FIELD ANALYSIS OF MERCURY IN WATER, SEDIMENT AND SOIL USING STATIC HEADSPACE ANALYSIS

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Abstract. We developed a field screening method for the rapid analysis of mercury in water, soil and sediment which can be applied cost-effectively at mercury-contaminated sites . The samples are chemically pretreated in ordinary containers, followed by analysis of the sample headspace mercury vapor using a portable commercially-available analyzer. Mercury in water samples is reduced directly by the addition of stannous chloride, while solids are first digested with aqua regia or piranha solution to liberate the mercury from the solids. Aided by vigorous agitation after addition of the reductant, the elemental mercury partitions between the solution and headspace according to Henry's Law. The method requires about 2 and 15 minutes to complete for water and solids, respectively. The method provides very useful detection limits for water (0.1 μg/L) and solids (2-3 μg/g). Intercomparisons with laboratory-analyzed environmental samples have shown good agreement.

1. Introduction

Techniques for the rapid field analysis of mercury in water, sediment and soil samples are needed to permit immediate screening of these environmental media at mercury-contaminated sites. Such capability can provide cost efficient guidance for locating sampling sites for laboratory analysis, and help direct cleanup activities. Mercury analytical technology is generally limited to laboratory applications, and existing field technology often suffers from poor detection limits, matrix restrictions, or extraction difficulties with solids.

We describe here a field method which employs static headspace measurements on samples pretreated to convert mercury to the elemental form. Aided by vigorous agitation, elemental mercury will partition between a solution and any headspace according to Henry's Law. The headspace can be sampled using a portable mercury vapor analyzer. The theory supporting static headspace measurement is governed by the solubility of elemental mercury vapor in water (Sanemasa, 1975). Henry's Law states that the concentration of the dilute solute in solution C_l, is proportional to its concentration in the gas phase, C_g, at equilibrium:

$$C_{l(eq)} = HC_{g(eq)}$$

where H is a proportionality factor called Henry's Law constant. The value for H depends on temperature, varying from 0.18 @ 5°C to 0.32 @ 25°C (Sanemasa, 1975).

2. Materials and methods

2.1. INSTRUMENTATION

The mercury vapor analyzer (Jerome Model 411 or 431, Arizona Instruments, Phoenix, Arizona) is small (15 cm x 33 cm x 10 cm), lightweight (2.3 kg) and analysis is rapid (single measurement obtained in 10-13 seconds). It is battery operated, and includes an internal air pump, which operates at a rate of 750 cm^3/min. The air flows through a guard column packed with sodalime, to remove moisture and acid gases. The dry vapor is then deposited onto a thin gold film which forms an amalgam selectively with mercury. The Hg/Au amalgam increases the electrical resistance of the gold film, which is measured using a Wheatstone bridge. The increase in resistance is proportional to the mass of the mercury incorporated by the film (McNerny et al, 1972; Murphy, 1979; McNerny, 1983).

A probe and external sodalime trap (Figure 1) were added to the instrument's sample path. Because the instrument was not designed for measuring samples with high moisture and acid content, the additional trap provides extra protection and an indication of sodalime saturation without opening the instrument. This modification does not affect the sample flow rate, and greatly reduces the chance of fouling the gold foil. It does, however, create additional dead volume, necessitating purging of the instrument between measurements until zero signal is obtained.
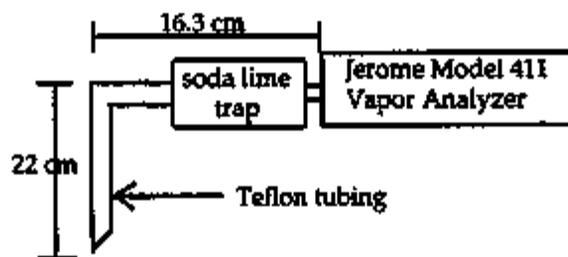

Fig. 1. Schematic of probe tip and external sodalime trap.

