Field Evaluation of an Electrochemical Probe for *in Situ* Screening of Heavy Metals in Groundwater

JANET HERDAN,
ROSEMARY FEENEY, AND
SAMUEL P. KOUNAVES*

*Department of Chemistry, Tufts University,
Medford, Massachusetts 02155*

ANTHONY F. FLANNERY,
CHRISTOPHER W. STORMENT, AND
GREGORY T. A. KOVACS

*Center for Integrated Systems, Stanford University,
Stanford, California 94305*

R. BRUCE DARLING

*Department of Electrical Engineering,
University of Washington, Seattle, Washington 98195*

The use of an electrochemically based probe for *in situ* determination of heavy metals in groundwater is described. The *in situ* probe, consisting of a microlithographically fabricated iridium ultramicroelectrode array sensor (UMEA), a custom-built miniaturized potentiostat and microcontroller, is connected to a laptop computer for control and data acquisition. The utility of this probe for rapid on-site screening of heavy metals was shown by conducting a proof-of-concept field demonstration at a metals contaminated landfill site located at Hanscom Air Force Base in Bedford, MA. Using the electroanalytical technique of square wave anodic stripping voltammetry (SWASV), the sensor was used to measure both the labile and total pH <2 forms of copper, lead, cadmium, and zinc at the parts-per-billion level. The on-site and *in situ* measurements were compared to laboratory-based electroanalytical measurements and to contract laboratory U.S. EPA Method 200.7 ICP analysis. The results indicate that *in situ* electroanalytical measurements of labile metal species are feasible, providing a rough estimation of metals concentrations and trends in their behavior. The *in situ* and on-site results agree to within an order of magnitude with the laboratory determinations. This study demonstrates that such electroanalytical-based devices may be of value for an initial, rapid, low-cost, screening of heavy metal contaminated sites.

Introduction

Contamination of groundwater by heavy metals is an important environmental concern because of the toxicity of such metals on a broad spectrum of organisms, including humans (*1*, *2*). Thus, it is crucial to develop the ability to easily obtain on-site (up-hole) and/or *in situ* quantitative measurements of these metals in order to provide for rapid,

low-cost, characterization and remediation of these sites. Environmental measurements of heavy metals in natural waters are normally obtained by the use of spectroscopic analytical techniques such as atomic absorption (AA), induced coupled plasma (ICP), and fluorimetry. These techniques normally require samples to be collected and sent to the laboratory for analysis. The instrumentation itself is expensive and requires significant maintenance and operator expertise. Thus, the determination of heavy metals for a large site can be costly, time consuming, and labor intensive. The need for a portable, low-cost, and fast, *in situ* heavy metal analysis system for initial screening of heavy metal contaminated sites has remained a high priority, especially since a significant percentage of these sites still remains to be assessed.

The speciation of heavy metal ions ultimately determines their bioavailability and toxicity. Strongly bound metals are less of an environmental concern because they are not necessarily bioavailable. On the other hand, heavy metals, which are weakly complexed or exist only in the ionic form, can be a threat to the environment because of their increased bioavailability and their toxicity. Thus, measuring total metal content by using conventional analytical techniques may not necessarily provide a true indication of the actual toxicity of these metals. It appears important to us that any measurement of metals in natural waters should provide some differentiation between total and bioavailable. Several electroanalytical techniques can be used to give both the concentration of the ionic form and, after acidification, an approximation of the total metal content. The problems related to metal speciation and measurement have been recently discussed in detail by Buffle *et al.* (*3*).

