
DEVELOPMENT OF POLAROGRAPHIC SENSORS FOR HEAVY METAL DETECTION SENSING APPLICATIONS

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ABSTRACT Field sensors offer potential improvements over laboratory-based methods for heavy metal analysis because concentration assays of environmental specimens are more rapidly obtained. This allows easier pollution hot spot detection and minimizes artifacts caused by sample transport and storage. This research project involves a field sensor concept based on polarographic techniques. Polarography is an electroanalytical method that performs trace level analysis with speciation capability. Several modifications of basic laboratory methodology, though, are needed to produce a practical, portable polarographic field sensor. These include changes in instrumentation, power supply, data acquisition, experiment control, and methods of metal extraction from test samples. The use of cyclic voltammetry (CV) at a graphite substrate to analyze for lead in water and spoil bank samples is presented in this work. Cold acid extraction was employed for the spoil bank material. Based upon comparison of these measurements with accepted methods of laboratory extraction and metal analysis, it can be concluded that the CV/graphite method is a promising candidate for a heavy metal field sensor. Further technique development will include construction of a full field measurement prototype, extension to analysis of additional metals, and use of high surface area electrodes to lower concentration detection thresholds.

KEYWORDS: field sensors, polarography, heavy metals

INTRODUCTION

Pollution is a major concern in all industrialized and developing countries. In recent years there has been increasing need for estimating damage done by contamination of water, especially in states such as Louisiana where wetlands occupy a major portion of the land area. Ideally the extent of heavy metal pollution should be assessed as it occurs, so that it may be remedied before it becomes hazardous to the biota that inhabit these aquatic areas. There is a pressing need for accurate and sensitive methods to determine total metallic concentrations in polluted water and sediment in the field. There is an additional important need, though, for methods to discern the specific chemical forms in which the metals are found, since the forms may differ substantially regarding toxicity. To illustrate this need for speciation capability,

consider the case of chromium. Chromium can exist in a relatively benign trivalent form (Cr^{+3}) or in the hexavalent state (Cr^{+6}) that has been implicated as a carcinogen [1].

Rationale and requirements for field sensors to detect heavy metal pollution

Pieces of analytical equipment designed and developed for field use have many advantages. For example, they increase the ease and speed of determining metallic concentrations *in situ*. Field sensing thus minimizes artifacts associated with sample transport and storage. A second reason for employing field sensors to detect heavy metal pollution is to identify “hot spots”: areas that have a greater concentration of pollutants compared to the total area sampled. Direct field sensing makes such “hot spots” easier to identify and survey.

The third reason for developing field sensors is to reduce the time between sampling and measurement so as to obtain results more rapidly. A field sensor bypasses time-consuming steps such as sample storage, transport, and storage again once it arrives at the laboratory. This can be a real concern considering that some EPA standard methods require field specimens to be tested within 24 hours of sampling.

For successful operation outside the laboratory setting, though, field sensors must meet a stringent set of requirements. The sensor must be light-weight and portable to allow transport in a variety of locales by vehicle or, ideally, manually. The sensor must be battery operated in order to function outdoors away from line power. Protocols for metal extraction from the sample matrix may need to be modified to be practically implemented under field conditions. For example, high temperature and pressure extraction methods such as microwave digestion, may need to be replaced by “cold” sediment digestion at ambient temperature. As with any analytical technique, field sensor detection limits must be low, ideally approaching those attainable in the laboratory. Other requirements include ease of data acquisition and storage. To fulfill the weight and data handling requirements, a laptop computer linked to the sensing device and driven by appropriate software appears to be the optimal configuration. The research described in this paper involves the beginning phase of an effort to develop such a sensor for monitoring heavy metals.

FIELD SENSOR HEAVY METAL DETECTION PRINCIPLE

The first question facing us was to evaluate the scientific principles and phenomena that

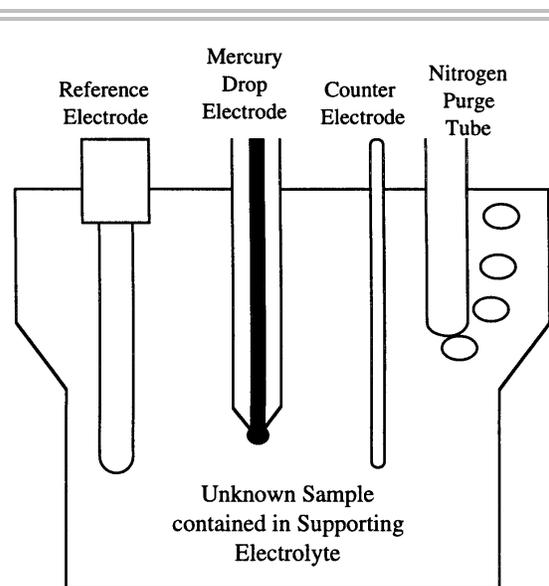
most effectively could form the basis for such a sensor.