2.2. ANALYSIS OF WATER

The initial water studies were done with mercury-dosed water samples. Deionized distilled water was added to 1-L polypropylene bottles in 100-mL aliquots. A stock solution containing 10 mg Hg^{2+}/L in 1.0 N HNO_3 was used to produce water samples at the desired mercury concentrations (0.2 - 30 μg/L). Saturated stannous chloride solutions were prepared by dissolving 200.0 g $SnCl_2$ dihydrate (J. T. Baker, analytical grade) in 100 mL of 30% hydrochloric acid (EM Science, suprapur), and diluting to 1.0 L with deionized distilled water. The solution was stirred for 24 hours at room temperature while bubbling with "mercury-free" air. A reagent blank was then measured using the portable mercury vapor analyzer to verify that no signal was produced by the solution alone.

To the 100 mL of mercury-dosed water in the 1-L bottle, 10.0 mL of a saturated $SnCl_2$ solution was added after which a small square (7.5 cm x 7.5 cm) of parafilm was rapidly secured atop the bottle. The cap was then pressed gently over the parafilm and the bottle vigorously shaken (manually) for one minute. Next, the cap was removed and the parafilm seal was punctured using the probe tip illustrated in Figure 1. A 10-s air sample was taken. The parafilm seal reduces the possibility of variable amounts of unequilibrated air entering the bottle while sampling and thus increases precision of replicate measurements.

To identify the time interval necessary for establishment of equilibrium between the aqueous phase and the headspace vapor, seven 1-L bottles containing 100.0 mL of deionized water were dosed with 100.0 μL of a 5.0×10^{-5} M $Hg(NO_3)_2$ solution. A 10.0-mL aliquot of a saturated $SnCl_2$ solution was added to each bottle, followed by vigorous manual agitation for 30 s for one sample, and 1.0 min for the other six samples. The headspace vapor in the bottle equilibrated for 30 s, and the vapor in one of the bottles agitated for 1.0 min, were analyzed immediately following agitation. The five remaining bottles were placed on the benchtop following the one minute agitation, until the headspace was analyzed using the field analyzer technique at intervals of 5 min, 2 hr, 5 hr, and 22 hr. Results from the kinetic study showed that equilibrium between the aqueous phase and the headspace vapor is reached between 30 seconds and a one minute reaction time.

Environmental water samples were collected from surface water outfalls, storm sewers and sumps in several buildings at the U.S. Department of Energy's Y-12 Plant in Oak Ridge, Tennessee. Additional samples were collected from the East Fork Poplar Creek (EFPC), which originates at the Y-12 Plant. The 100-mL aliquots were transferred to 1-L polypropylene bottles for field analysis. Laboratory analyses were performed using EPA method 245.1 (EPA, 1982).

A signal of ≤ 0.003 mg/m^3 in air (corresponding to ≤ 0.09 μg/L in water) is believed from experience to be spurious and therefore this value is reported as the approximate detection limit. The upper limit for an undiluted water sample is determined by the maximum instrument reading (1.99 and 0.99 mg/m^3 for the Jerome Model 411 and 431, respectively) and varies from about 10 to 45 μg/L depending on the model being used. A typical relative standard deviation for replicate measurements is about 10%. The formula converting signal to aqueous mercury concentration follows:

$$\text{Signal (mg Hg/m}^3 \text{ air) x Constant} = \mu\text{g Hg/L water}$$

The constant, which should be determined using one or more aqueous standards, converts mg/m^3 of air to μg/L of water, accounts for the aqueous and vapor volumes in the system, and adjusts for partitioning between phases according to Henry's Law. This constant varies among, and with the condition of, each instrument (Jerome Model 411 vs. 431).

2.3. SOIL/SEDIMENT METHOD

Two procedures were developed for soil/sediment analysis. For both methods, 50.0 mg of homogenized soil or sediment was weighed into 125-mL glass bottles with Teflon-lined silicone septum caps and chemically treated using aqua regia (two parts concentrated HCl to one part concentrated HNO_3) or piranha solution (four parts concentrated H_2SO_4 to one part 30 % H_2O_2). For soil method 1, the extracted mercury was reduced by addition of $SnCl_2$ (saturated solution) directly in the 125-mL bottle, followed by agitation for about a minute. A 1.0-mL sample of the headspace gas was collected in a gas-tight syringe, and injected into the vapor analyzer using the septum arrangement provided by the instrument manufacturer for calibration checking. The gas sample transfer was necessary because in most cases, Hg-contaminated soils would yield headspace vapor values too high to measure by direct headspace analysis with the portable analyzer.