One of the most useful electroanalytical techniques, which has low limits of detection for a number of priority metal pollutants and the potential to be implemented at very low cost, is anodic stripping voltammetry (ASV) (*4*–*5*). This is a preconcentration technique where the metal ion of interest is electrochemically deposited, by applying a negative potential, into a thin film (usually of mercury or a polymer) which has been predeposited on the electrode. In a typical system, a preconcentration time on the order of a few minutes will yield sensitivities at the parts-per-billion level. With longer preconcentration times, parts-per-trillion can be achieved. After the metal is preconcentrated, the potential is scanned from the applied negative potential toward a more positive potential. The metals are then "stripped" from the electrode, providing a current signal in the form of a peak at a redox potential characteristic of the metal and proportional to its concentration in solution. Multiple metals can be detected as long as the redox potentials of the different metals do not overlap. By using a special form of ASV, where a square waveform is used to generate the signal, square wave ASV (SWASV) (*6*, *7*), the analysis can be performed faster and with increased sensitivity. With the combination of SWASV and UMEs, detection limits of 10^{-12} M have been attained (*8*).

In this paper, we describe an electrochemically based system for the measurement of heavy metals in ground water. The system consists of a laptop computer with an attached probe containing the potentiostat and sensor. The sensor consists of a microlithographically fabricated array of 20 interconnected $10\,\mu$m diameter iridium ultramicroelectrodes (UMEA) coated with mercury hemispheres (*9*). Iridium substrates have been proven to be advantageous due to their insolubility in mercury (*10*, *11*). Mercury-coated iridium UMEs have been characterized and evaluated previously (*12*–
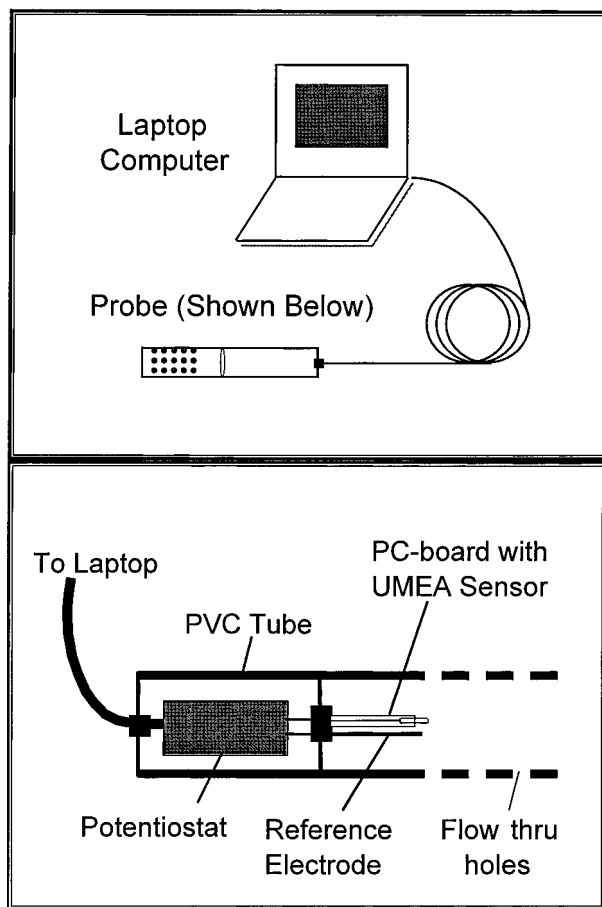
FIGURE 1. Diagram of the complete *in situ* electrochemical system consisting of a laptop computer connected to a 5 cm diameter PVC cylinder (probe) containing a miniaturized potentiostat, microcontroller, and the UMEA sensor.

14). The advantages of UMEs (*15–18*), and their application for heavy metal analysis have been well documented (*9, 12, 19–21*). The microlithographically prepared UME sensor arrays used in this study are easily fabricated leading to reduced cost, reproducible geometries, and ease in incorporating other transduction technologies to give multisensor devices.

The utility of the electrochemically based probe for rapid on-site screening of heavy metals is shown by conducting a proof-of-concept field demonstration at a metals contaminated landfill site. The system was used to measure both the labile and total pH 2 forms of copper, lead, cadmium, and zinc at the parts-per-billion level. The results are compared with those obtained from both laboratory-based electroanalytical measurements and a contract laboratory analysis (EPA Method 200.7, Analysis of Metals in Water Using ICP Spectroscopy).

