Electrochemical Techniques: Anodic Stripping Voltammetry

Quantitative Determination of Copper, Lead and Cadmium in Tap Water at a Thin Mercury Film Electrode.

1. Aim

To use a standard additions method to determine the levels of Copper, Lead and Cadmium in a typical tap water sample by Anodic Stripping Voltammetry (ASV) at a thin mercury film electrode.

2. Background

Anodic Stripping Voltammetry (ASV) is a very sensitive electroanalytical techniques where a reducing potential is initially applied to a working electrode which can immobilise the reduced analyte species onto its surface. Subsequently an oxidising potential sweep is applied to the electrode and the analyte is re-oxidised at its characteristic oxidation potential and the cathodic current generated is proportional to the amount of analyte initially deposited onto the electrode.

In this experiment copper, lead and cadmium ions are reduced at the surface of a thin mercury film electrode plated onto a glassy carbon disk electrode. The metals produced are immobilised by forming an amalgam with the mercury. The sensitivity of this technique arises due to the pre-concentration of the analyte species prior to analysis. **Figure 2.1** illustrates the processes occurring at the electrode surface during ASV.

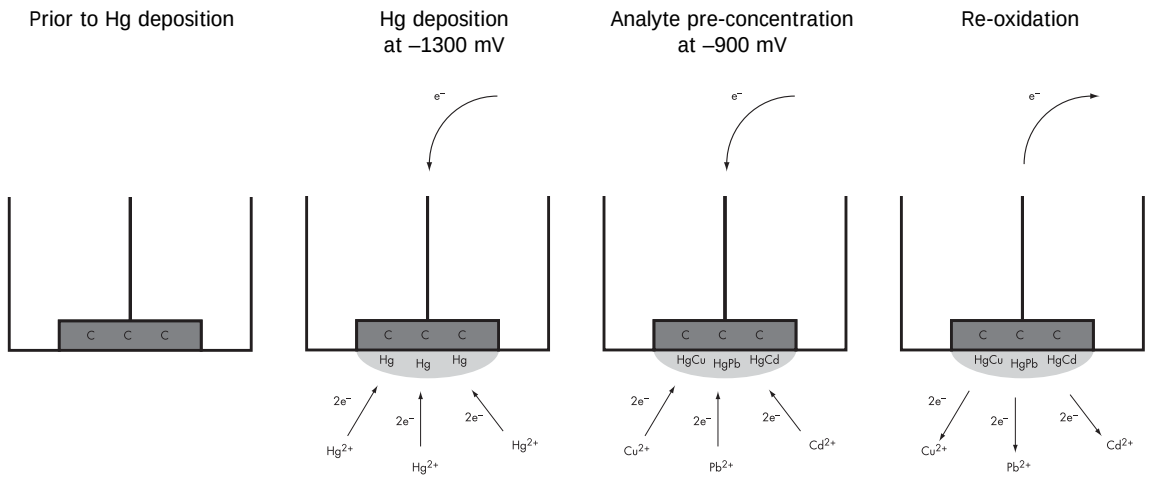

Figure 2.1 Formation of the thin mercury film electrode, pre-concentration and re-oxidation of analyte.

3. Equipment Required

Per Group:

- Computer with Echem software installed
- ER466 Integrated Potentiostat System, or an e-corder unit with EA161 Potentiostat
- From the ET014 EChem Electrode Kit:
    - Glassy Carbon voltammetric disk electrode
    - Leakless Ag/AgCl Miniature Reference electrode
    - Pt/Ti Auxiliary electrode
    - 3 mL mini cells with stirrer bar
- Magnetic stirrer
- Retort stand with 3 bosheads & clamps
- 1 mL auto-pipette and tips
- 500 mL beaker
- 3 x 20 mL beakers
- 4 x 10 mL beakers
- Nitrogen gas cylinder with a needle valve and hose terminating in Teflon tubing drawn down to a 1 mm OD at the tip
- 250 mL filter flask
- Tap fitted with a vacuum adapter
- 1 m of Teflon tubing with one end drawn down to 1 mm OD at the tip, and the other end inserted through the rubber bung that fits into the neck of the filter flask
- 100 mL volumetric flask
- 50 mL volumetric flask
- A wash bottle filled with milli-Q water

