

An Environmentally Friendly, Cost-Effective Determination of Lead in Environmental Samples Using Anodic Stripping Voltammetry

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Contamination of the environment with heavy metals such as lead presents many health risks to humans as well as aquatic life. In some areas, especially those near mining and smelting operations, Pb contamination of the sediment is the leading cause of most waterfowl deaths (1). Simple, effective, and field-portable methods for the measurement of these metals in environmental samples are vital tools for evaluating the risks that these contaminants pose. Anodic stripping voltammetry (ASV) is an effective electroanalytical method for the determination of a several metals, including Pb, Cd, Cu, and Zn (2). ASV is an advantageous technique in that it is field-portable and the required instrumentation is relatively low-cost as compared to other techniques. In ASV, analyte ions are deposited onto a working electrode by application of a negative potential. Then, the applied potential is swept in the positive direction to re-oxidize (strip) the deposited metals, and the corresponding current signal is recorded by the potentiostat. Analyte concentrations are proportional to peak areas, and each analyte is identified by its characteristic redox potential. ASV can commonly measure concentrations at levels of parts-per-billion and lower.

Traditionally, ASV required co-plating of analytes onto the working electrode with mercury (2). This is referred to as a mercury film electrode (MFE). Alternatively, a hanging-drop mercury electrode (HDME) could be employed (2, 3). The increasing aversion to mercury use (notably in academic laboratories) and the cost of mercury-containing waste disposal make these electrodes less desirable. Bismuth film electrodes (BiFEs) have been reported as alternatives to MFEs (4–9). While BiFEs require more attention to sample pH, the elimination of mercury makes BiFEs more attractive from safety, environmental, and cost perspectives. Additionally, the performance of the BiFE suffers little from the presence of dissolved oxygen; thus, purging samples with inert gas is not required, in contrast to MFEs and HDMEs.

Traditional electrode materials such as glassy carbon (GC) (10) may be utilized with mercury films and bismuth films. These renewable electrodes are available from a variety of manufacturers, but they typically cost hundreds of dollars, require routine polishing, and have limited lifetimes. A number of disposable screen-printed electrodes are commercially available, but these typically cost several dollars apiece and must be purchased in bulk quantities (11, 12). Homemade electrodes for the classroom can reduce some of the costs (13, 14). More practical electrodes for both classroom laboratory and field analysis applications should be inexpensive and require little to no maintenance; preferably they would be disposable after each experiment to reduce maintenance time and contamination across multiple samples. Graphite pencil "lead" re-fills have been

shown to function as working electrodes with both mercury and bismuth films (15–18). These are not only inexpensive (~12 per U.S. dollar) and readily available, but in our work they have shown better performance than the glassy carbon electrode in conjunction with bismuth films.

This article describes the use of new developments in ASV in an experiment that analyzes environmental samples for Pb content. In this experiment, students extract a sample such as riverbed sediment with dilute acid, facilitated by sonication, and analyze it for Pb content using ASV. This experiment replaces traditional working electrodes with inexpensive, disposable graphite pencil "lead" electrodes. Additionally, bismuth films are used, which are more environmentally friendly than traditional mercury films and eliminate the cost and hazards of mercury usage and disposal. The primary goal of this experiment is to teach the analytical electrochemical method of ASV for trace metal analysis. It is targeted for an upper-level undergraduate instrumental methods course, with possible applications in an environmental chemistry course.

Experimental

Reagents, Supplies, and Instrumentation

Concentrated nitric acid was obtained from Pharmco (Dallas, TX). Sodium acetate trihydrate, sodium hydroxide, bismuth(III) nitrate, and a 1000 ppm lead atomic absorption standard solution were obtained from Fisher Scientific (Hampton, NH). While ultra-pure reagents are often recommended for trace metal analysis, reagent-grade chemicals gave no observable Pb contamination and were used in the bulk of the work.

ASV was performed on a PalmSens portable potentiostat (Houton, The Netherlands). The working electrodes were Pentel SuperHiPolymer 2H pencil "leads" (0.7 mm thickness) purchased from Pentel (Torrance, CA). (The 3H rated pencil "leads" also worked; however, "leads" rated 1H, B, or HB performed poorly.) The counter-electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode from Cypress Systems, Inc. (Chelmsford, MA). Samples were extracted using a Branson B220 sonicator (Danbury, CT). Samples were prepared in 15 mL polypropylene Falcon tubes with caps (Fisher Scientific). PTFE or Nylon syringe filters (0.45 μ m pore size) and 10 mL plastic syringes were used to filter the sample extracts (Fisher Scientific).

Sample Collection, Preparation, and Extraction

River and lake sediment samples from locations in southwestern Ohio were used in our work. Sediments were collected by scooping the sediment (2–5 g) into 15 mL polypropylene

tubes and decanting excess water at the site. Samples were collected within a meter of the shoreline in water no deeper than ankle-depth. In the laboratory, the samples were sifted to remove large particles and filtered to isolate the sediment solid. The solid was pulverized with a mortar and pestle and dried in an oven at $\sim 100^\circ\text{C}$ for at least an hour.