The piranha solution evolves oxygen when the reagents behave properly. It is important to note this evolution since aqueous solutions of hydrogen peroxide spontaneously disproportionate to water and oxygen. Soil/sediment samples were allowed to react with the piranha solution for 15 minutes prior to the addition of 20 mL of a saturated $SnCl_2$ solution. This addition produces an exothermic reaction. As this step involves addition of a strong reductant to a strong oxidant, appropriate safety measures should be taken. The bottles should be cooled in a refrigerator or ice bath for about 10 minutes and then allowed to return to ambient temperature prior to analysis. The sample was manually shaken for one minute, then the headspace vapor was sampled as described above.

Using aqua regia, it was necessary to remove the acid gases from the bottle prior to addition of $SnCl_2$ solution (headspace was changed with mercury-free air for two minutes in benchtop studies). In the field, bottles can be left uncapped and the acid gases allowed to diffuse out of the vessel or a battery-powered air pump may be used to ventilate the samples. After addition of $SnCl_2$, the bottles were cooled to room temperature, followed by manual shaking for one minute. The headspace vapor was sampled (1.0 cm^3) using a gas-tight syringe and measured using the vapor analyzer.

The calculation for soil measured using soil method 1 involves a correction for sample dilution (1.0 mL of headspace vapor is injected and the instrument collects 125 mL of air) followed by application of Henry's Law constant to find the aqueous mercury concentration. The following relationship may then be used to find the total mass of mercury in the system.

$$C_{(aq)}V_{(aq)} + C_{(vap)}V_{(vap)} = \text{total Hg}$$

Where $C_{(aq)}$, $V_{(aq)}$, $C_{(vap)}$ and $V_{(vap)}$ are aqueous concentration, aqueous volume, vapor concentration and vapor volume, respectively. Dividing the total mercury value by sample weight yields μg Hg/g soil.

An alternative soil method (soil method 2) involved extracting the soil in 5.0 mL of aqua regia or piranha solution, followed by transferring a 0.5 - 1.0-mL aliquot of the extract to a 1-L polypropylene bottle and diluting to a final volume of 100 mL with deionized water. A 10-mL aliquot of a saturated $SnCl_2$ solution is then added and the headspace measured directly (as in the water method).

2.4. EXTRACTION EFFICIENCY

Two replicates of NIST Standard Reference Material 2710 (Montana soil, 0.05 g each) containing 32.6 ± 1.8 μg Hg/g, NIST Research Material 8407 (soil) 50 μg/g and a soil from the EFPC floodplain containing 2500 μg Hg/g (as measured by EPA method 245.5), were weighed into clean Erlenmeyer flasks. A 5.0 mL aliquot of piranha solution (1.0 mL 30 % H_2O_2 and 4.0 mL 30 % H_2SO_4) or a 3.5 mL aliquot of aqua regia (3.0 mL 30 % HCl and 0.5 mL 90 % HNO_3) was added to each flask. The flasks were swirled and then placed on the benchtop for exactly 15 minutes. Next, the slurries were poured and rinsed quantitatively through 25 mm glass fiber filters (Gelman Sciences, Ann Arbor, MI), and the filtrate was collected in 250-mL polypropylene bottles which contained 1.0 mL of concentrated HNO_3 (as a preservative) and about 175 mL distilled deionized water. The extraction filtrates were submitted for laboratory analysis using EPA method 245.1.

Data in Table I indicate that both aqua regia and piranha solution are good extraction reagents for mercury in soil. Perhaps at very high mercury concentrations, the aqua regia is slightly more effective in the 15 minute reaction interval used in this procedure. The interval is sufficient to expect nearly complete metal ion extraction by piranha solution and complete extraction by aqua regia. The EFPC soil (2500 μg/g) and NIST RM 8407 were extracted with high efficiency, in spite of the observation that sediment from this location has been characterized (Revis et al., 1989) as containing about 85 % of the total mercury present in the highly insoluble sulfide form.

