

# **Determination of Copper in Drinking Water by Anodic Stripping Voltammetry (ECD)**

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CHEM438 - 021L

*I submit this laboratory report as an original document. I assert that all ideas and discussion of data contained herein are my own work, unless otherwise referenced.*

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## ABSTRACT

The concentration of copper was measured in two types of water, distilled and tap water, by the standard addition method. 0, 400, 600, and 800  $\mu\text{L}$  of 20 ppm of Cu stock solutions,  $[S]_f$  were used as the spikes for the standard additions. The responses in terms of peak current height,  $i_p$  were measured for distilled water at spikes of 0, 440, 640, and 840  $\mu\text{L}$  of the same stock solution instead, which were corrected to the desired spike volumes from the calibration line:  $i_p = (-11.9 \pm 4.4) \frac{\mu\text{A}}{\text{ppm}} [S]_f + (4.82 \pm 5.42) \mu\text{A}$ . Corrected  $i_p$  of tap water from the  $i_p$  of distilled water lead to a standard addition calibration curve of the following:  $I_{S+X} \left( \frac{V}{V_0} \right) = (4.92 \pm 1.99) \frac{\mu\text{A}}{\text{ppm}} \cdot [S]_i \left( \frac{V_s}{V_0} \right) - (8.61 \pm 2.47) \mu\text{A}$ , where the x-intercept of the calibration curve represented the concentration of Cu in tap water samples, which was found to be  $1,750 \pm 3,456$  ppb (95% C.I.,  $n = 3$ ). Calibration of micropipette for 20  $\mu\text{L}$  of distilled water yielded an average of 21.31  $\mu\text{L}$  with a standard deviation of 0.33  $\mu\text{L}$  of water actually pipetted.

## INTRODUCTION<sup>1</sup>

Drinking water can contain a trace amount of metal ions, which can have some possible adverse effects upon consumption. The typical approach to determine the concentration of metal ions in water includes flame atomic emission and x-ray fluorescence. These two approaches have a smaller detection limit, which is suitable in detecting traces. However, they involve complex instrumentation, which leads to an easier method of electrochemical measurement.

Voltammetry is a technique which employs the current-potential behavior of a redox reaction at the electrodes of the electrochemical cell. To be specific, stripping voltammetry is the approach to determine the traces of metal ions in water. The approach involves two parts: 1) electrolytic cathodic deposition of chemical species onto the working electrode at constant potential, measured by using the reference Ag/AgCl electrode, and 2) scans performed in order for electrolytic dissolution or stripping of the metal ions from the surface of electrode back to the solution to occur, which involves an increasingly positive anodic potential. In turn, the data measured from the second process shows the relationship between the current and stripping potential. The peak produced by each metal ion is proportional to the metal concentration in the solution.

## PROCEDURE <sup>1</sup>

### *Part I: Preparing for the analysis.*

A standard addition method was used to determine the concentration of copper in the water. Two sets of samples were analyzed: distilled and tap water. For each type of water, three standard additions were performed in addition to a blank measurement consisting of the sample alone with the ammonium citrate buffer (pH = 3). 8 samples were measured in total (4 for each type of water) and 5 mL of buffer were added into each sample. Specifically for tap water, it was ensured that the sample was analyzed within a window time of 10 - 15 minutes after it was collected. A 1000 ppm stock solution of copper was used to prepare for the standard addition solutions. For each sample, about 20  $\mu$ L were pipetted into the electrochemical cell for measurement.

### *Part II: Assembling the electrochemical apparatus.*

The scrubber and the nitrogen flow were pre-set before starting the measurement. 5 mL of sample solution and 5 mL of buffer were pipetted into the clean electrolysis cell. A clean magnetic stirrer was added into the cell. Platinum wire was used as the counter electrode, followed by Ag/AgCl as the reference electrode. The electrodes were ensured to be free of bubbles prior to taking the measurement. The electrodes were connected to the potentiostat cables and were ensured to not touch each other.