Extraction of the samples was performed in dilute nitric acid using the following procedure (19): Approximately 0.5 g of the dry solid was weighed and placed into a clean 15 mL polypropylene tube, and 10.0 mL of 25% nitric acid (1:4 dilution of concentrated HNO_3) were added. The lid of the tube was closed, and the tube was shaken. The tube was then placed in a sonicator ($30\text{--}40^\circ\text{C}$) for 30 to 60 minutes. After sonication, the sample was filtered using $0.45\ \mu\text{m}$ PTFE or Nylon syringe filters into a new 15 mL polypropylene tube. Blank samples should be prepared following the same procedure above, excluding the solid sediment. A spiked sample can be prepared by addition of a known quantity of Pb standard solution to the solid sediment prior to extraction and filtration.

Voltammetry

For the BiFE to function properly, a solution pH of 4.0 to 4.5 is required. Thus, the sample was prepared as follows: 2.50 mL of 1.0 M sodium acetate were added to a sample vial (in our work, a 5 mL glass conical vial with stir bar). Next, 1.00 mL of the sample extract (in 25% HNO_3) was added, followed by 0.100 mL of 100 ppm Bi (in 25% HNO_3). Lastly, 1.00 mL of 3.0 M NaOH was added to the sample. A pH of 4.0–4.5 should be verified before continuing.

Square-wave ASV was performed using a Pentel Super-Hipolymer 2H graphite pencil "lead" working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The potentiostat was connected directly to the pencil "lead", and approximately 1 cm of the pencil "lead" was submerged in the sample solution (since the volumes of the standard additions are very small, the length of pencil "lead" submerged remains essentially constant). ASV was performed using the following parameters: conditioning step, $E = +0.500\ \text{V}$, $t = 20\ \text{s}$; deposition step, $E = -1.000\ \text{V}$, $t = 120\ \text{s}$; equilibration step, $E = -1.000\ \text{V}$, $t = 10\ \text{s}$; stripping step, $E_{\text{final}} = +0.500\ \text{V}$, $E_{\text{step}} = 0.005\ \text{V}$, pulse amplitude = $0.025\ \text{V}$, $\nu = 20\ \text{Hz}$. After recording the data (area of peak near $-0.55\ \text{V}$), $0.025\ \text{mL}$ of a 2.5 ppm Pb standard (in 2.5% nitric acid) was added, the solution was stirred, and voltammetric data were collected under the same conditions as above. Standard additions and data collection were repeated until the desired number of additions (typically 3–4) was complete. A blank sample should be analyzed before each new sediment sample to ensure that no Pb signal arises from reagent or apparatus contamination, and a control sample can be analyzed to verify the accuracy of the method. Ideally, at least three determinations of Pb in the sample should be performed, and multiple samples could be analyzed to identify results from anomalous samples.

Hazards

Chemical Hazards

Nitric acid is a strong acid that can cause severe burns. Sodium hydroxide is a strong base that is caustic and can cause severe burns. Samples and standards contain Pb and possibly other toxic substances that can cause health problems if ingested or inhaled.

In humans, Pb is known to cause neurological impairment as well as disorders of the kidneys, blood, and digestive system.

Physical Hazards

Areas near shorelines can be dangerous, including but not limited to such hazards as drowning potential and falls from slippery rocks. Sample collection in the field should be performed cautiously. Samples should not be collected from areas where this is prohibited. Sample collection, as with all experimental procedures, should never be performed alone. If desired, the instructor may choose to provide samples in lieu of the field sample collection activity.

Results

Voltammetry of the extracts of the river and lake sediments from the southwestern Ohio region exhibited well-behaved responses. Representative data from a sample from the Little Miami River are shown here, with Pb peaks clearly identified and quantified near $-0.55\ \text{V}$ (Figure 1). Other peaks were observed, including Bi (near $+0.1\ \text{V}$) and Cu (near $-0.05\ \text{V}$). The Pb peak clearly and predictably increased in area with subsequent standard additions of Pb.

Plots of the peak area versus the total concentration of Pb added to the sample were constructed (Figure 2). The concen-

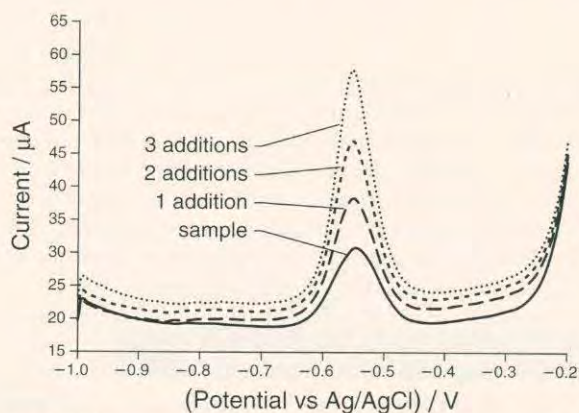


Figure 1. Voltammograms from a river sediment extract sample and three successive standard additions of Pb.

