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DETERMINATION OF COPPER IN SOLUTIONS OF URANYL SULFATE BY INTERNAL ELECTROLYSIS

O. Menis
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Oscar Menis, D. L. Manning, R. G. Ball

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ABSTRACT

A method is described for the determination of copper in solutions of uranyl sulfate by internal electrolysis. An electrolytic cell, composed of a platinum cathode and a cadmium anode which are separated by an alundum thimble, is used to deposit the copper from test solutions. The method is applicable to solutions that contain from 1 to 40 mg of copper. The precision of the method is related, however, to the quantity of copper that is deposited.

The precision of the electrogravimetric method was compared with that of the diethyldithiocarbamate colorimetric procedure and no sifnificant variation between the two methods was found to exist. The advantage of the electrogravimetric method is that copper can be determined by weighing after electrodeposition, thus combining the separation and determination of copper in the analysis of solutions of uranyl sulfate.

THE DETERMINATION OF COPPER IN SOLUTIONS OF URANYL SULFATE BY INTERNAL ELECTROLYTIC DEPOSITION

O. Menis, D. L. Manning, and R. G. Ball

INTRODUCTION

In making analyses of solutions of uranyl sulfate in the HR Laboratory, it has been the practice to determine the amount of copper in these solutions by a spectrophotometric method. It was necessary, however, to remove the copper from these samples of uranyl sulfate by a constant current, electrodeposition method before the amount of uranium and any other constituents could be determined. Consequently, it was believed that a considerable savings in time would be realized if the separation and determination of copper could be accomplished by means of the same electrogravimetric method. The use of constant current methods, however, has tended to yield black, porous deposits, which were not generally suited for quantitative measurements. Therefore, the purpose of this investigation was to develop a controlled potential method for the electrogravimetric determination of copper in solutions of uranyl sulfate.

Although controlled electrodeposition methods[1] appeared to offer a solution to the problem in that quantitative deposition of copper can be achieved in this manner, the equipment that is needed for supplying the external voltage regulation for constant electrode potentials, as described by several authors,[2,3,5] is bulky, expensive, and is not readily adaptable to the analysis of a large number of samples. On the other hand, the use of internal electrolysis as a means of a electrogravimetric separation of copper without an external source of electrical energy offers a direct, simple method for the determination of copper.

Early workers in electrochemistry have described the spontaneous electroplating of metals by the use of various electrodes, while Sand[7] was the first to use the term "internal electrolysis". Lingane,[6] in his text, presents an extensive treatment of this subject and also a method for the determination of copper by using zinc and platinum electrodes. In another method, Horton and Thomason[4] reported the removal of copper from radioactive solutions with cadmium metal. The procedure that is outlined herein is essentially that of Lingane with the innovation of a cadmium anode to provide closer potential control for the deposition of copper.

The net reaction of any internal electrolysis cell is the same as in the direct displacement of one metal by another, as, for example, when copper is precipitated by placing metallic zinc in a solution of a cupric salt. In the latter case the precipitated metal does not adhere well to the base metal because the surface is continually disintegrating. In internal electrolysis, the conditions at the platinum cathode are identically the same as if an external voltage source were used, and the metal is deposited in an adherent form. The cadmium anode is separated from the cathode by a porous alundum thimble to prevent any cementation of copper at the anode.

The advantage of the electrogravimetric procedure is that copper can be determined by weighing after deposition from solutions of uranyl sulfate. This combines the separation and the determination of copper into one step.

A schematic diagram of the internal electrolysis apparatus is shown in Figure 1.

PROCEDURE

Reagents

1. Sulfuric Acid, 1 N. Fill a liter volumetric flask approximately half-full with water. Cautiously add 28 ml of concentrated sulfuric acid; then dilute the solution to volume with water.

2. Anolyte Solution, 2 w/v per cent Na_2SO_4 in 1 N H_2SO_4. Dissolve 2 g of analytical, reagent grade, sodium sulfate in 100 ml of 1 N sulfuric acid.

Apparatus

1. Cathode, platinum gauze, 3.5-mm dia. x 3.5-mm high.

2. Anode, cadmium. The electrode is prepared from a strip of cadmium metal 4-inches long x 1/2-inch wide x 1/16-inch thick. The surface of the electrode is activated by dipping it into 1 N nitric acid before use.

