	15.5	8.3	38.5	66.7	30.1
Mod. 7471	13.4	10.7	16.0	12.0	14.2
Bio	66.0	25.0	63.0	40.0	40.0

Relatively high precision values for NIST standards reflect the same problem already described in Section 5.1, wherein the low number of analyzed NIST standards (only three pairs of duplicates) results in use of a high probability distribution parameter yielding a relatively high $\pm$ precision range. Again, the same formula is applied for each analytical method and does not represent any inherent disadvantage. Precision calculated for such a small number of duplicate pairs is more reasonably expressed by simple average error reflecting $\pm$ range from the duplicate mean (Table 8). This common sense approach eliminates disproportionality resulting from application of distribution parameter t for less than 5 degrees of freedom, i.e., less than six pairs of duplicates.

Figure 4. Precision as $\pm$ range in percent.

Figure 5. Average absolute error as the measure of precision.

Figure 6. Regression analysis as the parameter of precision.

Relatively high values in the <20-mg/kg concentration group in Table 8 reflect the similar disproportionality discussed previously in Section 5.2. The minute differences in absolute scale translate to a significant contribution to overall error when expressed in percent. The precision values calculated in concentration groups 20–260 and >260 mg/kg in Table 7 compare favorably with the average error calculated in Table 8. Values for BioNebraska are informative only and were obtained by interpretation of semiquantitative data, as described in Section 5.1.

Regression analysis was used to approach the tightness of relationship between pairs of duplicates. Correlation coefficients in Table 9 and Figure 6 generally support the results obtained by previously described methods.

TABLE 9

Regression Analysis as the Parameter of Precision					
Correlation	EPA 7471	SHSA	ASV	XRF	Mod. 7471
>260	0.82	0.66	0.96	0.98	0.99
20–260	0.71	0.66	0.74	0.94	0.92
<20	0.97	0.95	0.97	0.69	0.96
r-total	0.88	0.79	0.97	0.99	0.99

5.4 Semiquantitative Analysis

In an effort to provide a common benchmark for the comparison of each technique to EPA Method 7471, in terms that are the most meaningful to someone faced with the decision of choosing a technique for application, an examination of the frequency with which each of the techniques would correctly identify a sample within a particular concentration group was undertaken. The previously selected concentration groups were utilized. Figure 7 displays the results of this examination. In an effort to elucidate the sensitivity of this type of data analysis, an additional examination, with the randomly selected concentration groups 0-40, 10-300, and > 300 mg/kg, was undertaken. The results of that analysis are represented in Figure 8. It follows that there is indeed some sensitivity based on the arbitrary selection of concentration groups. In other words, the choice of concentration groups will obviously affect the results of such comparison.

5.5 Discussion

The results of the performance evaluation of mercury field screening techniques in the framework of this unique project confirmed the profound influence of critical variables already described in Section 5.1. In spite of the maximum effort that was made to homogenize samples, the residual heterogeneity resulted in highly variable concentrations analyzed in contaminated soils and, consequently, in the relatively wide ranges of calculated values of accuracy and precision for both respective sample groups and analytical methods. In terms of the project goals, however, the results are within expectations. Extremely well-homogenized NIST standard samples were analyzed with expected high accuracy and precision by laboratory techniques, as well as some of the field screening methods. This ideal situation, however, is practically not achievable under field conditions, where time and field equipment do not allow for laborious sample preparation and homogenization. It follows from the results that numerous measurements of the same sample will greatly reduce possible errors and will minimize the impact of randomly occurring extremes. Fast and relatively cheap field methods which are frequently calibrated by analyzing samples of known concentration within specific ranges will provide reliable data that are extremely useful in the field.

Computational methods and specific problems encountered in the determination of the accuracy and precision of samples with low mercury concentrations, or limited number of duplicate pairs, are described in detail in the respective sections. The 10% level of significance (90% confidence level) selected for certain calculations is generally used for soil gas monitoring in the vadose zone (ASTM D5314). With regard to the specific nature of mercury occurrence in soils, a lower confidence level might seem to yield better statistical results. A careful analysis of distribution parameters (Davis, 1986), however, indicates that this would generally apply only to calculations with an extremely small number of samples, which may frequently be considered not representative. Simple calculations based on $\pm$ range from either standard or duplicate means yield reliable results; however, only careful, common sense interpretations based on targeted concentration ranges can eliminate disproportionalities associated with the analyzed low concentrations described in Sections 5.2 and 5.3.

Figure 7. Semiquantitative comparison, <20, 20-260, and >260 mg/kg.

Figure 8. Semiquantitative comparison, randomly selected concentration groups (in mg/kg).

6.0 ECONOMIC AND OTHER CRITERIA

In order to facilitate the decision-making process of an ultimate user of these analytical techniques, the following information is provided. It is important to note that these data are subject to periodic revision by the developers of the respective technologies and that leases, rentals, or even subcontracted services may be arranged. Therefore, the only utility of this information is for quick economic comparisons of the techniques. Table 10 highlights the approximate cost of the capital investment and incremental cost per analysis for each field technique.

TABLE 10

Capital Investment and Cost per Analysis		
	Capital Investment (purchase)	Incremental Cost
SHSA	~\$6000	~\$1.50
ASV	~\$15,000	~\$1.50
XRF	~\$60,000	~\$0.50
Bio	~\$1000	~\$25.00

Direct economic comparisons require that a specific number of sites and/or samples be specified. If, for example, ten field screening analyses were required at 100 sites, resulting in 1000 analyses, the following cost per analysis can be computed (see Table 11).

TABLE 11

Economic Criteria			
	1000	5000	10,000
SHSA	\$7.50	\$2.70	\$2.10
ASV	\$16.50	\$4.50	\$3.00
XRF	\$60.50	\$12.50	\$6.50
Bio	\$26.00	\$25.20	\$25.10

It must be noted that, in the above comparisons, no salvage value for any of the equipment required for the tests is calculated. For instance, if we assume that 50% of the capital costs of the equipment can be recovered for each of the respective techniques, then Table 12 can be generated.

TABLE 12

Economic Criteria with 50% Capital Salvage Value			
	1000	5000	10,000
SHSA	\$4.50	\$2.10	\$1.80
ASV	\$9.00	\$3.00	\$2.25
XRF	\$35.00	\$6.50	\$3.50
Bio	\$25.50	\$25.10	\$25.05

With respect to the aforementioned economic data, it should be noted that neither the SHSA, as demonstrated by ORNL, nor the ASV system, as provided by GE, is commercially available as a turnkey system at this time. The XRF and ASV systems possess significantly greater analytical capabilities (detection of a wider variety of metals) than the other systems; thereby, the capital expenditures may be spread over other analytical applications that a company may have. However, the material provided in the appendices of this report will be sufficient for the configuration of such systems from readily available equipment. It also deserves mention that these economic projections assume that the analyst or field technician has previous experience with the respective technique (see section 6.3). Please note that these projections have only attempted to address the initial capital cost and the cost of expendable/consumable items (plastic bottles, acids, etc.) associated with the application of each technique; no labor costs have been included. Another factor that is not considered is that of secondary waste disposal (e.g., unused sample digests). All of these factors need to be addressed before a detailed economic analysis could ultimately be made by a potential end user.

6.1 Other Considerations

Each of the field analytical techniques discussed in this report, with the exception of the field-transportable XRF technique, employs a digestion/extraction step. The SHSA and BiMelyze® digestion/extraction step utilize aqua regia, which is an extremely corrosive acid. It is imperative that significant precautions be undertaken in handling aqua regia in the field; in particular, disposable gloves and safety glasses must be used. In addition, these acids should only be used outside, with careful attention paid to wind direction so as to avoid fumes, or in a laboratory fume hood. The ASV technique utilizes a KI/I₂ extraction solution, which eliminates the previous concerns specific to acids.

6.2 Ease of Use

A subjective analysis of the degree of difficulty in applying these techniques, based on observations of each technique's application by the authors of this report, suggests that the XRF technique is by far the easiest technique to use, primarily because of the minimal sample preparation it requires. The other three techniques all require rather laborious sample preparation and, as such, are considered to be about equally difficult to apply. However, since the BioNebraska BiMelyze® method is marketed in kits, with prelabeled containers, direction booklets, etc., it follows that it is slightly easier to use than are the ASV and SHSA techniques.

6.3 Time

Time is a significant consideration when choosing one of these techniques, i.e., both analytical time and necessary staff training time prior to conducting the analyses. From the previous section (6.2), it also follows that the training time, here expressed solely as the author's opinions, is as follows: XRF < BioNebraska BiMelyze® < SHSA < ASV.

7.0 CONCLUSIONS

A total of 96 discrete analyses of mercury in soil samples were performed by each of the four field and two laboratory analytical techniques. The results of analyses indicate that each of the tested field techniques is capable of providing reliable screening-level data.

Relatively large variation in analytical results observed in collected samples from Louisiana and Alberta indicates that even when significant efforts are undertaken to homogenize actual field samples, significant heterogeneity within those samples will likely exist. Sample heterogeneity generally reflects either 1) insufficient analytical size (variation within the sample) or 2) the site heterogeneity (variation between samples), which is typical for mercury occurrence. The effect of small analytical size can be reduced by incorporating larger aliquots into the analytical technique or better homogenization. The variation reflecting site heterogeneity can be reduced either by analyzing more samples across the site or employing significantly larger, well homogenized samples and subsequent resampling to subaliquots. It follows that the sampling strategy at a specific site and homogenization play a more critical role in representative site characterization than does the choice of analytical technique.

The application of these techniques in a field setting promises the potential for significant economic benefits, when the cost savings resulting from periodic mobilization/demobilization of field crews is considered. Further, the simple fact that time, in and of itself, is a very valuable commodity stresses the utility of these techniques. Their use in a field campaign designed to either delineate an area for excavation, or to confirm that the desired materials have been excavated, should employ multiple analyses of well homogenized soil samples to account for the previously discussed issue of heterogeneity. This holds true for both the field screening and fixed laboratory techniques. Such an approach will logically produce more representative data on the respective environmental setting and provide critical information prior to and during remedial action decisions.

8.0 REFERENCES

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APPENDIX A1

STATIC HEADSPACE ANALYSIS FOR MERCURY IN SOILS (DEVELOPED AT OAK RIDGE NATIONAL LABORATORY)

Static Headspace Analysis for Mercury in Soils (Developed at Oak Ridge National Laboratory)[Revision 1.1, 10/22/95]

1.0 Scope and Application

This is a field screening method for the rapid determination of mercury concentration in soils. Soil samples are first digested (oxidized and extracted) with aqua regia and then an aliquot of the digest is transferred to another container for chemical reduction and analysis of the mercury vapor in the sample headspace. While this method has a detection limit comparable to typical laboratory methods employing cold vapor atomic absorption, it is not intended to be an alternate to formal laboratory methods. However, when carefully applied the method is fully capable of producing results comparable to laboratory methods. The method requires a portable mercury vapor analyzer and the description given here assumes use of a Jerome Model 431-X Mercury Vapor Analyzer (manufactured by Arizona Instrument Inc., Phoenix, AZ, and widely available in the hazmat equipment rental market). Other portable detectors may also function satisfactorily but this method has not been tested nor optimized for any other detector. Applications include field selection of soil/sediment samples for formal laboratory analysis, rapid field definition of the areal and depth boundaries of mercury contamination in soil, and rapid field guidance of cleanup activities, including verification sampling.

2.0 Summary of Method

A 0.20- to 0.40-g sample of homogenized soil is extracted with 8 mL of an acid mixture, aqua regia (three parts concentrated hydrochloric acid and one part concentrated nitric acid) in a 40-mL glass bottle with Teflon-lined silicone septum cap. The glass bottles are left loosely capped to vent any gas pressure created during digestion (which requires a minimum of 15 min). A 0.01- mL to 1.0-mL aliquot of the well-mixed diluted extract is transferred to a 1-L polyethylene bottle containing 100 mL of deionized water. A 5-mL aliquot of a saturated stannous chloride (SnCl_2) solution is added to the sample. The bottle is capped and vigorously shaken manually for 1 min. The cap is removed and a square of parafilm is quickly stretched over the bottle opening. The parafilm seal is punctured using a special probe tip fitted to a portable mercury vapor analyzer. A sample of the headspace gas is taken with a mercury vapor analyzer and the results recorded.

Quantitative results can be obtained in the range of 0.1 to 14 $\mu\text{g/L}$ in the diluted extract. Method detection limit for soil depends largely on the extract aliquot size transferred for reduction and analysis. For example, the method detection limit for a 0.2-gram soil sample, with a total extract volume of 23 mL and a transferred extract volume of 1.0 mL, would be approximately 1 $\mu\text{g/g}$. Lower detection limits for soil

can be achieved by digesting larger samples and/or by increasing the extract aliquot volume transferred for analysis. Use of the smallest aliquot size transferred (e.g., 0.01 mL) or extract dilution can bring even very high mercury concentrations in soil extracts within the operating range of the method. See Kriger and Turner (1995) for additional information about method development.

3.0 Interferences

This method is relatively free of interferences due to separation of mercury from other non-volatile constituents of soil and the high selectivity of the Jerome mercury vapor analyzer. However, there are some potential interferants. Iodine compounds (iodides, iodates) are known to suppress the reduction of mercury by stannous chloride (reference). Fortunately, soils do not ordinarily contain enough iodide to cause any detectable interference. Free halogens, especially iodine and bromine, are not always effectively removed by the soda lime traps and may cause a positive response on the analyzer. While the addition of SnCl_2 , in great excess beyond that necessary to reduce mercury, is intended to assure complete reduction of any free halogens, on rare occasions these may survive in the sample headspace if samples are not adequately shaken. Halogen interference is typically characterized by inability to obtain a zero instrument reading (i.e., $<0.001 \text{ mg/m}^3$) in ambient air. Regeneration of the gold film at this point restores ability to zero and thus proper function. Although unlikely to be encountered in the highly acidic soil digests, unionized ammonia will also cause a false positive reading on the Jerome mercury vapor analyzer. If ambient air in the work area contains ammonia the only recourse is to move to another area. Similarly, high ambient air concentrations of organic sulfur compounds (e.g., mercaptans, volatile thiols) may also produce false positives and difficulty obtaining a zero reading on the Jerome prior to sample headspace measurements. Lastly, the Jerome analyzer should always be operated in a thermally stable environment as sudden temperature changes can greatly affect instrument response. Thus, outdoor areas likely to experience rapid temperature fluctuations (e.g., alternately full sun and shade) should be avoided. Thermal effects are often characterized by wildly varying instrument readings in ambient air otherwise expected or known to be free of elemental mercury.

4.0 Safety

Extreme care should be exercised when handling concentrated acids. The use of appropriate gloves, protective clothing and face shields is strongly recommended. The samples should be extracted in a well-ventilated area or fume hood. Caps on the vials should never be tightened until the samples have been diluted. Even after dilution, the soil digests are corrosive and exhibit a strong odor of chlorine. Note that dilution of the concentrated aqua regia with water should be conducted with

particular care, as the reaction is slightly exothermic (generates heat).

A soil extraction kit which employs aqua regia has recently become available commercially and is recommended as a safer approach for digesting soils for this procedure. The kit is available from Mercury Science, 4802 Glendarion Dr., Durham, NC 27713, Phone 919/493-0688.