Heavy metal concentration detection methods

There are several laboratory methods that determine heavy metal concentrations with accuracy down to the ppm range or below: atomic absorption spectroscopy (AAS), colorimetry, inductively coupled plasma atomic emission spectroscopy (ICP-AES), polarography, selective ion electrodes, X-ray fluorescence, energy dispersive analysis via X-rays (EDAX), and electron microprobe analysis.

AAS, ICP-AES, x-ray fluorescence, EDAX, and the microprobe, though, all determine total metal concentration only, and cannot directly provide speciation information. Selective ion electrodes, colorimetry, and polarography, on the other hand, not only allow for an unknown heavy metal to be identified; its valence state can also be distinguished. Also, of all of the detection methods listed above, colorimetric, polarographic, and selective ion electrode devices are the equipment that can most easily be made portable. Of the three candidate techniques best suited for field application, particularly where speciation questions are at issue, polarography generally has the lowest detection limit. Additionally, polarographic apparatus also has relatively low cost when compared to many of the other analytical methods (AAS, ICP-AES, EDAX, and microprobe for example).

As with any analytical technique, the polarographic method has certain limitations associated with it. It is rather difficult to efficiently use for multi-element analysis. Fouling of the electrode in complex media containing macromolecules may be a



Diffusion Control:

$$i_L = D_i Z_i F C_i / \delta$$

D_i = diffusion coefficient
 F = Faraday constant
 δ = diffusion layer thickness
 i_L = limiting current density

FIGURE 1. BASIC CONCEPTS OF POLAROGRAPHY.

problem. Interferences from other ions with similar half-wave potentials also can produce problematical results.

Characteristics of polarographic techniques and instrumentation

Polarographic methods used in the laboratory must be substantially modified for field use, as detailed later. In order to clearly see the reasons why these modifications are required, though, it is first necessary to describe standard laboratory methods. A polarographic measurement is accomplished by first placing a test sample in a special cell (as shown in Figure 1). It is important to use a supporting electrolyte solution in the cell that does not react with the sample to be analyzed. The polarographic method is an electrochemical technique based on

reduction of the ion being assayed, and measurement of the current associated with the reduction. Three electrodes are used in the polarographic process. The first is the cathode, the substrate upon which the reduction occurs, consisting of a small drop of mercury (Hg). The second electrode is the counter electrode which provides a return path for the current passing through the supporting electrolyte. In our laboratory device (an EG&G Model 303A Static Mercury Drop Electrode), the counter electrode is a platinum wire. The third electrode is a reference electrode to measure the potential of the mercury drop immersed in the solution. In our instrument a Ag/AgCl reference electrode is used. Nitrogen is bubbled into the supporting electrolyte to remove any oxygen present that could be reduced at the mercury electrode. Oxygen is electroactive and present at roughly the 6 ppm level (in the absence of nitrogen purging) and so would cause interferences if not removed.

The concentration of the ions of interest can be determined in the following manner. The supporting electrolyte carries a large excess of ions whose transport is the main cause of the electric field-driven current. The electrochemical reduction of the ion being assayed thus occurs under diffusion control conditions, which means that the limiting current (i.e., the maximum value) is proportional to concentration C_i as shown in Figure 1. Since current can be measured at low (nA) levels, so can concentration (down to ppb levels). The potential where the current reaches half of its limiting value (in a DC polarographic measurement) is termed the half-wave potential. The half-wave potential is a constant independent of the concentration of the unknown and is unique for each oxidation state of a given element. Equation 1 gives the Heyrovsky-Ilkovic

equation, which relates potential and current:

$$E = E_{1/2} + (2.3RT/ZF)\log([I_L - I]/I) \quad (1)$$

where E = potential of the reduction substrate, $E_{1/2}$ = half-wave potential, I_L = limiting current, I = measured current, F = Faraday's constant, T = absolute temperature, Z = number of electrons transferred, and R = gas constant.