### *Part III: Setting up the experiment in the software.*

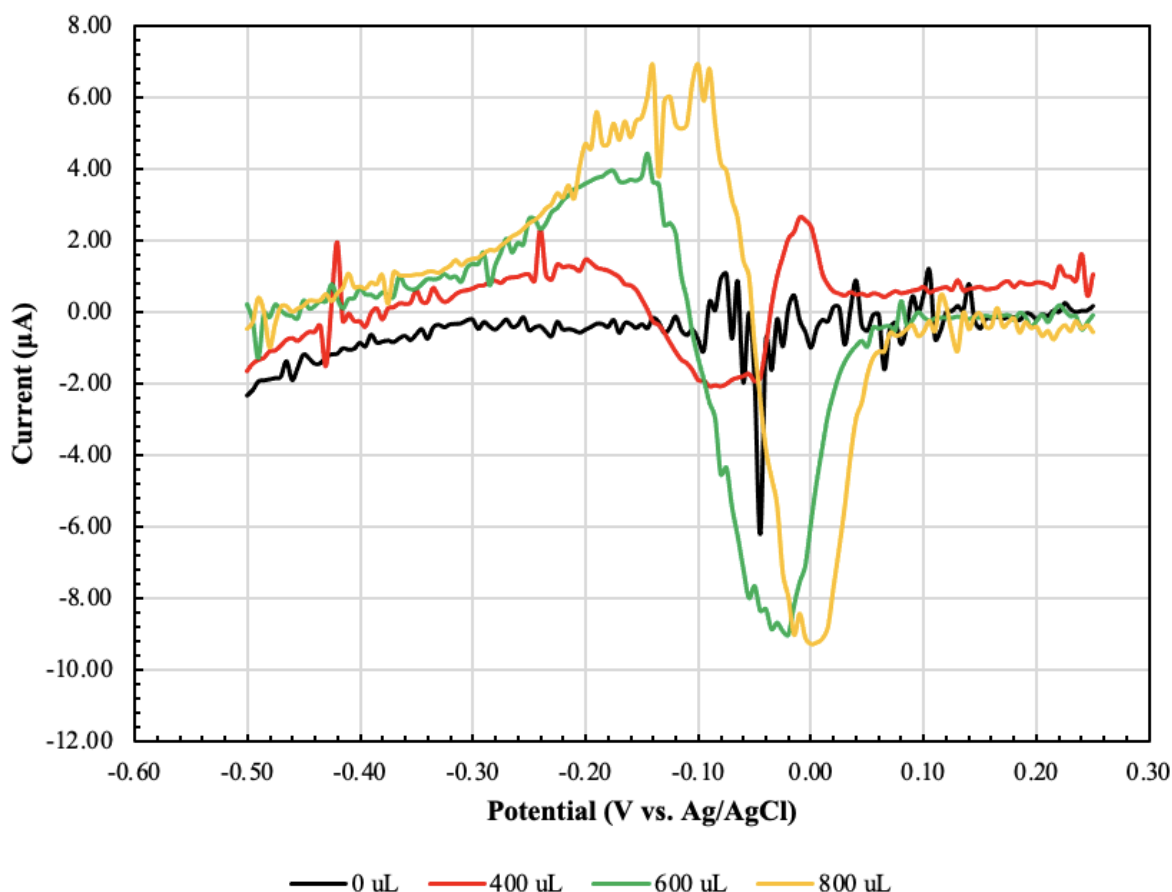
Three different sets of experiments were prepared: deposition, equilibration and stripping. For deposition, a constant reductive potential of -500 mV vs. Ag/AgCl. Simultaneously applying the reductive potential, the solution was stirred and deaerated while the stir rate and deposition time were controlled carefully. Other than that, for equilibration, the same deposition at constant potential as previously stated was performed, instead the stirring and any deaeration were halted. For stripping, a voltage scan in the positive direction from -500 mV up to a maximum potential of 300 mV vs. Ag/AgCl was performed. The measurement could be done in either square-wave or differential-pulse mode. The stirring was also halted during the stripping process.

### *Part IV: Calibrating the micropipette.*

A bottle and its cap were weighed. An aliquot of water of 20  $\mu$ L was added into the bottle. The bottle was recapped and reweighed. The measurement was repeated 10 times.

## RESULTS AND DISCUSSION

Two different sets of data were collected: distilled water and tap water. The signal measured for distilled water acted as the “blank” measurement for the determination of Cu concentration in tap water. Thus, the signal response from tap water was corrected by subtracting the measurement collected with the signal of the distilled water, at the same concentration of solution.