Residual headspace gas in the used 1-L polyethylene analytical bottles will contain mercury vapor even after the spent SnCl_2 has been rinsed out. Although this presents a small source of mercury vapor per bottle, many bottles stored in a poorly ventilated or confined space could pose an inhalation hazard. To minimize mercury vapor exposure, the used polyethylene bottles should be recapped tightly and stored in a well-ventilated area pending disposal. Rinsing the bottles with a dilute bleach (sodium hypochlorite) solution will reduce this hazard. In addition, inability to obtain a zero reading ($<0.001 \text{ mg/m}^3$) on the analyzer between samples should indicate a possible buildup of mercury vapor in ambient air in the work area and should trigger further investigation of the source.

5.0 Apparatus and Materials

5.1 Portable balance capable of weighing to 0.01 g (e.g., Acculab Pocket Pro C/50).

5.2 Mercury Vapor Analyzer-Jerome Model 431X (Arizona Instrument Inc.)
Jerome Model 411 may also be used but is somewhat less sensitive.

5.3 Soda lime trap and probe (See Figure 1)

- * Glass wool
- * Polyethylene drying tube: Bel-Art Products (6.5 cm in length)
- * Soda lime-indicating type (4-8 mesh): J.T. Baker
- * Teflon 1/4" tubing and 90° elbow
- * Silicone tubing (3/16" I.D.)

A small quantity of glass wool is placed at both ends of a polyethylene tube (Note that these tubes are cut in half for use). Each tube is filled with soda lime. The trap should be replaced at least daily or as needed. *This trap should prevent accidental aspiration of any liquid into the Jerome and serves the*

redundant function of removing acid gases. The Jerome is equipped with a similar internal trap. Under some circumstances, the external trap may begin to absorb mercury vapor and thus reduce the true signal from the sample. Thus if aqueous standards suggest the calibration is changing, this external trap should be changed immediately and the calibration rechecked.

Figure 1. Schematic of probe tip and soda lime trap

- 5.4 Parafilm (PM-992, 2-inch by 250-foot roll)
- 5.5 Polyethylene 1-L bottles, small-mouthed: HDPE bottle for the analysis of metals (e.g., I-Chem 313-1000)
- 5.6 Gloves, safety glasses, face shield
- 5.7 Paper towels
- 5.8 Laboratory tissue
- 5.9 Liquid waste container
- 5.10 Pipettors: Eppendorf or similar, 10-100 μL , 0.1-1.0 mL
- 5.11 Glass vials with Teflon-lined silicone septum closures (40 mL capacity)
- 5.12 Graduated cylinder (100 mL capacity)

5.13 Liquid dispenser: Repipet II or similar (0-10 mL capacity)

6.0 Reagents

6.1 Deionized water

6.2 Hydrochloric acid: concentrated, J.T. Baker or equivalent

6.3 Nitric acid: concentrated, J.T. Baker or equivalent

6.4 Stannous chloride solution: Saturated SnCl_2 solution is prepared by dissolving 200.0 g SnCl_2 dihydrate in 100 mL of 30% hydrochloric acid and diluting to 1.0 L with distilled water. The solution was stirred for 24 h at room temperature while bubbling with "mercury-free" air. The latter procedure is not typically necessary if SnCl_2 for Hg analysis (e.g., J.T. Baker) and a low-Hg-content batch of HCl are used.

6.5 Bromine monochloride solution: Potassium bromide (KBr), 5.4 g, is dissolved in a 0.5-L bottle of concentrated HCl, stirring for 1 h in a fume hood. Finally, 7.6 g of KBrO_3 is added while stirring.

6.6 Mercury standards: The assay is linear in the range of 0.1 to 14 $\mu\text{g/L}$. A secondary standard (1.0 $\mu\text{g/mL}$ Hg^{+2}) is prepared using a NIST traceable mercury standard for atomic absorption (1000 $\mu\text{g/mL}$ Hg^{+2}) or NIST SRM 3133 (10 $\mu\text{g/mL}$). The secondary standard should be preserved with 5 mL of bromine monochloride solution. The secondary standard is stable for up to one year. An external calibration curve is constructed by making a series of dilutions of the secondary standard. This is most easily accomplished by dispensing aliquots (e.g., 0.0, 0.1, 0.2, 0.5, 1.0 mL) of the secondary mercury standard into the 1-L analytical bottles which contain 100 mL of deionized water. *Although Jerome readings can be used directly with Henry's Constant to calculate the concentration of mercury in the analyzed aliquot, this practice is not recommended because it relies only on the internal calibration of the Jerome using a gaseous standard. The reduction and headspace equilibration portions of the complete procedure are thus not taken into consideration. In addition, experience has demonstrated that this internal calibration can drift over time and even over the course of a field analytical session. Thus, frequent verification of the mercury reduction and detection portion of the complete procedure is recommended. A low aqueous standard of 2.0 $\mu\text{g/L}$ (0.2 mL of the secondary standard) run after every five to ten samples has proven useful in tracking calibration.*

7.0 Sample Collection, Preservation, and Handling

The soil samples should be collected and stored in screw-cap glass or plastic containers. They should be analyzed as soon as possible, but not later than a few days after collection if not preserved by refrigeration (4°C) or drying (<60°C overnight). Mercury contaminated soil samples may be classified as hazardous waste, and the acid extracts *will* be classified as hazardous when disposal is required. After the addition of SnCl_2 , the aqueous portion of samples will be considered hazardous waste because of a pH less than 2 (corrosive under RCRA). The waste SnCl_2 is collected in a bottle until it can be neutralized, and then it may be discarded into a sanitary sewer under most conditions as non-hazardous waste. Specific regulations governing waste handling and disposal at each site should be consulted prior to disposal. Note that no cost effective means of cleaning the 1-L polyethylene bottles for reuse has been discovered.

8.0 Procedure

8.1 Sample processing, extraction, and headspace vapor measurement

- * A small quantity of soil (e.g. 0.2 ± 0.01 g) is weighed into a 40-mL glass vial with Teflon-lined cap.
- * 6.0 mL of concentrated HCl and 2.0 mL of concentrated HNO_3 are dispensed directly into the glass vial. *Do not premix these acids.*
- * After not less than 15 minutes carefully add 15 mL of distilled water to each sample.
- * A 0.01- to 1.0-mL soil extract aliquot is transferred to a 1-L polyethylene bottle which contains 100 mL of distilled water. *Note that selecting the lowest extract aliquot which gives an instrument response between about 0.010 and 0.100 mg/m³ is desirable to prolong the interval between regenerations of the detector (see Jerome manual for details about regeneration).*
- * Saturated SnCl_2 solution, 5 mL from a liquid dispenser, is added directly to the sample in the polyethylene bottle.
- * The bottle is capped and manually shaken vigorously for 1 min. to assure thorough mixing of the SnCl_2 with the sample and to achieve equilibration of mercury vapor between the solution and gas phase.

- * A small square (2 x 2 inch) of parafilm is pressed tightly over the top of the bottle. *The parafilm seal reduces the possibility of variable amounts of unequilibrated air entering the bottle while sampling and thus increases precision of replicate measurements.*
- * The parafilm seal is punctured with the probe tip of the mercury vapor analyzer. *Care should be taken not to aspirate liquids into the mercury vapor analyzer.*
- * The headspace vapor is sampled for one 7-second interval. *Note that the Jerome Model 411 uses a 10-second interval and has no purge intervals.*
- * The mercury vapor concentration is recorded.
- * The probe tip is removed from the bottle, and two or three air samples are taken to zero the instrument before the next sample is analyzed.

8.2 Determination of moisture content in the soil samples: Soil samples can be analyzed even if wet, but results are usually required to be reported on a dry weight basis. Whenever possible, the samples should be dried and homogenized before the analysis (dry homogenization is often more effective than wet). To determine the moisture content of a soil sample, a given amount of wet soil is weighed in a disposable weighing boat, placed in a microwave oven for approximately 7 min, and then weighed again after the sample cools. *Note that losses of mercury from samples during drying by microwaves has not been explored and thus this method of drying soils/sediments should not be used except to obtain moisture content of a separate sample.* Also, the sample can be dried overnight in a well-ventilated area or fume hood.

8.3 Regeneration of the gold film in analyzer: The Jerome Model 431-X and its predecessor Model 411 must be "regenerated" when the internal gold film reaches a certain level of mercury saturation. This level can be reached rapidly after just a few samples which are high in mercury, necessitating taking the analyzer out of service for about 30 min while regeneration and thermal restabilization occur. This process requires line voltage (110-130 VAC) for 10 min after which the unit can be removed from line power if battery charging is not required. Selection of the smallest extract aliquots for analysis will prolong the time between regenerations. Furthermore, it is recommended that two instruments be available and operated alternately if many samples are to be run. A portable generator may be used to regenerate the gold film and recharge the batteries of one unit while the other unit is in

service. The manufacturer suggests allowing 20 minutes for thermal stabilization after the regeneration before resuming instrument use.

9.0 Calculations

- 9.1 Determination of Hg calibration:** A calibration curve is generated by making a plot of the Hg concentration of the aqueous standards versus the Jerome readings (mg/m^3). A calibration blank (distilled water only) should also be included to verify a "zero" response on the analyzer. The slope of the calibration curve can be used as the slope factor (e.g., Figure 2). Multipoint calibration is optional once the analyst has established linearity between aqueous mercury concentrations and instrument readings. When only one standard is used for calibration purposes, the slope factor is calculated as follows:

$$\text{Slope factor } (\mu\text{g m}^3/\text{mg L}) = [V \cdot C / I] \cdot [1000 \text{ mL}^{-1} / G]$$

where

V=volume of standard (mL)

C=concentration of the mercury standard ($\mu\text{g}/\text{mL}$)

I=Jerome readings (mg/m^3)

G=volume of water (mL)

- 9.2 Determination of Hg concentration in soil samples:** The amount of Hg in the diluted extract of unknown soil samples is determined by using the formula:

$$\text{Amount of mercury } (\mu\text{g}) = [A \cdot B \cdot C / D] \cdot [E + F] \cdot [0.001 \text{ L mL}^{-1}]$$

where

A=slope factor ($\mu\text{g m}^3/\text{mg L}$)

B=Jerome readings (mg/m^3)

C=reduced volume (mL)

D=aliquot volume (mL)

E=acid volume (mL)

F=diluent volume (mL)

The amount of mercury per weight of soil is obtained as follows:

$$\text{Amount of dry soil sample (g)} = [1 - (\% \text{moisture} \cdot 0.01)] \cdot \text{sample weight}$$

$$\text{Amount of Hg per gram of soil } (\mu\text{g/g}) = \text{Amount of mercury } (\mu\text{g}) / \text{Amount of dry soil sample (g)}$$

A spreadsheet program which contains all the necessary calculations is included (see Appendix). The program can be used with Lotus, Quattro Pro, or Excel spreadsheet programs.

Standard Curve for Jerome 431

Figure 2. Example Calibration Plot for Jerome Model 431-X

10.0 Quality Control

The Jerome mercury analyzer should be checked for proper operation and internal calibration before each use in accordance with the instruction manual provided by Arizona Instrument, Inc. Return of this analyzer to the factory for service and calibration at least annually is strongly recommended. The need for calibration is readily determined if a "Functional Test Kit" is purchased from the manufacturer. The Jerome may still be used for the method described here even if the internal calibration drifts out of specifications, but the instrument should be returned when it no longer indicates proper calibration. *Use of an analyzer which lacks proper internal calibration must be accompanied by the external calibration described here and the analyzer must not be used further in the main application (industrial hygiene/protection of human health) for which it was designed.*

Quality assurance of the results being generated by this method can be tracked by inclusion of NIST, or equivalent, reference soils with each batch of site soils, and by regularly verifying/adjusting the slope factor determined by external calibration with a low- or midrange aqueous standard. Experience has shown that at least one such aqueous standard run with each group of ten soil samples is sufficient. If significant drift is detected, standards should be run more frequently and the slope factor adjusted accordingly. Analysis of a continuing calibration blank and a soil extraction reagent blank should also be incorporated at a frequency of 10%.

Replicate analyses of the same soil extract is a useful measure of method precision and should be performed at the rate of one per 20 soil samples. Replicate digests of the same soil are also useful but sample inhomogeneity can confound detection of the major source of poor precision. This is particularly true for soils analyzed in the naturally moist or wet state, or which contain visible elemental mercury. Such soils simply cannot be adequately homogenized for an analyzed aliquot size of a few hundred milligrams. True method precision is best established using NIST SRMs.

11.0 Method Performance

Three reference soil samples were used to evaluate the extraction efficiency of aqua regia under the conditions of this method. Two NIST Standard Reference/Research Materials, SRM 2710 (Montana soil, containing $32.6 \pm 1.8 \mu\text{g Hg/g}$), RM 8407 (mercury in sediment, $50 \pm 2 \mu\text{g Hg/g}$), and a soil from the East Fork Poplar Creek (EFPC) floodplain (containing $2500 \mu\text{g Hg/g}$ as measured by EPA Method 7471; EPA 1986), were weighed into clean Erlenmeyer flasks. These were extracted with 8 mL of aqua regia for 15 min. The slurries were filtered, diluted with 175 mL of distilled deionized water, and 1 mL of concentrated HNO_3 was added as a preservative. The extraction filtrates were submitted for laboratory analysis using

EPA Method 245.1 (EPA 1982). The results (Table 1) indicated that digestion of soil in aqua regia at room temperature for 15 minutes adequately recovered mercury. Notably, the EFPC soil, which has been characterized (Revis et al 1989) as containing 85% mercuric sulfide, was extracted with high efficiency.

Numerous NIST reference/research soils have been analyzed during the development and testing of this method. Table 2 summarizes results for NIST soils analyzed by this method. In addition, several suites of soil or sediment samples for which mercury results were available by approved EPA protocols (Methods 7471/245.5) have also been run by this field method for comparative purposes. In most cases analyzed samples were dried and pulverized prior to analysis by both the field and laboratory protocols. In many cases, the aliquots for the field method were taken from the same containers used to supply aliquots for the formal laboratory methods. Table 3 provides summary data for actual soils analyzed by both the field method described here and by the EPA-approved Method 7471 (EPA 1986). Figure 3 displays the results graphically.

Table 1
Extraction Efficiency of Aqua Regia at 22-24°C after 15-min Digestion.

Sample	Reference Value ($\mu\text{g/g}$)	Observed Value ($\mu\text{g/g}$) ¹	Average % Extracted
NIST RM 8407	50 $\pm$ 2	50 (14) ²	100
NIST SRM 2710	32.6 $\pm$ 1.8	31 (7.8)	96
EFPC soil	2500	2600	103

¹ Average of duplicate (except EFPC soil) extracts analyzed using EPA Method 245.1 (EPA 1982).