Experimental Section

***In Situ* Electrochemical Sensor System.** The complete device consisting of the probe (sensor, potentiostat, and microcontroller) and laptop computer is shown in Figure 1. The UMEA sensor and reference electrode are mounted in a modified 1.25 cm PVC connector with a water-resistant epoxy. This is covered with a 5 cm diameter PVC tubing which has drilled holes to allow water flow. This lower unit of the probe is connected to a second piece of PVC tubing which encapsulates the "custom"-built, miniaturized potentiostat and microcontroller. An o-ring and screws hold the two PVC tubes together. A 33 m shielded cable is attached

to the top of the PVC tube and feeds through to the electronics compartment. This end is capped and glued with rubber cement to seal it thoroughly. The other end of the cable is connected to the serial port of the laptop computer. Power for the potentiostat is supplied by four 9 V batteries. Potentiostat control and data acquisition via the microcontroller is accomplished by custom-written software. For the on-site (up-hole) experiments, the same sensor system was used after removing the protective PVC cover tube.

The electrochemical sensor utilizes a three electrode system, consisting of the iridium UME array, an on-chip iridium counter electrode, and an external miniature solid state Ag/AgCl reference electrode (Model M216, InVivo Metric, Healdsburg, CA). The iridium UME array is coated with a mercury hemisphere just prior to the beginning of the analysis. The mercury is deposited by applying a potential of -0.4 V (vs Ag/AgCl) for 480 s using an 8×10^{-3} M Hg(II) solution. This procedure provides a uniform mercury hemisphere on each array element. The sensor appeared to be stable for at least several hours in the water samples. Unless otherwise indicated, a frequency of 120 Hz, pulse height of 25 mV, scan increment of 2 mV, and a deposition potential of -1.2 V were used as the SWASV parameters. The frequency of 120 Hz was chosen because higher frequency levels would produce higher noise levels in our system. The time for preconcentration of the metal analyte varied from 100 to 300 s. SWASV peak heights were used for determination of concentration.

UMEA Fabrication. The procedure for the microlithographic fabrication of the iridium UMEA has been previously described in detail (*9, 22*), and only a very brief summary is given here. A 4 in. diameter Si wafer is thermally oxidized to grow an SiO_2 layer. A liftoff masking layer is photolithographically defined on the wafer and an Ir UME layer is deposited by d.c. magnetron sputtering. The excess Ir is removed, and the wafer is cleaned. Another liftoff mask to form the bondpads and metal interconnects is defined and Au is deposited by electron beam vacuum metal evaporation. The excess Au is removed, and again, the wafer is cleaned. The wafer is then coated with an insulating layer of Si_3N_4 deposited by plasma enhanced CVD (PECVD). Holes are plasma etched through the Si_3N_4 to expose the Ir UMEs, counter electrode, and Au bond pads. Each wafer produces approximately 40 arrays which are carefully saw diced and the photoresist is cleaned off with a 9:1 mixture of sulfuric acid and hydrogen peroxide, followed by a thorough rinsing with deionized water. The individual chip arrays were glued onto a custom designed PC-board and gold wire (0.001 25 in. diameter, Williams Advanced Materials) bonded with a West Bond 5000 wire ball bonder. The Au wire bonds were protected by a "glob-type" epoxy (87-GT, Epoxy Technology Inc., Billerica, MA) which was cured for three hours at 70 °C.

Laboratory System. An EG&G Princeton Applied Research (Princeton, NJ) Potentiostat/Galvanostat Model 263 with Model 270 software was used for all laboratory measurements of the samples and standards. A 3 mm diameter Hg-film coated glassy carbon electrode (Bioanalytical Systems, West Lafayette, IN) was used as the working electrode vs a commercially available Ag/AgCl reference electrode (Bioanalytical Systems, West Lafayette, IN) and a platinum wire counter electrode.