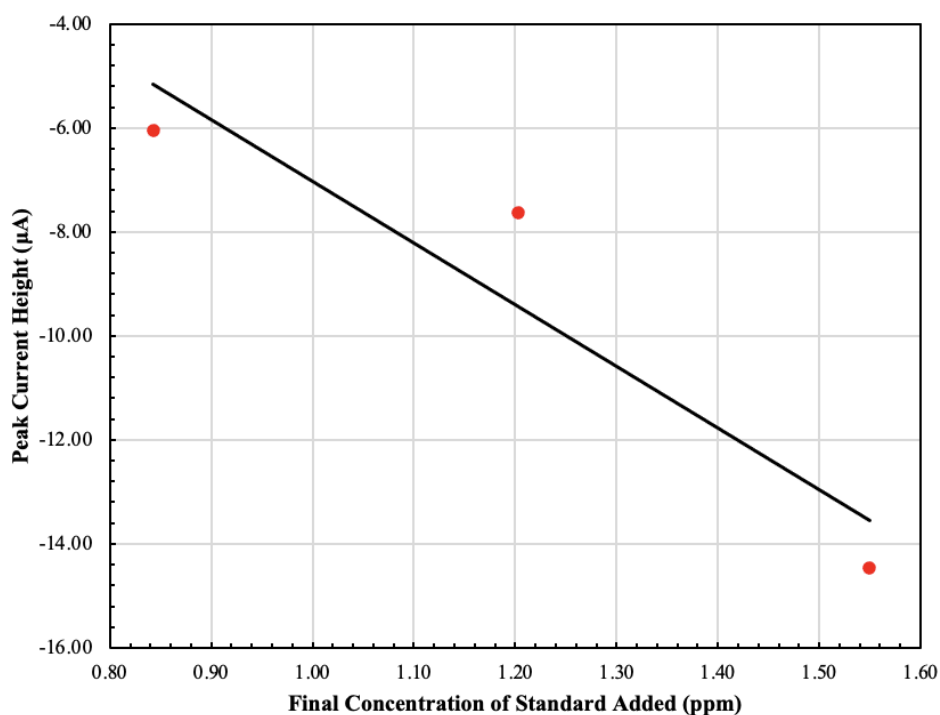


**Figure 1.** 4 scans of current versus potential for the copper response in tap water.

**Figure 1** showed the response measured as current for 4 different solutions of tap water. For the standard addition of 0 μL, no significant peaks could be observed, aside from a slight dip around -0.05 V vs. Ag/AgCl. This could be associated with some traces of Cu in the buffer solution used. It could also be due to the signal noise in the instrument, causing the unsteady measurement taken, as presented as “squiggly” lines in the same figure. Addition of standard (400, 600, and 800 μL) produced significant peaks around -0.10 to -0.05 V vs. Ag/AgCl.

**Table 1.** Response of copper for distilled water sample.

<sup>a</sup> $V_s$ ( $\mu\text{L}$ )	<sup>b</sup> $[S]_f$ (ppm)	<sup>c</sup> $E_p$ (V)	<sup>d</sup> $i_{p, \text{DI water}}$ ( $\mu\text{A}$ )
0.0	0.00	0.0000	0.00
440.0	0.84	-0.0450	-6.05
640.0	1.20	-0.1075	-7.64
840.0	1.55	-0.0850	-14.46

<sup>a</sup> Volume of standard added<sup>b</sup> Final concentration of the standard solution<sup>c</sup> Peak potential vs. Ag/AgCl<sup>d</sup> Peak current height for distilled water sample**Figure 2.** Calibration plot of distilled water sample.

Shown in **Figure 2** was the calibration plot of the distilled water sample sets, with data sets tabulated in **Table 1**. Upon taking the measurement for distilled water samples, the volume of standard added into each solution did not align with the volumes of standard added for the tap water samples. In order to obtain the response for the same volume of standard as that of the tap water, a calibration line in **Figure 2** was used. The equation of the calibration line was as shown in **Eq. 1**.

$$i_p = (-11.9 \pm 4.4) \frac{\mu\text{A}}{\text{ppm}} [S]_f + (4.82 \pm 5.42) \mu\text{A} \quad \text{Eq. 1}$$

The calibration was obtained by removing the first data point ( $V_s = 0 \mu\text{L}$ ) from the plot. There should be some response although no standard was added due to the possible presence of Cu in the sample itself and the buffer solution used. This could be due to improper handling of the instrument to collect data when performing the experiment in person. It did not behave linearly as expected if the point was not omitted in the calibration.