Bond [2] has given a more complete description of polarographic techniques.

MODIFICATION OF POLAROGRAPHIC APPARATUS FOR FIELD USE

The basic analytical techniques described previously that are used for analysis in the laboratory must, however, be modified in several ways before they can be applied in the field.

Reduction substrate considerations/Graphite as a sensing electrode

In order to reduce potential environmental harm from accidental spills of the mercury reservoir, an appropriate reduction substrate must be found to replace the dropping mercury electrode in common use in polarographic equipment. Further modification of existing polarographic techniques includes developing a means to prevent fouling to ensure proper electrode functioning under field conditions.

Graphite has certain obvious advantages over mercury for use as an electrode in voltammetric measurements. Intrinsically, graphite is not nearly as harmful to the environment as is mercury. Since it is a solid, accidental dispersal in the field area is a remote possibility. Graphite, in principle,

seems suited for voltammetric or polarographic environmental specimen analysis due to its highly conductive nature. Also, solid graphite electrodes (as opposed to liquid mercury) will contribute to the overall ease of mobility of the measurement apparatus, a major requirement for a field sensing system.

Data presented later suggest that a larger electrode surface area may be required to detect substances present at low concentrations. An additional positive feature of graphite is that various sizes and surface areas are commercially available, including yarns, felts, and fabrics.

The effectiveness of a graphite electrode, though, can be affected and compromised by various aspects of its complex surface chemistry. Care must be taken to ensure that the electrode surface is reproducible from measurement to measurement. Fouling by adsorption of environmental macromolecules could be a major potential problem. Means to renew the surface such as with cathodic cleaning or application of a renewable paste to the surface should be investigated.

Various oxidative electrochemical pretreatments have been proven to enhance graphite electrode sensitivity and response time for use in detecting dopamine concentrations in brain tissue [3, 4]. Perhaps similar treatments can be devised to enhance the properties of graphite for detecting environmental heavy metals. Surface atomic structure of the graphite is also relevant to its response [5]. The basal plane of the graphite structure is almost inert electrochemically. Most electron transfer reactions occur at the edges of the basal planes. Often large numbers of oxygen-containing functional groups (phenol, carbonyl, quinone, carboxyl, etc.) may be

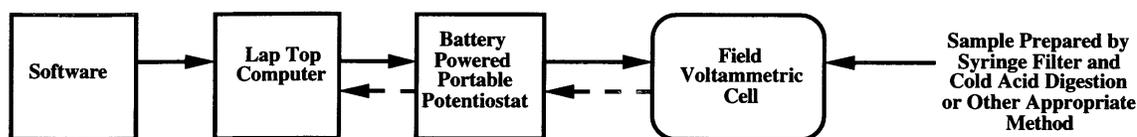


FIGURE 2. SCHEMATIC OF VOLTAMMETRIC MEASUREMENT SYSTEM SUITABLE FOR FIELD USE.

present on this surface and can participate in electrochemical reactions. Thus the percentage of the surface of the electrode comprised of non-basal planes is an important feature affecting electrode response.

Adaptation of extraction techniques to field use

Appropriate sample separation and metal extraction techniques are required for field use since often the equipment used in the laboratory for this purpose is not suitable for deployment under field conditions.

Extraction techniques should be simple, employing reagents and equipment able to be carried easily to the field site. In addition, before chemical analysis of certain types of samples can be performed (e.g., sediments or water-suspended particulates), the solid and aqueous phases must first be separated, by vacuum filtration or centrifugation for example. Syringe filtration may be adapted to field use to accomplish particulate and aqueous phase separation. After separation, though, extraction or digestion of the sample may still be required before analysis. For speciation studies, it is very important that this step does not change the oxidation state of the element one wishes to assay for.

Acid extraction processes, such as the ASTM Standard D 3974-81 [6] protocol, are difficult to implement under field conditions because of the heating required. This protocol calls for the mixing of four grams of sediment plus one ml concentrated HNO_3 , 10 ml concentrated HCl , and 100 ml H_2O .

The mixture is then heated at 95°C until ~10-15 ml liquid remains. The sample is centrifuged and supernatant removed.

In this research project, the following digestion technique was investigated as an alternative method that would be practical to implement in the field at ambient temperature. The sample was mixed with 100 ml of 150 mM HCl and then shaken for five minutes. Another extraction method for field use that could be useful in some circumstances is H_2O extraction. H_2O extraction may oxidize sulfides to sulfates, for example. Since sulfates are soluble in water, they may leach out in an aqueous environment. H_2O extraction was performed as follows: the sample was mixed with 100 ml deionized water and then shaken for five minutes. The effectiveness of these methods for analyzing 20 g dredge spoil bank samples is presented later.