Per class:

- Heavy metal waste container
- Printer
- Parafilm to cover reagents in beakers

3. Reagents Required

Per Group:

- Deionised water (milli-Q grade)
- 50 mL Chloride-Acetate Buffer Electrolyte (CLAC)
- 1 mL 1000 ppm Mercury Plating Solution (MPS) in CLAC
- 250 mL of Tap Water
- 1 mL each of 1000 ppm Copper, Lead and Cadmium standards

4. Safety Notes & Instrument Care

- Dispose of all solutions in the heavy metal waste container
- Wear gloves and protective eyewear throughout the experiment
- Avoid spilling liquids on the hardware by mixing reagents away from the units
- Do not touch the tip of the glassy carbon electrode. This will coat the electrode with an greasy film which prevents mercury from being deposited.

5. Procedure

5.1 Equipment Setup

5.1.1 Set up the potentiostat using the instructions in the manual on the eDAQ Software Installer CD.

5.1.2 Place the magnetic stirrer onto the base of the retort stand and attach the bossheads and clamps in the configuration shown in **Figure 5.1**.

5.1.3 Attach the filter flask to the clamp facing the rear of the setup and attach a length of rubber hose between the suction nozzle of the vacuum adapter and the nozzle of the flask.

5.1.4 Place the bung with protruding tubing into the neck of the filter flask. The tubing will be used to suck out solutions from the mini-cell when the tap fitted with the vacuum adapter is turned on. Only apply suction when solutions need to be removed from the cell.

5.1.5 Inspect the tip of the glassy carbon electrode (NB: avoid touching the tip with your fingers). The surface should be black and shiny. If it is dull and grey (from previous use), gently wipe the surface with a small piece of lint free tissue. Dispose of tissue in heavy metal waste container.

5.1.6 Place the stirrer bar into the mini cell and pipette 2 mL of CLAC and 40 µL of MPS into the cell.

5.1.7 Insert the glassy carbon working electrode into the largest hole in the lid of the mini cell. Adjust the rubber o-ring on the electrode so the electrode tip is immersed and

there is a clearance of at least 3 mm between the tip and the stirrer bar. Insert the reference electrode into the medium sized hole and the auxiliary electrode into one of the smaller holes. Align the tips of the two electrodes with that of the working electrode. Tape the pin ends (not the pins though) of the electrode together to keep everything in place.

5.1.8 Place the mini cell onto the magnetic stirrer and secure with the lower clamp. Turn on the magnetic stirrer and set to a medium rate. Check that the electrode tips are still immersed whilst the magnetic stirrer is on.

NB, DO NOT ADJUST THE RATE OF STIRRING DURING THE EXPERIMENT. TURN THE MAGNETIC STIRRER ON AND OFF USING A SWITCH OR AT THE POWER POINT.

5.1.9 Make sure that needle valve of the nitrogen supply is closed and insert the fine Teflon tube end of the gas line through the remaining hole in the lid. Adjust the cylinder regulator to give a pressure reading of not more than 0.5 bar. (0.1 bar ideal). Slowly open the needle valve, adjusting the flow to give a slow steady stream of gas bubbles.

5.1.10 Gently bubble nitrogen gas through the solution for approximately 1 minute, then adjust the nitrogen tube so nitrogen gas is still being pumped into the cell, but does not affect solution convection in the cell.

5.1.11 Connect the Red alligator clip from the potentiostat cable to the Auxiliary Electrode, the Green to the Working Electrode and the Yellow to the Reference Electrode.