TABLE I

Extraction efficiency results

Sample	Reference Value (μg/g)	Extractant	Observed Value (μg/g)[1]	% Extracted
NIST RM 8407	50	piranha	49	98
NIST RM 8407	50	aqua regia	50	100
NIST SRM 2710	32.6 ± 1.8	piranha	24.5	75
NIST SRM 2710	32.6 ± 1.8	aqua regia	31.4	96
EFPC soil	2500	piranha	2300	92
EFPC soil	2500	aqua regia	2600	103

[1] Average of duplicate extracts analyzed using EPA Method 245.1 (EPA 1982).

Although the field use of either aqua regia or piranha solution presents safety concerns, less hazardous extractants were ineffective for short interval extraction or caused interferences in the reduction or analysis steps.

3. Results and Discussion

3.1. WATER RESULTS

Figure 2 illustrates the good agreement between field and laboratory values and suggests that the method is useful as screening tool for measuring mercury in water. The average relative percent difference (RPD) between field and laboratory values was 37%. Although perfect agreement between laboratory and field results was not achieved in all cases, the field results are close enough to provide an indication of mercury concentrations with reasonable confidence. In a very few instances, the field method produced a false positive; that is, the result suggested there was a small amount of mercury present when actually was less than 0.2 $\mu g/L$. More importantly, however, in no case did the field technique indicate that mercury was not detectable when laboratory results indicated it should have been detected (false negative). A much higher concentration of mercury was examined in sump water collected at the U.S. Department of Energy's Y-12 Plant. Laboratory analysis indicated the mercury concentration was 400 $\mu g/L$, while the value obtained (required 10-fold dilution) using the field analyzer was 460 $\mu g/L$.
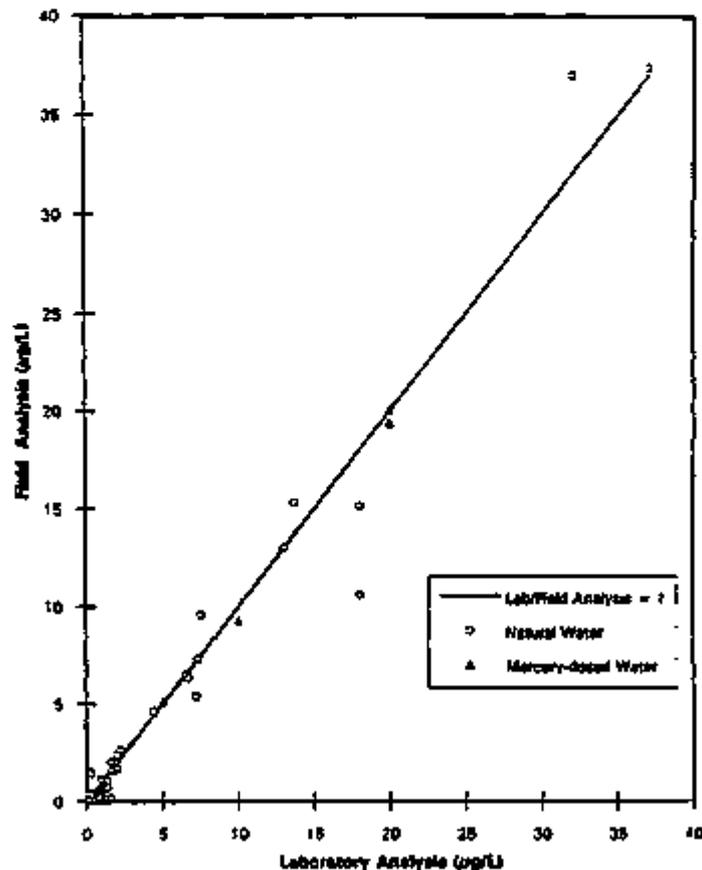

Fig. 2. Field analyzer performance for natural and Hg-dosed water samples.