The Hg films were formed by applying a constant potential of -0.4 V for 600 s using chronoamperometry. The film quality was confirmed by optical inspection with a Metaval-inverted incident-light microscope (Jena, Germany).

The parameters for the SWASV experiments were the same as in the *in situ* experiments with the exception of the square wave frequency and deposition times which were 60 Hz and 240 s, respectively.

TABLE 1. Summary of General Chemistry of Wells 6-11, 6-22, and 6-23[a]

	well 6-11	well 6-22	well 6-23
pH	6.64	6.03	5.92
dissolved oxygen	19.9	2.3	4.1
alkalinity (CaCO₃)	138	599	166
nitrate	<0.02	<0.02	0.05
total dissolved solids	1300	590	970
chloride	510	29	350
fluoride	0.9	0.8	0.8
petroleum hydrocarbons	<0.5	<0.5	<0.5
sulfate	99	4	130
iron	28.7	186	179

[a] All values are given in parts per million.

Reagents. Glacial acetic acid (Fisher) and nitric acid (Fisher) for the acidification of the samples were of trace metal grade. Standard solutions for Pb, Zn, and Cu were prepared from their respective salts $Pb(NO_3)_2$, $Zn(NO_3)_2$, and $Cu(NO_3)_2$ (ALFA-Johnson & Matthey, Ward Hill, MA), which were of ultrapure grade (99.999%). A 0.1 M KNO_3 solution (Alfa-Johnson & Matthey, 99.999%) and 0.1 M HNO_3 were used as the supporting electrolytes for the standard metal solutions. $Hg(NO_3)_2$ (Alfa-Johnson & Matthey, 99.999%) in 0.1 M $HClO_4$ (Fisher, trace metal grade) solution was used for Hg plating. The samples were filtered through cellulose nitrate filter paper with a 0.2 μm pore size. Filtering is an acceptable part of the scheme in water analysis (2), and even though metals may be absorbed by the filter, it is more important to remove the particulate matter which will interfere with the electroanalysis. All solutions were prepared with 18 MΩ cm deionized water (Nanopure, Barnstead Co., Dubuque, IA). All glassware was soaked in 8 M HNO_3 for 1 week followed by thorough rinsing with deionized water. High-density polyethylene bottles for sample storage were soaked for 1 week in a 1:1 HNO_3 and HCl solution followed by thorough rinsing with deionized water.

Sampling. The site used for this demonstration was located at the Hanscom Air Force Base (HAFB) in Bedford, MA, and is on the National Priority List (NPL) for remediation. According to information supplied by the HAFB Environmental Engineering Office, Site 6 (DP-07), had been contaminated with a variety of heavy metals including Pb, Cu, Cd, and Zn during its former use as a landfill and a filter bed to dewater sewage sludge from an Imhoff tank. The three monitoring wells chosen (6-11, 6-22, and 6-23) were located over the former buried filter bed. The dominant aquifers of this site are an upper and lower one separated by a lacustrine deposit. Well 6-11 was in the lower and well 6-23 and 6-22 were in the lacustrine aquifer. Well 6-11 was 8 m deep with a screened interval of 1.4 m and a water level of 2.3 m. Well 6-23 was 6 m deep with a screened interval of 1 m and a water level of 1 m. Well 6-22 is 9 m deep with a screened interval of 1.4 m and a water level of 2.9 m. The available general chemical analysis of the wells was provided by the Environmental Engineering Office at the HAFB and is given in Table 1.

Prior to the *in situ* analysis, two bailers (approximately 3 L) of water were taken from the wells to remove any stagnant water. All three wells were analyzed for Cu, Cd, Pb, and Zn, both by placing the probe *in situ* (down-hole) and by bringing a sample to the surface, i.e., on-site (up-hole). Well 6-23 was sampled again on August 22, 1996, to check if any temporal changes had occurred and also test the reproducibility of the probe. Three liter bailer samples were taken at the same time, acidified to pH 3 with concentrated HNO_3, and stored in a refrigerator. Aliquots of each well also were sent to an EPA certified lab (Lapuck Labs, Watertown, MA) for ICP analysis using EPA Method 200.7.

