Original: 1/21/13, 3/6/13, Revised: 4/15/13 SDB, 10/15/18, 12/27/18 10/3/19 FGC

Determination of Copper in Drinking Water by Anodic Stripping Voltammetry

Read section 17.5 in Harris.

Introduction. Awareness of the possible adverse effects of trace amounts of metal ions in drinking water, in food supplies and wastewater has led to a demand for metal analysis methods with detection limits in the sub - ppm range. Flame atomic emission and x-ray fluorescence often have the necessary detection limits but involve more complex instrumentation than an electrochemical measurement.

Voltammetry is an electrochemical technique in which the current-potential behavior of a redox reaction at an electrode surface is measured. The potential is varied in some systematic manner to cause electroactive chemical species to be reduced or oxidized at the electrode. The resultant current that flows under diffusion control in the working electrode circuit is proportional to the concentration of the chemical species.

Stripping voltammetry is a two-step technique. The first step is the electrolytic deposition of a chemical species onto an inert "working" electrode at a constant potential, as measured by the "reference" (Ag|AgCl) electrode. This pre-concentration step can involve either an anodic or cathodic deposition process. The most common form of stripping voltammetry involves a cathodic deposition process in which a metal ion species is reduced from the solution onto an electrode, resulting in the formation of a metal film on the electrode surface. The second step consists of a "scan" done by imposing systematic change in voltage of the working electrode, which causes electrolytic dissolution, or "stripping", of the various species in the deposited film back into solution, each at a characteristic electrode potential. For a cathodic deposition process, the stripping step involves application of an increasingly positive (anodic) potential, so the method is called *anodic stripping voltammetry, or "ASV"* for short.

The high sensitivity of stripping voltammetry results from the pre-concentration that takes place during deposition. For pre-concentration to take place, the deposited material must adhere to the electrode surface. Mercury is often the electrode of choice in reductive electrochemistry, but mercury does not work well for deposition of copper because copper oxidizes and strips off near the potential where the mercury film electrode itself begins to oxidize. Also, copper is not highly soluble in mercury. We will use a glassy carbon electrode here. Copper forms small crystals on glassy carbon and strips off cleanly. Because the electrode surface is very important to the analysis, it is important that it be kept clean. The glassy carbon film electrode should never be touched or handled. It is also important that the glassy carbon electrode not be oxidized by application of a large positive potential to the cell. A damaged glassy carbon electrode will give high, noisy backgrounds, and it may not permit the copper film to adhere.

PRE-LAB ASSIGNMENT

Write the answers to these questions in your notebook, and be prepared to show them to your TA at the beginning of the lab period. Be ready to discuss these with your teammates and the TA.

1. Why is a square-wave stripping voltammetry experiment more sensitive than a regular square wave experiment? How does stirring the solution during the deposition step in the experiment increase sensitivity? What does this say about the need to control stirring carefully?
2. What is the purpose of the citrate buffer in this experiment? It is possible that the citrate buffer has a small amount of copper. What effect would the presence of copper in the buffer cause in this experiment? How could that be corrected?
3. On the web, find a supplier of reagent-grade ammonium citrate and citric acid, and record the level of impurities that they report in their citric acid and ammonium citrate. (Sigma-Aldrich and Fisher are suppliers that list impurity levels.) Usually, the "heavy metals" are reported as only lead, so determine the maximum amount of lead impurity in the sample **as analyzed**, based on the procedure given here, and assuming that all the lead came from the ammonium citrate buffer. The stock solution of ammonium citrate/citric acid buffer is about 0.1M. The pH of the buffer is about 3, and 50 mL of buffer contains about 46.5 mL of 0.1M citric acid and 3.5 mL of 0.1M ammonium citrate.

EXPERIMENTAL

Prepare for the Analysis. You and your partner(s) will work together to analyze a sample of water collected from a drinking water fountain in Brown laboratory. The analysis will be for Cu^{2+}, which should be reported as ppb of Cu in the tap water sample by weight.

This is a trace analysis, so your glassware and the surrounding area where you work must be especially clean. ***Clean all equipment and containers thoroughly. Trace contamination can significantly influence your results!*** Clean collection and cell glassware by rinsing with 6 M HNO_3, then rinsed with distilled water. Plastic ware should be washed carefully with soapy water and rinsed thoroughly. Use distilled water for all rinsing and dilutions.

Warning: Nitric acid is a strong, oxidizing acid! It will ruin jewelry, clothes and will stain your hands. Handle it carefully with gloves and wash your hands! Clean up any spills promptly and completely.

