Recovery of Copper in Effluent from Advancement Placement Chemistry Labs

James Dorn, Sophie Fuller, Allison Glazer, Patrick Hsu, Bethany Lane, Grace Martin, Anders Niemi, Danica Pietrzak, Megan Smith, Tom Talasek[*]

[*]*Faculty advisor, Basis High School, Flagstaff, AZ*

Summary

Solutions containing copper are commonly generated in high school chemistry laboratories. Currently these wastes must be collected and submitted to a hazardous waste facility for treatment, often at a considerable expense. This paper describes a method for extracting copper from solutions using equipment commonly found at most high schools.

Introduction

The prevailing copper guidelines by the US Environmental Protection Agency are 1.3 mg Cu per L in public water sources; a value that many experts agree is too high and may have undesired effects. Professionals in the field recommend maximum concentration of 1.0 mg·L⁻¹ copper[1] to ensure no detrimental effects in public drinking water.

In small doses copper exposure has been linked to variant gastrointestinal symptoms such as nausea and abdominal pain. By randomly selecting dosage (0,2,4,6 or 8 mg·L⁻¹ copper) for 200 participants a study was able to establish a correlation and possibly causation of effects of high copper concentration in drinking water. The most common side effect after the 5-week trial was nausea, often within only 15 minutes after digestion[2]. Both sources agree in the harmful effects of acute copper poisoning but there are some arguments as to what the maximum concentration should be. Significant injuries were observed on the kidney, spleen, and liver of mice as their copper concentration was increased, as well as increasing the presence of the amyloid beta protein in the brain, increasing risk for Alzheimer's disease[3].

The Journal of Industrial and Engineering Chemistry[4] examines copper reduction prevalent in industrial settings. Electrochemical removal methods, such as electrocoagulation and electrodialysis, as well as other techniques including absorption, cementation, membrane filtration, and photocatalysis have been used to treat the effluent from industrial applications like electroplating. These techniques are both too capital-intensive and impractical in a small-scale high school lab scenario.

As a result, high school laboratories produce copper solutions that are typically either collected in a container for professional treatment and disposal as a hazardous waste, or simply poured down the drain. In particular, College Board, the administrators of Advanced Placement (AP) courses, includes a lab "How Can Color Be Used to Determine the Mass Percent of Copper in Brass?" in their publication AP Chemistry Guided-Inquiry Experiments: Applying the Science Practices.[5] With the widespread usage of this lab across high school AP chemistry classes, it is estimated that 22 kg of copper can be removed every year from industrial effluent and hazardous waste that requires further processing.

Described here is an electrochemical method for capture of copper from laboratory-generated solutions in a high school environment. The method uses low cost equipment that is likely already present in the laboratory or can be acquired inexpensively. Despite the relatively low reduction of copper within the water supply, this was intended for the use of AP scholars, not in an industrial setting.

Materials and Method:

A photograph of the setup is shown in Figure 1. A square of copper sheet was cut into a rectangular shape to serve as a cathode. A neck was fashioned into the sheet, preserving at least a

3x3 inch square surface area available to place in the solution being treated. The copper electrode was attached to a ring stand using a Vernier nonmetallic electrode support and secured with a tightly wrapped rubber band. The anode was a graphite electrode 12 in long and 1 in in diameter attached to a second ring stand with a clamp. A beaker was placed on a stir plate with a Teflon stir disk inside to maintain constant agitation. The size of the beaker can be varied based on the volume of liquid to be processed. The ring stands were arranged in a manner that allowed the electrodes to be situated so that the voltage drop was minimized in the cell, with at least the bottom two inches reaching into the solution. In order to evaluate recovery efficiency, 0.1 M copper (II) nitrate solution was accurately measured and placed in the beaker. A TEKPower DC Regulated Power was used to supply the power to the corresponding electrodes. Several voltages were evaluated, but based on the results described below, the optimum voltage was found to be 6 V. The power supply was used in constant voltage mode, and the current was allowed to float.

Copper concentration, temperature and current were monitored periodically throughout the run. A Vernier SpectroVis Plus spectrometer with Logger *Pro* was used to determine copper concentration. Colorimetric determination of copper was conducted at a wavelength at 693.4 nm. A background absorbance was also measured at 500 nm. A typical calibration curve is shown in Figure 2.