Results and Discussion

The results of this study for the *in situ*, on-site, laboratory and ICP analyses are summarized in Table 2. Keeping in mind that the aim of this device is to provide low-cost, rapid, order-of-magnitude initial screening, the results obtained are promising. If we compare the *in situ* values for Pb to those from the laboratory ICP method, there is a correlation (within an order of magnitude) between the levels at which Pb is present and the values given by the probe. Note that the *in situ* concentrations obtained for labile Pb are 302, 32, and 210 ppb, while the lab ICP analysis for total Pb gives 898, 174, and 687 ppb, respectively. These are reasonably good numbers considering the *time* and *cost* differential when compared with laboratory ICP analysis.

***In Situ* Measurements.** By using *in situ* techniques, one can hope to obtain measurements of the heavy metal contamination levels without any modification of the sample caused by changes in pressure, temperature, or sample contamination. This is especially important when electrochemical techniques are intended to provide speciation and bioavailability information. In this study, even though feasible, no such demands were made of the sensor. The sensor easily distinguished the differing metals and their concentrations in wells 6-11 and 6-23 (Table 2). The detection levels varied from a low of 4 ppb for Cu (6-23A) to a high of 302 ppb for Pb (6-23B). The general trend for the concentration of metals in the samples was supported by the ICP data. The *in situ* data collected at this site supports the concept that electroanalytical techniques are capable of providing reasonable representations of heavy metal contamination for initial, rapid, order-of-magnitude, field screening.

The data collected for well 6-23 on two different days indicated a 4-fold increase in the Cu and a 10-fold increase in the Pb concentrations. This large variation, which was later confirmed by ICP and laboratory measurements, is most likely due to a change in the water composition caused by the groundwater movement. The fact that the electrochemical-based probe detected this change is very encouraging in demonstrating its ability to accurately reflect real-time concentration fluctuations at the parts-per-billion levels.

A typical square wave voltammogram obtained *in situ* for well 6-23 (8/19/96) is shown in Figure 2. In this voltammogram, a well-formed peak at -0.62 V and a smaller peak at -0.02 V are observed for Pb and Cu, respectively. The sharp gaussian shape of this peak provides reassurance that the electrochemistry during the SWASV technique is not being significantly affected by any of the organic or complexing material in the sample.

In order to confirm the SWASV relationship between current and concentration and also as an indication of metal complexation effects during the stripping step, the effect of changing the deposition time on peak current response was performed with the *in situ* sensor in well 6-11. For variations of deposition times between 240 and 60 s, the peak height of Pb, the main contaminant, linearly increased with longer deposition times. The reproducibility of three consecutive SWASV measurements was ± 3%.

On-Site Measurements. On-site (up-well) analysis can be another important aspect in estimating the heavy metal contamination in the field. On-site sampling may still provide valuable information about the metals present even though the sample has been removed from its natural environment. This is especially true for water samples for which shifts in chemical equilibrium occur slowly or where it may be necessary to bring samples to the surface and to add reagents in order to do an analysis for certain metals.