² Values in () are relative percent differences in duplicates

Table 2. Results of Application of Field Method to NIST Reference/Research Materials

NIST Soil ID	Date Analyzed	Field Mercury ($\mu\text{g/g}$)	Certified Mercury ($\mu\text{g/g}$)	Percent Difference
RM 8407	12/14/94	44	50 ± 2	-12
RM 8407	12/14/94	46	50 ± 2	-8.0
SRM 2710	12/14/94	30.4	32.6 ± 1.8	-6.7
SRM 2710	12/14/94	31.2	32.6 ± 1.8	-4.2
SRM 2709	12/30/94	1.88	1.40 ± 0.08	34
SRM 2709	2/8/95	2.2	1.40 ± 0.08	57
SRM 2709	2/8/95	3.4	1.40 ± 0.08	142
SRM 2710	2/8/95	33	32.6 ± 1.8	1.2
RM 8407	2/8/95	39	50 ± 2	-22
RM 8407	2/8/95	45	50 ± 2	-10
SRM 2710	2/9/95	33	32.6 ± 1.8	1.2
SRM 2710	2/9/95	33	32.6 ± 1.8	1.2
SRM 2710	2/9/95	36	32.6 ± 1.8	10
SRM 2710	2/10/95	31	32.6 ± 1.8	-5.0
SRM 2710	2/10/95	29	32.6 ± 1.8	-11
SRM 2711	2/10/95	6.5	6.25 ± 0.19	4.0
SRM 2710	2/11/95	36	32.6 ± 1.8	10
SRM 2711	2/11/95	6.0	6.25 ± 0.19	-4.0
SRM 2710	2/11/95	31	32.6 ± 1.8	-4.9
SRM 2710	2/11/95	38	32.6 ± 1.8	16
SRM 2709	2/11/95	2.4	1.40 ± 0.08	71
SRM 2709	2/11/95	2.4	1.40 ± 0.08	71
RM 8407	2/11/95	50	50 ± 2	0
SRM 2709	2/11/95	1.9	1.40 ± 0.08	36
SRM 2710	2/11/95	26	32.6 ± 1.8	-20
RM 8407	2/11/95	49	50 ± 2	-2.0
SRM 2710	2/21/95	32	32.6 ± 1.8	-1.8

NIST Soil ID	Date Analyzed	Field Mercury ($\mu\text{g/g}$)	Certified Mercury ($\mu\text{g/g}$)	Percent Difference
RM 8407	2/21/95	50	50 ± 2	0.0
RM 8407	2/21/95	39	50 ± 2	-22
RM 8407	2/21/95	53	50 ± 2	6.0
RM 8407	2/21/95	47	50 ± 2	-6.0
SRM 2710	5/4/95	31	32.6 ± 1.8	-4.9
SRM 2710	5/4/95	32	32.6 ± 1.8	-1.8
SRM 2710	5/4/95	30	32.6 ± 1.8	-8.0
SRM 2710	5/4/95	32	32.6 ± 1.8	-1.8
RM 8407	5/4/95	44	50 ± 2	-12
RM 8407	5/4/95	50	50 ± 2	0.0
SRM 2710	5/28/95	31	32.6 ± 1.8	-4.9
SRM 2710	5/28/95	30	32.6 ± 1.8	-8.0
RM 8407	5/31/95	46	50 ± 2	-8.0
RM 8407	5/31/95	48	50 ± 2	-4.0
SRM 2710	6/1/95	30	32.6 ± 1.8	-8.0
RM 8407	6/1/95	50	50 ± 2	0.0
RM 8407	6/7/95	52	50 ± 2	4.0
RM 8407	6/7/95	50	50 ± 2	0.0
RM 8407	6/7/95	47	50 ± 2	-6.0
RM 8407	6/7/95	47	50 ± 2	-6.0
RM 8407	6/28/95	54	50 ± 2	8.0
RM 8407	6/28/95	52	50 ± 2	4.0
RM 8407	6/30/95	50	50 ± 2	0.0
RM 8407	6/30/95	50	50 ± 2	0.0
RM 8407	6/28/95	48	50 ± 2	-4.0

Table 3. EFPC Soils Analyzed by Both Field and Laboratory Methods

Sample ID	Date Analyzed	Field Mercury ($\mu\text{g/g}$)	Laboratory Mercury ($\mu\text{g/g}$)	% Difference ^a
ZE5150717	12/14/94	213	230	-7.42
ZE3181013	12/14/94	27	28	-5.36
ZE3740918	12/14/94	53	55	-3.32
ZE5380512	12/14/94	66	67	-1.77
ZE5150717	12/14/94	211	230	-8.21
ZE5470412	12/14/94	78	85	-8.01
ZN3210115	12/14/94	241	260	-7.38
ZN3340211	12/14/94	285	270	5.41
ZN3210127	12/14/94	2471	2630	-6.06
ZE5380524	12/14/94	1720	2100	-18.09
ZE3770822	12/15/94	24	15.3	56.91
ZE3740920	12/15/94	442	780	-43.28
ZE3181025	12/15/94	338	390	-13.38
ZE3770810	12/15/94	366	480	-23.75
ZE5150729	12/15/94	942	900	4.62
ZE5340621	12/15/94	1038	1200	-13.54
ZE5670424	12/15/94	1282	1300	-1.41
ZN3210127	12/15/94	2633	2630	0.12
ZN3340223	12/15/94	1721	1900	-9.40
ZN3340324	12/15/94	1818	2100	-13.43
ZN3340324	12/15/94	1852	2100	-11.79
ZE3740920	12/15/94	554	780	-29.02
BA1	2/21/95	2500	2500	0.00
BA2	2/21/95	620	570	8.77
BA3	2/21/95	920	790	16.46
BA4	2/21/95	200	220	-9.09
BA5	2/21/95	510	550	-7.27
BA6	2/21/95	1300	1300	0.00
BA7	2/21/95	1800	1800	0.00
BA8	2/21/95	250	250	0.00
BA9	2/21/95	550	520	5.77
BA10	2/21/95	1000	980	2.04

^a $100 \times ((\text{Field} - \text{Lab}) / \text{Lab})$

Figure 3. Intercomparison of Results for EFPC Soils Analyzed by Both Field and Laboratory Methods

12.0 References

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APPENDIX A2

SAMPLE SPREADSHEET FOR CALCULATION

Example Spreadsheet and Data for Calculation of Soil Mercury Concentration

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Project: Jacobs			Analyst: N. Ayala / R. Turner					Instrument Serial No: 1782				
2	Date: May 4-7, 1995												
3	Sample ID	Time Start Digestion	Time Start Analysis	Moisture Content	Sample Weight	Acid Volume	Diluent Volume	Transferred Volume	Reduced Volume	Jerome Reading	Slope Factor ^a	Field Mercury	
4				(%)	(g)	(mL)	(mL)	(mL)	(mL)	(mg/m3)		(µg/g) ^b	Comments
5	2701	5/4 1930	5/5 1005	0	0.24	8	15	0.02	100	0.015	18	129	
6	2702	5/4 1930	5/5 1025	0	0.24	8	15	0.01	100	0.008	18	138	
7	2703	5/4 1930	5/5 1010	0	0.26	8	15	0.02	100	0.039	18	311	
8	2704	5/4 1930	5/5 1020	0	0.3	8	15	0.02	100	0.048	18	331	
9	2705	5/5 1600	5/7 1254	0	0.33	8	15	0.02	100	0.008	20	56	
10	2706	5/4 1930	5/5 945	0	0.25	8	15	0.02	100	0.066	18	546	
11	2707	5/4 1930	5/5 955	0	0.37	8	15	0.2	100	0.021	18	12	
12	2707	5/4 1930	5/5 1040	0	0.37	8	15	0.2	100	0.021	18	12	Duplicate analysis
13	2708	5/4 1930	5/5 935	0	0.25	8	15	0.02	100	0.098	18	811	
14	2709	5/4 1930	5/5 925	0	0.25	8	15	0.02	100	0.116	18	960	
15	2701-B	5/5 1600	5/6 2130	0	0.22	8	15	0.02	100	0.011	20	115	Duplicate digestion
16	NIST2710	5/4 1930	5/5 1000	0	0.23	8	15	0.2	100	0.034	18	31	32.6 ± 1.6
17	NIST2710	5/4 1930	5/7 1418	0	0.23	8	15	0.2	100	0.034	19	32	32.6 ± 1.6
18	NIST2710	5/4 1930	5/7 1426	0	0.23	8	15	0.2	100	0.032	19	30	32.6 ± 1.6
19	NIST2710	5/4 1930	5/5 1700	0	0.23	8	15	0.2	100	0.035	18	32	32.6 ± 1.6
20	NIST8407	5/4 1930	5/5 1010	0	0.24	8	15	0.2	100	0.051	18	44	50 ± 2
21	NIST8407	5/4 1930	5/7 1422	0	0.24	8	15	0.2	100	0.056	19	51	50 ± 2
22	NIST8407	5/8 1312	5/8 1340	0	0.3	8	15	0.2	100	0.082	16	50	50 ± 2

^a Aqueous standard in µg/L divided by Jerome reading in mg/m³

^b (((J*K*I)/H)*(F+G))/((1-D*0.01)*E)*0.001

APPENDIX B

RAPID ELECTROANALYSIS OF MERCURY IN ENVIRONMENTAL WASTES

RAPID ELECTROANALYSIS OF MERCURY IN ENVIRONMENTAL WASTES

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ABSTRACT

An electroanalytical method for detecting total mercury in a wide range of solid and aqueous matrices has been developed for rapid field analysis. The method is based on the selective removal of mercury species from solid substrates into a KI/I_2 extracting solution followed by anodic stripping electroanalysis. The stripping current and charge have been found to be linear with Hg concentration. Oxygen present in solution has essentially no influence on the electroanalysis, which thus eliminates the time-consuming solution deoxygenation procedure and the need for carrying an inert gas cylinder to the field. Small variation in iodine and iodide concentrations due to various degrees of KI/I_2 consumption by different substrates has practically no effect on the stripping results. The method possesses a great selectivity to Hg and no interference from other heavy metals such as Cd, Pb, Fe and Cu has been observed. The method's sensitivity increases with increasing electrodeposition time. A detection limit of 20 ppt has been achieved with 10 minute deposition time. Application of this method has also been extended to simultaneous detection of other metals. The electroanalytical results for real-world samples contaminated with a wide range of Hg concentration in a variety substrates agree very well with the analytical results based on a modified EPA atomic absorption method. Compared with other fieldable methods such as X-ray fluorescence and absorbance spectrometry, this method has advantages in its combination of speed, simplicity, selectivity, sensitivity and multi-metals capability. Furthermore, this electroanalytical probe is not only very useful for rapid field screening and on-site remediation analysis, but also for manufacturing process on-line monitoring and medical diagnosis for almost all heavy metals.

INTRODUCTION

Because of the environmental significance of mercury and its compounds due to their high toxicity to humans, a large number of studies¹⁻¹⁹ have been carried out to develop and improve methods for characterizing and detecting mercury in various environmental wastes and industrial process streams. The most commonly used analytical methods are Atomic Absorption (AA), Inductively Coupled Plasma Atomic Emission (ICP-AE), and Mass Spectroscopy (MS), and Neutron Activation. However, these methods were designed and developed for trace mercury analysis in laboratories, not for rapid field screening and on-line process monitoring. They require well-controlled experimental conditions, expensive instrumentation, frequent maintenance/calibration, and more importantly lengthy sample preparation, which is necessary for analyzing total mercury and for eliminating the interference of other components in environmental samples. Due to the high cost and extensive time delay of these analytical methods and the requirement of large number of samples necessary for a site characterization, there is a real need for developing rapid and fieldable or portable techniques for field screening and remediation on-site monitoring. There are a few reported fieldable or potentially fieldable analytical methods such as X-Ray Fluorescence (XRF),^{20,21} Colorimetry²² Ion-Selective Electrode (ISE)²³ and Anodic Stripping Voltammetry (ASV)^{24,25}. XRF is probably the most widely used fieldable method because of its great

advantage of simultaneously detecting multi metals with minimum sample preparation. However, the detection limits for XRF (25-50 ppm for soil samples and 100 ppb for water samples) are not low enough for determining action-limit Hg concentrations in solid wastes and water samples. The current regulatory standard for Hg is 20 ppb in drinking water. 10-50 ppm Hg is often the action level for solid wastes. Colorimetric methods can be complicated and time-consuming and/or are usually targeted only for one specific Hg species. For example, Draeger tubes can only be used to analyze elemental Hg. Ion-Selective Electrode is suitable only for inorganic Hg ions and its measurement is strongly dependent on the composition of sample substrate because its voltammetric response differs not only with various Hg species, but also with different concentration of halides and sulfide existing in the substrate. Anodic Stripping Voltammetry has been widely used to detect a variety of heavy metals in many laboratories because of its great sensitivity. However, most of its applications are directed to analyze other heavy metals rather than Hg because Hg is the most preferred working electrode in ASV. Solid electrodes have been evaluated in several laboratories²⁴⁻²⁶ for analyzing mercury in environmental samples. But both sample preparation and electroanalysis procedure are long and complicated, so the methods are very difficult to be applied to the field.

In the present paper we report the development of a rapid and fieldable electroanalytical method²⁷ for analyzing total mercury in a wide range of solid and aqueous matrixes. The method is based on the computer-controlled anodic stripping voltammetry assisted by the KI/I_2 oxidative extraction. Different mercury species existing in an aqueous solution or a solid substrate are first converted into a mercuric iodide complex (HgI_4^{2-}) by reacting with the KI/I_2 extraction solution. The HgI_4^{2-} complex is subsequently electrochemically reduced and accumulated at the electrode surface as elemental Hg which is finally oxidized off the electrode surface by anodic stripping voltammetry. The electroanalysis takes place in a diluted KI/I_2 extraction solution, thus no solution medium exchange is needed. Furthermore, the strong adsorption of iodide and iodine at Au electrode surface guarantees a reproducible electrode surface for Hg analysis in the solutions extracted from various substrates. Compared with other fieldable methods such as X-ray fluorescence and colorimetry, this method is more advantageous in the combination of speed, simplicity, selectivity, sensitivity and multi-metal detection capability. For example, detecting sub-ppb level of Hg in aqueous medium requires essentially no sample preparation and takes about 1 minute. Detection of Hg in solid matrixes takes about 15 minutes and requires only one step extraction before electroanalysis. No interference from other heavy metals such as Cd, Pb, Fe and Cu has been observed. The method's sensitivity increases with the increase of electrodeposition time. A detection limit of 20 ppt has been achieved with 10 minute deposition time. The method is inexpensive and computerized, and the instrument is rugged and fieldable. The experimental results have also demonstrated that this electroanalytical probe is not only very useful for rapid field screening, but also for on-line manufacturing process monitoring, on-site remediation analysis and medical diagnosis for almost all heavy metals.

EXPERIMENTAL

1. Apparatus and Electrodes

Shown in Figure 1 is the schematic diagram of the computer-controlled electroanalytical system (Cypress Systems, Inc. Lawrence, KS) used for this study. Although a desk-top computer was employed in the laboratory to conduct all experiments reported here because of the convenience of data storage and manipulation, a manual-driven battery operated potentiostat can be used in the field. A typical 3.0 ml V-shaped micro-vial was used as the electrochemical cell. A piece of Pt wire served as an auxiliary electrode. A home-made Ag/AgI (0.1 M KI saturated with AgI) or a commercial Ag/AgCl (3 M KCl saturated with AgCl; Cypress Systems, Inc.) was used as the reference electrode. The potential difference

between two reference electrodes was about 260 mV. Since most of the electrolytes used for Hg electroanalysis contained 0.1 M KI, a Ag/AgI reference electrode was obviously the choice because its potential was more stable and reproducible while long exposure of the Ag/AgCl electrode in KI solution often resulted in a large potential shift due to the diffusion of KI into the reference solution cavity.

Figure 1. Schematic Diagram of Electroanalytical System.

The working electrode used for stripping analysis was either a Glassy Carbon (GC) or Au disk (1 mm in diameter) electrode, which was embedded in a Kel-F or glass body. Since field application was the primary objective of this study, no attempt was made to obtain the most active electrode surface, rather it was to obtain the most stable electrode surface. All electrodes were initially polished with 1 μM polishing diamond followed with 0.05 μM polishing alumina, then stored in purified water. No mechanical polishing was necessary for the Au electrode after use because its surface activity can be regenerated by in-situ electrochemical oxidation-reduction cycling if needed. Due to strong adsorption of iodide/iodine at the Au surface, the Au electrode has the most reproducible surface for Hg deposition in a KI solution since its surface is constantly covered with a monolayer of chemisorbed iodine, thus preventing other species from adsorbing onto its surface. For the GC electrode, ultrasonication in solution for 3 minutes or electrochemical cycling in 1 M sulfuric acid solution has been found to be effective to regenerate surface activity in some cases. However, mechanical polishing may be necessary if the surface has been severely deactivated.