INSTRUMENTATION MODIFICATIONS

A generic block diagram outlining the basic requirements of a polarographic system that can be used in the field is shown in Figure 2. A variety of equipment can be used to assemble a system such as that shown in Figure 2. Any laptop PC computer will suffice as long as the system requirements for the software are met. Three specific systems that we are considering are shown in Figure 3. Possible choices for the software include CorrWare for Windows[®] and EG&G M270 Electrochemical Analysis Software.

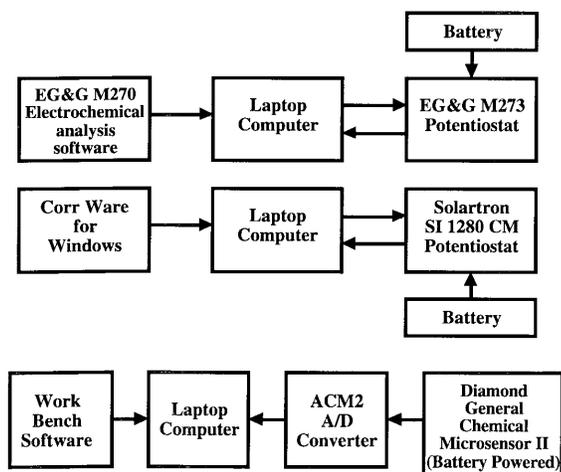


FIGURE 3. THREE POSSIBLE SPECIFIC FIELD SENSING SYSTEMS.

Possible candidates for the potentiostat include the Solartron SI 1280 CM or the EG&G M273. The Solartron would seem to have the advantage in regard to portability. The third system considered does not employ a potentiostat, but rather uses a chemical sensing system (Diamond General Chemical Microsensor II). Electrodes can be made from commercially-available graphite in various shapes and sizes to obtain targeted specific surface areas, an important factor related to the lower limits of concentration detection, as discussed later.

LABORATORY SIMULATION OF FIELD SENSORS

Equipment and technique considerations

The instrument configuration shown in Figure 4 was used to conduct a series of tests to assess the basic feasibility of these field sensor concepts. Polarography is actually not just one method of analysis, it is a family of closely related methods that differ from each other depending upon the potential

versus time waveform applied to the reduction substrate. The first question to answer when using a nonstandard reduction substrate is which of these techniques is most effective. To answer this question, the following methods were investigated: cyclic voltammetry, linear sweep voltammetry, normal pulse polarography, differential pulse polarography, square wave voltammetry, and sampled DC polarography. Graphite rod counter electrodes (6 mm in diameter) were used for these tests. Two types of experiments were conducted. In the first, lead (Pb) was added to the aqueous supporting electrolyte at a concentration of 25 ppm. The supporting electrolyte used to test the field sensor methodology was 0.1 M citric acid with added NH_4OH to adjust the pH to 3. Such a reagent can be easily stored in containers suitable for transport to the test site along with the polarographic field sensing equipment. This first test series yielded an effective method for analysis using a graphite substrate. This method, cyclic voltammetry (CV), was then used for a more difficult analysis, determining the lead content from dredge spoil bank samples from Bayou Trepagnier, a contaminated site near Norco, Louisiana. Such samples were first analyzed using the extraction protocols previously described for field use. To further characterize the method, the sample was analyzed using differential pulse polarography (DPP) and cyclic voltammetry with a mercury electrode, in order to compare the proposed field sensing method with the more usual laboratory techniques. Specimens were also tested with differential pulse polarography using a mercury electrode when lead was extracted with H_2O and via ASTM D 3974, again in order to compare potential field methods with laboratory techniques.

