

EXPERIMENT 8

Determination of Copper by Electrogravimetry

UNKNOWN

Submit a clean, labeled 100-mL volumetric flask to the instructor so that your unknown copper solution may be issued. Your name, section number, and your locker number should be written legibly on this flask. The flask does not need to be dry on the inside, but needs to have been rinsed with deionized water after it has been washed. *The flask must be turned in at least 1 lab period before you plan to do the experiment* so that the Teaching Assistants will have time to prepare the unknown. Each student will have his or her own unknown to analyze even if you are working in pairs.

BACKGROUND

In *electrogravimetry*, a metal ion is *quantitatively* (>99.9%) electroplated onto a preweighed “working” electrode almost always as the solid metal. This takes place at the negative electrode or *cathode*, which is defined as that electrode at which *reduction* takes place. From the gain in mass of the electrode, the amount of metal in the sample can be calculated – assuming no interferants are also electroplated onto the electrode. A few metal ions can be deposited in some chemical form onto the *anode*, the electrode at which oxidation takes place. For example, under the appropriate experimental conditions, Pb^{2+} can be deposited onto an anode as PbO_2 .

The two critical factors in performing a good quantitative analysis are finding the conditions so that 100% of the analyte of interest in the sample at hand is plated onto the electrode, and that nothing else is.

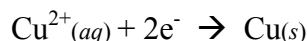
Electrogravimetry is capable of very high precision and accuracy, $\pm 0.1\%$ or better, because the only measurements made are pairs of weighings, and weighing is readily capable of very high precision and accuracy. All the instrument does is apply a potential to the working electrode that is sufficiently high to force the deposition electrochemistry to proceed to completion. This can be accomplished with equipment as simple as a battery, some wire, and a few resistors.

There are two basic variations of electrogravimetric method – controlled-potential or controlled-current. In *controlled-potential electrogravimetry*, a known constant potential is applied to the electrode for a sufficiently long enough time to plate out 100% of the analyte. The current decreases as the metal is plated out until only the small *charging* or *background current* flows. This provides a measure of selectivity if there are two or more metals that can plate out; the metal ion that is more easily reduced can often be plated out quantitatively without any of the

other metal also plating out. This procedure generally provides a nice smooth coating, but requires more sophisticated and expensive instrumentation and quite a long analysis time.

In *controlled-current electrogravimetry*, a fairly large voltage is applied to the working electrode in order to force a constant relatively large current to flow through the cell. The current is often on the order of milliamps (mA) instead of microamps (μA), as is typically the case in controlled-potential electrogravimetry. If the concentration of metal ion in the electrolysis solution is insufficient to consume *all* the current, then other reactions such as hydrogen ion reduction must occur in order to consume all the current that is forced to pass through the cell. Obviously, if any interferences are present, they will also plate out; but the method is significantly faster than using a controlled potential and the required instrumentation is simpler and cheaper. In either electrolysis variation, the solution is stirred or agitated in some manner in order to speed up the analysis.

In this experiment, you will plate a dilute, acidified solution of copper ion onto a pre-weighed platinum electrode:



The determination of copper is one of the easiest, oldest, and most important applications of electrogravimetry. One reason is that cupric ion does not require very negative potentials to be plated out quantitatively. Thus, most common metals do not also plate out and serve as interferences. The E° for Cu^{2+} reduction is only +0.34 V, as opposed to the E° 's for Pb, Sn(II), Ni, and Cd, and which are -0.13, -0.14, -0.25, -0.40, and -0.76 V, respectively. In general, the more positive the E° for a redox couple, the easier a species can be reduced. Of the more common metals that can plate out under the conditions used in this experiment, only Ag(I), Hg(I), and Hg(II) with E° 's = +0.80, +0.80, and +0.85 V, respectively, would interfere.

INSTRUMENTATION

Sargent-Slomin Electrolytic Analyzer.

This is a (very old, if not positively ancient) dual-cell, constant-current electrolysis unit. These were first marketed probably before your parents were born, and the units in the laboratory are undoubtedly older than you are, perhaps twice your age. So much for "Waste, Fraud, and Inefficiency" in the CHE 226 Lab.

PROCEDURE

Preparation of Electrodes

1. Check out one or two pairs of Pt electrodes from the Teaching Assistant. Be very careful with these throughout the entire experiment; they are quite fragile, and **extraordinarily**

expensive. The larger, gauzy electrode is the cathode; the smaller one is the anode, which will rotate during electrolysis to stir the solution.