2. Electroanalytical Techniques

Two basic electroanalytical techniques, cyclic voltammetry (CV) and Anodic Stripping Voltammetry (ASV), have been applied for mercury analysis. Cyclic voltammetry was used mainly for screening new samples to probe the potential windows, possible interference and Hg concentration levels. Anodic stripping voltammetry was the principal technique for quantitative analysis of Hg, especially at below ppm concentrations. The ASV technique can be operated in many modes, but all involve three basic steps: first, an oxidative potential or a series of oxidative potential steps is applied to a working electrode to make sure the electrode surface is free of the metal of interest and to obtain a reproducible electrode surface for each experiment; then the electrode potential is stepped to a more negative value at which the detecting metal ions will be reduced to metallic state and deposited (accumulated) onto the electrode surface. The deposition time varies from seconds to hours in either steady-state (quiescent) or non steady-state (stirred) solution conditions depending on metal concentration and the requirements of

detection limit, speed and simplicity. Finally, the working electrode is subjected to a positive potential scan in either a linear scan (LS), differential pulsed (DP) or square-waved (SW) pattern to oxidize (strip off) the metal from the electrode surface back into the solution. This oxidation process produces an anodic stripping current proportional to the metal concentration in solution. The method's detection limit for most heavy metals is typically in the range of low ppb to high ppt.

Among the three ASV methods, LS-ASV is the fastest and simplest but least sensitive method, while DP-ASV is regarded as a highly sensitive but the slowest one. SW-ASV is the most preferred method because it possesses the similar high sensitivity as DP-ASV with the speed close to that of LS-ASV.

3. Chemicals and Solutions

All chemicals, KI (Aldrich Chemical Co.), HgI_2 (Fisher Scientific Co.), I_2 (Mallinckrodt, Inc.), and K_2SO_4 (Aldrich Chemical Co.) were used as received. The analytical solutions were prepared with water purified through Milli-Q water purification system (Millipore Co.), while the extraction solution was prepared with the deionized water. All Hg standard solutions were made by dissolving HgI_2 into an appropriate KI/ I_2 solution. The extract solution for solid samples was either 1.0 M KI/0.5 M I_2 or 1.0 M KI/0.1 M I_2 . The extract was further diluted 10 times with the purified water or 100 times with 0.1 M KI electrolyte.

4. Extraction Procedure

A general extraction and electroanalysis procedure for solid samples contaminated with Hg can be described briefly as following :

- 1) Weigh 1.0 g of sample into a threaded tube.
- 2) Add 10.0 ml extract solution (e.g. 1.0 M KI/0.5 M I_2) into the above tube and tighten the cover.
- 3) Extract for 10-30 minutes at 100 °C under stirred condition.
- 4) Filter the sample and save the filtrate.
- 5) Dilute the above filtrate 10 times with the purified water or 100 times with 0.1 M KI solution. Transfer the diluted solution into an electrochemical cell.
- 6) Immerse the electrode assembly (an Au electrode, Pt auxiliary electrode and Ag/AgI reference electrode) into the cell and connect them to the potentiostat.
- 7) Run one of pre-determined ASV programs for Hg analysis. It should always start with the program having the shortest deposition time. If no Hg peak is visible or too small for quantitation, run a program with longer deposition time until the amplitude of the stripping peak falls into the calibration range.
- 8) Wash the electrode assembly thoroughly with water, then run a background check in the pure electrolyte solution before proceeding to another sample. Method calibration in Hg standard solutions should be conducted periodically during the course of electroanalysis of environmental samples.

RESULTS AND DISCUSSION

Dependence on Hg Concentration

Presented in Figure 2 are the square-wave anodic stripping voltammograms of 0, 20, 50, 100, and 200 ppb Hg in the 0.1 M KI/0.005 M I_2 electrolyte solution at Au electrode. Both stripping current (peak height) and charge (peak area) were found to observe a linear relationship with the Hg concentration in solution. What should be mentioned here is that the stripping current and charge are strongly dependent on the deposition time, therefore different deposition times yield different working curves. Displayed in Figure 3 are three Hg electroanalysis calibration curves at three different deposition

Figure 2. Square-Wave Anodic Stripping Voltammograms of Hg at Au Electrode. SW-AS voltammograms of 0, 20, 50, 100, and 200 ppb Hg in 0.1 M KI, 0.005 M I_2 and 0.25 M K_2SO_4 solution. Deposition at -100 mV in a quiescent solution for 10 minutes followed by 20 seconds at 0.0 V before SW anodic stripping. Amplitude 30 mV, step height 4 mV, period 16.67 ms. Other experimental Conditions: Electrochemical cell volume: 3 ml; working electrode, Au disk (1 mm in diameter); auxiliary electrode, Pt wire; reference electrode, Ag/AgI (0.1 M KI). All solutions were not deoxygenated.

Figure 3. Calibration Curves for Hg Electroanalysis at Different Deposition Times. A: Deposition at -100 mV for 600 seconds, followed by 10 seconds at 0.0 mV before SW anodic stripping. B and C: Deposition at -100 mV for 30 and 5 seconds, respectively, followed by 5 seconds at 0.0 mV before SW stripping. Other experimental conditions as in Figure 2.

times for a wide range Hg concentrations. These curves clearly demonstrate that this electroanalytical method has an extremely wide dynamic working range. For example, when a sample contains a high Hg concentration, we can use a short deposition time and when Hg concentration is very low, longer deposition time should be employed. Thus, no tedious dilutions and/or preconcentrations are needed for analyzing a large number of samples with very a wide range of analyte concentrations. Such procedures are necessary for other analytical methods because samples have to be prepared so that they fall into the method's working range. For anodic stripping electroanalysis, only the change of deposition time is needed. This translates into a great reduction in analysis time and expense.

Dependence on Deposition Time

Presented in Figure 4 is the dependence of stripping current with the deposition time for 400 ppb Hg in 0.1 M KI at GC electrode. As the deposition time increases, the stripping current increases but the background current remains the same. This result thus demonstrated that in order to increase the method sensitivity and decrease the method detection limit, longer deposition time should be used. When 10 minute deposition time was used, the method detection limit based on three times the signal to noise ratio is about 20 ppt. Since this detection limit is sufficient for rapid field analysis, further study in lowering the detection limit has not been conducted. However, based on the existing results, we are confident to predict that the detection limit can be further reduced to sub ppt level.

Figure 4. Effect of Deposition Time on Stripping Current at GC Electrode. Stripping currents were measured from the linear scan anodic stripping voltammograms for 0.40 ppm Hg in 0.1 M KI solution. Deposition at: -0.54 V in non steady-state solution for various lengths of time, followed by 10 sec at the same potential in steady-state solution before stripping at 300 mV/s. Other conditions as in Figure 2.

Dependence on Deposition Potential

Shown in Figure 5 are the dependence of Hg stripping current and charge against the electrode deposition potential. Hg stripping signals were measured from square-wave anodic stripping experiments in 0.1 M KI solution containing 1.0 ppm Hg. As demonstrated by the plots in Figure 5, both stripping current and charge increase as the deposition potential shifts towards a more negative value. The increase can be explained by the combination of electrode overpotential and different nucleation formation mechanisms. When the potential exceeds -1.4 V, the signal decreases as the result of vigorous hydrogen gas evolution at electrode surface. What should be cautioned here is that the optimum deposition potential obtained for Hg standard solution may not be the one for environmental samples because they may contain other metals. Deposition at very negative potential may cause those metals to co-deposit at the electrode surface with Hg, thus there is a possibility to form some sort of metal compounds at the electrode which complicates the electroanalysis.

Figure 5. Effect of Deposition Potential on Stripping Electroanalysis at GC Electrode. The Stripping currents and charges were measured from the square-wave anodic stripping voltammograms for 1.00 ppm Hg in 0.1 M KI solution. Deposition conditions: 60 seconds at various electrode potentials in steady-state solution, followed by square-wave anodic stripping (amplitude 30 mV, step height 2 mV, period 30 ms). Prior to deposition, a predeposition potential of 200 mV was applied for 2 seconds and after deposition a postdeposition potential of -200 mV was applied for 2 seconds. Other conditions as in Figure 2.

Experiments have also been carried out to investigate the dependence of electroanalysis on deposition potential at a Au electrode. Presented in Figure 6 are the stripping current and charge obtained from a series of square-wave anodic stripping experiments for 200 ppb Hg at a Au electrode in the electrolyte of 0.1 M KI, 0.005 M I_2 and 0.25 M K_2SO_4 as a function of deposition potential. Prior to the

Hg deposition, a potential of 400 mV was applied to the electrode to make sure the electrode was free of any trace of Hg. After the Hg deposition at various electrode potentials, a rest potential of 0.0 mV was applied so that the deposition time at different deposition potentials was the same and the square-wave scan took the same time to complete. From both the current vs. potential and charge vs. potential responses displayed in Figure 5, one can conclude that there is essentially no effect of deposition potential (0.00 to -0.60 V) on Hg stripping electroanalysis at aAu electrode under the experimental conditions, compared with that at GC electrode shown in Figure 5. This is probably be due to the strong surface Au-Hg amalgamation and I-Au chemisorption. It has been reported that iodine molecules and iodide anions in solution strongly adsorb at Au, Ir and Pt surfaces to form a monolayer of chemisorbed iodine atoms.²⁸⁻³¹ Metal deposition onto this iodine covered surface has revealed some interesting surface phenomena. For example, deposition of Ag onto an iodine-preadsorbed Pt electrode surface results in place exchange between the Ag and I atoms.²⁷ That means that the deposited Ag atoms are underneath the I layer rather on the top of it. It is most likely that this place exchange has also taken place during the course of Hg deposition at the iodine-preadsorbed Au electrode surface. If this is the case, the I layer at Au electrode surface plays a very important role for Hg electroanalysis because it not only protects the electrode from deactivated by preventing surface contamination by other adsorbers in a solution, but also selectively filters Hg into its layer to avoid Hg interaction with other species in solution.

Figure 6. Effect of Deposition Potential on Stripping Electroanalysis at Au Electrode. The Stripping currents and charges were measured from the square-wave anodic stripping voltammograms for 200 ppb Hg in the solution of 0.1 M KI, 0.005 M I_2 and 0.25 M K_2SO_4 . Deposition condition: 60 seconds at various electrode potentials in steady-state solution, followed by square-wave anodic stripping. Prior to deposition, a predeposition potential of 400 mV was applied for 5 seconds and after deposition a postdeposition potential of 0 mV was applied for 20 seconds. Other conditions as in Figure 2.

Dependence on Oxygen in Solution

We have also investigated the effect of dissolved O_2 in solution on the result of electroanalysis at a Au electrode. A cyclic voltammetric experiment was conducted for 5 ppm Hg solution with deoxygenation by purging the solution with N_2 gas and also for the same solution without deoxygenation. The experimental results displayed in Figure 7 clearly demonstrate that solution

deoxygenation has no effect on Hg stripping current and potential (171 mV), although oxygen reduction at the electrode obviously occurred as indicated by the large cathodic background current in the potential range from 0.0 to -1000 mV (curve a). This independence of stripping results on O_2 in solution had also been observed at the GC electrode, as demonstrated by the experimental results shown in Figure 8. Compared in the figure are the stripping currents obtained for the Hg solutions (5 ppm Hg in different KI concentrations) with the O_2 removal by N_2 purging with those without the O_2 removal under otherwise the same experimental conditions. This finding is very important for rapid field analysis because there is no need for a time-consuming deoxygenation procedure and for carrying an inert gas cylinder to a field.

Figure 7. Effect of Oxygen on Stripping Analysis at Au electrode. The cyclic voltammograms of 5 ppm Hg in non-deoxygenated (curve a) and deoxygenated (curve b) electrolyte solution (0.1 M KI, 0.005 M I_2 and 0.25 M K_2SO_4). Scan rate: 200 mV/S; 4th scan recorded. Other experimental conditions as in Figure 2.

Dependence on KI Concentration

The obvious advantage of using KI as the electrolyte for Hg electroanalysis is its simplicity because KI is used as the extractant, thus no solution exchange is needed from extraction to electroanalysis. More importantly, due to HgI_4^{2-} complex formation, the Hg stripping peak can be shifted by changing the KI concentration to avoid any possible overlapping with other metals. Presented in Figure 9A are three representative stripping voltammograms of 0.40 ppm Hg in three different KI concentrations. The resulting stripping peaks were plotted against the KI concentration in Figure 9B. The plot gave a slope of 117 mV which agrees very well with the theoretical value of 118 mV based on the Nernst equation. Another phenomenon observed from Figure 9A is that the stripping current is almost independent of the KI concentration, which is more clearly illustrated by the stripping results presented in Figure 8.

Figure 8. Effect of Oxygen and KI Concentration on Stripping Current. The stripping currents were measured from the 4th cyclic voltammograms of 5 ppm Hg solution with O₂ removal (open symbol) and without O₂ removal (solid symbol) in different KI concentrations at GC electrode at scan rate of 200 mV/s. Experimental conditions: the electrolyte of 0.25 M K₂SO₄ was used for all experiments except for the case of 500 mM KI where no K₂SO₄ was added. The cathodic limit of all cyclic scans was set at -1240 mV more negative and anodic limit at 260 mV more positive than the stripping peak potential. Other experimental conditions as in Figure 2.

Figure 9. Dependence of Hg Stripping Potential on KI Concentration at GC Electrode.

A: The stripping portion of 4th cyclic voltammograms of 5 ppm Hg in different KI concentrations. **B:** Hg stripping peak potential vs. log [KI]. All solutions were oxygenated. Other conditions as in Figure 7.

Dependence on Iodine Concentration

High I_2 concentration was necessary for rapid extraction of various mercury species from a variety of solid matrices, but it can also interfere with Hg electroanalysis. Chemical reduction of I_2 with several chemicals such as ascorbic acid, hydroxylamine and $CaSO_3$ has been successfully tried. However, chemical reduction did not help in producing more reproducible electroanalytical results because of reagent adsorption at the electrode surface and/or the electrochemical reduction of the oxidized species. It definitely complicates the analysis procedure. Since ASV has extremely high sensitivity, it is much simpler to avoid problems associated with high I_2 concentration just by diluting the extract 10 to 100 times with purified water or an other electrolyte. The dilution not only reduces the I_2 reduction current, but also minimizes the substrate interference. It has also been demonstrated to be effective by using a higher current scale during the deposition period to avoid possible potentiostat saturation and a lower current scale during the Hg stripping to maximize current peak. The dependence of the stripping current on I_2 concentration is shown in Figure 10.

Figure 10. Effect of I_2 Concentration on Stripping Current at GC Electrode. The stripping currents were measured from linear scan anodic stripping voltammograms of 4 ppm Hg in 0.1 M KI and different concentration of I_2 . Deposition at -1000 mV for 60 seconds in steady-state solution, followed by linear scan of 200 mV/s anodic stripping. Other conditions as in Figure 2.

Metal Interference

Several heavy metals such as Cd, Pb, Fe and Cu have been studied for possible interference to Hg stripping in KI solutions. Except for Fe, other metals do not interfere with the Hg stripping analysis in 0.1 M KI solution. Separation of the Fe and Hg stripping peaks can be achieved by changing the KI concentration. Displayed in Figure 11 are the square-wave anodic stripping voltammograms of 0.1 M KI solution containing 1.00 ppm Cd and Pb (dotted curve) and that containing 1.00 ppm Cd, Pb and Hg (solid curve) at a GC electrode. Deposition took place at -900 mV in steady-state solution, followed by square-wave anodic stripping. As can be seen from the voltammograms, each metal has its distinct stripping peak which is well separated from the others.