5.1.12 Open EChem software.

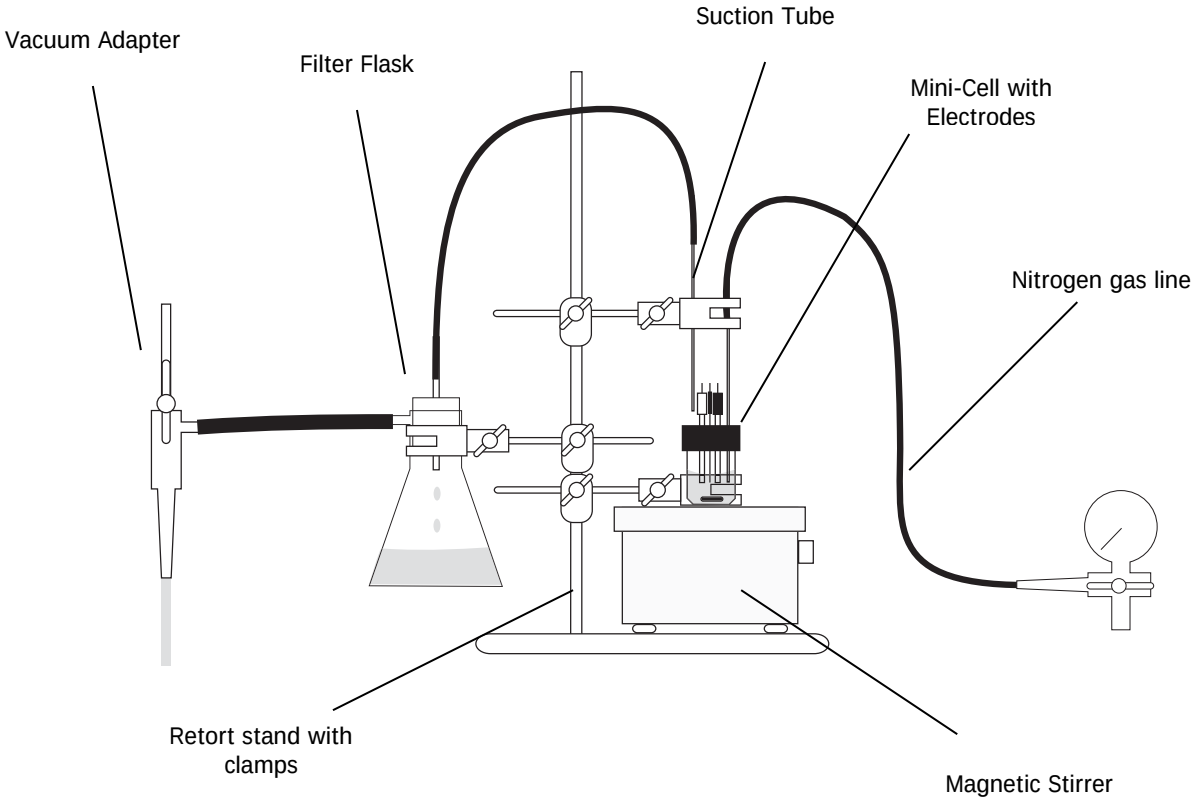

Figure 5.1 ASV Equipment Setup

5.2 Plating the Thin Mercury Film onto the Glassy Carbon Electrode

5.2.1 In EChem, set the current range of the potentiostat to 20 µA in the potentiostat dialog box.

5.2.2 Select Linear Stripping Voltammetry from the **Technique...** menu and use the following parameters to plate the mercury film:

Range	±2 V
Speed	10 kHz
Deposition Potential	-1300 mV
Deposition Time	300 s
Ramp Rate	1000 mV/s
Start Potential	-1300 mV
Finish Potential	100 mV
Sample Width	0.5 ms
Rest Time	10 s

5.2.3 Run the procedure SWITCHING THE MAGNETIC STIRRER OFF DURING THE REST AND STRIPPING STEPS. Label the resulting voltammogram “mercury plating” in the page comments.

5.3 Sample Collection and Preparation of Standard Additions

5.3.1 Collect approximately 250 mL of tap water. Each group should select different taps from around campus and make an estimate of the frequency of the taps use.

5.3.2 Using the tap water sample as the diluent, prepare a combined standard with an addition concentration of 5 ppm Cu, 1 ppm Pb and 1 ppm Cd in the 100 mL volumetric flask. For now assume that the concentration of these elements in the tap water is zero.

5.3.3 Make a second serial dilution with tap water to 250 ppb Cu, 50 ppb Pb and 50 ppb Cd, using the 50 mL volumetric flask (i.e. dilute 2.5 mL of the standard produced in **5.3.2** to 50 mL). This is the top standard to prepare other standards for analysis.