TABLE 2. Summary of Analytical Results for Three Wells Tested at Hanscom Air Force Base on 8/19/96 and 8/22/96

method	well 6-11B (8/22/96)	well 6-22A (8/19/96)	well 6-23A (8/19/96)	well 6-23B (8/22/96)
in situ	-[a] 5 ppb Cu 210 ppb Pb -	- - - -	- 4 ppb Cu 32 ppb Pb -	- 12 ppb Cu 302 ppb Pb -
on-site (neat)	- - -	- 15 ppb Cu 275 ppb Pb -	- 2 ppb Cu 105 ppb Pb 10 ppb Zn	- 5 ppb Cu 280 ppb Pb 17 ppb Zn
ASV in lab, acidified and filtered	- 5 ppb Cu 50 ppb Pb -	- - 200 ppb Pb 90 ppb Zn	- - 180 ppb Pb 20 ppb Zn	- - 1000 ppb Pb 25 ppb Zn
ICP EPA method 200.7	<2 ppb Cd <2 ppb Cu 687 ppb Pb 27 ppb Zn	<2 ppb Cd <2 ppb Cu 168 ppb Pb 49 ppb Zn	<2 ppb Cd 14 ppb Cu 174 ppb Pb 20 ppb Zn	<2 ppb Cd 34 ppb Cu 898 ppb Pb 65 ppb Zn
physical appearance	clear with small amounts of particulates	clear with tiny suspended particulates	turbid and a lot of particulates	clear

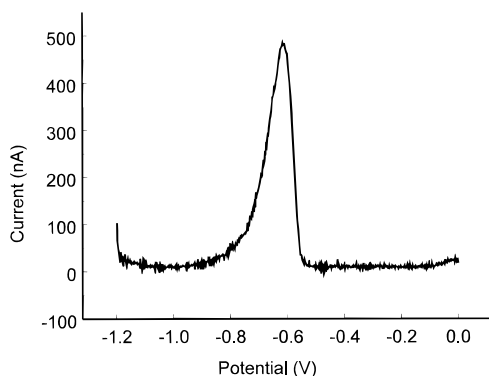[a] (-) Not detected or not measured.

FIGURE 2. A typical *in situ* square wave anodic stripping voltammogram with a peak at -0.62 V and a smaller peak at -0.02 V for Pb and Cu, respectively, obtained at groundwater well 6-11. SWASV parameters: frequency = 120 Hz, pulse height = 25 mV, scan increment = 2 mV, deposition potential = -1.2 V, and deposition time = 240 s.

One of the problems encountered during the on-site measurements was the physical change of the sample caused by removing it from the well. The temperature of the well samples, which was initially about 15 °C, increased to match that of the air temperature, which was almost 27 °C during the analysis. Simultaneously, the turbidity and color of the samples changed noticeably from clear to murky yellow. During the on-site measurements, the UMEA sensor had to be cleaned and reactivated more frequently due to the fouling caused by the higher level of particulates in the water. However, we were surprised by the reasonably good peaks that were obtained even under these conditions.

Fouling of the electrode is a serious problem in the analysis of natural water systems. It is commonly caused by the accumulation of organic matter onto the electrode surface. It has been shown that fouling may be minimized by the application of polymers onto the electrode to form a protective layer (*23*). In this study, fouling may have contributed to some inconsistencies in the data. However, since one aim of this study was to show the potential of this type of system for rapid, low-cost, on-site screening (i.e., to see if any heavy metals are present at higher-than-acceptable limits), we did not intend to demonstrate a high degree of precision or accuracy, but simply an order of magnitude correlation with laboratory ASV and ICP data. Another problem which may contribute to inaccurate data is the saturation of the UMEA Hg-film, especially since the concentration of the metals in some samples was so high. However, with the deposition times used and from calculations, we did not expect this to occur and did not see any evidence for it in the stripping peaks.

Another problem which may be encountered with thin Hg-film UMEs is the formation of intermetallic compounds such as between Cu/Zn and Hg (*24*). This could account for some of the variation seen in the peak current heights for Zn and Cu. However, for the rapid analysis times used with SWASV the error introduced by this problem should not be significant.

Overall, the *in situ* and on-site measurements proved to be successful at demonstrating that the electrochemically based sensor in its simplest form and without any manipulations or modifications can detect heavy metal contamination in groundwaters. Such a portable system can be advantageously used for a rapid on-site initial field screening. We confirmed that our system could detect trends throughout these studies which were later verified by ICP and in-laboratory experiments. Its ease of operation, low cost, and time efficiency are other major benefits.