Figure 11. Simultaneous Detection of Multi Metals. Square-wave anodic stripping voltammograms of 0.1 M KI solution containing 1.00 ppm Cd and Pb (curve a) and that containing 1.00 ppm Cd, Pb and Hg (curve b) at GC electrode. Deposition condition: 1 second at -900 mV in steady-state solution, followed by square-wave anodic stripping (amplitude 30 mV, step height 2 mV, period 30 ms). All solutions were deoxygenated. Other conditions as in Figure 2.

Environmental Sample Analysis

Summarized in Table 1 is a comparison of Hg analytical results from an analytical laboratory using AA method vs. those from rapid electroanalysis with SW-ASV at a Au electrode for 11 real-world environmental samples and 10 soil samples doped with different Hg species. The experimental conditions were the same as those in Figure 3. The Hg concentrations were determined by comparing the experimentally determined stripping charge with the appropriate calibration curve in Figure 3. The presented values in Table 1 are the Hg concentration in solid samples, not in the dilute extract, which differs by 1000 times. Also listed in Table 1 are the electroanalytical results at a GC electrode for two Hg environmental samples by linear scan anodic stripping voltammetry. The following observations are made by examining Table 1 and other detailed ASV results:

- 1) The electroanalysis reproducibility is very good for soil, phosphor, brick and concrete samples, as demonstrated by the experimental results in Figure 12. However, the reproducibility is poor for all phenolic samples. The anodic stripping current and charge for these samples decrease during the course of sequential measurements. This phenomenon is most likely caused by the Au electrode surface deactivation as the result of strong adsorption of organic species extracted from the phenolic samples. However, this reproducibility problem can be overcome by cleaning the electrode prior to the Hg electroanalysis by electrochemical oxidation-reduction potential cycling in 1 M H_2SO_4 . Ultrasonication of the electrode in 1 M H_2SO_4 for 3 minutes has also been found to be moderately effective for improving the reproducibility of electrode surface activity, as illustrated by the results shown in Figure 13.

Table 1. COMPARISON OF LAB-AA AND RAPID ASV METHODS FOR MERCURY ANALYSIS

<u>Sample #</u>	<u>Source</u>	<u>Media</u>	<u>Form of Hg</u>	<u>AA -Hg.ppm</u>	<u>ASV -Hg.ppm</u>
1	Real	Phenolic	?	11	9.1
2	Real	Phenolic	?	52	33.51
3	Real	Phenolic	?	623	633.1
4 [#]	Real	Phenolic	?	280	270
5 [#]	Real	Phenolic	?	460	440
6	Doped	Soil	Hg ⁰	100	114
7	Doped	Soil	Hg ⁰	1000	989.1
8	Doped	Soil	Hg ⁰	10,000	8742
9	Real	Soil	-	ND*	ND
10	Real	Soil	HgS	3347	3125
11	Real	Soil	HgS	113	92.36
12	Real	Soil	Hg ⁰	6217-32,000**	22678
13	Doped	Soil	HgO	955	950.2
14	Doped	Soil	HgS	1007	889
15	Doped	Soil	(Hg) ₃ (PO ₄) ₂	1102	994.7
16	Doped	Soil	HgCl ₂	941	1000
17	Doped	Soil	Hg ₂ O	1099	749.9
18	Doped	Soil	Hg ₂ Cl ₂	984	1123
19	Doped	Soil	CH ₃ HgCl	240	266.1
20	Real	Phosphor	Hg ⁰	3666	4037
21	Real	Phosphor	Hg ⁰	<10	<5
22	Real	Brick	Hg ⁰	3080***	4804
23	Real	Concrete	Hg ⁰	1164***	1006

A GC electrode was used for these two samples. Others were analyzed at a Au electrode.

* ND: not detectable; Hg-free soil sample.

** The sample contains visible Hg beads, thus there is a large Hg concentration variation due to sampling.

*** Estimated values.

Ave Q=0.182; SD=0.003; SD%=1.6%

Ave i=0.528; SD=0.009; SD%=1.7%

Figure 12. An Example of Hg Electroanalysis Reproducibility for Soil Samples. Stripping currents and charges were measured from the square-wave anodic stripping voltammograms for a soil sample doped with elemental Hg in the solution of 0.1 M KI, 0.005 M I_2 and 0.25 M K_2SO_4 . Deposition condition: -100 mV for 30 seconds in steady-state solution, followed by square-wave anodic stripping. Prior to deposition, a predeposition potential of 400 mV was applied for 5 seconds and after deposition a postdeposition potential of 0 mV was applied for 5 seconds. Other conditions as in Figure 2.

Figure 13. Effect of Electrode Cleaning on Hg Electroanalysis. Stripping currents were measured from the square-wave anodic stripping voltammograms for a phenolic residue sample contaminated with mercury. The electrode was cleaned after the 4th run by ultrasonication in 1 M H_2SO_4 for 3 minutes. Other conditions as in Figure 12.

- 2) Most of the electroanalytical results are in good agreement with the results from those obtained by a GE-CRD analytical laboratory using a cold vapor atomic absorption method as shown in Table 1. However, it should be pointed out that, for most of the samples, we are comparing the same solid samples analyzed by two different techniques, not comparing the same extract by two different techniques. The difference found between two methods can be contributed by variations of sampling, extraction and analysis. Since the method's accuracy is not extremely important for rapid field analysis, a direct comparison of rapid electroanalysis and cold vapor atomic absorption method for the same electrolyte has not been performed. All soil samples give consistent and relatively correct analytical results without any treatment of working electrode between sample analysis. However, phenolic samples have a tendency to yield lower Hg analytical results (although they are still in the same order of magnitude to the AA results) if no pretreatment of the working electrode is performed. This tendency may be explained by the strong adsorption of phenolic residues onto electrode surface, thus decreasing the deposition efficiency. By cleaning the electrode between runs and taking measurement immediately after electrode immersion into the Hg solution, one can obtain higher and comparable Hg values for all phenolic samples. Brick and concrete samples produce great uncertainty due to the heterogeneity of Hg existing in the samples. Thus, the same extracts were used for both AA and ASV methods for Hg analysis.

CONCLUSIONS

Stripping voltammetry has been used extensively to detect Hg in KI solution. A linear relationship has been found between stripping current and Hg concentration. No interference from other heavy metals has been observed primarily as a result of the use of Hg-specific extraction reagents, the method's ability to avoid stripping peak overlap by changing the KI concentration and the mechanism to avoid metal co-deposition to form complicated metal compounds through selection of the proper deposition potential. The presence of oxygen in solution has essentially no effect on the electroanalytical results. The detection limit calculated on the basis of three times the signal to noise ratio is 20 ppt with a 10 minute deposition time. As the deposition time increases, the detection limit will decrease accordingly. The electrochemical results for real-world Hg samples in a wide range of solid substrates agree very well with the analytical results based on flame AA. The method has been also applied to simultaneously monitor Cu, Fe, Cd, Pb and Hg. The advantages of ASV (anodic stripping voltammetry) method can be summarized as Simple, Fast, Inexpensive, Selective, Sensitive and Versatile (multi-element capability):

1) Simple

One step extraction: add KI/I₂ solution to a sample;

One step analysis: immerse electrode into the extract and take the measurement.

2) Fast

The current analysis takes less than 3 minutes per sample depending on Hg concentration. The extraction time varies with the sample matrix from 5 to 30 minutes. With multi-electrode and flow cell design, one can easily measure 10 samples per minute.

3) Inexpensive

Assuming 10 mL extractant solution (1M KI/0.1M I₂) is used for a 1.0 g solid sample. The total analysis cost (not including labor) is less than \$3/sample.

Chemicals: \$0.22/sample.

Disposable filter: \$1.8/sample.

Misc. (weighing paper, wipes, etc.): <\$1.

The initial cost for a stripping electroanalysis system ranges from \$3000 with manual control to \$15,000 with lap-top computer control.

4) Selective and sensitivity

Both extraction and electroanalysis are very specific to Hg due to the large formation constant of HgI_4^{2-} and easy and precise control of deposition potential. The KI/I_2 extraction is very selective towards Hg species. Interference which is the main obstacle to a method's selectivity and sensitivity has been not found because Hg stripping potential can be manipulated by changing the KI concentration to avoid any possible interference signals.

5) Reproducibility

The method possesses great reproducibility because it is insensitive to many experimental variables. For example, oxygen in solution has virtually no influence on Hg electroanalysis. Small changes in KI and I_2 concentration have practically no effect on the stripping current intensity. Another important factor for the method's reproducibility is the strong adsorption of iodine at the Au electrode surface, which ensures a reproducible electrode surface in a variety of extract solutions.

6) Multi-Element Capability

The described stripping method can be applied to screen a wide range of metals including Ni, Pb, Hg, Cd, Cr, Ag, Cu, Tl and As simultaneously or step-by-step individually in aqueous solution. This capability provides significant savings in time and money for sample analysis, and more importantly is extremely useful in on-site monitoring and automatic controlling an industrial metal plating or cleaning process.

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APPENDIX C

BIMELYZE IMMUNOASSAY

BIMELYZE[®] MERCURY IMMUNOASSAY ANALYSIS OF SAMPLES FROM NATURAL GAS SITES

INTRODUCTION

This report summarizes the mercury analyses of 96 soil samples taken from natural gas sites for a study sponsored by the Gas Research Institute (GRI) and the U.S. Department of Energy (DOE). The study was organized by John Harju of the Energy and Environmental Research Center (EERC). The goal of the project is to evaluate four different field portable techniques for their utility to measure mercury contamination at sites associated with the natural gas industry. The samples were analyzed by Craig Schweitzer (Product Development Manager, BioNebraska, Inc.) using the BiMelyze[®] Mercury Immunoassay, manufactured by BioNebraska Inc. Analysis took place at the EERC laboratories in Grand Forks, North Dakota (March 7-9, 1995).

SUMMARY OF METHOD

Enzyme Linked ImmunoSorbent Assays (ELISA) have been used for over twenty years in the medical diagnostic field, both in the home (e.g. pregnancy testing) and in clinical settings (e.g. AIDS diagnosis). Immunoassays are based on highly specific interactions of antibodies with specific analytes. ELISA technology has been adapted in the last ten years to detect contaminants in environmental matrices, with current environmental immunoassays on the market detecting numerous analytes (e.g. heavy metals, such as mercury, and organics such as polychlorinated biphenyls (PCB's)). The BiMelyze Mercury Immunoassay is an ELISA based test for mercury in environmental matrices using mercuric ion monoclonal antibodies (patent 5,503,987). The assay has been validated for solid environmental matrices such as soils and sludges by both BioNebraska and independent investigators (see reference 1). The assay has also been demonstrated successfully for other matrices such as paint and cinderblock (2). The assays specificity and sensitivity has been described in detail (1,2,3) and is not affected by typical constituents in environmental matrices. It is being used commercially in remediation projects at sites such as battery recycling plants, chemical and dye manufacturing plants, mining sites, munitions and nuclear processing facilities and natural gas metering and compression stations throughout the country. The method is approved for use in Department of Energy (DOE) projects and is assigned method number MB 100 in the DOE methods compendium (4). The BiMelyze immunoassay has also been certified by the California Environmental Protection Agency (EPA), certificate number 95-01-014, and has passed technical work group approval of the federal EPA. Draft method number 4500, has been assigned by the office of solid waste (OSW) for inclusion in the OSW-846 methods manual.

The field portable tube assays format allows analysis of up to 13 samples and 3 controls in approximately 1.25 hours at approximately \$25 per sample (5). BioNebraska also markets the same assay in a 96-well plate assay for quantitative measurements of numerous samples in a

laboratory setting (6). The extract and tube assay kits are virtually self-contained, using dropper bottles for the addition of the reagents or, alternatively, pipettes for greater precision. Two positive controls, generally at 5 and 15 parts per million (ppm) mercury, and a negative control are supplied with the extraction kit. Standards at other concentrations can be supplied to meet the end users requirements/action levels. The standards and unknowns are extracted and analyzed at the same time for semi-quantitative mercury determination. The lower limit of quantitation for the assay is 0.5 ppm in soils and 0.25 ppb for aqueous samples (3).

Three major steps comprise mercury detection using the BiMelyze Mercury Immunoassay system: sample preparation, immunoassay and interpretation. For a complete description of the steps refer to the BiMelyze Soil Extraction Kit protocol (7) and the BiMelyze Mercury Assay Tube Kit protocol (8). These protocols contain: summary of the method, contents of the kits, user supplied materials, safety warnings, storage conditions and the actual step-by-step instructions with descriptive illustrations. The major steps are illustrated in the reference "Principles of ELISA" (9).

SAMPLE PREPARATION

The operator/analyst labels the soil sample bottles with identification numbers and places 5 g of soil into the corresponding bottles. Proper sampling technique is necessary to ensure the soil is homogeneous and representative of the area tested. Sample preparation is especially important when measuring the presence of elemental mercury.

Hydrochloric acid and nitric acid are added to the water in the supplied acid mixture bottle (final dilution of 2:1:1). The contents are mixed and 4 milliliters (mL) of the acid solution are added to each of the samples and controls. The soil samples and controls are vigorously swirled at least fifteen seconds of each minute during the ten minute extraction. Glass beads enclosed in the bottles aid in sample dispersion and extraction.

After extraction, 7 mL of Sample Buffer are added to each of the acidic Soil Sample bottles, the samples are swirled to mix the contents, and then filtered using supplied filter tips. Three drops (0.105 mL if using pipettes) of the extract solution are added to the supplied dilution bottles containing 35 mL dilution buffer. The large dilution is necessary to adjust the extract solution to pH 7 and to dilute the mercury concentration into the assay working range. The prepared samples are then ready to be analyzed by the immunoassay.

IMMUNOASSAY

Prepared samples and standards are added to tubes labeled with identification numbers. Quantitative additions are accomplished by dropper bottles up to a fill line or, alternatively, using pipettes capable of measuring 0.5 mL. The samples are incubated at ambient temperature for 5 min., then emptied and the tubes rinsed three times with distilled water. Next is the addition of 0.5 mL of monoclonal antibody solution to the tubes. The antibody is supplied as a lyophilized powder and dissolved into Antibody Diluent prior to use. After the 5 min. antibody incubation, the tubes are emptied and washed three times with a detergent solution then rinsed three times

with distilled water. The third 5 min. step is the addition of Conjugate, a secondary, horseradish peroxidase complexed antibody that binds to the mercury antibodies. The tubes are emptied, detergent washed three times, and distilled water rinsed three times. The final step is the addition of Substrate which is oxidized by the horseradish peroxidase complexed antibody, turning the liquid from colorless to a blue-green. The resulting color intensity is dependent on the mercury concentration in the original sample. After the 5 min. incubation, color development is terminated by three drops of Stop Solution added to each tube. The tubes are swirled at least once during each of the incubations and after the addition of the stop solution to facilitate thorough mixing.

INTERPRETATION

The final color intensities are measured visually or, preferably, with a differential photometer available from BioNebraska that reads at 405 nanometers. The final color intensity is directly proportional to the *log* of the mercury concentration. The data are interpreted in a semi-quantitative manner relative to the standards. By comparing the unknown sample color intensities to those of the standards, the unknown samples are classified as being less than, between, or greater than the mercury concentrations of the standards. For example in Table 1, experiment 1; the negative soil gave an absorbance of 0.08, the 1 ppm standard gave an absorbance of 0.73 and the unknown sample C4 gave an absorbance of 0.27. Sample C4 is classified as having a concentration of mercury that is between the negative control and 1 ppm mercury (neg-1 ppm).

