Experiment 5: Determination of Lead or Copper by Anodic Stripping Voltammetry

Key Experimental Concepts	Electrochemistry, redox reactions, anodic stripping voltammetry (Review Ch. 17.5)
Analysis Goals	Calibration by standard addition (Review Ch. 5-3) Prelab: posted on the ELN

Organization

~~Since there are only two voltammetry set-ups, we will split our time in lab today between voltammetry and measuring glucose using enzymes – both using the method of standard additions. Half the class will start with voltammetry, and the other half with enzymes. After 2 hours, we will switch.~~

See the ELN for the pre-lab assignment.

Introduction

How Lead[1] and Copper Get into Drinking Water

Lead and copper can enter drinking water when plumbing materials that contain lead or copper corrode. This can be triggered by water with high acidity or without corrosion inhibitors, which is what happened in Flint, Michigan in 2014. The most common sources of lead in drinking water are lead pipes, faucets, and fixtures. In homes with lead pipes that connect the home to the water main, also known as lead services lines, these pipes are typically the most significant source of lead in the water. Lead pipes are more likely to be found in older cities and homes built before 1986. Among homes without lead service lines, the most common problem is with brass or chrome-plated brass faucets and plumbing with lead solder. Newer homes and buildings contain copper pipes instead of lead. In order to reduce the potential for lead corrosion, the Safe Drinking Water Act (SDWA) reduced the maximum allowable lead content [in plumbing materials] -- that is, content that is considered "lead-free" -- to be a weighted average of 0.25 percent calculated across the wetted surfaces of pipes, pipe fittings, plumbing fittings, and fixtures and 0.2 percent for solder and flux. There are currently no restrictions on copper plumbing.

In the lab, we will work with an electrochemical method called anodic stripping voltammetry to quantify lead and copper in unknown samples, specifically drinking water collected first thing in the morning from drinking fountains in USD's Shiley Center for Science & Technology.

Please note, because of the health risks of lead, some additional precautions are noted in the procedure for this experiment. ~~Please be sure to summarize this information under "Safety" in your ELN Data & Obs section.~~

Procedure – Sample Collection:

Reagents and Equipment

- 250-mL prewashed Pyrex beaker
- ~~Conc. Nitric Acid (Corrosive! Oxidant!)~~

Water samples:

From each drinking fountain with a totally dry surface (indicating no use since the previous day), a 100-mL sample was drawn into the beaker. The samples were ~~stabilized by adding nitric acid to reach 1% by volume and stored at 4 °C until~~ analyzed immediately.

[1] * https://www.epa.gov/ground-water-and-drinking-water/basic-information-about-lead-drinking-water

Anodic Stripping Voltametry (ASV)

Voltammetry is the measurement of electrical current under controlled potential (voltage) conditions. Voltage may be stepped to a pre-set level and kept constant, or swept through a range of voltages at a fixed rate. In order to achieve good analytical data, a three-electrode electrochemical cell must be used. Unlike a traditional two electrode cell, which contains a cathode and an anode, a three electrode cell features a working electrode, a counter electrode and a reference electrode. Each electrode plays a particular role in the measurement:

1. Working electrode: This is where the reaction of analytical interest takes place. It may be a reduction or an oxidation reaction. In ASV, this is the electrode that metal ions in solution are reduced onto, and then oxidized back off into solution.
2. Reference electrode: This electrode is made of a material with a very stable standard reduction potential, which will remain inert in your reaction solution. A very high resistance is placed between the reference electrode and the rest of the electrochemical cell, to minimize the current which can flow to this electrode. (Reference electrodes also have a very high internal resistance.) The reference electrode voltage is used the fixed reference point for measuring the voltage on the working electrode. Since there is almost no current flowing to the reference electrode, no reactions can occur to alter its thermodynamic voltage (via the Nernst equation).
3. Counter electrode: To maintain charge neutrality, the counter electrode provides current to balance any reaction occurring at the working electrode. If the reaction at the working electrode is oxidation, a reduction reaction will occur at the counter electrode to use up the electrons produced. If the reaction at the working electrode is a reduction, then an oxidation will occur at the counter electrode to supply the electrons being consumed at the working electrode. Counter electrodes generally have larger surfaces than working electrodes, to ensure that the reaction at the working electrode is the rate (current) limiting reaction. Look at pictures of the electrodes in the standard operating procedure for our set-up, and verify this size difference.