We will measure the copper in the water by standard additions because there may be complexing agents present in the tap water. There may be significant amounts in the lab's distilled water, as well. We will need a measurement of the response from the tap water, and then measurements with added copper standard. Plan on measuring three standard additions, if possible. We will also want a blank measurement (use 5.00 mL of distilled water here) to check on copper in the citric acid/citrate electrolyte we are using. You'll need to carefully clean the cell and electrodes again before analyzing the blank, of course.

We will use an ammonium citrate buffer (pH = 3.0) as the supporting electrolyte. This has been prepared for you, but for the record, it is a mixture of 0.1M ammonium citrate and 0.1M citric acid. You will add 5.00 mL of the citrate buffer to each solution, including the blank. The blank measurement will help determine the amount of trace copper in the citrate buffer.

Collect a water sample from your favorite drinking fountain in Brown or Drake lab. You will need a clean container to make the collection. A clean beaker or clean plastic bottle of at least 250 mL will work. The tap water needs to be analyzed soon after it is collected. The trace metals will deposit on the glass (and maybe even on the plastic) container if the water stands for long. Plan on analyzing the water within 10-15 minutes of collecting it. Be aware that very little copper is being measured – so it is easy to contaminate the sample if you touch the solution or if you touch the cell or electrode surfaces! This experiment requires care and cleanliness!

Prepare a copper standard from 1000 ppm stock copper solution. You'll need to think about what concentration this should be to make appropriate standard additions. Guess that there are copper levels of about 10 ppb in the tap water. Your first standard addition should about double the copper level in the water.

For each standard addition, an aliquot (about 20 μL, but known accurately) of your standard copper solution is added to the cell using the micropipette. The aim is to increase the copper peak height by roughly a factor of 20-50% with each addition. The sample is stirred and de-aerated as above. The deposition, equilibration, and stripping steps are repeated.

Assemble the electrochemical apparatus. The scrubber solution should be purple (the V(II) ion in it will reduce any oxygen in the lab nitrogen flow). The scrubber is pre-set for use and does not require student set-up or adjustment. The nitrogen flow should be pre-set – only a ***very*** gentle flow is needed, and you should be sure that the valve is positioned to allow that gentle flow before connecting the tubing to the bubbler.

Clean the bubbler tube by rinsing with dilute nitric acid, then distilled water, Sample solution (5.00 mL) and 0.1M ammonium citrate buffer used as supporting electrolyte (5.00 mL) are then pipetted into the CLEAN electrolysis cell. A CLEAN mini-stirrer magnet should then be added. Do not use kimwipes or paper towels to dry any item in this experiment, as these will contaminate the solution.

Rinse the electrodes with distilled water. The working (glassy carbon) electrode and the reference (Ag|AgCl) electrode go in the openings in the cell cover and are adjusted using the O-rings on the electrodes. The counter electrode is the fixed platinum wire with the gold-colored connector on the cell cover. The cell is fitted to the top and the electrodes are immersed into the solution. Position the bubbler tube away from the electrodes; it can sit above them. Check for bubbles sticking on the frit of the reference electrode (***important!)*** and on the bottom of the working electrode. Tap the cell vial gently with a pencil or finger or jostle the electrodes, if necessary, to remove any adhering bubbles.

Next, connect the electrodes to the potentiostat cables – there are 3 to connect, and these are labeled to match the electrodes they connect to. **It is important that you connect these clips**

correctly, and that the clips do not touch one another. It is also important that you do NOT touch electrodes or these clips when the cell is switched "on" because the static electricity you may carry can damage the potentiostat. Have the TA check the set up BEFORE you begin the experiment.

Once you have verified that there are no bubbles, power the potentiostat on.

Set up the Experiment in the Software You'll need to set up the experiment in the instrument software. You'll consider 3 issues:

Deposition. A potential is applied that is sufficiently negative to reduce a reproducible fraction of the copper ions to copper metal film on the surface of the working electrode. This should be about -500 mV vs. the reference electrode. The solution may be de-aerated with stirring while the deposition proceeds. The solution is stirred with the stirrer motor during deposition to maximize the amount of dissolved copper ion arriving at the electrode surface. The stir rate setting and the deposition time must be carefully controlled, since this control the fractional amount of analyte deposited. Remember that the amount of metal concentrated on the electrode determines the size of the stripping peak, the quantitative basis for the analysis.

Equilibration. During the equilibration time, usually 5-10 seconds, the deposition potential is maintained, but the stirring and any deaeration is halted by raising the bubble tube above the level of solution. This allows any convection from bubbling and stirring to die down so that the stripping process occurs under diffusion control. You must stop the stirrer and adjust the bubbler position manually, so watch the time displayed on the screen.