3.2. SOIL/SEDIMENT

Soil method 1 was used to analyze a series of surface soil samples and one soil core collected in the mercury-contaminated EFPC floodplain (Oak Ridge, Tennessee). These samples were also submitted for laboratory analysis. Figure 3 illustrates the linear relationship between laboratory and field data up to about 60 μg/g, at which point a plateau in the field data is observed. Complete saturation of the headspace volume will occur at 24 °C (Hg°_{sat} = 18 ng/mL; Weast, 1980) for soil samples having concentrations which are $\geq$ 66 μg/g. The leveling in the plot of experimental data is in very good agreement with the calculated point where this phenomenon should occur. The measured values above about 20 μg/g also fall a little short of the actual soil concentrations (average RPDs for samples $\leq$60 μg/g was 54%). This effect could be due to assuming Henry's Law constant is 0.3 even when the aqueous phase is a strong acid mixture.

To further investigate the accuracy and precision of the field analyzer method, several NIST soil standards were measured using soil method 1. Figure 3 shows that reasonable accuracy is obtained at low mercury concentrations, while the most contaminated soils are less accurately measured. This is consistent with the saturation effect noted earlier for soil containing $\geq$ 66 μg/g. Additionally, using soil method 1 the partitioning between the extractants and the headspace may be unlike that in water. Therefore, the use of Henry's Law constant for water in the calculation converting the instrument's signal to soil concentration may cause the measured values to deviate from the ideal line.

Extension of the application of this analysis to include soil concentrations above 66 μg/g required the development of soil method 2. Data from the analysis of NIST standards appearing in Figure 4 were measured using soil method 2, which involved extracting the sediment in glass bottles into 5.0 mL of piranha solution, then transferring a small aliquot to a 1-L bottle where the extract was diluted to 100 mL with water. The procedure for water samples was then followed. The standards were measured accurately (RPDs <1%). Since the dilution (soil method 2) involves addition of a large volume of water relative to the volume of acid, Henry's Law constant for water appears more reasonable. Thus, this method permits accurate mercury measurements in soils exceeding the 66 μg/g upper limit established for method 1. Figure 4 also illustrates the accurate (average RPD = 18%) measurement of mercury in dry finely sieved sediment obtained from the Clinch River near Oak Ridge, Tennessee. These soil samples were extracted into 5 mL of aqua regia in a 1.0 L polypropylene bottle, diluted to 100 mL with distilled deionized water and analyzed by direct headspace analysis (water technique).