2. Clean the platinum electrodes by immersing them in the beaker of concentrated nitric acid provided (see the instructor) for about 5 min. This will dissolve any Cu that has already been plated on the cathode as well as removing traces of grease and other materials from the surface. Remove from the acid and rinse well with deionized water into a waste beaker.
3. Rinse off the wet cathode (larger outer electrode) with a few squirts of alcohol from a wash bottle, **but not into any container containing acids.**
4. Place the electrode on a conventional watch glass in an oven at about 105 °C for 5 min. Cool in a desiccator and weigh accurately. **Don't touch the electrode body with your fingers.** Grease will prevent copper from adhering properly and can increase the mass of the electrode.

Electrolysis

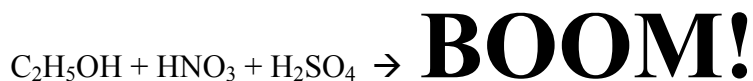
1. Carefully dilute the unknown solution to the mark and mix well.
2. Pipet 25.00-mL aliquots of the unknown copper solution into each of two tall-form beakers and add about 50 mL of deionized water, 2 mL of concentrated sulfuric acid, and 1 mL of concentrated nitric acid.
3. Properly connect one set of electrodes to the apparatus. **Make sure they do not touch each other even when rotating.** This would result in a “short circuit”.
4. Gently and carefully lower the electrode assembly into the tall-form beaker so that the top of the cathode is about $\frac{3}{4}$ inch below the rim of the beaker. Start the stirring motor (labeled **A**). Add sufficient deionized water to raise the level of the solution to about a half inch from the top of the cathode. Cover the beaker with a split watch glass.
5. With the autotransformer control knob (labeled **B**) turned fully counter-clockwise and the control knob (labeled **D**) in the **NORMAL** position, turn on the current switch (labeled **C**). Rotate the autotransformer knob (**B**) clockwise until the ammeter reads 1 to 2 A and the voltage remains below 4 V.
6. Repeat Steps **4** and **5** for the second sample.
7. Electrolyze at this voltage until the blue-green color of copper ion has disappeared (about 15-30 min). Add 1 mL of urea solution (**Notes 1 & 2**) and continue the electrolysis for an additional 5 min.
8. Add sufficient deionized water to cover the cathode completely. Make this addition with a wash bottle and use this opportunity to wash drops of solution from the surface of the split watch glass and the sides of the beaker into the bulk of the solution.

9. Continue the electrolysis for an additional 15 min at 0.5 A current. If no additional copper is deposited on the fresh cathode surface, the deposition is complete. (**Note 3**)
10. To stop the electrolysis, turn off the stirrer **but do not interrupt the current at this time**. Slowly raise the electrode assembly with one hand while washing the exposed portion of the cathode with a stream of deionized water from a wash bottle. As soon as the cathode is completely out of the solution, turn off the current and replace the beaker with a beaker of deionized water. Raise the beaker of deionized water to cover the electrodes and **gently** swirl. Wash the electrodes with a second portion of deionized water and carefully disconnect the cathode.
11. Rinse the cathode with alcohol (wash bottle) and place it in a beaker in an oven at 105 °C *for no more than 5 minutes* to dry. Do not heat longer because the fresh copper surface oxidizes easily, the electrode will gain mass, and your results will be high.
12. Cool the electrode to room temperature in a desiccator and weigh accurately. It is important to rinse, dry, cool, and weigh the plated electrode in the same manner as was the cleaned electrode previously, because the *difference* in mass will represent the total mass of copper in the 25.00-mL aliquot of your unknown.
13. **Clean up your work areas.**
14. ***Return the set of electrodes to the TA.***

HAZARDOUS WASTE DISPOSAL

Pour all electrolyzed Cu solutions, any remaining unknown Cu solution, any extra nitric or sulfuric acid into the properly labeled Hazardous Waste Container for this experiment, which is located in a hood in the lab. If you are unsure of the proper container, ASK.

*Any of the small amount of ethanol left over from rinsing your electrodes may be safely washed down the sink with copious amounts of cold water. **DO NOT POUR THE ETHANOL INTO THE HAZARDOUS WASTE CONTAINER FOR THIS EXPERIMENT. AN EXPLOSION CAN RESULT.***

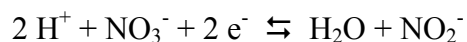


NOTES

1. Electrogenerated nitrite prevents complete deposition of copper and is removed by urea according to the reaction:



Nitrite is formed by the reaction:



2. Preparation of Urea Stock Solution. Dissolve 250 g of urea in 500 mL deionized water. This solution should have been prepared for you and already available.
3. As an additional check, you can add 2 or 3 drops of the solution to a few drops of concentrated ammonium hydroxide in a test tube. The deep blue color of the copper-ammine complex indicates incomplete deposition of copper.

TEXT REFERENCE

D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, *Analytical Chemistry: An Introduction*, 7th ed., Chapter 20, pp. 508-522.

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