Laboratory Analyses. SWASV at a Hg-film glassy carbon electrode was used to corroborate the electroanalytical results field analyses. The laboratory analysis scheme, shown in Figure 3, involved filtration and acidification of the sample. Filtration was necessary in order to remove particulates which could interfere with the electroanalysis of the metal species. Acidification to pH <2 frees the complexed metals (increasing the peak response) and allows for differentiation into labile and total forms. Metal concentrations were determined from standard calibration curves. The reproducibility was verified by doing three consecutive analyses.

The voltammogram obtained for the preserved sample from well 6-22 indicated the presence of Pb and Cu. The sample was spiked with a known quantity of these metals. The two peaks in the voltammogram increased proportionally thereby confirming the identity and quantity of the species. Upon acidifying the sample, an increased response for Pb
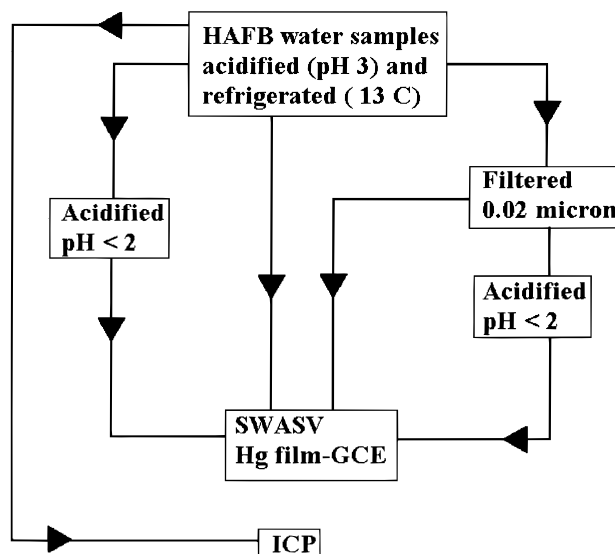
FIGURE 3. The sample preparation and analysis scheme used for the laboratory analyses.

was noted and a small signal for Zn appeared. The Zn and Pb were quantified at 90 and 200 ppb, respectively. The Cu peak could not be seen in this voltammogram because of the large increase in the Pb peak.

Voltammograms of the preserved sample of well 6-23 (8/19/96) showed a broad peak for Pb. Upon acidification, the Pb peak increased and became sharper and a broad Zn peak appeared. The quantity for these metals was estimated at 180 and 20 ppb for Pb and Zn, respectively.

An aliquot of well 6-23 (preserved, sampled on 8/22/96) was analyzed; however, only minor peaks were seen in the voltammogram. Current signals were very low in comparison to other voltammetric data. Another aliquot was filtered for the analysis, and Pb was found to be the major contaminant. Zinc was also present, but could not be detected because of its lower current response (*vide infra*). For the third aliquot, which was also acidified to pH <2, the well-formed peak for Pb shown in Figure 4A was observed. The concentration of Pb was estimated to be about 1000 ppb. To quantify the Zn in the sample, the potential window was shortened from −1.2 to −0.8 V, thus excluding the large Pb peak. The concentration of Zn was determined from the peak at −1.0 V, shown in Figure 4B, to be 25 ppb. Well 6-11 yielded a poor response with very low currents. The sample was filtered and acidified and Pb and Cu were approximated to be 50 and 5 ppb, respectively.

The laboratory results added complimentary information to the analysis of the groundwater. Analyses were done in the preserved sample, after filtration and also acidification. This scheme provided a broader picture of the metal speciation of the sample under the conditions described. Filtration was necessary because of the particulate matter visible in the samples. Acidification generally gave a higher value over the preserved sample. By acidifying the water sample to pH <2 and analyzing it electrochemically, a total metal concentration could be approximated. The temporal and spatial trends in the *in situ* and on-site data were consistent with the ICP and laboratory experiments as shown in Table 2.