4. Conclusions

The field analyzer method described here provides a new field screening tool for the analysis of mercury in water, sediment and soil. Over the tested range of concentrations in water (0.1 - 400 μg/L), precision and accuracy were quite good. The method is sufficiently simple and easily implemented for field studies. However, this method is not intended to replace submission of samples for laboratory analysis, but rather to locate regions which should be sampled for laboratory analysis.
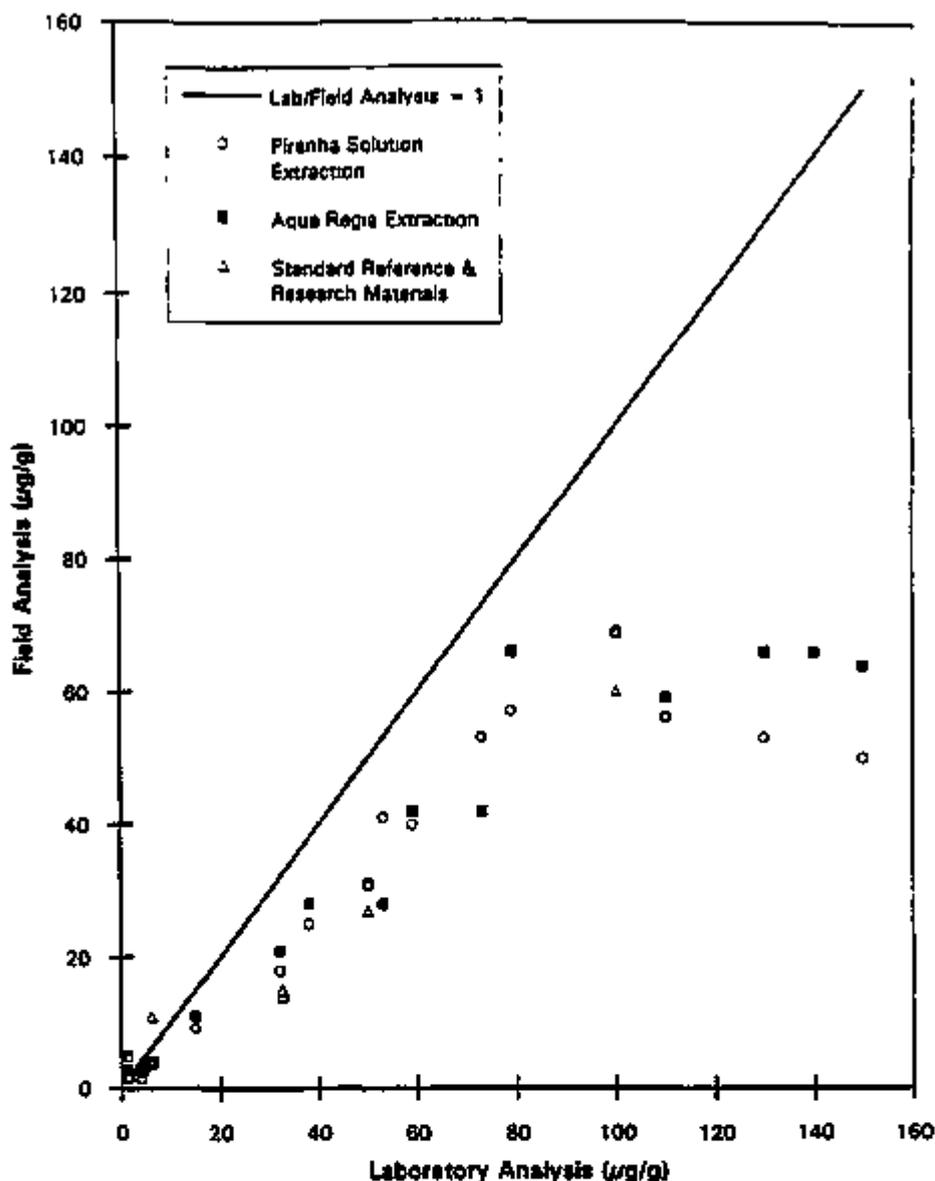
Fig. 3. Field analyzer performance for soils using method 1.

