

Thomas Fillmore
Will Wickun

AN INTRODUCTORY-LEVEL EXPERIMENT FOR THE ELECTROCHEMICAL RECOVERY AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER

ABSTRACT

Procedures suitable for an introductory-level laboratory experiment were developed for the electrogravimetric determination of copper. The method involves deposition of the reduced metal onto the working electrode at low current levels. The electrolysis reaction is driven without the need for potentiometric control and the cathodic reduction of the metal proceeds to near thermodynamic completion. When separate cell compartments are used, purity of the recovered metal should also be high. These characteristics of electrolysis were confirmed by the electrogravimetric analysis of copper that yielded a recovery of 93.93 ± 5.74 percent. Purity of the recovered copper, determined through spectrophotometric methods, was shown to be 97.82 ± 3.24 percent.

Key words: electrolysis, electrogravimetric analysis, spectrophotometric analysis.

INTRODUCTION

The electrolytic cell is commonly used throughout industry for electrorefining metals, electroplating, and recovering valuable metals from solution. Established industrial procedures indicate that the currents required are generally unachievable with the standard power supplies available in an academic laboratory. In addition, little information is readily available on the simple electrolytic recovery of metals for analytical purposes. Many procedural approaches used in a quantitative chemistry laboratory (Petrucci and Moews 1964, Tackett and Knowles 1966, Kennedy and Adams 1970) are controlled potential electrolysis experiments requiring precise current monitoring.

Other electrogravimetric methods (Skoog, West, and Holler, 1992) require the use of expensive platinum electrodes. For these reasons, a simple, inexpensive experiment for the electrolytic recovery of copper from solution was developed. The scope of the experiment can be expanded easily to include the spectrophotometric determination of the purity of the recovered metal.

PROCEDURE

The 0.25 M salt solution used for this investigation was prepared from reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. This salt was selected for its high solubility in water and its brilliant blue color, which was useful in visually monitoring the progress of the reaction and in spectrophotometrically establishing the purity of the recovered metal.

Salt bridges were prepared from a saturated solution of KCl in agar (Harris, 1995) and constructed with approximately 50 cm of folded 24 gauge nichrome wire anode embedded within

Thomas Fillmore, Department of Biological and Physical Sciences, Montana State University - Billings, Billings, MT 59101-0298.

Will Wickun, Department of Biological and Physical Sciences, Montana State University - Billings, Billings, MT 59101-0298.

them in order to maximize the current flow. For the cathode, a premassed copper strip, approximately 1 cm, (5 cm) was connected to a standard regulated laboratory power supply with an alligator clip and immersed in the center of a 250 mL beaker containing 100.0 mL of the copper sulfate solution. The beaker was periodically swirled without removing the salt bridge or cathode. The current was monitored with the power supply's internal ammeter. Faraday's constant and the relationship of current and time allowed a rough estimate of the time required for total deposition. However, since the concentration of the Cu (II) in solution continually decreases as the experiment progresses, the time required to reach completion increases accordingly.

For the percent recovery determination, the contents of the cathode compartment were quantitatively transferred into a glass funnel containing premassed filter paper and the premassed cathode with copper deposits. The filter paper and cathode with deposits were washed with deionized water, dried for several hours at 110°C, cooled in dessicator, and then weighed (Table 1). For purity determinations, most of the recovered copper was dissolved in 6 M HNO₃ and the solution was heated without boiling until the evolution of NO₂ was no longer evident. An excess of 6 M NH₃ was added and absorbances were measured against standards on a Shimadzu UV2100 UV-vis recording spectrophotometer. From absorbance data, corresponding concentrations were established by comparison with the concentrations of standard tetraammine Cu (II) solutions (Table 2 and 3). The standard deviations for the data in Tables 1 and 2 were calculated using the equation

$$s = \sqrt{\frac{\sum(x - \bar{x})^2}{N - 1}}$$

where N is the number of replicate data in the set.