Stripping. A voltage scan in the positive direction is applied to strip the copper off of the electrode. The oxidation current that flows when the copper strips off is measured as a function of applied potential. The waveform selected for the scan should be either square-wave (more sensitive) or differential-pulse. The scan rate and some pulse parameters must also be set. Faster scans give bigger current signals but also give broader peaks and larger backgrounds. ***Don't scan to a potential more positive than +300 mV vs. the reference, or you may damage the working electrode and get erratic current measurements.*** You will want to deposit copper at a potential of -500mV for a fixed time and under stirring, equilibrate for a fixed time with no stirring, and then apply an anodic scan from about -500mV to about +250 mV vs. the reference to strip the copper deposit off of the electrode, again with no stirring. Your ability to perform these three steps reproducibly determines the quality of the analysis.

You'll want to set the potentiostat as follows:

Setup:
You can download the MicroPStat app for your iPhone or iPad.
Make certain to set-up your data storage by using either iCloud, Dropbox or Google Drive.
See page 8 or handout for instructions.

Electrode conditioning time 60 sec (this is the deposition time)
Potential during conditioning -0.500 V (this is the deposition potential)
Quiet time: 60 sec (this is the rest time, to allow stirring effects to dissipate)
Select square-wave (this is faster) or differential pulse voltammetry

For **differential pulse voltammetry** (DPV) use these acquisition parameters:
Init -0.500 V
Final +0.250 V (no higher than +0.300 V)
Scan rate: 100 mV/sec
Frequency: 25
Pulse height: 50 mV (Amplitude)
Current range: 100 uA
I/F filter: toggle on
R/T plot: toggle on
Frequency: toggle on

For **square wave voltammetry** (SWV), use these acquisitions parameters:
Init -0.500 V
Final +0.250 V (no higher than +0.300 V)
Scan rate: 100 mV/sec
Frequency: 25
Pulse height: 50 mV (Amplitude)
Current range: 100 uA
I/F filter: toggle on
R/T plot: toggle on
Frequency: toggle on

You can change these to see the effects of these settings on the response if you like, but do not set the ending potential higher than +0.30 V; otherwise the glassy carbon electrode can be damaged and the results will be erratic. Remember that to get quantitative results, the potentiostat scan settings and the conditions of deposition (stirring, bubbling, etc.) should not change over the complete set of measurements.

Reconditioning the Electrode. If the electrode surface becomes damaged or if the water has any surface-active components in it, you may see a smaller response or not see any copper response at all. This can happen when surface-active material deposits on the electrode surface or when the anodic stripping runs use +0.3 V or higher as the end potential, which can oxidize the electrode surface. If you don't see any signal with addition of copper, the electrode may need to be reconditioned. If necessary, your TA will polish the electrode to renew the glassy carbon surface. After polishing and thorough rinsing, the TA will help you condition the electrode for use by performing 5 cycles of cyclic voltammetry (CV) from -0.5 V to +0.25V at 1 V/sec scan rate with 0 s deposition and quiet times. If the CV trace that results is "consistent" (that is, if the current responses are more or less the same), the electrode is then ready to use in the stripping experiment. If not, more polishing and another CV conditioning run may be required.

Analysis of the unknown and standards. The deposition voltage used should be set to -0.50 V, applied for 60 seconds, with stirring. The quiet time (with no stirring) should be 60 seconds

followed by a voltage scan from –0.500 v to + 0.250 v using either DPV or SWV mode. The peaks for Pb^{2+} (if present) and Cu^{2+} appear at about -0.40v and +0.10V vs. Ag|AgCl, respectively.

