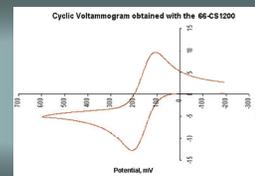


Experiments in Analytical Electrochemistry



5. Analysis of Trace Lead in Water by Anodic Stripping Voltammetry

PURPOSE: To use Anodic Stripping Voltammetry (ASV) to determine low levels of dissolved Pb

BACKGROUND: Why Lead? Lead contamination of drinking water is a major global problem. Acute lead poisoning in children can cause anorexia, vomiting, malaise, convulsions and even, permanent brain damage. Chronic lead poisoning can cause weight loss, weakness and anemia. Lead can leach into water from either solder used to join copper pipes or from lead pipes in older buildings. Other sources of lead are paints in older buildings, and dust/soil contaminated with tetraethyl-lead (formerly a gasoline additive.)

The following websites provide information about toxicity levels of lead, how it is manifested in children, treatments and risk assessment/management.

<http://esainc.com>. After opening the site, click “Lead Analysis” and then “Understanding Pediatric Blood Lead Levels” for a table ranging from lead levels of <math>< \mu\text{g}/\text{dL}</math> (normal) to $> 44 \mu\text{g}/\text{dL}$ (serious).

<http://www.atsdr.cdc.gov/HEC/CSEM/lead>. This comprehensive article, titled, “Case Study in Environmental Medicine, Lead Toxicity.” Covers symptoms of lead in young children, blood lead toxicity levels, sources of lead, etc.

<http://www.manbir-online.com/diseases/lead/htm>. This is a short article that discusses the sources of lead and its clinical manifestations, toxicity levels and treatments.

<http://www.epa.gov/lead/403risk.htm>. This site contains the U.S. EPA’s comprehensive information regarding “Lead in Paint, Dust and Soil” and includes risk assessment, risk management and data on lead. Recommended reading for anyone interested in researching the subject.

THEORY: ASV is one of the most sensitive, convenient, and cost effective analytical methods for detection and determination of metal ion contaminants, such as lead, in water whether from rivers, lakes, process streams or drinking sources. With ASV, it is possible to analyze simultaneously very low levels of several metals such as Pb, Cu, Cd and Zn. ASV can detect levels in the range of part-per-million (ppm) or even part-per-billion (ppb) (i.e., $\sim 10^{-10}$ M). Example linear sweep ASVs of Pb are shown in Figure 1.

ASV involves a deposition step (often called pre-concentration) at an applied negative potential for a specified period of time. The metals, as ions in solution, are concentrated by plating them onto the electrode in their metallic form. Then the electrode is scanned linearly toward positive potentials so that the metals, one at a time, are stripped from the electrode and re-oxidized at a potential characteristic of each metal. The resulting current-voltage peaks can be compared with those in a calibration curve done

with standard solutions of known quantities of metal ions. Besides determining which metals are present, the quantity of each metal can be correlated to the peak height of the current or the integrated charge under the peak.

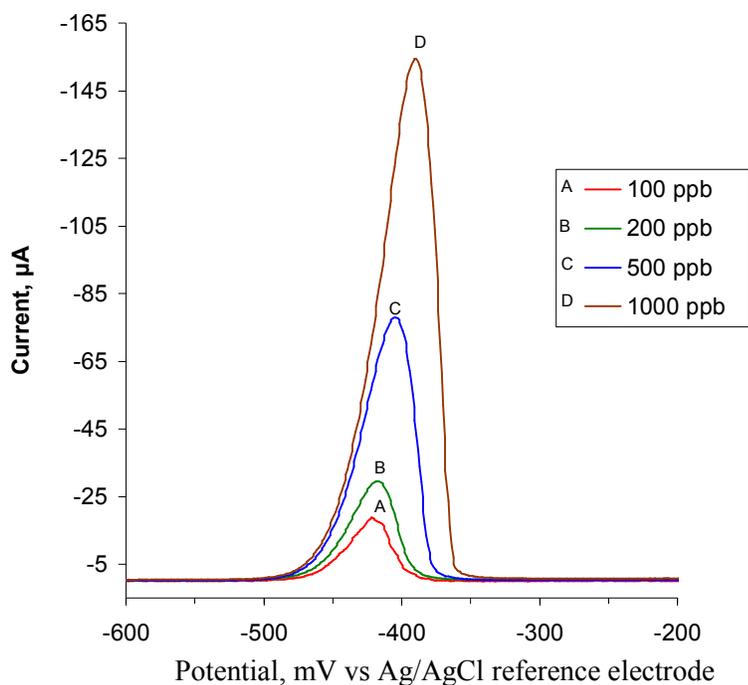


Figure 1. Linear scan ASV of Pb using a thin Hg film electrode on glassy carbon. Experimental conditions: deposition time 2.0 minutes a with 30 second rest period before scanning. Initial potential at -1,000 mV and final potential at +200 mV. Scan rate = 2 V/s with the Hg film co-deposited with Pb during the deposition step. Data files were exported to Excel and plotted with the potential scale set from -200 to -600 mV. If you are unfamiliar with the use of Excel program, please consult the Technical Note on Excel in this eChem Manual.