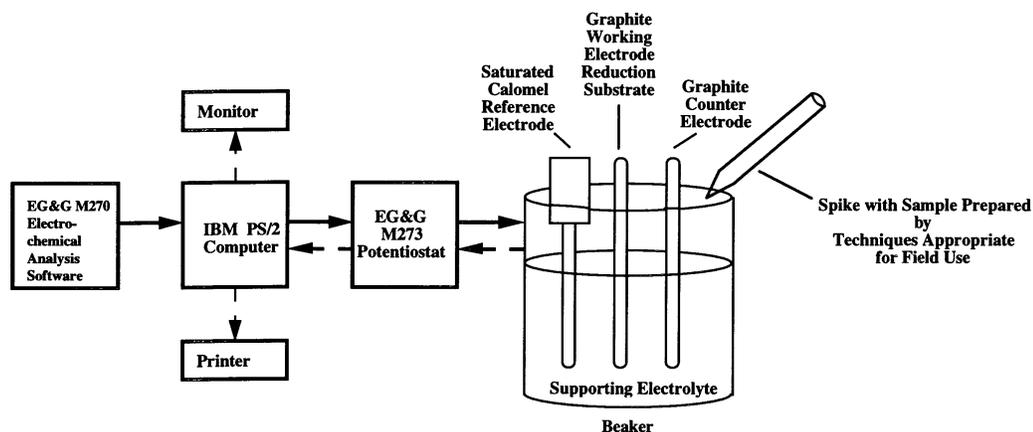


FIGURE 4. EQUIPMENT USED IN THE LABORATORY TO SIMULATE FIELD TESTING.

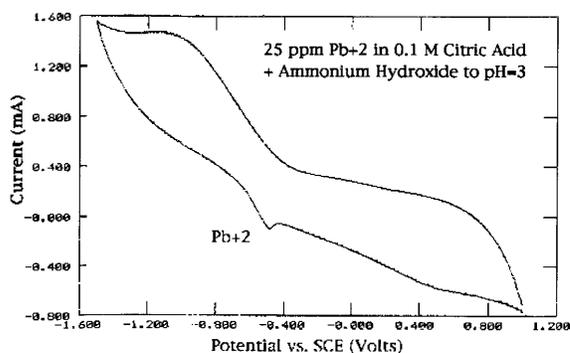


FIGURE 5. CYCLIC VOLTAMMOGRAM USING GRAPHITE ELECTRODE.

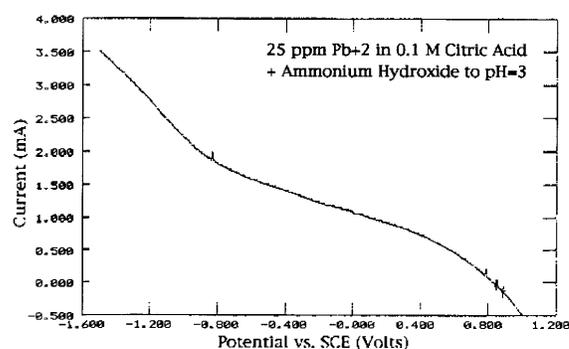


FIGURE 6. SQUARE WAVE VOLTAMMOGRAM USING GRAPHITE ELECTRODE.

RESULTS

Of all of the polarographic methods investigated, cyclic voltammetry (CV) produced the best results in preliminary laboratory trials. This can be seen from inspection of Figures 5-7 which show voltammograms for various test methods. Only CV shows a clear peak at the Pb^{+2} half-wave potential (~ -0.5 V versus SCE). Cyclic voltammetry was accordingly used to analyze the spoil bank specimens. An example of the standard addition calibration curve for a spoil bank sample is shown in Figure 8. An actual CV spoil bank voltammogram recorded with the simulated field sensor apparatus of Figure 4 is shown in Figure 9. A Pb^{+2} peak on the oxidation

branch of the voltammogram is clearly visible at a half-wave potential of -0.52 V (SCE). The values of current used in Figures 8 and 9 are based on the peak current (i.e., the current above that of the hysteresis loop). The Pb^{+2} concentration found from the measurements depicted in Figure 9 was 773 ppm.

Differential pulse polarography (DPP) with a Hg electrode was used to compare spoil bank metal content recovery after using three extraction techniques (cold HCl, cold H_2O , and D3974-81). The values of Pb^{+2} concentration obtained from these three extraction methods are shown in Figure 10. The values are 666, 53, and 1,609 ppm, respectively, for HCl cold digestion, H_2O

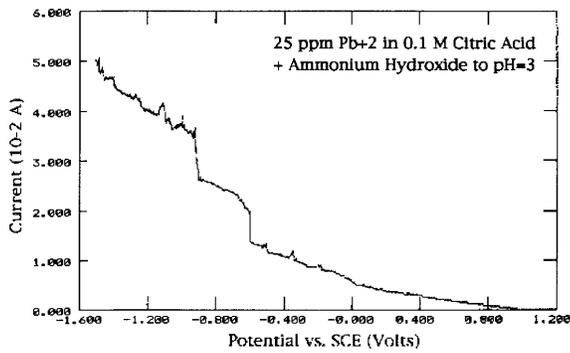


FIGURE 7. NORMAL PULSE POLAROGRAM USING GRAPHITE ELECTRODE.