The absorbance values can also be used to subjectively determine the mercury concentration of the unknown soil, relative to the standards. Sample C1, in Table 1, experiment 1, is classified as having 1-5 ppm whereas C2 is neg-1 ppm mercury. The absorbencies of these samples (0.74 and 0.72 respectively) are quite close to the absorbance of the 1 ppm standard (0.73) so, it can be inferred that both samples contain approximately 1 ppm mercury.

SAMPLES

Samples in this study were grouped, prior to analysis by EERC personnel, into three classes consisting of A, B and C's depending upon their approximate concentrations of mercury. Thirty "A" samples had mercury levels in the range of 50-2000 ppm, 34 "B" samples were in the range of 1-200 ppm and 32 "C" samples were in the background to 5 ppm range. The standards used for this study were 1, 5, 20 ppm mercury and a negative control. The results are therefore interpreted semi-quantitatively as: neg-1, 1-5, 5-20, >20 ppm mercury for the standard extraction and dilution of a 5 g sample. The current commercial test kit is designed and manufactured for detecting mercury in the 0.5 to 50 ppm range, but some samples in this study were in the thousands of ppm range; therefore, a dilution scheme which was 50 times more dilute than the standard protocol was used for semi-quantitation of the higher concentration samples. This dilution was accomplished by extraction of a smaller sample size (1 g) and an increase in dilution. The data for the 1 g samples are compared to the same standards of neg, 1, 5 and 20, but concentrations are interpreted as neg-50, 50-250, 250-1000 or > 1000 ppm mercury. When all of the data is combined, as in table 2, the classifications become neg-1, 1-5, 5-20, 20-50, 50-250, 250-1000 and >1000 ppm mercury.

DISCUSSION

The "B" and "C" series were first analyzed by the standard 5 g extraction protocol with samples classified greater than 20 ppm re-tested with the 50 fold dilution scheme described previously. Since the "A" samples were known to contain high amounts of mercury, they were initially tested with the higher dilution scheme. Some of the "A" series were classified as neg-50 ppm after the initial extraction and were subsequently analyzed with the standard protocol.

The raw data, presented in Table 1, is comprised of 10 separate experiments, each presenting the weight of soil extracted, photometer readings, and classifications produced by a distinct kit. Finalized data, presenting the final classifications, are listed in Table 2. Samples absorbance close to that of the standard are in bold and underlined in both tables.

An error associated with sample A22, experiment 8, produced an absorbance reading of 0.00. The sample was then extracted by the standard protocol in experiment 10 and produced an absorbance which was much greater than the 20 ppm standard. The sample was not re-analyzed with the 50 fold dilution scheme and can only be classified as >> 20 ppm. Samples A6, A11 and B27 gave absorbencies which were identical to that of the 250 ppm standard, therefore the concentrations are not listed as a range, but as 250 ppm.

The absorbencies of the 20 ppm standards are generally near 1, if the absorbance of the unknown samples in Table 2 were greater then the 20 ppm control, but less than 2.0 the symbol ">1000" was used. If the unknown sample had an absorbance greater than 2.0, the symbol ">>1000" was used.

Table 1 Raw data from BiMelyze Mercury Immunoassay analysis, March 7-9, 1995.

Experiment 1

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
C1	5.01	0.74	1-5 ppm
C2	5.09	0.72	neg-1 ppm
C3	5.04	0.72	neg-1 ppm
C4	5.10	0.27	neg-1 ppm
C5	5.09	0.36	neg-1 ppm
C6	5.10	0.14	neg-1 ppm
C7	5.08	0.40	neg-1 ppm
C8	5.11	1.18	5-20 ppm
C9	5.13	0.58	neg-1 ppm
C10	5.09	0.14	neg-1 ppm
C11	5.11	0.14	neg-1 ppm
C12	5.12	0.12	neg-1 ppm
neg	NA	0.08	NA
1 ppm	NA	0.73	NA
5 ppm	NA	1.04	NA
20 ppm	NA	1.26	NA

Experiment 2

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
C13	5.10	0.88	1-5 ppm
C14	5.10	0.72	1-5 ppm
C15	5.12	0.54	neg-1 ppm
C16	5.14	1.08	1-5 ppm
C17	5.14	0.67	neg-1 ppm
C18	5.15	0.84	1-5 ppm
C19	5.10	0.41	neg-1 ppm
C20	5.14	1.01	1-5 ppm
C21	5.12	0.28	neg-1 ppm
C22	5.14	0.46	neg-1 ppm
C23	5.18	0.31	neg-1 ppm
C24	5.17	0.52	neg-1 ppm
neg	NA	0.13	NA
1 ppm	NA	0.71	NA
5 ppm	NA	1.16	NA
20 ppm	NA	1.69	NA

Experiment 3

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
C25	5.11	1.10	5-20 ppm
C26	5.17	0.44	neg-1 ppm
C27	5.15	0.19	neg-1 ppm
C28	5.16	0.39	neg-1 ppm
C29	5.15	0.16	neg-1 ppm
C30	5.13	0.19	neg-1 ppm
C31	5.13	0.32	neg-1 ppm
C32	5.11	0.54	neg- ppm 1
B1	5.11	1.18	>20 ppm*
B2	5.14	>2.0	>20 ppm*
B3	5.17	>2.0	>20 ppm*
B4	5.14	0.88	5-20 ppm
neg	NA	0.00	NA
1 ppm	NA	0.60	NA
5 ppm	NA	0.80	NA
20 ppm	NA	1.15	NA

Experiment 4

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
B29	5.05	1.30	>20 ppm*
B30	5.07	1.12	5-20 ppm
B31	5.17	1.10	5-20 ppm
B32	5.08	>2.0	> 20 ppm*
B33	5.09	>2.0	>20 ppm*
B34	5.12	1.31	>20 ppm*
A1	1.04	1.34	>1000 ppm
A2	1.02	1.25	>1000 ppm
A3	1.06	0.21	< 50 ppm*
A4	1.05	0.47	< 50 ppm*
A5	1.06	1.32	>1000 ppm
A6	1.05	0.82	250 ppm
neg	NA	0.09	NA
1 ppm	NA	0.63	NA
5 ppm	NA	0.82	NA
20 ppm	NA	1.16	NA

* Samples tested over/under the standards and were re-tested using the alternative dilution scheme.

Table 1 Raw data from BiMelyze Mercury Immunoassay analysis, March 7-9,1995.

Experiment 5

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
B17	5.18	1.96	>20 ppm*
B18	5.16	1.69	> 20 ppm*
B19	5.18	>2.0	>20 ppm*
B20	5.13	0.94	5-20 ppm
B21	5.14	1.29	>20 ppm*
B22	5.10	0.16	neg-1 ppm
B23	5.14	1.55	>20 ppm*
B24	5.13	0.68	1-5 ppm
B25	5.11	1.05	5-20 ppm
B26	5.12	1.09	5-20 ppm
B27	5.19	>2.0	>20 ppm*
B28	5.15	0.53	1-5 ppm
neg	NA	0.00	NA
1 ppm	NA	0.42	NA
5 ppm	NA	0.72	NA
20 ppm	NA	1.10	NA

Experiment 6

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
B5	5.14	0.95	5-20 ppm
B6	5.11	1.09	5-20 ppm
B7	5.13	0.79	5-20 ppm
B8	5.13	>2.0	>20 ppm*
B9	5.17	1.05	5-20 ppm
B10	5.14	1.08	5-20 ppm
B11	5.14	0.71	5-20 ppm
B12	5.16	1.23	>20 ppm*
B13	5.15	0.31	neg-1 ppm
B14	5.17	0.95	5-20 ppm
B15	5.16	0.73	5-20 ppm
B16	5.17	1.86	>20 ppm*
neg	NA	0.10	NA
1 ppm	NA	0.47	NA
5 ppm	NA	0.66	NA
20 ppm	NA	1.17	NA

Experiment 7

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
A7	1.07	1.32	250-1000 ppm
A8	1.07	1.44	>1000 ppm
A9	1.07	1.47	>1000 ppm
A10	1.02	>2.0	>>1000 ppm
A11	1.08	0.84	250 ppm
A12	1.04	>2.0	>>1000 ppm
A13	1.03	0.96	250-1000 ppm
A14	1.03	>2.0	>>1000 ppm
A15	1.09	1.87	>1000 ppm
A16	1.05	1.89	>1000 ppm
A17	1.06	>2.0	>>1000 ppm
A18	1.04	0.85	250-1000 ppm
neg	NA	0.05	NA
1 ppm	NA	0.67	NA
5 ppm	NA	0.84	NA
20 ppm	NA	1.35	NA

Experiment 8

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
A19	1.02	>2.0	>>1000 ppm
A20	1.04	0.82	250-1000 ppm
A21	1.02	>2.0	>>1000 ppm
A22	1.08	0.00	neg-50 ppm
A23	1.08	1.70	>1000 ppm
A24	1.05	>2.0	>>1000 ppm
A25	1.03	0.73	50-250 ppm
A26	1.07	1.00	250-1000 ppm
A27	1.02	0.65	50-250 ppm
A28	1.08	0.22	neg-50 ppm
A29	1.08	1.46	>1000 ppm
A30	1.07	1.80	>1000 ppm
neg	NA	0.25	NA
1 ppm	NA	0.56	NA
5 ppm	NA	0.78	NA
20 ppm	NA	1.06	NA

* Samples tested over/under the standards and were re-tested using the alternative dilution scheme.

Table 1 Raw data from BiMelyze Mercury Immunoassay analysis, March 7-9, 1995.

Experiment 9 Second analysis of samples

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
B1	1.05	0.32	20-50 ppm
B2	1.04	0.76	250-1000 ppm
B3	1.04	1.04	>1000 ppm
B8	1.07	0.68	250-1000 ppm
B12	1.07	0.85	250-1000 ppm
B16	1.04	0.74	250-1000 ppm
B17	1.04	0.50	50-250 ppm
B18	1.05	0.47	50-250 ppm
B19	1.04	0.62	50-250 ppm
B21	1.03	0.23	20-50 ppm
B23	1.06	0.72	250-1000 ppm
B27	1.03	0.63	250 ppm
neg	NA	0.12	NA
1 ppm	NA	0.45	NA
5 ppm	NA	0.63	NA
20 ppm	NA	0.94	NA

Experiment 10 Second analysis of samples

SAMPLE	WEIGHT(g)	ABSORBANCE	CLASSIFICATION
B29	1.04	0.34	neg-50 ppm
B32	1.04	1.05	250-1000 ppm
B33	1.02	0.75	250-1000 ppm
B34	1.01	0.32	neg-50 ppm
A3	5.05	0.92	5-20 ppm
A4	5.02	1.34	20-50 ppm
A22	5.09	>2.0	>>20 ppm
A28	5.12	0.90	5-20 ppm
neg	NA	0.12	NA
1 ppm	NA	0.55	NA
5 ppm	NA	0.60	NA
20 ppm	NA	1.07	NA

* Samples tested over/under the standards and were re-tested using the alternative dilution scheme.

Table 2 Results of BiMelyze Mercury Immunoassay analysis, March 7-9, 1995.

SAMPLE	CLASSIFICATION (PPM)
A1	>1000
A2	>1000
A3	5-20
A4	20-50
A5	>1000
A6	<u>250</u>
A7	<u>250-1000</u>
A8	>1000
A9	>1000
A10	>>1000
A11	<u>250</u>
A12	>>1000
A13	250-1000
A14	>>1000
A15	>1000
A16	>1000
A17	>>1000
A18	<u>250-1000</u>
A19	>>1000
A20	<u>250-1000</u>
A21	>>1000
A22	>>20
A23	>1000
A24	>1000
A25	<u>50-250</u>
A26	<u>250-1000</u>
A27	<u>50-250</u>
A28	5-20
A29	>1000
A30	>1000

SAMPLE	CLASSIFICATION (PPM)
B1	<u>20-50</u>
B2	250-1000
B3	>1000
B4	5-20
B5	5-20
B6	<u>5-20</u>
B7	<u>5-20</u>
B8	<u>250-1000</u>
B9	<u>5-20</u>
B10	5-20
B11	<u>5-20</u>
B12	250-1000
B13	NEG-1
B14	5-20
B15	<u>5-20</u>
B16	250-1000
B17	50-250
B18	<u>50-250</u>
B19	<u>50-250</u>
B20	5-20
B21	20-50
B22	<u>neg-1</u>
B23	250-1000
B24	1-5
B25	<u>5-20</u>
B26	<u>5-20</u>
B27	<u>250</u>
B28	1-5
B29	20-50
B30	<u>5-20</u>
B31	<u>5-20</u>
B32	250-1000
B33	250-1000
B34	20-50

SAMPLE	CLASSIFICATION (PPM)
C1	<u>1-5</u>
C2	<u>neg-1</u>
C3	<u>neg-1</u>
C4	<u>neg-1</u>
C5	<u>neg-1</u>
C6	<u>neg-1</u>
C7	<u>neg-1</u>
C8	5-20
C9	<u>neg-1</u>
C10	<u>neg-1</u>
C11	<u>neg-1</u>
C12	<u>neg-1</u>
C13	1-5
C14	1-5
C15	<u>neg-1</u>
C16	1-5
C17	<u>neg-1</u>
C18	1-5
C19	<u>neg-1</u>
C20	1-5
C21	<u>neg-1</u>
C22	<u>neg-1</u>
C23	<u>neg-1</u>
C24	<u>neg-1</u>
C25	5-20
C26	<u>neg-1</u>
C27	<u>neg-1</u>
C28	<u>neg-1</u>
C29	<u>neg-1</u>
C30	<u>neg-1</u>
C31	<u>neg-1</u>
C32	<u>neg-1</u>

REFERENCES

1. Evaluation of field test kits including immunoassays for the detection of contaminants in soil and water.
2. Waste Testing & Quality Assurance Symposium. Enzyme-linked immunoassay (ELISA) for the detection of mercury in environmental matrices.
3. BiMelyze® Field Screening Test for Mercury in Soil.
4. DOE Methods for Evaluating Environmental Waste Management Samples. MB 100.
5. BiMelyze Price List.
6. BiMelyze Laboratory Screening Test for Mercury In Soil.
7. BiMelyze Soil Extraction Kit (protocol).
8. BiMelyze Mercury Assay Tube Kit For Solid Matrices (protocol).
9. Principles of the Mercury ELISA.

APPENDIX D

X-RAY FLUORESCENCE SPECTROMETRY

Analysis of Mercury in Soil Using Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry

The Spectrace 6000 was used in a study to determine the effectiveness of EDXRF for the analysis of mercury in soil. The following report will summarize the technique by describing the theory of energy dispersive X-ray fluorescence, the hardware and software of the Spectrace 6000, and the general procedure for sample preparation and analysis.

ENERGY DISPERSIVE XRF ANALYSIS

Energy dispersive X-ray fluorescence spectrometry, developed in the early 1970's, is a flexible elemental analysis method used for quantitative determinations of solid, liquid and thin film (filters or wipes) samples. EDXRF spectrometry is capable of analyzing elements with atomic number 11-sodium and higher in the periodic table in concentrations ranging from a few parts per million to 100 % by weight. The Spectrace 6000 is a benchtop EDXRF spectrometer that is interfaced with a personal computer for data handling, storage and automation of the analysis method.

EDXRF THEORY AND SPECTRACE 6000 HARDWARE

Excitation

The Spectrace 6000 uses an X-ray tube for sample excitation. The X-ray tube is an evacuated glass envelope containing a filament and a pure metal anode which is typically rhodium. The tube voltage and current are automatically controlled through the software to produce the necessary X-rays to excite elements in a sample. The X-rays produced in the tube radiate towards the sample through a window that is sealed with beryllium.