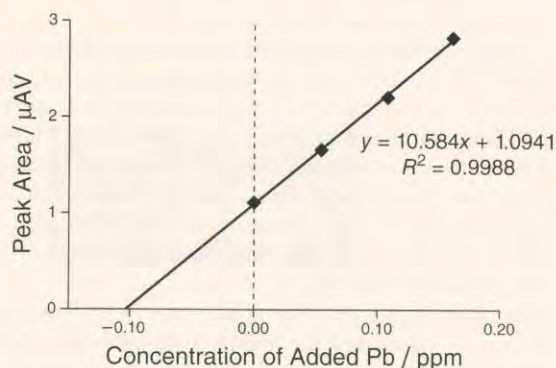


Figure 2. A representative data set of Pb peak area vs the total concentration of Pb added to the sample.

tration of Pb in the diluted sediment extract solution was determined from the absolute value of the x intercept of the linear fit, adjusting for the dilution factor when preparing the sample. From this and the mass of solid sample, the concentration of Pb in the sediment sample can be calculated. In a representative set of data from one student, three determinations of Pb in sediment from the Little Miami River show an average Pb level of 9.3 ± 1.4 ppm ($\mu\text{g Pb per g sediment}$). This is consistent with values recently reported by the U. S. Geological Survey (USGS) (20).

Discussion

This experiment provides students with opportunities to learn techniques in analytical electrochemistry and possibly environmental chemistry, while also engaging them in real-world experiment. From a curricular viewpoint, this activity covers concepts and techniques such as electrochemistry, voltammetry, ultrasonic extraction, and the standard addition method.

This experiment is optimal for a course in which students are permitted to work at their own schedule or in which students rotate through a set of experiments over several weeks. The voltammetry can be completed within 15–20 minutes per determination, depending on the number of standard additions (IUPAC recommends 3–4) (21). In a 3-hour period, several individuals can complete the voltammetry experiments on a single potentiostat. However, the other required steps can be logistically time-challenging. Students must prepare many solutions, which can consume significant lab time. For time-restricted courses, instructors may consider preparing solutions and possibly even sediment samples. In classes with fewer constraints, students may collect and dry samples days or weeks before extraction and analysis. Most to all of the class' samples could be extracted simultaneously. Lastly, while students are encouraged to perform three determinations, with proper blanks, spiked samples, and control samples, the instructor may, at his or her discretion, trim these activities to meet the desired time constraints.

For instructors who do not have access to appropriate samples or who wish to avoid the field activity altogether, a number of standard reference materials (SRMs) performed well. In our work, analyses of SRMs 8704 (Buffalo River Sediment), 1944 (NY/NJ Waterway Sediment), and 2711 (Montana Soil) from the National Institute of Standards and Technology gave excellent results, with Pb levels consistent with the certified values (22). Such samples would work well for instructors who wish to assess the accuracy of students' results.

It is notable that the PalmSens potentiostat used here costs about one-half the price of a traditional bench-top unit, with essentially the same capacities, which may allow institutions to equip their laboratories with more units at lower cost. Additionally, the PalmSens instrument is compact, battery-powered, and field-portable, allowing instructors to adapt this experiment to field applications. This possibility is not available with some other laboratory-based analytical methods such as GFAAS or ICP spectrometric methods.

Instructors may wish to emphasize the significant propagated error associated with the standard addition method (23). Students could also compare results from the standard addition and the calibration curve methods. As our work has shown, the calibration curve method will provide lower Pb concentrations

(and when analyzing SRMs, inaccurate Pb concentrations), owing to matrix effects in the sediment samples. Examination of errors associated with sampling aspects could also be considered (24), especially for courses in environmental analysis.

Conclusions

The experiment was performed using a pilot group of four students who each performed the experiment on actual sediment samples as well as two sets of SRMs to assess their analytical accuracy. The primary goal of the experiment is to teach experimental analytical electrochemistry, along with associated procedures such as sample preparation through extraction. Additionally, in performing the experiment students become more familiar with concepts in electrochemical methods such as applied potentials and measured currents. The participating students had no prior experience with or formal training in electrochemistry of any kind (except for the use of standard pH electrodes and meters). ASV is an excellent technique for the introduction of electrochemistry to students owing to the relative straightforwardness and ease of understanding of the method.

The students in this experiment succeeded both in terms of analytical results as well as understanding of the principles of applied potential electrochemistry. All were able to successfully explain the physical functioning of the method in their reports, and their experimental results, especially for the SRM samples, were accurate with respect to known values. Additionally, the use of actual samples from the students' environment added to the students' interest in the experiment. While the SRMs were excellent samples for verifying method performance and assessing accuracy, work on river sediment samples was much more eagerly performed by the students. An additional learning goal of this experiment was to teach the application and value of the standard addition method of analysis. While it was not uncommon in the students' results to see relative errors from 10% to 20%, even with relatively linear calibration plots, the students understood well the necessity of using the standard addition method, even in light of its moderately high level of relative error. The alternative calibration curve method with simple calibration standards yielded much lower determined concentrations of Pb in their analyses, which were clearly less accurate when analyzing SRMs with certified values for comparison.

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Disclaimer

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