**Table 2.** Response of copper corrected for tap water sample.

<sup>a</sup> $V_s$ ( $\mu\text{L}$ )	<sup>b</sup> $[\text{S}]_f$ (ppm)	<sup>c</sup> $E_p$ (V)	<sup>d</sup> $i_{p, \text{DI water}}$ ( $\mu\text{A}$ )	<sup>e</sup> $i_{p, \text{tap water}}$ ( $\mu\text{A}$ )
0.0	0.00	0.0000	0.00	0.00
400.0	0.77	-0.0275	-4.29	-4.05
600.0	1.13	0.0600	-8.59	-3.42
800.0	1.48	0.0750	-12.73	-0.26

<sup>a</sup> Volume of standard added

<sup>b</sup> Final concentration of the standard solution

<sup>c</sup> Peak potential vs. Ag/AgCl

<sup>d</sup> Peak current height for distilled water sample

<sup>e</sup> Corrected peak current height for tap water sample

The corrected current responses for tap water samples were calculated as tabulated in **Table 2**, by using **Eq. 1** to determine the actual peak current height for the designated concentration of distilled water.

**Table 3.** Data points for standard addition for tap water samples.

<sup>a</sup> $[\text{S}]_i$ (ppm)	<sup>b</sup> $V_s$ ( $\mu\text{L}$ )	<sup>c</sup> $V_0$ (mL)	$[\text{S}]_i * V_s / V_0$ (ppm)	<sup>d</sup> $I_{s+x}$ ( $\mu\text{A}$ )	<sup>e</sup> $V$ ( $\mu\text{L}$ )	$I_{s+x} * V / V_0$ ( $\mu\text{A}$ )
20.00	0.0	10.0	0.00	0.00	10,000	0.00
20.00	400.0	10.0	0.80	-4.05	10,400	-4.21
20.00	600.0	10.0	1.20	-3.42	10,600	-3.62
20.00	800.0	10.0	1.60	-0.26	10,800	-0.28

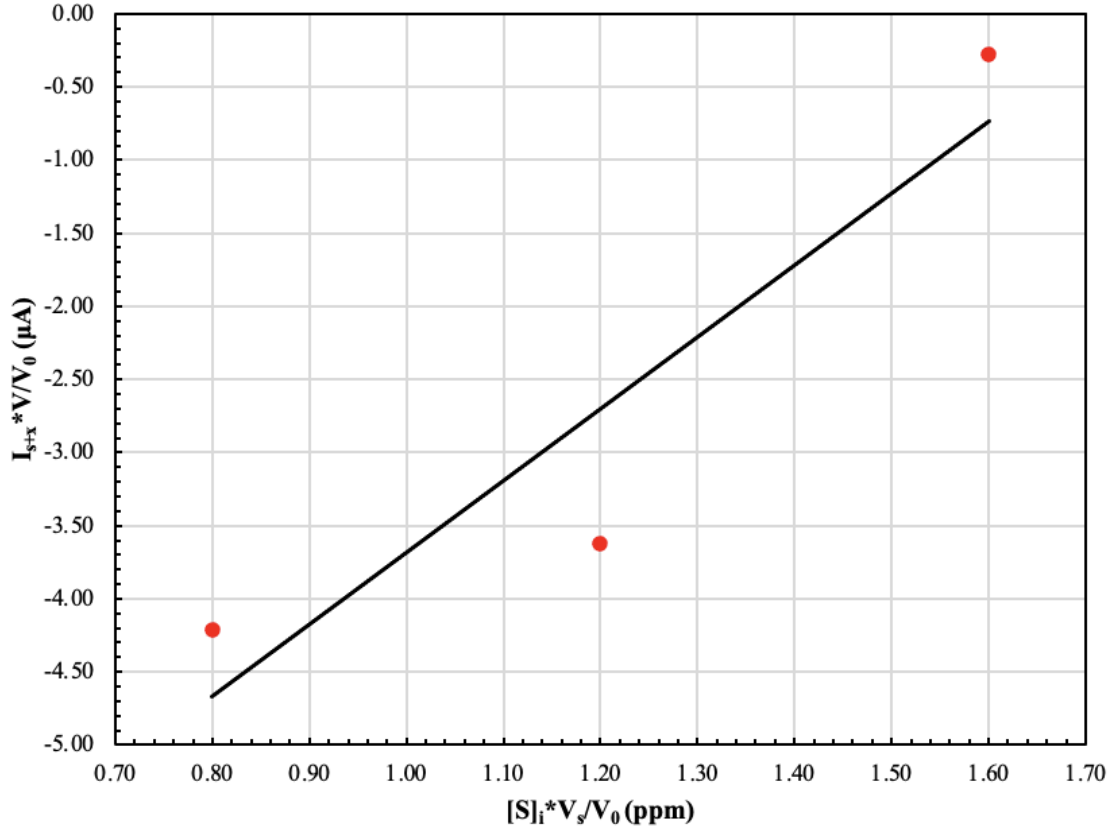
<sup>a</sup> Initial concentration of the standard solution