5.3.4 Using the top standard, prepare the following 5 standards in the 10 mL beakers, again using the tap water sample as the diluent.

	Addition Concentration		
	[Cu] (ppb)	[Pb] (ppb)	[Cd] (ppb)
Addition 1	50	10	10
Addition 2	100	20	20
Addition 3	150	30	30
Addition 4	200	40	40
Addition 5	250	50	50

5.4 Removing Solution from Mini-Cell and Cleaning

5.4.1 Make sure that the sink is not blocked and turn on the tap connected to the vacuum adapter, to apply suction to the filter flask.

5.4.2 Switch off the magnetic stirrer.

5.4.3 Leaving the electrodes *in situ*, remove the nitrogen gas line, and replace with the suction tube. Suck the entire contents of the cell into the filter flask.

5.4.4 Remove the suction tube and fill the cell with milli-Q water using the wash bottle.

5.4.5 Repeat steps **5.4.3** to **5.4.4** a total of three times.

5.4.6 Pipette 2.5 mL of fresh CLAC into the empty mini-cell for the next run.

5.4.7 Switch magnetic stirrer back on.

5.5 Running Tap Water Sample

5.5.1 Pipette 0.5 mL of the Tap Water sample into the cell with the 2.5 mL of CLAC.

5.5.2 Rinse the nitrogen gas line and repeat the de-gassing step outlined in **5.1.10**.

5.5.3 In the Linear Stripping Voltammetry dialog box, select the following parameters:

Range	±1 V
Speed	10 kHz
Current range	20 µA
Deposition Potential	-900 mV
Deposition Time	60 s
Ramp Rate	1000 mV/s
Start Potential	-900 mV
Finish Potential	50 mV
Step Height	2 mV
Step Width	2 ms
Sample Period	0.5 ms
Rest Time	10 s
Cleaning Potential	50 mV
Cleaning Time	2 s

5.5.4 Collect a total of three voltammograms for the Tap Water sample, labelling each page accordingly. If the measured current exceeds 20 µA during a run, increase the current range to a suitable value and repeat the run.

5.5.5 The voltammograms should look similar to **Figure 5.2**. The largest hump should be around –100 mV, which corresponds to copper. There may also be smaller humps at around –400 mV and –600 mV, which corresponds to lead and cadmium respectively.

5.5.6 When you are happy with your voltammograms for the Tap Water sample, clean the mini-cell using the procedure outlined in **5.4**, and pipette 2.5 mL of fresh CLAC into the mini-cell.