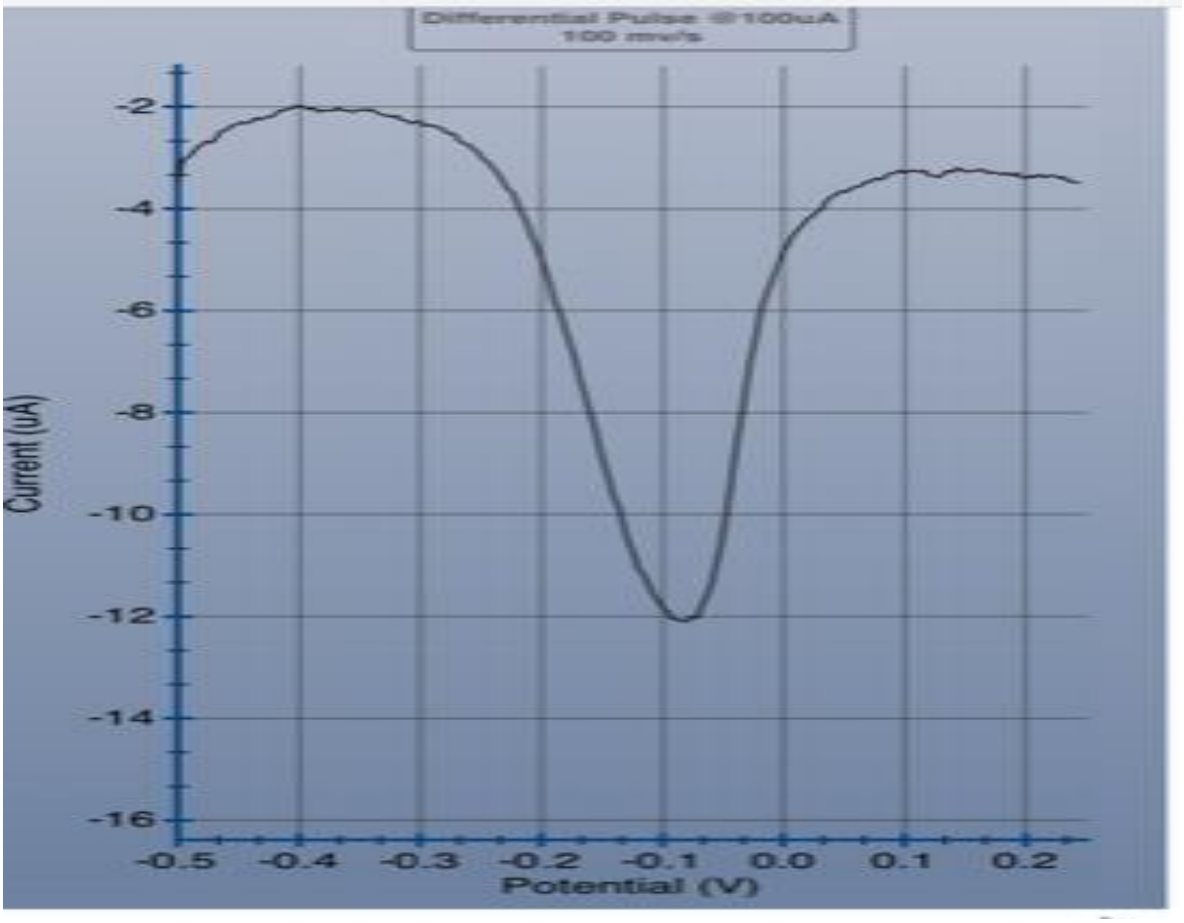

Figure 1. Anodic stripping voltammogram for copper in water

A voltammogram plotting current vs. stripping potential like that shown in Figure 1 is recorded at the end of each scan – you see the computer-generated peak from the scan run (see Figure 1) and can get other information from this screen. The scans are saved in the in either the iCloud, Dropbox or Google Drive – along with the computer-generated peak heights and peak position (i_p and E_p) just click the peak to get the i_p and E_p. A peak is produced for each metal ion that is stripped from the electrode. The peak height (i_p) is proportional to the metal concentration in the solution.

Measure the blank (distilled water) sample and 3 standard additions. Clean the cell, then measure a tap water made from 5.00 mL of tap water and 5.00 mL of the citrate buffer. Make 3 standard additions to the tap water sample.

Rinse, but do not wipe, the electrodes between runs. Wiping may contaminate the electrode and solution.

Correct for the blank signal on all other scans if necessary. Make a standard additions plot for the corrected copper peak height vs. amount of copper standard added. Calculate the amount of copper in the tap water from this plot.

Calibrate the micropipette. It is necessary to calibrate the micropipette to know the volume of standard delivered. Pre-weigh a weighing bottle and cap to +/- 0.1 mg. Using the micropipette set at 20 μL, add an aliquot of water to the weighing bottle, replace the cap and re-weigh. Repeat 10 times to obtain an average volume delivered and the standard deviation. Repeat the calibration at other volume settings as needed.

SAFETY AND DISPOSAL

The citrate buffer and copper solutions used in this experiment require only normal handling precautions.

Warning: the 6M HNO_3 can cause severe chemical burns and will leave a yellow strain on skin. Use gloves and plastic tongs when removing the glassware from the acid rinse. Immediately and thoroughly wash any skin area on which nitric acid is spilled. Carefully neutralize and clean up any spills at once.

Carefully remove and clean all electrodes with distilled water. Remove the electrode cell and clean it in 6M HNO_3.

Dispose of all solutions and acid rinses in the non-organic waste jug.