ASV was originally developed with a hanging Hg drop electrode where the metals often form an amalgam. However, to limit the quantity of toxic Hg used, thin Hg films can be pre-deposited onto an electrode such as glassy carbon or co-deposited simultaneously with the analyte metal ions. The amount of Hg deposited is very little and can be readily removed at potentials less negative than those of the analyte metals, such as Pb, Cd and Cu. References 1-5 include web-based online ASV articles and hardcopy references on the subject.

EXPERIMENT

Equipment

- Use an analog or computer-controlled potentiostat with appropriate data acquisition equipment for this experiment (ask your lab instructor for directions on use of potentiostat)
- Electrochemical cell and electrodes
 - Small volume cell
 - 1.0 mm or 3.0 mm flat tipped glassy carbon electrode
 - Pt auxiliary electrode
 - Ag/AgCl reference electrode
 - Polishing kit
- A magnetic stirrer and a small bar inside the cell

- A timer
- 50 ml and 100 ml volumetric flasks

Chemical Solutions

- A. Prepare three separate 100 mL solutions at 100 ppb, 500 ppb and 1,000 ppb of $\text{Pb}(\text{NO}_3)_2$ containing 0.1 M KNO_3 , 50 mM HNO_3 and 40 ppm $\text{Hg}(\text{NO}_3)_2$. Use doubly distilled water or other high purity water for dilutions.
- B. Prepare a background solution containing 0.1 M KNO_3 , 50 mM HNO_3 and 40 ppm $\text{Hg}(\text{NO}_3)_2$.
- C. Dilute a sample of tap water or an unknown sample from your instructor. Prepare the sample by adding an equal volume of 0.1 M KNO_3 containing 50 mM HNO_3 and 40 ppm $\text{Hg}(\text{NO}_3)_2$.

Note: It is important that glassware is cleaned thoroughly, rinsed several times with pure water and then dried prior to use. You should look at the bottle labels of chemicals to note the amount of heavy metal impurities, if any are present. High purity reagents, absent of heavy metal impurities, can be purchased. Discuss this issue with the laboratory instructor. Calibration using the method of standard addition can correct for impurity if it is the same as the sought for metal.

PROCEDURE

1. Connect the cell (3- electrodes) to potentiostat (see instructor for direction or manual for potentiostat use)
2. Place the cell on top of the magnetic stirrer and put the stirring bar, the auxiliary Pt and the Ag/AgCl reference electrode in place.
3. Polish the glassy carbon electrode under light pressure with an alumina slurry on a micro-cloth polishing pad using a figure 8 motion. Five to 10 complete figure 8 tracings should be sufficient. Rinse the electrode immediately with pure water and remove any excess water by touching an edge to a Kimwipe™ or clean adsorbent paper. Fit the electrode into the cell. Further discussion on the activation of glassy carbon electrode may be found in the technical notes of this manual.
4. Add the 100 ppb Pb sample in the cell and replace the cover with the electrodes.
5. Set the applied potential, E_i , at -900 mV, the final potential, E_f , to $= 0.00$ mV and the sensitivity to $1 \mu\text{A/V}$.
6. Turn the magnetic stirrer ON, set the timer for 2 minutes and then switch the potentiostat to the ON position so that -900 mV is applied to the glassy carbon electrode. Turn the stirrer off/on with an inline switch and leave the speed controller set to the same setting to maintain the same stirring rate from experiment to experiment.
7. If the current overload light turns on, decrease the sensitivity.
8. After 90 seconds, turn the stirrer off so that the solution quiets.
9. When the timer goes off after 2 minutes, push the scan button ON so that the potential is scanned from E_i of -900 mV to 0.00 mV. A scan rate of 500 mV/sec is recommended. A higher scan rate lessens the possibility of error due to oxygen in the solution oxidizing the deposited metal, like Pb, on the electrode.
10. Remove the Hg film by stepping the potential to $+400$ mV for 30 seconds. Do not re-polish the electrode between runs.

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11. Repeat the experiment with the background solution and then with all three standard Pb solutions, running duplicates for each concentration. Always remove the Hg film between runs. Next, run duplicates on the unknown water sample.
 12. Plot the peak heights vs. concentration for the blank and standards and then determine the amount of Pb in the tap water from the calibration plot (noting where the peak height of the sample lies on the plot of the standard solutions).
 13. Do a linear regression analysis to confirm the ppb lead in the unknown water sample (run at least duplicates on the standards and the sample if time permits).

Note: If you are using a computer-controlled potentiostat like the CS-1200, the procedure for the analysis of lead is the same as that described above. With this instrument, you can and should scan at rates as high as 1 or 2 V/s. The timing and potentials can be set with the computer menu but please remember to turn the stirrer off at the preset time of 2 minutes.