For mercury extraction from soil and sediment, both aqua regia and piranha solution are effective. The aqua regia may work a little better under these experimental conditions; however, using the piranha solution does eliminate one step because removal of acid gases before reduction is not necessary. For general soil surveys, method 1 is recommended. The limit of detection using this technique is 1.4 $\mu g/g$ and the linear dynamic range extends to about 66 $\mu g/g$ at which point the headspace vapor in this system becomes saturated (24 °C). Reasonable precision is obtained by method 1, but results become progressively less accurate with increasing mercury concentration. This may be due to the assumption that Henry's Law constant is 0.3 in the formula converting signal to soil mercury concentration since partitioning from a strong acid mixture is likely different than when water is the sole solvent. Alternately, extracting the sample in a 1-L bottle, then diluting and following the analysis procedure for water permits accurate soil/sediment measurements to be made at concentrations up to at least 30 $\mu g/g$ (Figure 4).
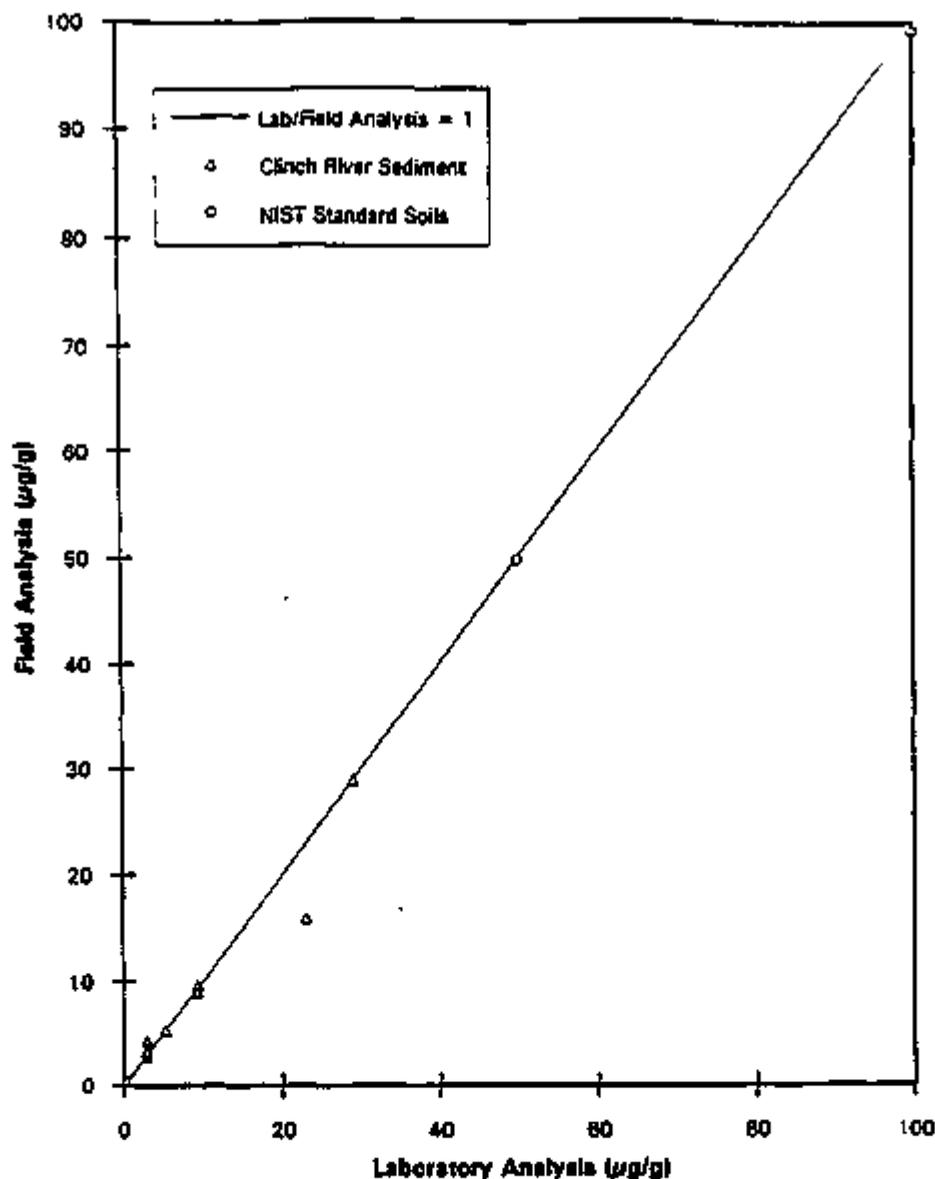
Fig. 4. Field analyzer performance for soil and sediment using water method (Clinch River sediment) and soil method 2 (NIST standard soils)

Soil method 2 also offers improved accuracy and has the advantage that digest can be conducted in a glass container. The limit of detection is determined mostly by the quantity of soil/sediment digested and the volume of digest transferred for reduction. Linearity can be maintained at even high concentrations as long as the quantity of mercury transferred and reduced is kept below the air saturation value. The method is applicable when greater accuracy is desired at sites where soil mercury concentrations may be high ($> 50\ \mu g/g$). For field screening, high accuracy may not be necessary at extremely high concentrations as one would primarily be interested in the presence or absence of high mercury levels in soil. Rigorous quantitation would be obtained by laboratory analysis.

Practical applications for this field screening technique include defining the boundaries of shallow groundwater mercury plumes (e.g., using push screen sampling),

tracking surface water sources of mercury in an industrial complex, preliminary site mapping of soil/sediment contamination, selecting soil/sediment samples for laboratory analysis, field monitoring of the progress of soil remedial action, and detecting initial breakthrough in sorbent column studies or full-scale treatment systems. Using our method, the number of samples collected for laboratory analysis may be greatly reduced as a rapid field method exists to direct the collection.

Acknowledgments

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