REPORT

Do a full report, including an introduction and an error analysis. Report the metal ion concentration as ppb copper. Include a single plot of your scans of current vs. potential for the copper response.

In your discussion, answer the following questions:

1. What are the likely sources of copper ion in tap water?
2. List advantages and disadvantages of the standard addition method as compared to conventional calibration of copper in tap water, as measured by stripping voltammetry.
3. What are the advantages of using regular volumetric pipettes (1 - 5 mL) over using micropipettes? What are the disadvantages?
4. What purpose does the ammonium citrate buffer serve in this experiment? Given the potential for contamination that you calculated in the pre-lab, why do we use it in the analysis?

Setting up your Data Storage

Connecting your Application to Cloud Storage

A primary feature of the MP-1 is that while connected to wifi, it can automatically upload data files to the cloud service of your choice. To set this up you must enter your device settings, find the settings entry for MicroPStat, and select your Cloud Provider. Currently the app supports Google Drive, Dropbox, and iCloud Drive.

Restart the app to allow the changes to take effect. In the app from the bottom menu tabs, go to Settings and turn on Automatically Log Results to your cloud service. Logging onto each service is slightly different and explained below.

- iCloud Drive
    - While "Automatically Log Results to iCloud" is on, the app will automatically log the data to the device's primary Apple user account. To log in you must sign in the general device settings.

- Dropbox
    - For a single use you may log in on the login page that pops up when you turn on "Automatically Log Results to Dropbox". If you wish to remain logged in, you must download the Dropbox App.
- Google Drive
    - When you turn on "Automatically Log Results to Google Drive", you will be taken to your device's default browser to log in to Google. **Note: To fully sign out of Google you must do so from that browser, otherwise your account may remain accessible after closing the app.**

Data Storage

Whenever an experiment is run on the MicroPStat-1, the data may be logged to the Micro SD card and/or the cloud service you specify. The choice of where files are stored must be made in the Settings tab of the app. Whether files are named according to timestamp or a numbering system may also be changed in Settings. Additionally, the name of the cloud file (but not the SD file) will appear on the screen after an experiment is completed, write this down in your laboratory notebook to correlate it to a specific experiment.

- Micro SD Storage
    - All files are stored in the "RESULTS" folder. Experiment data can be further found in the "EXP" folder. After this, all data files are stored into folders named with the current date. Each data file will be specifically named according to the timestamp or numbering system. **Note: When switching between timestamp and numbering settings for the SD card, it is possible that the numbering will continue from a higher number than expected.** All data will still be saved, but it is recommended for simplicity that a single system should be chosen and used. If you plan on using the SD card as your primary data logger, it is suggested

you make careful note of the date and time of each experiment, so you can accurately correlate data files with experimental conditions.

- iCloud Drive
    - All files are stored in your iCloud Drive in a folder named DLK-MP-1. Experiment files will be then be stored in a subfolder with the name set in Settings as “Dir Name”. If the folder does not yet exist it will be created. Each data file will be named with the chosen “Data Prefix” followed by a timestamp or number. After each experiment is completed, this filename should appear in a popup.
- Dropbox
    - All files will be stored in Dropbox in a folder named microPStat, which can be found in the “Apps” folder of your Dropbox. Experiment files will be then be stored in a subfolder with the name set in Settings as “Dir Name”. If the folder does not yet exist it will be created. Each data file will be named with the chosen “Data Prefix” followed by a timestamp or number. After each experiment is completed, this filename should appear in a popup.
- Google Drive
    - All files will be stored in a folder with the name set in Settings as “Dir Name”. If the folder does not yet exist it will be created. Each data file will be named with the chosen “Data Prefix” followed by a timestamp or number. After each experiment is completed, this filename should appear in a popup.

Acquisition Parameters for Differential Pulse

Initial Potential: -0.50 V
Final Potential: +0.25 V
Scan Rate: 100 mV/S
Frequency: 25
Pulse Height: 50 mV
Current Range: 100 μA
I/F Filter: ON
R/T Plot: ON
Limit Frequency: ON

Acquisition Parameters for Square Wave

Initial Potential: -0.50 V
Final Potential: +0.25 V
Scan Rate: 100 mV/S
Frequency: 25
Pulse Height: 50 mV
Current Range: 100 μA
I/F Filter: ON
R/T Plot: ON
Limit Frequency: ON

Pre-Acquisition Parameters

Degas/Stir: Degas/Stir
Total Time: 60 seconds
Equilibrium Time: 60 seconds

Cond/Depos 1: ON
Cond1 Pot: -0.50 V
Cond1 Time: 60 seconds
Cond1 Stir: No
Cond/Depos2: OFF
Cond/Depos3: OFF