Fluorescence

These X-ray photons from the tube are passed through a primary radiation filter for the purpose of optimizing the incident X-ray beam. The X-rays then strike the sample and excite elements by photojecting an inner-orbital electron. Once an element has a vacancy in an inner-orbital electron shell, this element is in an excited state. In order to return to the ground state, an electron from an outer orbital undergoes electron shell transfer to fill the vacancy. This transition will emit an X-ray photon that is characteristic of the element. Common emission lines are termed $K\alpha$, $K\beta$, $L\alpha$ and $L\beta$. For analysis of mercury, the spectrometer will detect the $L\alpha$ and $L\beta$ of mercury at 9.987 keV and 11.823 keV, respectively. Upon excitation, these X-rays are emitted in all directions from the sample.

Detection

The detector sits at 45° from the sample (90° from the X-ray tube) to detect the elemental fluorescence from the sample. The X-ray detector is an electrically cooled semi-conductor made of lithium drifted silicon or Si(Li). When an X-ray photon enters the detector region, it's energy is dissipated into the semi-conductor region by creating electron hole pairs. The number of electron hole pairs is proportional to the energy of that X-ray

photon. This charge is swept off the detector region by a voltage bias across the detector region. This signal is amplified and converted to a digital energy value which is then assigned to a channel on a 2048-channel multichannel analyzer. That X-ray photon is now considered one count in the assigned energy channel.

SPECTRACE 6000 SOFTWARE

Spectral data is transferred to the interfaced personal computer (PC) for storage of spectra and calculation of results. A spectrum of X-ray photon counts is acquired which results in a histogram containing element peaks. Once the spectrum has been acquired from a sample the PC software is responsible for data processing. The element peaks are integrated by the software to obtain counts/second data for each element of interest in the sample. Element intensities (counts/sec) are compared to those of known standards to calculate results for the unknown sample. The Spectrace 6000 software used a Fundamental Parameters algorithm to calculate mercury results for each sample.

For the analysis of mercury in soil, the following National Institute of Standards and Technology (NIST) certified soil materials were used to standardize the Spectrace 6000.

NIST 2709	San Joaquin Soil
NIST 2710	Montana Soil
NIST 2711	Montana Soil
NIST 8408	Mercury in Tennessee River Sediment

SAMPLE ANALYSIS

In order to analyze an unknown soil sample for mercury, the following general procedure was used.

1. The samples were stored in a jar in the freezer for preserving.
2. Prior to analysis, approximately 10 grams of each moist sample was placed into a dish and set in a fume hood for a few hours to air dry. This method of drying was chosen to prevent or minimize the volatilization of Hg.
3. The dried sample was then placed into a grinding vessel and pulverized in a shattermill for 1 minute. This reduces the particle size of the soil to around 100 mesh.
4. The sample was then put into a standard 32 mm XRF sample cup ($\frac{1}{2}$ to $\frac{3}{4}$ full) and sealed on the open end with Mylar (6.0 μ m) X-ray transparent film.
5. The sample cup was then placed into the sample chamber on the Spectrace 6000 for a 10 minute measurement.
6. While the previous sample was running, the grinding vessel was washed and steps 3, 4 and 5 were repeated until all samples were analyzed.

RESULTS

After a measurement, results of mercury and up to 17 other metals (Pb, As, Zn, Cr, Cu, U, Se, etc.) are displayed on the computer screen and stored and/or printed if desired. A measurement time of 10 minutes will achieve a 3-sigma detection limit for mercury of approximately 5 ppm.

REFERENCES

R.W. Chappell, R.L. Olson, "Assessing the Usability of X-ray Fluorescence Data" presented at the Field Screening for Hazardous Waste and Toxic Chemicals Symposium, Las Vegas, NV, January 1995.

W. Goldschmidt, D. Gallis, D. Catherman, "On-site Analytical Support: A Cost-Effective Alternative to Fixed Laboratory Services" Remediation, Autumn 1994 issue.

J. Ashe, "Accuracy of Lead Measurements of Paint, Soil and Dust Samples by Laboratory-Based XRF" presented at NIST Workshop, Peter Pella chairman, Boulder, CO, 1993.

APPENDIX E

**SUMMARY OF ANALYTICAL RESULTS AS
REPORTED**

SUMMARY OF ANALYTICAL RESULTS AS REPORTED

Sample ID	SHSA		ASV		Bio		XRF		EERC		EPA 7471	
Location	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2
	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
LOUISIANA SOILS												
OL - 1	651.43	963.33	1840	1748	>1000	>1000	874.019	9.49	907.462	9.448	1150	1261
MLG - 1	5521.41	586.99	730	1150	>1000	>>20	632.802	8.372	771.919	8.736	1365	760
GL - 1	3160.49	3971.17	5200	4000	>>1000	>>1000	1704.815	11.848	1701.173	11.539	2470	3720
GL - 4	106.45	161.7	350	220	250	250-1000	167.42	5.491	126.542	5.293	195	120
MLG - 4	8969.4	5920.4	1320	3100	>>1000	>>1000	6514.209	23.354	5995.946	22.468	3470	5420
MLG - 7	206.98	387.54	1860	1350	250-1000	250-1000	195.932	5.322	323.574	6.175	286	363
LL - 1	>9100	>6900	13500	9400	>>>1000	>>>1000	4217.611	17.703	4888.941	19.105	5480	7470
DARB - 1	1697.84	1335.66	1950	1730	>1000	>1000	816.911	8.673	1023.551	9.491	1230	1400
OL - 2	74.99	31.18	38	54.3	5-20	5-20	41.204	3.824	41.382	4.392	35.2	28.6
MLG - 2	11.01	10.56	18	22.5	5-20	5-20	9.619	3.956	7.017	3.822	14.7	14.4
GL - 2	13.56	5.13	4.3	6.9	5-20	1-5	8.467	3.862	7.984	4.487	1.71	1.76
GL - 5	0.28	0.29	<1	NR	Neg-1	Neg-1	ND		0.623	3.53	0.16	1.47
MLG - 5	23.58	25.09	21.5	26.5	5-20	20-50	19.811	3.51	16.152	3.563	23.2	19.1
MLG - 8	6.7	6.36	NR	NR	5-20	5-20	3.79	3.018	ND		9.16	1.35
LL - 2	221.86	98.9	142	140	250-1000	50-250	182.69	4.891	156.572	4.899	160	121
DARB - 2	50.5	82.76	47.8	49.5	50-250	50-250	51.317	4.258	65.688	4.023	57.7	49.2
OL - 3	1.25	1.39	0.5	<1	Neg-1	Neg-1	ND		ND		0.27	0.319
MLG - 3	0.17	0.12	<0.5	<1	Neg-1	Neg-1	ND		ND		<0.03	<0.03
GL - 3	0.38	2.21	<0.5	<1	Neg-1	Neg-1	3.034	3.694	ND		0.715	0.559
GL - 6	0.63	0.95	<0.5	<1	Neg-1	Neg-1	ND		ND		0.12	0.07
MLG - 6	1.48	2.11	NR	<1	1-5	1-5	ND		6.031	2.916	1.26	0.728
MLG - 9	1.78	1.26	NR	<1	1-5	Neg-1	ND		0.061	2.859	0.09	0.11
LL - 3	0.99	1.23	<0.5	<0.5	Neg-1	1-5	ND		3.522	3.617	0.424	0.454
DARB - 3	0.32	0.85	<0.5	1	1-5	Neg-1	ND		ND		0.915	0.29

ND not detected

NR not determined due to interference

Sample ID	SHSA	ASV		Bio		XRF					EERC		EPA 7471		
Location	#1	#2	#1	#2	#1	#2	#1	#1 (+/-)	#2	#2 (+/-)	#1	#2	#1	#2	
	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
ALBERTA SOILS															
E. Cross 1	420.7	1136.53	1400	800	>1000	>1000	497.345	7.923	522.69	8.284	848	798	790.0	ND	
WR 1	1235.71	488.59	950	950	>1000	>1000	453.364	7.434	443.952	7.374	911	699	654.0	536.0	
WD 1	7.04	6.95	7	5.5	5 - 20	5 - 20	8.593	3.454	4.886	3.559	9.49	11.3	5.76	7.1	
AN 1	26.3	20.81	46	70	20 - 50	50-250	23.271	4.032	29.288	4.1	37.6	32.4	27.5	45.7	
BN 1	171.14	124.86	257	170	>1000	250-1000	176.954	5.555	205.931	5.993	255	287	106.0	253.0	
CM 1	21.83	26.41	113	69	250	50-250	69.251	4.356	62.123	4.902	116	90.6	30.1	29.7	
CLM 1	3286.24	6472.88	5850	6200	250-1000	>1000	3364.223	19.708	2503.774	16.99	2760	3910	2330.0	3420.0	
E. Cross 2	12.41	14.97	16	16	20-50	20-50	6.211	3.876	18.344	3.997	17.9	14.3	14.4	16.7	
WR 2	200.78	466.55	320	243	250-1000	250-1000	163.038	5.49	193.837	5.587	388	281	218.0	408	
WD 2	717.23	279.56	340	460	>1000	250-1000	273.297	5.954	285.902	6.143	371	353	357.0	445	
TB 1	7.82	9.73	13	9	1-5	5-20	3.749	3.911	14.049	3.869	14.7	12.7	11.4	9.43	
PW 1	3.39	1.97	2.5	3.6	5-20	5-20	4.423	4.002	ND		1.65	1.36	6.07	5.51	
CM 2	1.00	0.57	1.8	2.1	5-20	1-5	ND		ND		0.722	0.3	0.643	0.707	
CLM 2	146.13	138.41	119	234	250-1000	250-1000	191.122	6.84	222.773	7.418	97.9	106	102	120	
WR 3	1.03	0.59	<0.5	<1	1-5	Neg-1	1.376	3.114	ND		0.45	0.391	0.262	0.202	
WD 3	0.65	0.48	0.5	<1	1	Neg-1	ND		1.457	3.362	0.055	0.053	0.103	0.112	
AN 2	<0.013	<0.01	<0.5	<1	1	Neg-1	ND		ND		<0.03	<0.03	ND	ND	
PW 2	0.08	0.21	0.5	<0.5	Neg-1	Neg-1	3.641	3.867	ND		<0.03	<0.03	ND	ND	
BN 2	0.73	0.76	<0.5	<0.5	Neg-1	Neg-1	ND		ND		0.054	0.054	0.088	0.137	
CM 3	0.19	0.14	<0.5	<1	Neg-1	Neg-1	ND		ND		<0.03	<0.03	ND	0.065	
CLM 3	0.55	0.23	<0.5	2	Neg-1	Neg-1	ND		ND		0.31	0.36	0.234	0.27	
NIST STANDARDS															
SRM - 2711	5.99	6.48	1.90	NR	5-20	20-50	4.844	3.217	ND		11.00	5.60	6.07	5.51	
SRM - 2710	36.36	30.92	NR	50.00	20-50	250-1000	27	5.54	ND		32.80	30.80	30.50	32.70	
SRM - 2709	2.43	2.43	<0.5	1.00	5-20	5-20	ND	ND	ND		1.41	1.40	1.43	1.37	

Sample ID	RT Corporation			
Location	Beginning (µg/g)	Middle (µg/g)	End (µg/g)	Mean (µg/g)

ALBERTA SOILS

E. Cross 1	590	2700	1300	1530
WR 1	550	360	560	490
WD 1	7.1	7.1	7.2	7.1
AN 1	28	30	25	28
BN 1	180	140	160	160
CM 1	32	82	33	49
CLM 1	4100	4400	5300	4600
E. Cross 2	13	12	14	13
WR 2	110	820	310	413
WD 2	590	410	280	427
TB 1	9.00	7.70	9.20	8.60
PW 1	2.20	2.00	2.20	2.10
CM 2	0.69	0.64	0.60	0.64
CLM 2	110	110	110	110
WR 3	0.46	0.13	0.18	0.26
WD 3	<0.099	<0.10	<0.10	<0.10
AN 2	<0.11	<0.10	<0.10	<0.10
PW 2	<0.11	<0.098	<0.10	<0.10
BN 2	<0.10	<0.10	<0.098	<0.10
CM 3	<0.10	<0.10	<0.10	<0.10
CLM 3	0.26	0.27	0.19	0.24

NIST STANDARDS

SRM - 2711	N/A	N/A	N/A	N/A
SRM - 2710	N/A	N/A	N/A	N/A
SRM - 2709	N/A	N/A	N/A	N/A

SUMMARY OF ANALYTICAL RESULTS AS REPORTED

Sample ID	SHSA	ASV		Bio		XRF		EERC		EPA 7471	
Location	#1	#2	#1	#2	#1	#2	#1 (+/-)	#2	#2 (+/-)	#1	#2
	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
LOUISIANA SOILS											
OL - 1	651.43	963.33	1840	1748	>1000	>1000	874.019	9.49	907.462	9.448	1150
MLG - 1	5521.41	586.99	730	1150	>1000	>>20	632.802	8.372	771.919	8.736	1365
GL - 1	3160.49	3971.17	5200	4000	>>1000	>>1000	1704.815	11.848	1701.173	11.539	2470
GL - 4	106.45	161.7	350	220	250	250-1000	167.42	5.491	126.542	5.293	195
MLG - 4	8969.4	5920.4	1320	3100	>>1000	>>1000	6514.209	23.354	5995.946	22.468	3470
MLG - 7	206.98	387.54	1860	1350	250-1000	250-1000	195.932	5.322	323.574	6.175	286
LL - 1	>9100	>6900	13500	9400	>>>1000	>>>1000	4217.611	17.703	4888.941	19.105	5480
DARB - 1	1697.84	1335.66	1950	1730	>1000	>1000	816.911	8.673	1023.551	9.491	1230
OL - 2	74.99	31.18	38	54.3	5-20	5-20	41.204	3.824	41.382	4.392	35.2
MLG - 2	11.01	10.56	18	22.5	5-20	5-20	9.619	3.956	7.017	3.822	14.7
GL - 2	13.56	5.13	4.3	6.9	5-20	1-5	8.467	3.862	7.984	4.487	1.71
GL - 5	0.28	0.29	<1	NR	Neg-1	Neg-1	ND		0.623	3.53	0.16
MLG - 5	23.58	25.09	21.5	26.5	5-20	20-50	19.811	3.51	16.152	3.563	23.2
MLG - 8	6.7	6.36	NR	NR	5-20	5-20	3.79	3.018	ND		9.16
LL - 2	221.86	98.9	142	140	250-1000	50-250	182.69	4.891	156.572	4.899	160
DARB - 2	50.5	82.76	47.8	49.5	50-250	50-250	51.317	4.258	65.688	4.023	57.7
OL - 3	1.25	1.39	0.5	<1	Neg-1	Neg-1	ND		ND		0.27
MLG - 3	0.17	0.12	<0.5	<1	Neg-1	Neg-1	ND		ND		<0.03
GL - 3	0.38	2.21	<0.5	<1	Neg-1	Neg-1	3.034	3.694	ND		0.715
GL - 6	0.63	0.95	<0.5	<1	Neg-1	Neg-1	ND		ND		0.12
MLG - 6	1.48	2.11	NR	<1	1-5	1-5	ND		6.031	2.916	1.26
MLG - 9	1.78	1.26	NR	<1	1-5	Neg-1	ND		0.061	2.859	0.09
LL - 3	0.99	1.23	<0.5	<0.5	Neg-1	1-5	ND		3.522	3.617	0.424
DARB - 3	0.32	0.85	<0.5	1	1-5	Neg-1	ND		ND		0.915