<sup>b</sup> Volume of standard added

<sup>c</sup> Initial volume of solution

<sup>d</sup> Signal notation for corrected peak current height for tap water sample

<sup>e</sup> Total volume of the solution:  $V = V_0 + V_s$



**Figure 3.** Standard addition plot of copper response for tap water samples.

$$I_{S+X} \left( \frac{V}{V_0} \right) = (4.92 \pm 1.99) \frac{\mu A}{ppm} \cdot [S]_i \left( \frac{V_s}{V_0} \right) - (8.61 \pm 2.47) \mu A \quad \text{Eq. 2}$$

Data points in **Table 3** were plotted as shown in **Figure 3**, with the calibration curve as shown in **Eq. 2**. Similar to previously stated, the first data point was omitted in the calibration line as it did not have an accurate representation of the solution as expected. For a standard addition method where multiple solutions with varying volumes were involved, the linearization in **Eq. 3** could be used to determine the unknown concentration of Cu.<sup>2</sup>

$$I_{S+X} \left( \frac{V}{V_0} \right) = \frac{I_X}{[X]_i} \cdot [S]_i \left( \frac{V_s}{V_0} \right) + I_X \quad \text{Eq. 3}$$

$I_{S+X}$ : signal from final solution

$I_X$ : signal from initial solution

$[S]_i$ : initial standard concentration

$V_s$ : volume of standard added

$V_0$ : initial volume of solution

$V$ : final total volume =  $V_s + V_0$



The x-intercept of the standard addition plot in **Figure 3**, and as derived in **Eq. 3**, represented the unknown concentration of Cu in the tap water samples. Within the 95% confidence interval, the concentration of Cu in the tap water was  $1,750 \pm 3,456$  ppb (95% C.I.,  $n = 3$ ). The error was bigger than the actual concentration could be due to several reasons: 1) only 3 sample points were used to obtain the calibration point, 2) the calibration curve did not fit the data points perfectly ( $R^2$ -value of only 0.860), and 3) incorrect measurement of the blank solutions (sample without standard solutions added). All three reasons contributed to the statistical standpoint of the error analysis, which caused the large intervals of concentration obtained within the 95 % confidence interval.

One of the sources of copper in tap water is through mining, farming, and/or industrial waste released into the river and lakes.<sup>3</sup> These contaminated water seeped through underground and contaminated the well/groundwater. The main cause of Cu traces found in tap water is that the flow of water through pipes causes the corrosion on the pipe wall.<sup>3</sup>

The advantage of using standard addition method as opposed to conventional calibration of copper in tap water is that it is more precise and accurate in determining the traces of Cu in tap water.<sup>4</sup> It also overcomes the matrix differences in the solution used. However, it requires at least three replicates for each sample point, which is delicate. More preparation time is required and the duration of experiment is also longer.

**Table 4.** Calibration data of micropipette for 20  $\mu$ L of water.

Calibration	Mass of Bottle + Cap (g)	Mass of Water (g)	<sup>a</sup> Volume of Water ( $\mu$ L)
0	16.1446		
1	16.1661	0.0215	21.56
2	16.1867	0.0206	20.66
3	16.2082	0.0215	21.56
4	16.2294	0.0212	21.26
5	16.2506	0.0212	21.26
6	16.2723	0.0217	21.76
7	16.2934	0.0211	21.16
8	16.3144	0.0210	21.06
9	16.3360	0.0216	21.66
10	16.3571	0.0211	21.16