To summarize, in the three-electrode cell, current is measured between the working electrode and counter electrode, while voltage is measured between the working electrode and reference electrode. Isolating these two measurements provides much greater accuracy and stability in electrochemical measurements than we would get with only 2 electrodes.

Anodic stripping voltammetry is a 2-step electrochemical technique for the detection of trace metals in solution. It works by reducing dissolved metal ions at the working electrode surface, converting them to neutral metal atoms which are insoluble and therefore plate out or deposit as a thin film of metals on the working electrode surface. That film is then "stripped off" via oxidation, so that the metal returns back to its ionic dissolved state. The current during the stripping step is used to determine the quantity of metal which was present, and the voltage at which metals oxidize off the electrode helps determine the identity of the metal. Calibration curves can be constructed from the peak current at known concentrations of metal ions to allow the determination of an unknown.

'Concentration step': A strong reducing potential is applied, and solid metals form on the electrode.

$$Cu^{2+}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)}$$

$$Pb^{2+}_{(aq)} + 2\ e^- \rightarrow Pb_{(s)}$$

'Stripping step': Working electrode potential is swept towards more positive potentials. When the potential is high enough, lead and then copper will be oxidized back to ions.

$$Pb_{(s)} \rightarrow Pb^{2+}_{(aq)} + 2\ e^-$$

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2\ e^-$$

In previous experiments we have only used external calibration curves, where the unknown sample was compared to a set of standards made from pure water + analyte. This method assumes that the sensitivity

(signal/conc) is the same for samples and standard, that the signal arises only from the analyte in most cases and that the sample matrix has no impact on the measurement. This assumption needs to be checked with a spike recovery test, as we did in the glucose / enzyme lab. If the spike recovery test result is not in a narrow range near 100%, this alerts us to the existence of a matrix effect, where other chemicals in our sample are changing the sensitivity of the method to the analyte and causing our results to be inaccurate. Whenever this happens, we must use the method of standard additions, where known amounts of analyte are added to aliquots of sample and the signals are measured as a function of the concentration added. The technique corrects for matrix effects and has the added advantage of producing less hazardous waste. For information on the standard additions method and how to prepare samples, see Harris section 5-3.

In this experiment, we will build both an external calibration curve and a standard additions analysis. This will allow us to simultaneously check for matrix effects and fix the problem if we find it.

Procedure – ASV measurements

Reagents and Equipment

- Concentrated Nitric acid, HNO_3 -- Use a spectroscopy grade acid certified for AA (low metals)
- Water Samples
- Pb and Cu AA Standard Solutions (1000 ppm)
- Pb and Cu Quality Control Samples (~100 ppm)
- Volumetric Glassware
- Micro-pipettes
- 1 M KCl (aq)
- nitric acid (1 M)
- Bio-Logic Potentiostat and gold screen-printed electrodes

1. Specific instructions for the instrument you are using will be provided (**refer to Standard Operating Procedure document**), to show how to connect the hardware and where to input all settings appropriately in the software.
   a. The ASV settings are as follows:
      i. deposition step: -0.8 V vs. Ag/AgCl reference electrode for 60s
      ii. stripping step: -0.8 V to 0.6 V at a scan rate of 20 mV/s
   b. Both instruments will use carbon screen-printed electrodes for this experiment. Be sure to rinse the electrodes with DI water before starting the experiment, and in between each sample. **Be very careful not to touch the gold electrode surface with your hands or even with kimwipes!**