ND not detected

NR not determined due to interference

Sample ID	SHSA	ASV		Bio		XRF			EERC			EPA 7471		
Location	#1	#2	#1	#2	#1	#2	#1	#1 (+/-)	#2	#2 (+/-)	#1	#2	#1	#2
	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
ALBERTA SOILS														
E. Cross 1	420.7	1136.53	1400	800	>1000	>1000	497.345	7.923	522.69	8.284	848	798	790.0	ND
WR 1	1235.71	488.59	950	950	>1000	>1000	453.364	7.434	443.952	7.374	911	699	654.0	536.0
WD 1	7.04	6.95	7	5.5	5 - 20	5 - 20	8.593	3.454	4.886	3.559	9.49	11.3	5.76	7.1
AN 1	26.3	20.81	46	70	20 - 50	50-250	23.271	4.032	29.288	4.1	37.6	32.4	27.5	45.7
BN 1	171.14	124.86	257	170	>1000	250-1000	176.954	5.555	205.931	5.993	255	287	106.0	253.0
CM 1	21.83	26.41	113	69	250	50-250	69.251	4.356	62.123	4.902	116	90.6	30.1	29.7
CLM 1	3286.24	6472.88	5850	6200	250-1000	>1000	3364.223	19.708	2503.774	16.99	2760	3910	2330.0	3420.0
E. Cross 2	12.41	14.97	16	16	20-50	20-50	6.211	3.876	18.344	3.997	17.9	14.3	14.4	16.7
WR 2	200.78	466.55	320	243	250-1000	250-1000	163.038	5.49	193.837	5.587	388	281	218.0	408
WD 2	717.23	279.56	340	460	>1000	250-1000	273.297	5.954	285.902	6.143	371	353	357.0	445
TB 1	7.82	9.73	13	9	1-5	5-20	3.749	3.911	14.049	3.869	14.7	12.7	11.4	9.43
PW 1	3.39	1.97	2.5	3.6	5-20	5-20	4.423	4.002	ND		1.65	1.36	6.07	5.51
CM 2	1.00	0.57	1.8	2.1	5-20	1-5	ND		ND		0.722	0.3	0.643	0.707
CLM 2	146.13	138.41	119	234	250-1000	250-1000	191.122	6.84	222.773	7.418	97.9	106	102	120
WR 3	1.03	0.59	<0.5	<1	1-5	Neg-1	1.376	3.114	ND		0.45	0.391	0.262	0.202
WD 3	0.65	0.48	0.5	<1	1	Neg-1	ND		1.457	3.362	0.055	0.053	0.103	0.112
AN 2	<0.013	<0.01	<0.5	<1	1	Neg-1	ND		ND		<0.03	<0.03	ND	ND
PW 2	0.08	0.21	0.5	<0.5	Neg-1	Neg-1	3.641	3.867	ND		<0.03	<0.03	ND	ND
BN 2	0.73	0.76	<0.5	<0.5	Neg-1	Neg-1	ND		ND		0.054	0.054	0.088	0.137
CM 3	0.19	0.14	<0.5	<1	Neg-1	Neg-1	ND		ND		<0.03	<0.03	ND	0.065
CLM 3	0.55	0.23	<0.5	2	Neg-1	Neg-1	ND		ND		0.31	0.36	0.234	0.27
NIST STANDARDS														
SRM - 2711	5.99	6.48	1.90	NR	5-20	20-50	4.844	3.217	ND		11.00	5.60	6.07	5.51
SRM - 2710	36.36	30.92	NR	50.00	20-50	250-1000	27	5.54	ND		32.80	30.80	30.50	32.70
SRM - 2709	2.43	2.43	<0.5	1.00	5-20	5-20	ND	ND	ND		1.41	1.40	1.43	1.37

SUMMARY OF ANALYTICAL RESULTS AS REPORTED

Sample ID	RT Corporation			
Location	Beginning	Middle	End	Mean
	(µg/g)	(µg/g)	(µg/g)	(µg/g)

LOUISIANA SOILS

OL - 1	820	1500	740	1020
MLG - 1	740	920	540	733
GL - 1	5100	3800	2600	3833
GL - 4	230	130	380	247
MLG - 4	4400	12000	4400	6933
MLG - 7	170	130	210	170
LL - 1	9600	12000	9000	10200
DARB - 1	1000	1000	1600	1200
OL - 2	25	33	30	29
MLG - 2	11	11	11	11
GL - 2	1.4	1.5	0.78	1.2
GL - 5	<0.11	0.24	<0.11	0.15
MLG - 5	19	15	15	16
MLG - 8	0.72	0.58	0.99	0.76
LL - 2	33	210	160	134
DARB - 2	47	44	55	49
OL - 3	0.42	0.41	0.28	0.37
MLG - 3	<0.099	<0.10	<0.098	<0.10
GL - 3	<0.097	<0.10	0.13	0.11
GL - 6	<0.097	<0.10	<0.096	<0.098
MLG - 6	0.66	0.66	0.94	0.75
MLG - 9	<0.10	0.13	<0.098	0.11
LL - 3	0.39	0.39	0.44	0.41
DARB - 3	0.12	<0.17	1	0.43

Sample ID	RT Corporation			
Location	Beginning (µg/g)	Middle (µg/g)	End (µg/g)	Mean (µg/g)

ALBERTA SOILS

E. Cross 1	590	2700	1300	1530
WR 1	550	360	560	490
WD 1	7.1	7.1	7.2	7.1
AN 1	28	30	25	28
BN 1	180	140	160	160
CM 1	32	82	33	49
CLM 1	4100	4400	5300	4600
E. Cross 2	13	12	14	13
WR 2	110	820	310	413
WD 2	590	410	280	427
TB 1	9.00	7.70	9.20	8.60
PW 1	2.20	2.00	2.20	2.10
CM 2	0.69	0.64	0.60	0.64
CLM 2	110	110	110	110
WR 3	0.46	0.13	0.18	0.26
WD 3	<0.099	<0.10	<0.10	<0.10
AN 2	<0.11	<0.10	<0.10	<0.10
PW 2	<0.11	<0.098	<0.10	<0.10
BN 2	<0.10	<0.10	<0.098	<0.10
CM 3	<0.10	<0.10	<0.10	<0.10
CLM 3	0.26	0.27	0.19	0.24

NIST STANDARDS

SRM - 2711	N/A	N/A	N/A	N/A
SRM - 2710	N/A	N/A	N/A	N/A
SRM - 2709	N/A	N/A	N/A	N/A

APPENDIX F

**NOVA GAS TRANSMISSION NEVIS SOUTH METER
STATION MERCURY CLEANUP**

NOVA Gas Transmission Nevis South Meter Station Mercury Cleanup

Nevis South M/S is located in Section 22 of Township 039 Range 22 West of the 4th meridian, near Stettler in the Province of Alberta. Nevis South is a receipt station that meters producer's gas entering the NOVA Gas Transmission (NGT) pipeline system. The station was rebuilt in 1992 to allow the metering of larger volumes of gas. The retired meter run building had at one time used two mercury containing manometers to measure gas flow

Cleanup started in 1995, with the following goals:

- the correct removal of asbestos from the run building, and disposal of the building and asbestos
- the excavation and disposal of all soils contaminated with greater than 10 ppm¹ of mercury
- the application of a new field screening technique for mercury, developed by A. A. Kriger and R. R. Turner and recently tested by the Gas Research Institute.
- the removal and recycling of all of the abandoned above and below ground piping

Surface soils around the run building and adjacent instrument building foundation were sampled on a triangular grid. Yard gravels and underlying soils at each sample site were excavated to 25 to 30 cm depth using a pick and shovel. A sample of the gravel and soil (0 - 30 cm) was collected from the wall of the hole using a decontaminated trowel. The sample was sealed in a labeled, heavy duty Ziploc bag that was agitated until the soils were broken up and mixed. Half of the sample was then removed using the same trowel and sealed in an identically labeled Ziploc, as a duplicate sample. A total of 82 soil samples were collected, labeled sequentially NEVSS95-1 to NEVSS95-82.

One duplicate sample was screened for mercury by shaking the bag for 15 seconds, placing it on the dash heater of a vehicle and heated to between 36 to 65 °C, shaking for another 15 seconds and measuring the headspace mercury vapour using a Jerome 431X. This screening technique does not provide a reliable correlation between the Jerome results and total mercury concentrations found by cold vapour atomic absorption laboratory analyses. However, the can indicate whether mercury is present in the soil and to a limited extent, the relative concentration.

The other set of duplicate samples were logged on chain of custody forms, stored in a cooler and delivered to Chemex Labs of Calgary, Alberta.

Grid sampling started in front of the run building and instrument building, the most common locations that mercury contaminated soil is found. An approximate triangular grid with 2m between sample nodes was used. Field headspace screening, as described above, was performed as samples were collected. The headspace screen results were used to indicate the presence or absence of mercury. The grid was developed until the headspace screening indicated the absence of mercury in the outer nodes of the sample grid on four sides of the building/foundation. A total of 82 nodes were sampled and screened. Field screening indicated mercury contamination of surface soils mainly in the front (south) of the run and instrument buildings, with some to the east of the instrument building.

NOTE: The sampling grid did not provide coverage for the whole site and does not provide statistical coverage.

Thirty-seven of the duplicate samples were selected for analysis for total mercury by cold vapour atomic absorption (CVAA). The samples were selected in order to confirm the presence or absence of mercury,

¹ Canadian Council of Ministers of Environment industrial cleanup criteria

- Approximately 20 g of each sample was placed in a clean mortar, gravel sized particles were removed, and the remainder of the sample was homogenized with a clean pestle.
- Approximately 1 g of the homogenized sample was weighed and the weight recorded.
- The 1 g of sample was placed in a 200 mL glass jar. 6 mL of hydrochloric acid and 2 mL of nitric acid was added and the sample left to digest for 15 minutes. After 15 minutes, 15 mL of distilled water was added to the extract.
- 0.5 mL of the extract was pipetted into a clean 1 L flask along with 100 mL of distilled water.
- 5 mL of tin (II) chloride solution was then added to the flask. The flask was immediately sealed with parafilm, shaken for 1 minute and the headspace vapours were analyzed with the Jerome 431X. The reading was recorded.
- The concentration of mercury in the soil sample was then calculated using the following formula:

$$[\text{Hg}] \text{ sample} = 46 \cdot \frac{\text{Jerome}}{\text{Slope}} \cdot \frac{1}{\text{Mass}}$$

Where,

[Hg] sample = Concentration of mercury in micrograms per gram (ppm) in the wet soil sample

46 = Total volume of the extract solution divided by the volume of the aliquot of the extract solution used for analysis, i.e. (6 mL + 2 mL + 15 mL) / 0.5 mL = 46.

Jerome = Jerome 431X reading of mercury headspace vapours in mg/m³.

Slope = The slope of the curve of standard solution concentrations versus Jerome readings, as calculated above (0.83).

Mass = the mass of the soil sample digested in grams.

- One or two concentrations of the standard solution were analyzed after the analysis of every five to ten soil sample, in order to check that the slope of the standard curve had not changed.

Results

The results of field and laboratory analyses are summarized in Appendix A. The laboratory reports are attached to this report.

Discussion of the Results

Statistical Analysis

For the Nevis South meter station a total of 48 samples were available for comparison between the field analysis method and the NGT laboratory and Chemex. Of the 48 samples, 15 samples produced a reading of 0 (zero) from the Jerome meter when performing the field test. These samples, when tested at Chemex and NGT, contained less than 0.3 ppm mercury. It is believed that for low mercury levels in soil, the 0.5 mL aliquot from the above procedure produces a mercury level in the headspace below the detection limit of the Jerome meter. As the detection limit appears to be more than an order of magnitude below the cleanup level it is not considered a problem. It should also be noted that an average moisture content for the soil at the site was assumed to be 10% for the purposes of calculating mercury contamination in the field technique.

Conclusions

Cleanup

The intention of the cleanup activity was to reduce mercury levels in the soil at the Nevis South meter station site to below 10 ppm. Location in the meter station site which were most likely to be contaminated were tested and excavated until mercury concentrations were below 10 ppm. The entire yard was not sampled. Sites most likely to be contaminated were based on judgment and experience from previous NGTL meter station sites.

Laboratory Analysis

A comparison of NGT and Chemex labs showed good agreement between the different techniques. At the 90% confidence level the correlation coefficient between Chemex and NGT is greater than 0.8. From this result it is apparent that the NGT lab results are equivalent to the Chemex result.

Field Analysis

A comparison of Field Analysis Techniques and Chemex labs showed good agreement between the different techniques. At the 90% confidence level the correlation coefficient is greater than 0.75. From this result it is likely that the Field Analysis Technique is an acceptable measurement technique for cleaning up mercury contaminated soils of the type encountered at Nevis South meter station.

Recommendations

- Further testing should be done to confirm the accuracy of the Field Analysis Technique in alternate soil types and to provide further data confirming the result for the soils tested at Nevis South.
- During these tests it is important to determine the soil moisture content for use in the Field Analysis Technique.
- Standard solutions used to calibrate the Jerome Vapour meter in the Field Analysis Technique should be sent for analysis to confirm the calibration curve.

Surficial mercury contamination was delineated using the field screen and laboratory results.

Appendix A Data from Nevis South mercury contamination measurements after cleanup.

Sample Number	Excavated	Field Analysis (ppm)	Chemex Lab (ppm)	NGT Lab (ppm)
93	n	0.000	0.023	0.180
101	n	0.000	0.039	0.040
102	n	0.000	0.059	0.020
121	n	0.000	0.063	0.030
99	n	1.555	0.064	0.070
83	n	0.000	0.068	0.100
94	n	0.000	0.087	0.001
122	n	0.000	0.122	0.030
98	n	0.000	0.150	0.090
117	n	0.000	0.152	0.200
128	n	0.000	0.153	0.190
118	n	0.000	0.168	0.260
108	n	0.334	0.233	0.330
95	n	0.000	0.243	0.170
127	n	0.000	0.270	0.250
84	n	0.000	0.289	0.290
129	n	0.172	0.315	0.550
115	n	0.329	0.374	0.580
114	n	0.723	0.408	0.570
85	n	0.282	0.462	0.630
110	n	0.332	0.510	0.660
86	n	0.000	0.556	0.790
109	n	0.553	0.556	1.400
119	n	0.278	0.589	0.550
100	n	0.607	0.710	1.070
111	n	2.923	0.926	1.950
120	n	1.113	1.050	1.260
106	n	1.487	1.140	2.070
112	n	0.971	1.160	1.290
113	n	0.832	1.250	1.910
116	n	1.003	1.320	1.630
105	n	0.946	1.510	1.080
126	n	0.177	1.520	2.420
107	n	1.604	2.190	2.900
104	n	1.555	2.210	2.110
96	n	2.250	2.730	3.910
97	n	3.405	3.530	6.850
103	n	1.683	3.640	4.510
130	n	6.285	7.010	12.590
125	n	3.426	0.874	5.180
124	n	0.599	1.180	1.420
123	n	3.985	3.985	3.985
122	n	3.804	4.700	7.840
121	n	5.215	6.876	6.450
120	n	3.147	6.350	7.820
119	n	6.315	12.700	18.560
118	n	7.205	15.600	19.600
117	n	25.036	18.000	18.510

APPENDIX G

METHOD 7471A MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

METHOD 7471A

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the

absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M KMnO_4 and 10% H_2SO_4 , or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO₃.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated KMnO_4 solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of KMnO_4 solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into

account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

METHOD 7471A
MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)