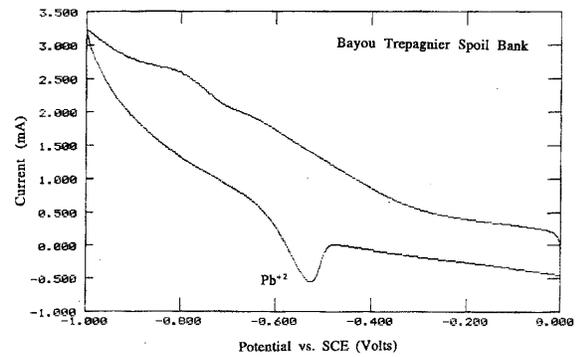


FIGURE 9. BAYOU TREPAGNIER SPOIL BANK Pb^{+2} VOLTAMMOGRAM USING CYCLIC VOLTAMMETRY.

Standard Addition Calibration Curve (forced through zero) of Bayou Trepagnier Spoil Bank Samples using Cyclic Voltammetry

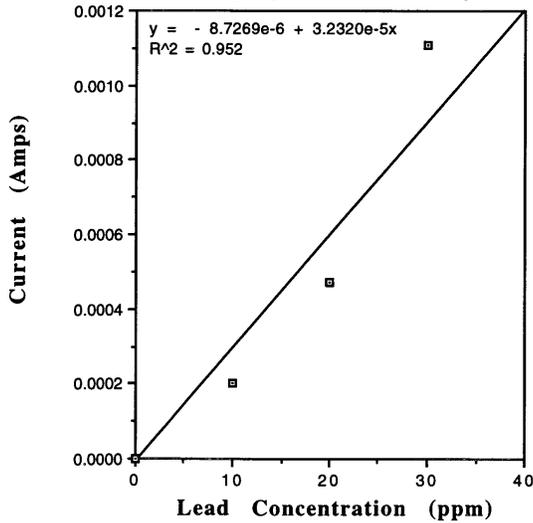


FIGURE 8. CALIBRATION CURVE FOR LEAD SAMPLE DETERMINED WITH THE CV/GRAPHITE METHOD.

Comparison of Extraction Techniques Used to Extract Lead from Bayou Trepagnier Spoil Bank

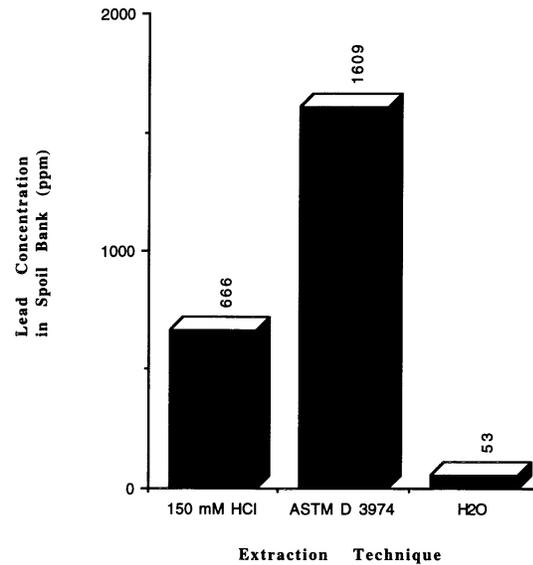


FIGURE 10. SPOIL BANK LEAD CONTENT DETERMINED USING VARIOUS EXTRACTION TECHNIQUES.

extraction, and ASTM D 3794-81. This indicates that the proposed field method (cold HCl digestion) has a recovery lower than the standard method, yet one that would be quite adequate for relative pollutant concentration surveys for hot spot identification.

The comparison of spoil bank lead content determined with the CV/graphite,

CV/mercury, and DPP/mercury methods is presented in Figure 11. These values were 773, 556, and 666 ppm, respectively. Since the field sensing method produced results similar to the conventional methods, this test gives reason for optimism with regard to the accuracy of the CV/graphite method.