5.6 Running Standard Additions

5.6.1 Repeat steps **5.5.2** to **5.5.6** substituting the tap water sample with 0.5 mL of Addition 1.

5.6.2 Repeat step **5.6.1** with the remaining Additions in turn.

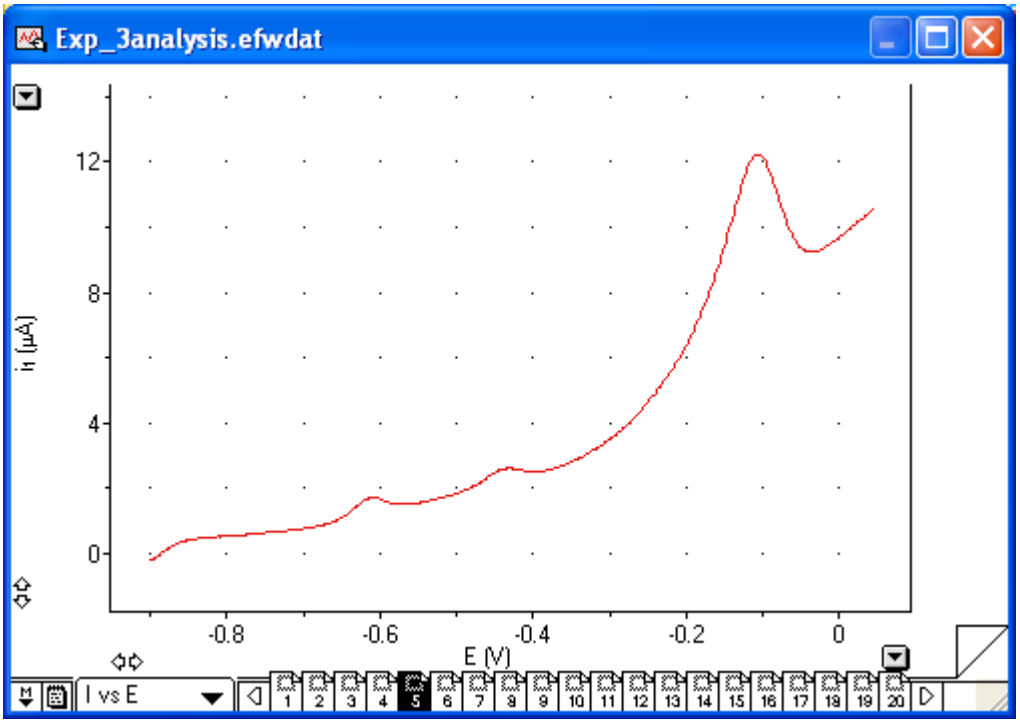

Figure 5.2 Typical Voltammogram Obtained

6. Analysis

6.1 Peak Areas

6.1.1 For integrating peak areas, change the display from I vs E to I vs t in the display pop-up menu on the bottom left hand corner of the main EChem window. See **Figure 6.1.**

6.1.2 Open the **Data Pad** window under the **Windows...** menu. In the first column select **Page Number** from the **Selection Information** options. In the second column select **Integral** from the **General Statistics** options.

6.1.3 Drag the marker from the bottom left corner of the main EChem window, to where you think the copper peak begins. Select a second marker by selecting **Ctrl** before clicking in the empty marker box. Drag the second marker to the other side of the copper peak. The tie line between the two markers represents the baseline of the voltammogram.

6.1.4 Adjust the markers until you feel that the tie line is a good approximation of the baseline of the peak. Using the mouse select the region between the markers, See **Figure 6.1.**

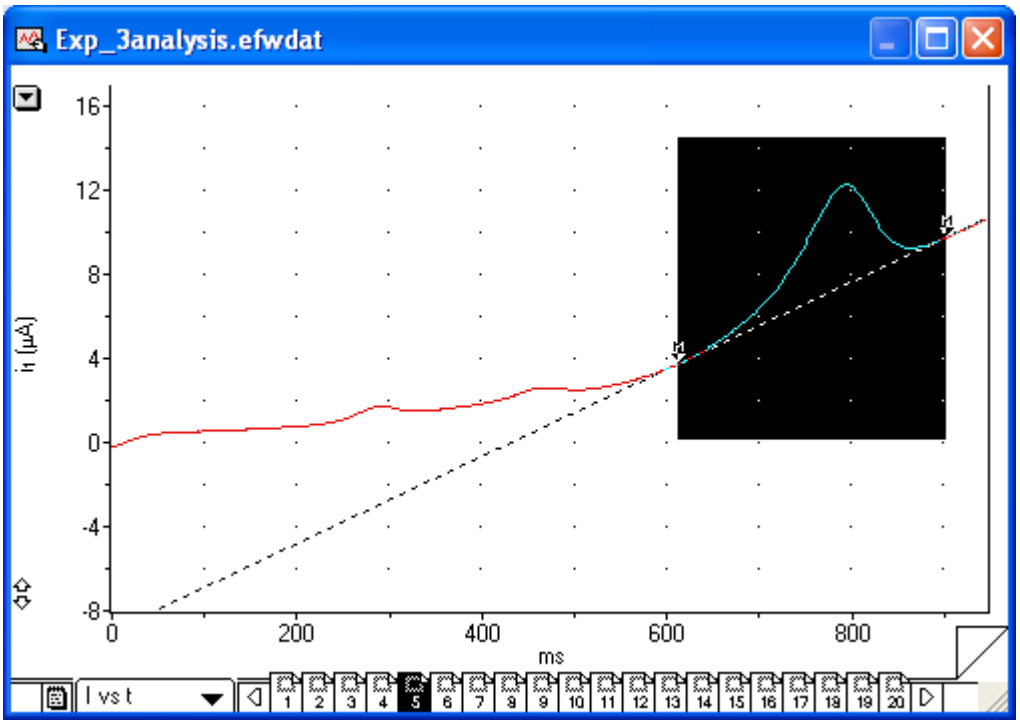

Figure 6.1 Selection of a Peak for Integrating

6.1.5 Select **Add to Data Pad** from the **Windows...** menu, or press **Ctrl+D** to record the page number and the area between the baseline and the curve for the selection.