<sup>a</sup> Density of water at 25°C is 0.99705 g/mL<sup>5</sup>

**Table 4** shown above tabulated the calibration data of micropipetting 20  $\mu$ L of water. The volume of water actually pipetted was found to be  $21.31 \pm 0.33$   $\mu$ L. This slightly higher volume than what it is supposed to be should be taken into account when preparing/diluting samples. The

advantage of using the regular volumetric pipette is that it can easily and accurately draw up the necessary amount of liquid at a time.<sup>6</sup> The pipettes are calibrated with small divisions and are often adjustable. Nevertheless, micropipettes are more accurate and precise as they can transfer microliters of volume. In contrast, micropipette requires calibration every few months as they are spring-loaded instruments and require more care than the regular volumetric pipette.<sup>6</sup>

For each sample solution, an ammonium citrate buffer was added. Although there is potential contamination of these metal ions in the buffer as calculated in pre-lab, in which it could alter the concentration of traces in tap water, it is still being used regardless. The buffer was essential to be used in the experiment as it could ensure the solution maintained its pH at 3.0.<sup>7</sup> Additional presence of solute in the solution would not change the overall pH due to the presence of buffer. Addition of buffer solution made the solution a good electrolyte, which makes the electrochemical cell to be active during the measurement taking. Presence of a buffer also improved the solubility of the solution.<sup>7</sup>

## CONCLUSIONS

Anodic stripping voltammetry is the go-to approach to determine the traces of metal ions in tap water as it employs a less complicated instrument and also has a low detection limit as flame atomic emission and x-ray fluorescence measurement. Standard addition method was used rather than the conventional calibration method as the solutions used have an interfering and complicated matrix, where only standard addition could take that into account in the data analysis of the metal ions' traces. The anodic stripping method produces responses in terms of current. At a particular potential, a current peak may be observed and it is directly proportional to the concentration of metal ions in the sample. On top of that, calibration of micropipette should be done regularly as it could determine the actual volumes of solution pipetted and precisely determine the concentration of a particular analyte in the solution.

## REFERENCES

<sup>1</sup> Cruz, F. *CHEM438 Instrumental Methods Laboratory - Determination of Copper in Drinking Water by Anodic Stripping Voltammetry lab*; University of Delaware: Newark, Delaware, 2019; pp 1-11.

<sup>2</sup> Harris, D. C.; Lucy, C. A. *Quantitative Chemical Analysis*; Macmillan Learning, 2020.

<sup>3</sup> Copper and drinking water from private wells.  
<https://www.cdc.gov/healthywater/drinking/private/wells/disease/copper.html> (accessed Oct 29, 2021).

<sup>4</sup> Sample Analysis Design – Step 2 – calibration/standard ...  
[https://www.researchgate.net/profile/J-Tarafdar/post/Whats\\_the\\_best\\_way\\_to\\_generate\\_calibration\\_curves\\_for\\_an\\_inductively\\_coupled\\_plasma-mass\\_spectrometry\\_ICP-MS\\_device/attachment/5a4207284cde266d587db911/AS%3A575732146294784%401514276648162/download/Lecture\\_8\\_10\\_11\\_2011.pdf](https://www.researchgate.net/profile/J-Tarafdar/post/Whats_the_best_way_to_generate_calibration_curves_for_an_inductively_coupled_plasma-mass_spectrometry_ICP-MS_device/attachment/5a4207284cde266d587db911/AS%3A575732146294784%401514276648162/download/Lecture_8_10_11_2011.pdf) (accessed Oct 29, 2021).

<sup>5</sup> Water - density, specific weight and thermal expansion coefficients.  
[https://www.engineeringtoolbox.com/water-density-specific-weight-d\\_595.html](https://www.engineeringtoolbox.com/water-density-specific-weight-d_595.html) (accessed Oct 29, 2021).

<sup>6</sup> Kozlowski, R. What is the purpose of a pipette?  
<https://sciencing.com/purpose-pipette-8743073.html> (accessed Oct 29, 2021).

<sup>7</sup> Boundless. Boundless Chemistry.  
<https://courses.lumenlearning.com/boundless-chemistry/chapter/buffer-solutions/> (accessed Oct 29, 2021).