3. Alundum Thimble, extraction, RA 360, 30-mm dia. x 80-mm high, available from the Central Scientific Co., Chicago, Ill.

4. Magnetic Stirrer, with Teflon covered stirring bar, available from the Arthur H. Thomas Co., Philadelphia, Pa.

5. Milliameter, 500-ma capacity, available from the Triplett Electrical Instrument Co., Bluffton, Ohio.

6. Beakers, Pyrex, 100 ml.

Transfer an aliquant of a sample into a 100-ml beaker. The size of the sample aliquant should be adjusted so that 1 to 40 mg of copper is present. Dilute this test portion to approximately 50 ml with 1 N sulfuric acid; then insert a small magnetic stirring bar into the solution. At this time, assemble the apparatus as shown in Figure 1. A milliameter that is incorporated in the circuit may be used to measure the current; however, this is optional, and, if desired, the milliameter may be eliminated. Before using the cadmium anode

for the first time, thoroughly cleanse the surface by dipping the anode into 1 N nitric acid; then, wash the anode with water. After washing the anode, insert it into the alundum thimble. In a similar manner, cleanse the surface of the platinum cathode by dipping it into concentrated nitric acid. After the cathode is clean, rinse it with water; then heat it over an open flame until the surface is dull-red. Cool; then weigh the cathode and record the weight. Adjust the cleaned and tared cathode in position around the alundum thimble; it is necessary to use a freshly cleaned and tared cathode for each determination. Fill the alundum thimble with approximately 25 ml of anolyte; then allow this solution to drip through the thimble for approximately one minute in order to saturate the pores of the thimble. The surface of the anolyte should be a little higher than the surface of the sample at the beginning of electrolysis to prevent diffusion of the sample into the thimble. After the pores of the thimble are saturated, immerse the electrodes in the sample; then short-circuit the electrodes and electrolyze the solution for 30 minutes with constant stirring. After this period of electrolysis, remove the sample from the electrolytic cell; then wash the cathode and alundum thimble with water. If the sample is to be analyzed for other components, add the wash solution to the sample. Leave the electrodes short-circuited during the wash operations in order to maintain the potential at the cathode, thus preventing the loss of deposited copper by dissolution in the acid medium. Remove the cathode from the cell. Wash again with water, then finally with acetone. Dry the cathode in an oven at 100°C for two to three minutes. Longer periods may promote the formation of an oxide on the deposited copper and thus lead to high results. Allow the cathode to cool to room temperature; then weigh the cathode and its deposit. Record the final weight of the cathode. The difference between the final

and initial weights corresponds to the amount of copper which was deposited from the sample.

EXPERIMENTAL

Advantages of the Alundum Thimble. In preliminary experiments on the deposition of copper by internal electrolysis, the anode compartment of the electrolysis cell was connected to the sample compartment by means of a bridge of agar and salt. Although quantitative deposition of copper from solutions of uranyl sulfate were obtained by means of such an arrangement, long periods of electrolysis, such as one or two hours for 10 mg of copper, were required for the deposition. This slow rate of deposition was related to a low flow of current through the cell due to the high resistance of the bridge. By using an alundum thimble to isolate the cadmium anode from the sample, however, the internal resistance of the cell was greatly reduced. When an alundum thimble was inserted in the apparatus, the current flow through the cell was increased by a factor of approximately 20, while an initial current of the order of 250 ma in the deposition of 10 mg of copper was realized. In addition, the period of electrolysis was decreased in an equivalent relationship in that a period of 30 minutes was sufficient for the quantitative deposition of 1 to 40 mg of copper.

Diffusion Studies. Since the test solutions of uranyl sulfate are analyzed for uranium and other substances after the electrolytic removal of copper, it is essential that no loss of these constituents occurs during the electrolysis by diffusing into the anode compartment. A study was made, therefore, of the deposition of copper from solutions of uranyl sulfate that contained known amounts of uranium, copper, and nickel. After the determination

of copper by this method of internal electrolysis, the uranium and nickel content in the test portion was determined by conventional laboratory methods. In every case, a quantitative recovery of the copper was realized after a 30-minute period of electrolysis. Insofar as the loss of uranium or nickel by diffusion was concerned, subsequent analyses of these two elements were found not to be affected by loss through diffusion into the anolyte.