ICP Analysis. The preserved water samples were analyzed by ICP analysis using EPA Method 200.7. This method provides total metal concentrations present in the water samples by dissociating the complexed metals. The ICP results confirmed that Pb, Cu, and Zn were the contaminants, consistent with the *in situ* and on-site electrochemical sensor
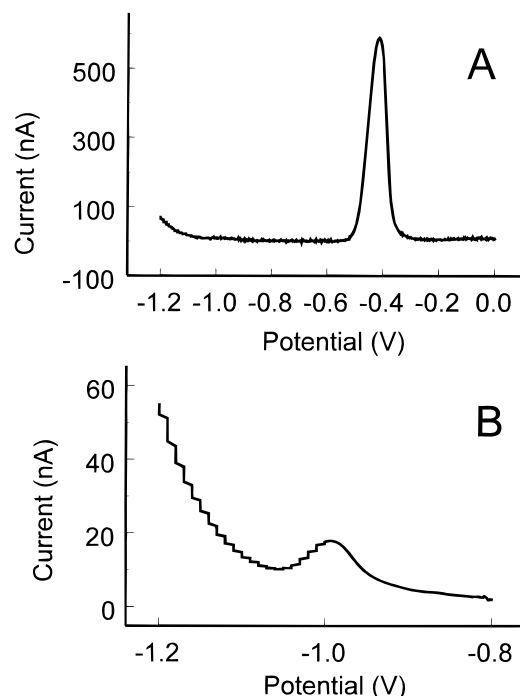

FIGURE 4. A typical voltammogram acquired in the laboratory for an acidified and filtered sample taken from well 6-23 (8/22/96) and showing the resulting (A) Pb and (B) Zn peaks. SWASV parameters: frequency = 60 Hz, pulse height = 25 mV, scan increment = 2 mV, deposition potential = −1.2 V, and deposition time = 240 s.

data. Pb was found to be the greatest contaminant, which also corresponded with the *in situ*, on-site, and laboratory data. The most interesting aspect of these split comparison results was that, even though the ICP concentration data was an order of magnitude higher, there was a reasonable correlation with the *in situ* and on-site data, especially when taking into account the substantial differences between the species measured and the technique used. This was vividly illustrated by the variations for well 6-23 taken 2 days apart. For example, the *in situ*/on-site data showed an increase of about 170% for Cu while the ICP data showed an increase of about 140%. For Pb, the *in situ*/on-site data showed an average increase of about 485% and the ICP data showed an increase of about 400%.

Conclusions. For the intended purpose of providing rapid, order-of-magnitude initial screening, the results obtained are promising. For example, comparing the *in situ* values for Pb to those from the ICP method, there is a correlation (within an order of magnitude) for the levels at which Pb is present and the values given by the sensor. Note that the *in situ* concentrations for Pb are 302, 32, and 210 ppb, while the lab ICP gives 898, 174, and 687 ppb, respectively. These are reasonably good numbers considering the *time* and *cost* differential when compared with laboratory ICP analysis.

Clearly, what this initial proof-of-concept study shows is that *in situ*/on-site measurements taken with such an electrochemically based sensor can be used to give rapid on-site information for these heavy metals in groundwater. Up-hole measurements using standard additions to the neat sample will give a number for the labile form of the metals. Acidification to pH 2 should then provide a value which is reasonably close to that given by a laboratory ICP measurement for the total/dissolved forms.

We believe that with slight modifications to the sampling protocol and the addition of an anti-fouling membrane on the sensor, this type of device can provide a low-cost and rapid method for on-site and *in situ* determination of heavy

metals. We are planning a larger scale demonstration in the near future with an updated version of the probe which will also allow for the detection of four additional metals, As(III), Cr(VI), Hg(II), and Se(IV).

Acknowledgments

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