Table 1: Mass and percent copper recovered

Sample	Theoretical mass (g)	Experimental mass (g)	Percent copper recovered
R-1	0.3176	0.2825	88.95
R-2	0.3176	0.2942	92.63
R-3	0.3176	0.2806	88.35
R-4	0.3176	0.3478	109.5
R-5	0.3176	0.2990	94.14
R-6	0.3176	0.2801	88.19
R-7	0.3176	0.2910	91.62
R-8	0.3176	0.3001	94.49
R-9	0.3176	0.3044	95.84
R-10	0.3176	0.2903	91.40
R-11	0.3176	0.3098	97.54
R-12	0.3176	0.3001	94.49

Mean percent copper recovered: 93.93 ± 5.74%

Table 2: Standard concentrations used to determine molar absorptivity

Standard	Concentration	Absorbance	Molar Absorptivity
S-1	3.809 x 10 ⁻³ M	0.192	50.4 M ⁻¹ cm ⁻¹
S-2	3.174 x 10 ⁻³ M	0.164	51.7 M ⁻¹ cm ⁻¹
S-3	2.592 x 10 ⁻³ M	0.132	50.9 M ⁻¹ cm ⁻¹

Mean molar absorptivity: 51.0 ± 0.8 M⁻¹ cm⁻¹

Because all samples have a similar composition and have been analyzed in the same way, the mean percent purities from the 12 sets of data in Table 3 were pooled to improve the reliability of the standard deviation, which was then calculated with

$$s_{pooled} = \sqrt{\frac{\sum(x - \bar{x}_1)^2 + \sum(x - \bar{x}_2)^2 + \sum(x - \bar{x}_3)^2 + \dots}{N_1 + N_2 + N_3 + \dots - N_{total}}}$$

where N₁ is the number of data in set R-1, N₂ is the number of data in set R-2, and so forth, and N_{total} the total number of data sets pooled, is 12 in this case.

Table 3: Purity verification based on absorption ($\lambda = 600 \text{ nm}$)

Sample and replicate	Theoretical conc x 10 ³ (M)	Exptl conc x 10 ³ (M)	Absorb	% purity	Mean % purity	
R-1	a	3.758	3.270	0.168	87.01	86.55
	b	3.132	2.706	0.139	86.39	
	c	2.505	2.161	0.111	86.27	
R-2	a	3.803	3.679	0.189	96.74	98.00
	b	3.169	3.212	0.165	101.40	
	c	2.535	2.433	0.125	95.98	
R-3	a	3.854	3.834	0.197	99.48	98.53
	b	3.212	3.309	0.170	103.00	
	c	2.570	2.394	0.123	93.15	
R-4	a	3.901	3.854	0.198	98.80	101.60
	b	3.251	3.464	0.178	106.60	
	c	2.601	2.589	0.133	99.54	
R-5	a	3.818	3.776	0.194	98.90	99.53
	b	3.182	3.192	0.164	100.30	
	c	2.546	2.530	0.130	99.37	
R-6	a	3.869	3.834	0.197	99.10	99.27
	b	3.224	3.270	0.168	101.40	
	c	2.580	2.511	0.129	97.33	
R-7	a	3.814	3.854	0.198	101.00	101.10
	b	3.179	3.270	0.168	102.90	
	c	2.543	2.530	0.130	99.49	
R-8	a	4.000	3.971	0.204	99.28	107.10
	b	3.333	3.698	0.190	111.00	
	c	2.666	2.958	0.152	111.00	
R-9	a	3.830	3.601	0.185	94.02	96.86
	b	3.191	3.134	0.161	98.21	
	c	2.553	2.511	0.141	98.35	
R-10	a	3.869	3.640	0.187	94.08	96.20
	b	3.224	3.134	0.161	97.21	
	c	2.580	2.511	0.142	97.33	
R-11	a	3.832	3.737	0.192	97.52	96.32
	b	3.193	2.978	0.153	93.27	
	c	2.554	2.511	0.129	98.32	
R-12	a	3.799	3.562	0.183	93.76	92.68
	b	3.166	2.842	0.146	89.77	
	c	2.533	2.394	0.123	94.51	

Overall mean purity: $97.82 \pm 3.24\%$

DISCUSSION

In the initial design of the electrolytic cell constructed for this investigation, the Cu cathode and Zn anode were immersed in the same 250 mL beaker. As concentration of the Cu (II) became very dilute, Zn (II), present in solution from the oxidation of the zinc anode, deposited on the copper cathode. Because of this, impurities were inherently present in the copper. The use of separate anode and cathode compartments produced reasonably good results. However, in order to keep the current flow sufficiently high, repeated hand-agitation of the anode compartment was necessary. This difficulty was overcome by completely eliminating the anode compartment and constructing the anode as an integral part of the salt bridge (Fig. 1). Current flow was optimized easily while

avoiding the zinc impurity in the deposited copper.