REPORT (Data Analysis and Discussion):

Consult with the laboratory supervisor about the content and format of your report for this experiment. Suggestions and questions to consider are as follows:

1. Write a short summary of what you did in this experiment, noting any deviations or substitutions in the procedure.
2. Show example stripping voltammograms for Pb at 2 or more concentrations. Plot I_p vs. Pb concentration (both the uncorrected and corrected for background) and from the plot, determine the concentration of the Pb in the unknown sample. [Note: If you could not detect a peak for Pb in your unknown, the amount of Pb is most likely below 10 ppb.]
3. Were there other metals present in the water sample as evidenced by other peaks? If yes, how can you identify the metal or metals?
4. If your unknown is tap water, the amount of Pb may depend on whether the water was left standing in the pipes for hours or days, or whether you let the water run for a few minutes before sampling. If time permits, you may wish to see whether there is a difference in the quantity of Pb depending on the sampling time.
5. If time permits, make a run with 100 ppb without the co-deposition of Hg and report what you observed in the way of the Pb ASV wave shape and height, and compare it to the result with the Hg film.

Note: It is important to use high purity water throughout in making solutions and high purity reagents that are designated as being free of heavy metals. Besides trace amounts of Pb in reagents, copper is usually the main contaminant.

REFERENCES:

1. http://www.luc.edu/chemistry/faculty/fitch/Fitchgroup/Service_Learning/service_learning.html A website maintained by Professor Alanah Fitch of Loyola University (Chicago, IL) on environmental Pb analysis, etc.
2. <http://www.tau.ac.il/~advanal/LaboratoryManual.htm> This is a laboratory manual with experiments in electroanalytical chemistry applications to the analysis of drinking water, as maintained by Tel Aviv University. Experiment #6 is a description of heavy metal analysis by stripping voltammetry.
3. Allen J. Bard and Larry R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*; Publisher, John Wiley & Sons 2nd Ed. 2001. Chapter 11, pgs 458-464.
4. Howard A. Strobel and Wm. R. Heineman, *Chemical Instrumentation: A Systematic Approach*; Publisher Wiley Interscience, 3rd Ed. 1989. Chapter 30, pgs. 1137-1141.
5. Joseph Wang, Anodic Stripping Voltammetry: An Instrumental Analysis Experiment, *J. Chem. Ed.* 60, December 1983, pgs. 1074-1075.

OPTIONAL EXPERIMENT – Differential Pulse Voltammetry (DPV)

Differential Pulse Voltammetry requires a computer-controlled or programmable potentiostat. DPV provides excellent high sensitivity. However, the method uses pulse waveforms so that ASV takes longer and interference from oxygen can become significant. Thus, it is advisable to remove oxygen from solutions by purging them with nitrogen for a few minutes. Otherwise, the procedure is the same as already outlined above. Discuss with the laboratory instructor about how to set the operating parameters of the potentiostat for DPV.

If you use computer data acquisition, it is useful to export the ASCII data to an Excel file and computers subtract the “blank” background scan from the Pb ones. The baseline will be nearly flat after background subtraction (e.g., Figure 2) so that it is easy to determine the peak heights.

Use the standard lead solutions from Part A, under Chemical Solutions, for the ASV experiment.

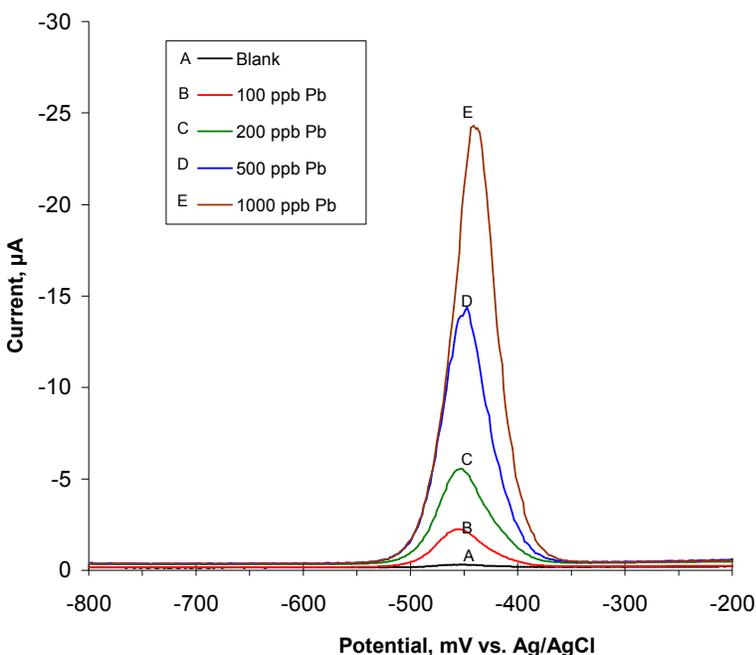


Figure 2. Example Pb ASV with differential pulse voltammetry. Deposition time is 2 minutes with 30 second rest period before ASV from $-1,000$ mV to $+200$ mV with a step height of 2 mV. The cycle period is 20 ms with a pulse height of 50 mV. The Hg film is co-deposited with the Pb during the deposition step. Data were obtained with CS-1200 computer-controlled potentiostat. Data exported to Excel and plotted with the potential scale set from -200 mV to -800 mV. If you are unfamiliar with the use of Excel program, please consult the Technical Note on Excel in this eChem Manual.