Current was determined from the digital readout of the power supply. Temperature was measured with a digital thermometer or with a Vernier temperature probe. Graphite recovery was determined gravimetrically.
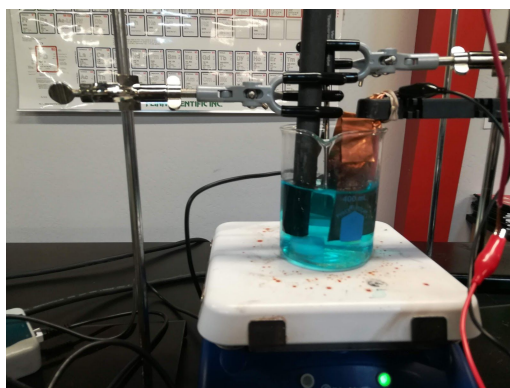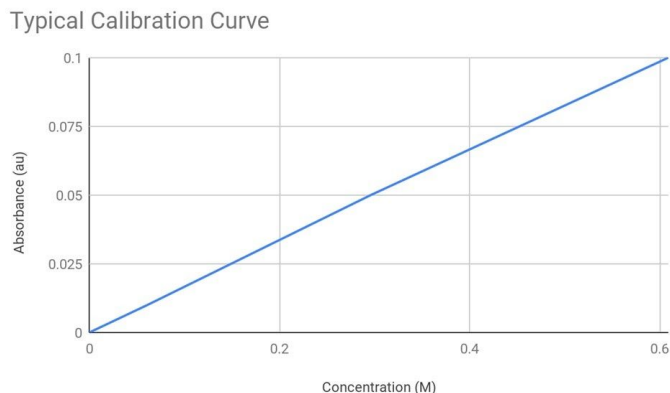

Figure 1: Equipment setup for copper recovery.

Figure 2: Typical calibration curve for determination of $[Cu^{2+}]$.

Results and Conclusions:

Initial trials were conducted using the setup described above. Pure copper was dissolved in nitric acid, copper was removed to below the detection limit of the method and equipment used. Additionally, brass was used under similar conditions to mimic the AP lab mentioned above. Similar results were achieved with respect to copper concentration. There was no attempt to determine whether the zinc concentration from the dissolved brass was affected, due to a lack of available instrument resources.

Initial experiments were run at higher voltages as described above, which provided some troubling results, that being a recovery of 103.826 %, indicating an error. Recoveries determined at lower voltage resulted in recovery rate of about 100%.

It was hypothesized that the recovery issue might be related to electro-etching of the graphite electrode due to the oxidation of water at the anode. This was somewhat supported by suspended particles in the copper solution. To further support this, the mass of the graphite electrode was measured before and after a recovery trial. The amount suspended particulate matter was assessed by gravity filtration and gravimetric analysis, and was determined to match the weight loss from the graphite electrode within the measurement capability of available equipment.

An extended run was conducted at 6 V to determine if the graphite electro-etching could be eliminated. The resulting data from this test is shown in Figure 3 and 4. While the appearance of particulate matter was slowed, it began to appear that the copper was exhausted from the solution. An increase in absorbance at wavelengths lower than copper absorbs was also observed as shown in Figure 5. When the particulate matter was removed, and the absorbance spectra measured, the absorbance in the range of 500 nm dropped to zero, and the absorbance at 693 nm corresponded with the difference between the absorbance at 693 and 500 nm. This was used to correct for the absorbance of the suspended matter.

A lower detection limit (LDL) of 0.02589 M was determined by using two times the RMS noise of the spectrophotometer, making it impossible to determine the effectiveness of this method below this level.
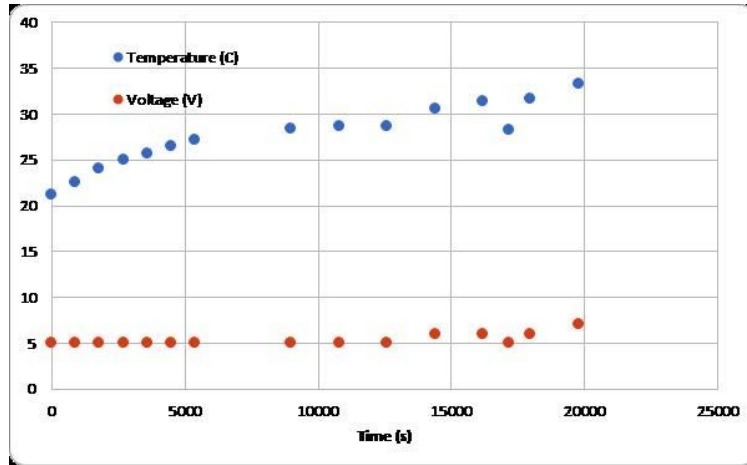
Figure 3: Temperature and applied cell potential as copper is recovered.