For this cell, an initial current of 1 A was applied for four to five hours or until the current became essentially zero. No attempt was made to control the working electrode potential. Using Faraday's constant and the relationship between charge and time, the theoretical minimum time for a complete reaction was calculated at 1.1 hours. However, this calculation does not account for iR drop nor the decrease in current with decreasing Cu (II) concentration. For this reason, the cell was allowed to run significantly longer than the theoretical time in order to maximize recovery of the copper. The disappearance of the blue color of the solution and the cessation of current were reliable indicators that deposition of the copper was complete.

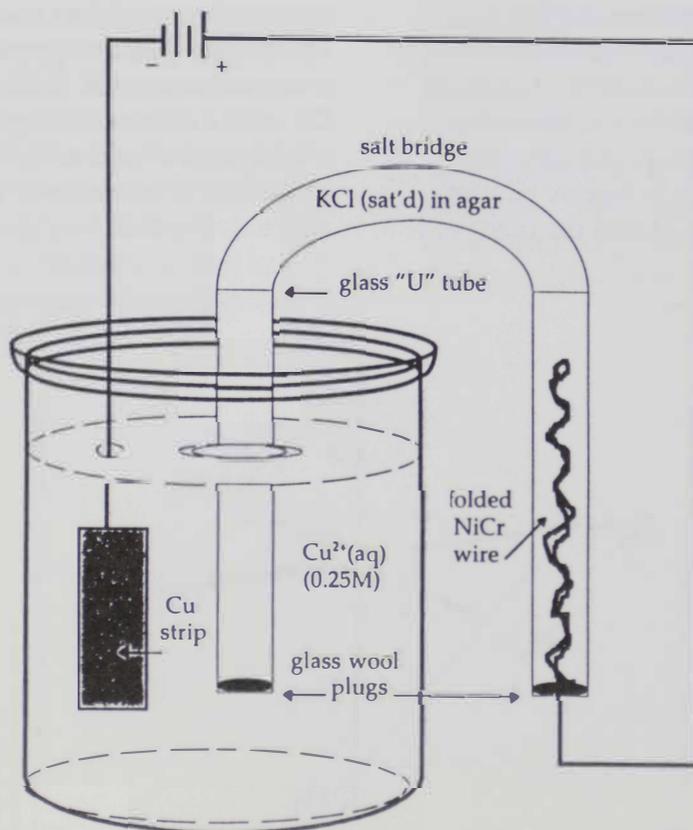


Figure 1. Sketch of electrochemical cell construction.

The purity of the 12 samples, split into three replicates each, was determined spectrophotometrically. Although the aqueous solution of the recovered Cu (II) was a faint blue color, the intensity of this absorption was insufficient to be quantitatively useful. Therefore, the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ was converted to the much more intensely blue $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ by the addition of an excess of 6 M NH_3 . Addition of ligands to such aqueous solutions leads to the formation of coordination compounds by successive displacement of water molecules (Cotton and Wilkinson 1972). Ammonia is a much stronger ligand than water, easily displacing the four water molecules from the equatorial positions of the Cu (II) ion and, at the same time, causing the absorption band to move from the far red to the middle of the red region of the spectrum (Fig. 2). However, the axial bond lengths are Jahn-Teller distorted by the presence of the four equatorial NH_3 . Because of this effect, it is impossible to displace the two axial H_2O molecules unless the solution is diluted with pure liquid ammonia. Comparison of the literature (Cotton and Wilkinson 1972) and the observed

maximum wavelength (~600 nm vs. 601.5 nm, respectively) unambiguously confirmed that the ion formed was indeed the octahedral $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. Initial serial dilutions of the sample were also made with 6 M NH_3 to ensure the predominance of the $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ even after subsequent dilution of the aliquots with water.