6.1.6 Annotate the data pad to record which element the peak belongs to and the repeat that was being performed.

6.1.7 Repeat **6.1.3** to **6.1.6** for all pages and for all peaks and record peak areas in **Table 7.1.** It may be difficult to identify peaks for lead and cadmium in the tap water sample, because these elements are usually less abundant in drinking water than copper.

6.1.8 For the tap water sample and each addition, work out the average peak area of each element for the three repeats performed and record in **Table 7.1.**

6.4 Standard Additions Calibration

6.4.1 Call the unknown concentration of Cu, Pb and Cd in the 0.5 mL tap water sample [Cu_{TW}], [Pb_{TW}], [Cd_{TW}]. Assuming the concentrations of these elements is zero in tap water, the concentrations of the additions would be equivalent to those listed in **5.3.4**.

For each element X:

$[X_{actual}] = [X_{TW}] + [X_{addition}]$ and

$Area_{measured} = Area_{TW} + Area_{addition}$

6.4.3 In a spreadsheet application, plot $X_{addition}$ on the x axis and $Area_{measured}$ on the y axis, and use least squares regression to fit a straight line through the points. Do this for each of the elements and report the R^2 value for each plot.

6.4.4 Determine the equations of the fitted lines in the form y = mx + b;

where m = slope

b = y-intercept

6.4.5 If the concentration of an analyte element is zero ($[X_{TW}]=0$), the fitted line should pass through the origin. If the analyte element is present in the tap water sample, the fitted line in the corresponding plot is shifted up.

6.4.6 To calculate the concentration of the unknown, either;

a. extrapolate the line fitted in **6.4.3** back to the x-axis. $[X_{TW}]$ is equal to the absolute value of the x-intercept.

b. substitute y=0 into the equation determined in **6.4.4**. $[X_{TW}]$ is equal to the absolute of x value when y=0.

7. Results

7.1 Peak Areas

Sample		Cd (ΔμA.ms)	Pb (ΔμA.ms)	Cu (ΔμA.ms)
Tap Water Run 1				
Tap Water Run 2				
Tap Water Run 3				
	Average=			
Addition 1 Run 1				
Addition 1 Run 2				
Addition 1 Run 3				
	Average=			
Addition 2 Run 1				
Addition 2 Run 2				
Addition 2 Run 3				
	Average=			
Addition 3 Run 1				
Addition 3 Run 2				
Addition 3 Run 3				
	Average=			
Addition 4 Run 1				
Addition 4 Run 2				
Addition 4 Run 3				
	Average=			
Addition 5 Run 1				
Addition 5 Run 2				
Addition 5 Run 3				
	Average=			

7.2 Tap Water Concentrations

$[Cu_{TW}]$	
$[Pb_{TW}]$	
$[Cd_{TW}]$	

8. Questions

8.1 What is the purpose of the reducing the analyte at the mercury film electrode?

To pre-concentrate the analyte, which increases the sensitivity of the technique.

8.2 Why should the rate of stirring in the mini-cell not be altered throughout the experiment?

The amount of analyte ions reduced at the mercury film electrode is dependant on both solution concentration, the period the reducing potential is applied and solution convection. Both the reduction period and the rate of convection need to remain constant so the signal due to changes in solution concentration is monitored.

8.3 What is the purpose of bubbling nitrogen gas through the solution?

To remove oxygen, which can interfere with the redox processes occurring at the surface of the electrode.

8.4 List some of the advantages and disadvantages of using the standards additions method of calibration?

The matrix of the standards are matched to the matrix of the sample and the magnitude of matrix interference is similar in both solutions. Matrix differences between samples and standards can often cause errors when normal calibration methods are used. The main disadvantage of using standard additions is that only one sample can be analyses per calibration run.