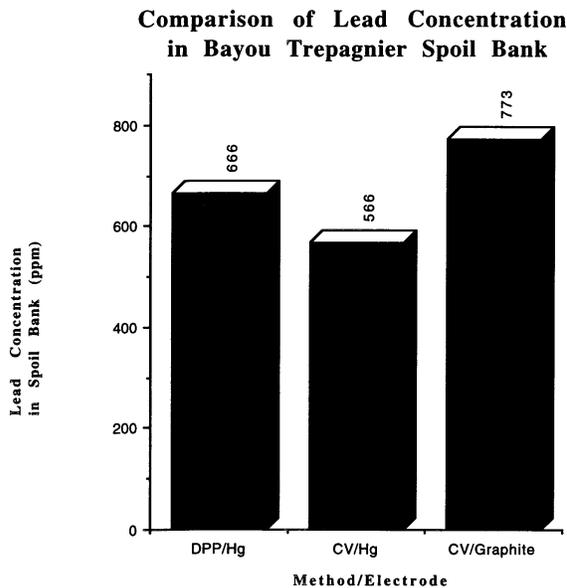


FIGURE 11. COMPARISON OF SPOIL BANK LEAD CONTENT MEASURED WITH DIFFERENT LABORATORY AND FIELD POLAROGRAPHIC TECHNIQUES.

Using 1,600 mm² of graphite electrode surface area exposed to the supporting electrolyte, the lower limit of Pb⁺² concentration detection was seen to be 5 ppm. To lower this limit, in principle, would require an increased current signal at a given concentration. Theoretically this can be obtained by increasing the surface area exposed to the electrolyte. This idea was investigated by measuring the CV current for a solution containing 50 ppm Pb⁺² dissolved in the supporting electrolyte while changing the area exposed in a controlled manner. The results are shown in Figure 12. In Figure 12, total current refers to the difference between the two currents at a given potential for the forward and reverse scans of a cyclic voltammogram (Figure 9, for example). Peak current is as defined above, and hysteresis current is the difference between total and peak current. The currents shown in Figure 12 were taken at E_{1/2}. Currents were

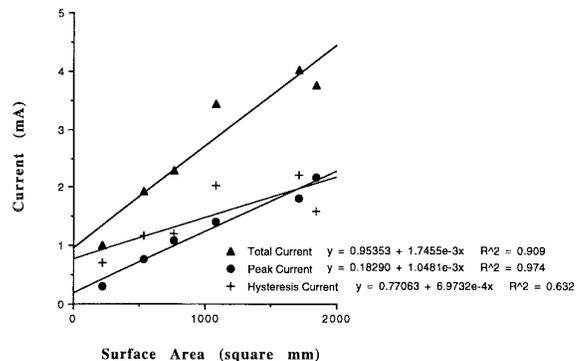


FIGURE 12. GRAPHITE ELECTRODE CURRENT VERSUS SURFACE AREA RESPONSE.

observed to scale linearly with area, as expected.

This implies that the sensitivity of a field electrode can be increased by increasing the area of graphite exposed to the supporting electrolyte. Commercially-available graphite can be obtained with very high specific surface areas—about 180 m²/g for yarn and 0.7 m² for felt. This gives reason for optimism that a graphite-based field sensor can approach the laboratory limits for detection sensitivity from a mercury electrode. Additionally, graphite is available in woven, sheet, and ribbon forms that may be useful in electrode construction.

DISCUSSION AND CONCLUSIONS

Polarography seems suited for field sensing of heavy metal concentrations based on portability, ability to perform speciation studies, and low detection limit capability. Laboratory polarographic instrumentation must be modified for field use to achieve adequate portability and ease of data acquisition, while using a reduction substrate less toxic than mercury to protect the environment.

Preliminary data has shown that cyclic voltammetry on a graphite substrate is a

technique suitable for use as a heavy metal field sensor. Measurements employing field sensing methods under simulated conditions are comparable to those obtained using standard laboratory polarographic techniques. Heavy metal extraction procedures with adequate metal recovery for use under field conditions have been developed that are easily performed with a minimum of specialized equipment and reagents. Further research and development is needed to 1) decrease the detection limit on the portable field device by increasing electrode surface area, 2) assess resistance to electrode fouling and poisoning, and 3) determine the applicability of the CV/graphite technique for assaying other heavy metals besides Pb^{+2} (chromium, arsenic, cadmium, and mercury, for example). Future research is planned to produce a working field sensor prototype and to test it under both laboratory and field conditions.

ACKNOWLEDGMENTS

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