Molar absorptivity was derived from the concentrations and the absorbances of the tetraammine Cu (II) standards. This absorptivity was used to determine the concentration of the recovered Cu (II) in each of the samples. Percent purity was then calculated from a comparison of the concentrations obtained for the recovered Cu (II) solutions to the concentrations of the standard solutions.

Based on the data collected and summarized in Tables 1 and 3, electrolytic deposition can serve well as an introductory-level analytical method. For this simple, inexpensive procedure, a mean recovery of 93.93 ± 5.74 percent Cu with a corresponding purity of 97.82 ± 3.24 percent was achieved. It was noted that when a lower current was applied, deposition of the copper

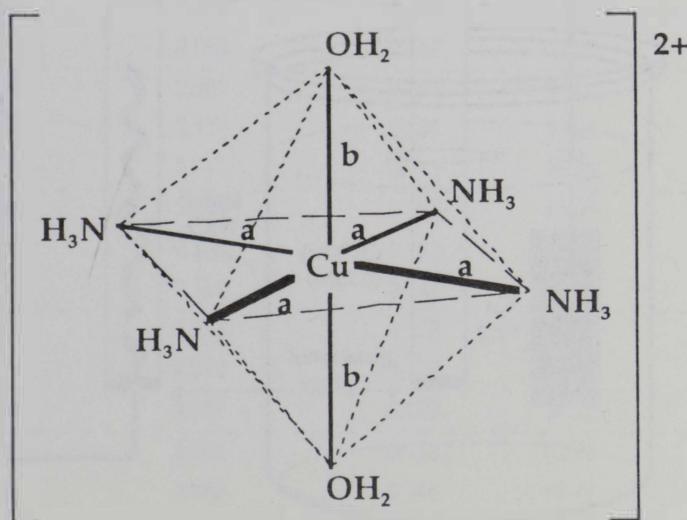


Figure 2. Jahn-Teller distortion (i.e. $b > a$) in the octahedral complex lowers symmetry and energy.

required a longer time, however, the copper was generally of higher purity. It is assumed here that, as in a rapid precipitation reaction, at high current and high deposition rates, other ions from the solution are likely to become trapped in the deposited copper. This phenomenon would account for the impure appearance of the copper resulting from deposition at high current levels. In industrial electrorefining, a low current is supplied over several weeks in order to recover large sheets of high-purity copper.

Although electrogravimetric analysis is an established method, many published procedures may be difficult or time consuming. The procedure presented in this paper is uncomplicated enough for an introductory-level chemistry student to follow and to retrieve valid data. Other metals in solution could also be recovered in a similar manner. With the possible exception of the recording spectrophotometer, for which a Spec-20 could be substituted, all apparatus and materials used are common to secondary and higher-level educational institutions. An informative review of ligand field theory and determination of a coordination compound, as well as quantitative determinations using the

UV-vis spectrophotometer, are additional pedagogic benefits of this otherwise simple experiment.

LITERATURE CITED

- Cotton, F. Albert and Geoffrey Wilkinson. 1972. *Advanced Inorganic Chemistry*, 3rd ed. John Wiley and Sons. New York, NY. p. 916-918
- Harris, C. Daniel. 1995. *Quantitative Chemical Analysis*, 4th ed. W. H. Freeman. New York, NY. p. 350.
- Kennedy, John H. and Frank Adams. 1970. Controlled potential electrolysis: An experiment for elementary quantitative analysis. *J. Chem. Educ.* 47: 461-463.
- Petrucci, R. H. and P. C. Moews. 1964. A simple quantitative electrolysis experiment for first year chemistry. *J. Chem. Educ.*, 41(10): 552-553.
- Skoog, Douglas A., Donald M. West, and F. James Holler. 1992. *Fundamentals of Analytical Chemistry*, 6th ed. Saunders. Orlando, FL. p. 874-876.
- Tackett, Stanford L. and John A. Knowles. 1966. Simple potentiostat for controlled potential electrolysis. *J. Chem. Educ.*, 43(8): 428-431.