2. Calibration check:
   a. Pipet 10.00 mL of the 100 ppm Pb calibration check sample into a 20 mL vial. Using a micropipette, add 100 µL of 1M KCl and 100 µL of 1 M HNO_3 to your vial.
   b. Run the ASV protocol and record the peak current, baseline current, and peak location – a peak should be clearly visible!
   c. Now add a 200 µL aliquot of 1000 ppm Cu standard to see if its peak is separate from the lead peak. Calculate the concentration of Cu in the solution based on dilution. Record peak current, baseline current, and peak location of both peaks if possible.
3. Unknown sample by standard additions:
   a. Pipet 10.00 mL of "unknown" water sample into a 20 mL vial. Using a micropipette, add 100 µL of 1M KCl and 100 µL of 1 M HNO_3 to your vial.
   b. Run the ASV protocol and record the peak current and location (if a peak is visible). Based on its location, what metal ion is likely causing this peak?

c. Add 100 μL of 100 ppm metal calibration check standard – choose the metal you'll be doing standard additions with based on your answer to part b). Repeat the ASV protocol and record the peak current, baseline current, and peak location.
d. Repeat step c four additional times.
e. Plot the peak current data vs. the concentration of lead added.

4. If time allows, run a blank by standard additions. This is the same as making an external calibration curve, because there should be nothing present but water, the analyte, and the reagents required for the method (KCl and HNO3):
    a. Pipet 10.00 mL of DI water into a 20 mL vial. Using a micropipette, add 100 μL of 1M KCl and 100 μL of 1 M HNO_3 to your vial.
    b. Run the ASV protocol and record the peak current (if a peak is visible).
    c. Add 100 μL of 100 ppm metal calibration check standard. Repeat the ASV protocol and record the peak current.
    d. Repeat step 2c four additional times.
    e. Plot the peak current data vs. concentration of lead added.
5. Be sure to include the names and descriptions of files created in your ELN. Exporting screenshots of sample data is encouraged.
6. Dispose of all solutions in the appropriate waste containers.

Calculations

a. Generate a standard addition curve for the blank using your data, or if necessary, class data from Blackboard. The linear fit will hopefully pass through the origin, but don't force it to do so.
b. Generate a standard addition curve for the unknown. If the unknown contains enough of the metal you selected to be detectable by this technique, the linear fit will pass *above* the origin.
~~c. Generate a standard addition curve for the performance standard solution.~~
d. Calculate the selected metal concentration in the unknown sample, and determine the uncertainty in this value.
e. Calculate the selected metal concentration in the blank, with uncertainty
f. Estimate the detection limit for Cu by ASV. This is the lowest concentration of copper that can be reliably detected by this method.

Results and Analysis guidelines

The goal of this experiment is to determine the concentration of Cu in the various samples, and to report the determined values with appropriate error. ~~You will be given the known concentration of the performance test sample after the experiment.~~ The water sample is a true unknown. See Jupyter notebooks for additional details on error propagation and standard addition.

For each sample, report the concentration of Cu in the unknown. All reported values should have appropriate error attached to them. Be sure to discuss possible sources of error for each method.

Be sure to address the following questions in your Results & Analysis section:

1. Is there any evidence of lead or copper contamination of the blank, or the nitric acid? Is there any evidence of lead in the drinking water sample?

2. Compare the slopes of the external calibration curve and the standard additions graph. This difference could be due to the matrix effect, or to random error. To find out, compare the difference in slopes with the standard uncertainty in the slope, ux. What does this tell you about which is more important in causing the difference, the matrix effect or random error?

3. Based on propagation of error calculations, what is the % random error in the concentration of copper in the final measurement (after 5 standard additions of 100 uL each)? How does this compare to the % error in the concentration of copper in the unknown sample? What does this tell you about the sources of error in this experiment?

4. Look up the EPA guidelines for allowable copper concentrations in drinking water. Do you think ASV is a valid method for measuring that level of copper? Why or why not?

5. Include a conclusion.