8.5 List some possible sources of error in the experiment?

Contamination in the reagents, variability in defining the peaks between runs, degradation of the mercury film, cross contamination between solutions, measurement errors, etc.

8.6 Why is copper expected to be the largest peak in tap water?

Most tap water runs through copper piping and copper is a more abundant element than lead and cadmium.

8.7 Do you think the method used in this experiment would be a suitable for the routine analysis of cadmium in drinking water?

No. On most occasions, the amount of cadmium in drinking water would be below the detection limits of the techniques.

9. Instructors Notes

9.1 Computer System and Software Required

One computer is required per group. EChem software must be installed for this experiment.

9.2 Reagents

Make sufficient Chloride-Acetate Buffer Electrolyte (CLAC) to supply at least 50 mL per group. An additional 100 mL is required to make the Mercury Plating solution.

Batch Volume 500 mL

7.3 g of Sodium Chloride

1.35 g of Sodium Acetate

0.6 mL of Glacial Acetic Acid

500 mL milli-Q water

1000 ppm Mercury Plating Solution (MPS) in CLAC

Batch Volume 100 mL

135 mg of Mercuric Chloride

100 mL of CLAC

It is best to supply each group with small vials of each of the 1000 ppm Cu, Pb and Cd standards to prevent contaminating expensive commercial standards. Only 1 mL of each is required per group.

9.3 Preparation of Glassware

Prior to practical class, all glassware should be soaked overnight in 0.2% HCl and then rinsed with milli-Q water. Air dry the glassware, as wiping may introduce contaminants. If beakers are to be left standing for some time, seal with parafilm.

9.4 Other Water Samples

The experimental technique outline works well with sea water and other natural water samples, however the solutions may need to be filtered to remove sediment and treated with UV light to destroy organic material. These treatments may need to be applied to tap water samples depending on the quality of the supply.

9.5 Hints and Tips

It is not uncommon for newcomers to analytical electrochemistry to have teething difficulties with ASV experiments.

The most common problems are:

1. The working electrode should be scrupulously clean before the experiment. Especially no oily deposits (eg fingerprints) should be left on the tip of the electrode as these stop the formation of an even mercury film.

2. The mercury film itself is actually a collection of small mercury droplets with an overall gray appearance. Inexperienced users often want to deposit more mercury to get a mirror like finish but this would require the deposition of more mercury than is required. Also excess mercury can fall from the electrode mid-experiment.

3. Control of solution pH is critical for most ASV experiments. Most transition metal ions are hydrolysed to an appreciable extent at pH 7. That is hexa-aquametal ions, $[M(H_2O)_6]^{2+}$, will convert to hydroxyl species eg $[M(H_2O)_5(OH)]^{+}$ as the pH is raised, eventually resulting in the formation of insoluble hydroxides and oxides. These processes interfere with the simple chemistry of the conversion of a metal ion in aqueous solution to a metal atom in the mercury phase in the ASV experiment. One of the first signs of trouble is a shift in the ASV peak position (and sometimes an unsymmetrical peak).

In general ASV of simple metal dications should be done at around pH 4 or less. Even pH 5 would be too high for copper. Use of a narrow range indicator paper can be useful to determine if the pH has drifted out of range far. However the pH should not be so low as to cause dissolution of the substrate metal out of the mercury amalgam. For example while pH 2 would probably be OK for copper determination it would be too low for ASV of zinc. A pH of about 4 is usually a good compromise.

4. Another problem can be the temptation to use too high concentration of substrate ions. ASV is normally used to detect metal ion in the ppb ranges (or even ppt). If using ppm solutions, you normally would have use very short deposition times to avoid putting too much substrate into the mercury film - which leads to a mercury amalgam that no longer behaves ideally (eg changes in viscosity can occur). Again the first sign of trouble can be changes in peak position, misshapen and peaks even double-humped peaks.

5. Changes in peak position (especially drift in the one direction over several days) can indicate that the reference electrode is in need of regeneration or replacement. Reference electrodes do age! If you are using a reference electrode without a knowledge of its history or age then do not be surprised by strange peak positions.