Red: Current (Amps) | Blue: Absorbance (693.4nm) | Green: Adjusted Absorbance | Yellow: Background (500nm)
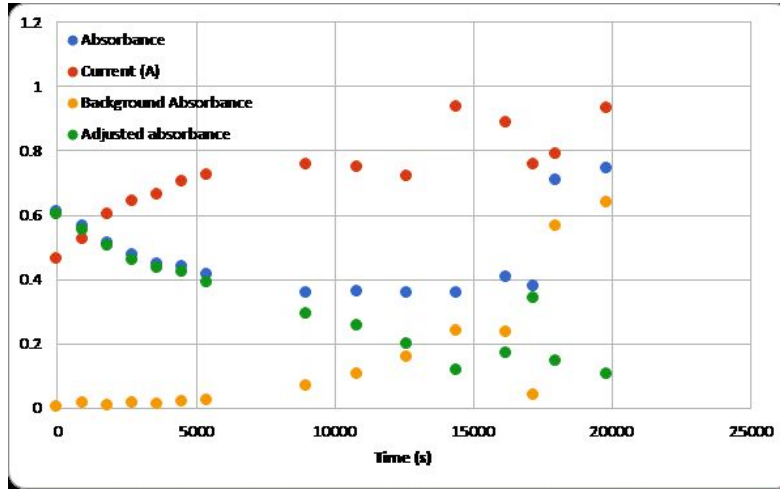

Figure 4: Current, absorbance, background absorbance, and corrected absorbance as copper is recovered.
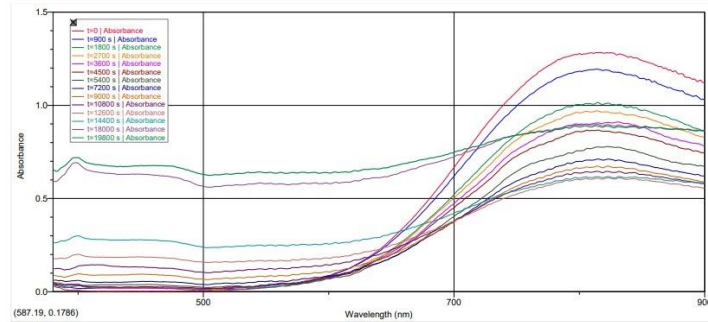

Figure 5: Absorbance vs. wavelength as copper is recovered.

References:

1. Fitzgerald, & J, D. (1998, June 01). Safety guidelines for copper in water. Retrieved from
https://academic.oup.com/ajcn/article/67/5/1098S/4666243

2. Determination of an Acute No-Observed-Adverse-Effect Level (NOAEL) for Copper in
Water. (2002, May 25). Retrieved from
https://www.sciencedirect.com/science/article/pii/S0273230001914928)

3. Sparks, D. L., Friedland, R., Petanceska, S., Schreurs, B. G., Shi, J., Smith, M. A., . . .
Stankovic, G. (2014). TRACE COPPER LEVELS IN THE DRINKING WATER, BUT NOT
ZINC OR ALUMINUM INFLUENCE CNS ALZHEIMER-LIKE PATHOLOGY. *PMC*.
Retrieved from https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3899576/.

4. Al-Saydeh, S. A., El-Naas, M. H., & Zaidi, S. J. (2017). Copper removal from industrial
wastewater: A comprehensive review. *Journal of Industrial and Engineering Chemistry,56*,
35-44. doi:10.1016/j.jiec.2017.07.026

5. Cacciatore, K. (2013). *AP Chemistry Guided-Inquiry Experiments: Applying the Science
Practices Student Manual* (T. Holme, Ed.). New York: The College Board.