## APPENDICES

### Lab Notebook

Exp. No. <b>6</b>	Experiment/Subject <b>CHEM 438 (ECD)</b>	Date <b>10/18/2021</b>	20
Name <b>Abdul Fayed</b>	Lab Partner	Locker/Desk No.	
			Course & Section No. <b>021L</b>

#### Prelab Questions

1. Square-wave stripping voltammetry is more sensitive than regular square-wave experiment because it employs the preconcentration step which accumulates the desired analyte on the surface of the electrode through electrodeposition. Stirring increases the sensitivity as it allows the desired analyte in the solution to constantly move and eventually reach the surface of the anode. However, too much stirring will also cause the lack of deposition of analyte on the surface as it is constantly moving around instead of being reduced onto the surface. Thus, the stirring has to be controlled carefully.
2. Citrate buffer is used to control the pH of the solution @ pH = 3. pH plays an important role when working with electrochemical system as it determines the range of appropriate voltage to be applied on the system to achieve the intended goal of the experiment (electrodeposition of  $\text{Cu}^{2+}$  on the surface before anodic stripping). It is possible that the citrate buffer has a small trace of Cu. The presence of Cu in buffer will interfere <sup>with</sup> the original sample (tap water) and gives out ~~false~~ wrong concentration of Cu in the ~~tap~~ water. To correct this standard addition method can be used to determine the concentration as it takes into account the "matrix" effect of the system.

#### 3. Sigma aldrich:

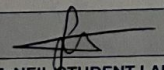
citric acid:  $[\text{Pb}] = 2 \text{ ppm}$

ammonium citrate:  $[\text{Pb}] = 5 \text{ ppm}$

$$0.046 \text{ L} \times \frac{0.1 \text{ mol}}{1 \text{ L citric acid}} \times \frac{2 \text{ mol Pb}}{10^6 \text{ mol of solution}} = 9.3 \times 10^{-9} \text{ mol Pb}$$

$$0.0035 \text{ L} \times \frac{0.1 \text{ mol}}{1 \text{ L ammonium}} \times \frac{5 \text{ mol Pb}}{10^6 \text{ mol soln}} = 1.75 \times 10^{-9} \text{ mol Pb}$$

$$\frac{(9.3 \times 10^{-9} + 1.75 \times 10^{-9}) \text{ mol}}{0.05 \text{ L}} \times \frac{207.2 \text{ g}}{\text{mol}} \left( \frac{1 \text{ mg}}{10^{-3} \text{ g}} \right) \left( \frac{1 \text{ ppm}}{1000 \text{ mg/L}} \right)$$

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$$[\text{Pb}]_{\text{tot}} = 0.046 \text{ ppm}$$



Purpose of experiment is to determine the copper concentration in drinking water by anodic stripping voltammetry. ~~Plot~~


There is a trace of Cu in drinking water that can be lethal to human health if not controlled properly. Anodic stripping voltammetry is one of the technique to determine the concentration of Cu in drinking water. FAf or X-ray fluorescence have the better detection limit but they involve complex instrumentation. The idea of this experiment is to deposit the Cu in the drinking water onto an anode which will then be oxidized and the amount of Cu that leaves the surface reflects the concentration of Cu in the solution, which will be detected by the amount of current produced.

↳ Procedure (Brief general overview only).

1. Collect the water sample from the tap.
2. <sup>Determine</sup> The concentration of Cu by standard addition method ( $n=3$ ).
3. Use ammonium citrate buffer ( $\text{pH} \approx 3$ ) in the sample.

Data for voltage vs. current are provided in TXT file (in this lab, all data should be provided  $\rightarrow$  dry lab).

[illegible]

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Exp. No. 6	Experiment/Subject CHEM 438 (ECD)	Date 10/18/2021
Name Abdul Foyeal	Lab Partner	Locker/Desk No. Course & Section No. 021C

4. Assemble the electrochemical apparatus
5. Set up the experiment in the software.  
(deposition, equilibration, stripping).

#### Calibration of micropipette

1. Weigh bottle and cap.
2. Micropipette 20  $\mu$ L water into the bottle.
3. Cap the bottle then reweigh.
4. Repeat 10 times to obtain the relative average volume and standard deviation.
5. Dispose of all chemicals appropriately and clean the glassware.

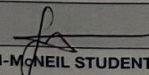
#### Conclusions

Anodic stripping voltammetry employs the setup of electrochemical cells, where it can ~~also~~ be used to determine the concentration of desired analyte in a system.

#### Micropipette calibration

~~# of calibra~~

Number	Mass(g)	Mass of H <sub>2</sub> O(g)
0		
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		

Signature 	Date 10/18/2021	Witness/TA	Date
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