Rate Studies. In controlled potential electrolysis, the rate of the electrode process is limited by the rate of transfer of the reacting substance from the body of the solution to the electrode surface by diffusion and electrical migration. Factors that influence the rate of deposition are the electrode area, the solution volume, the rate of stirring, the temperature, and to a lesser degree, the particular electrode reaction. The rate of deposition, however, is independent of the amount of electrode reaction, e.g. the amount of copper that is deposited.(6)

A study of the rate of deposition of copper by internal electrolysis revealed that quantitative recoveries of up to 40 mg of copper can be accomplished in a minimum time of 20 minutes at room temperature with rapid stirring by means of a magnetic stirrer. An electrolysis period of 30 minutes is recommended, however, in order to provide ample time for complete depositon. The presence of uranium does not affect the rate of deposition, although an increase in the current was observed.

Precision of the Method. The results of the determination of copper in standard solutions of three typical concentration ranges (49, 296, and 1480 μg/ml) normally encountered in solutions of uranyl sulfate are shown in Table II.

Table II

Determination of Copper in Uranyl Sulfate Solutions

Precision of the Method in Typical Concentration Ranges

Copper Added, µg/ml	Uranium Present mg/ml	Copper Found, mg	Copper Found, µg/ml	Average µg/ml	S µg/ml	V Per Cent
Low Conc. Range						
49	1.05	1.1	44	47	2.1	5
		1.2	48			
		1.2	48			
		1.1	44			
		1.2	48			
		1.2	48			
Median Conc. Range						
296	5.17	7.6	304	297	3.1	1
		7.4	296			
		7.3	292			
		7.4	296			
		7.5	300			
		7.4	296			
		7.4	296			
		7.4	296			
		7.5	300			
		7.4	296			
High Conc. Range						
1480	25.8	37.5	1500	1502	2.1	0.1
		37.6	1504			
		37.6	1504			
		37.5	1500			
		37.6	1504			
		37.5	1500			
		37.5	1500			
		37.5	1500			
		37.5	1500			
		37.6	1504			

Approximately one mg of copper can be weighed with a coefficient of variation of 5 per cent. In weighing larger quantities of copper, 10 to 40 mg, the coefficient of variation is 1 per cent and 0.1 per cent, respectively. The standard deviation in absolute units for all three ranges was found to be constant in concentrations from 2 to 3 μg/ml. The precision of the electrogravimetric method for the determination of copper is, therefore, governed mainly by the total amount of copper that is weighed.

Comparison of the Precision of the Method with the Diethyldithiocarbamate Colorimetric Method. In order to further evaluate the electrogravimetric method, the precision of the method was compared with the diethyldithiocarbamate, colorimetric method for copper.(8) This comparison was made by determining the amount of copper, 100 to 400 μg/ml, in a series of duplicate samples of uranyl sulfate, by both methods. The standard deviation for both methods was calculated from the difference between the duplicates for each sample type. Application of the "F" test showed that no significant difference exists between the results that are obtained by the two methods.

Interferences. Any metals, in the electromotive force series, that have more negative potentials than copper will interfere in this method of electrolysis. The most common ones more likely to be encountered are silver, mercury, and lead. Such materials would be preferentially reduced before copper; however, these substances were not present in any of the samples which were examined in this experimental work.

SUMMARY

A method of internal electrolysis was developed for the determination of copper in solutions of uranyl sulfate. In this method a simple, electrolytic cell, composed of a platinum cathode and cadmium anode that are separated by an alundum thimble, is used to deposit copper from the test solutions. The method was found to be applicable to solutions that contain from 1 to 40 mg of copper in a 25-ml aliquant. The precision of the method was found to be dependent on the quantity of copper that is deposited during the period of electrolysis.

In addition, the precision of this electrogravimetric method was compared with that of the diethyldithiocarbamate, colorimetric method. In this comparison, no significant variation in precision of the two methods was found, as calculated from the "F" test. The advantage of the electrogravimetric method is that copper can be determined by weighing after deposition from solutions of uranyl sulfate, thus combining the separation and the determination of copper into one procedure.

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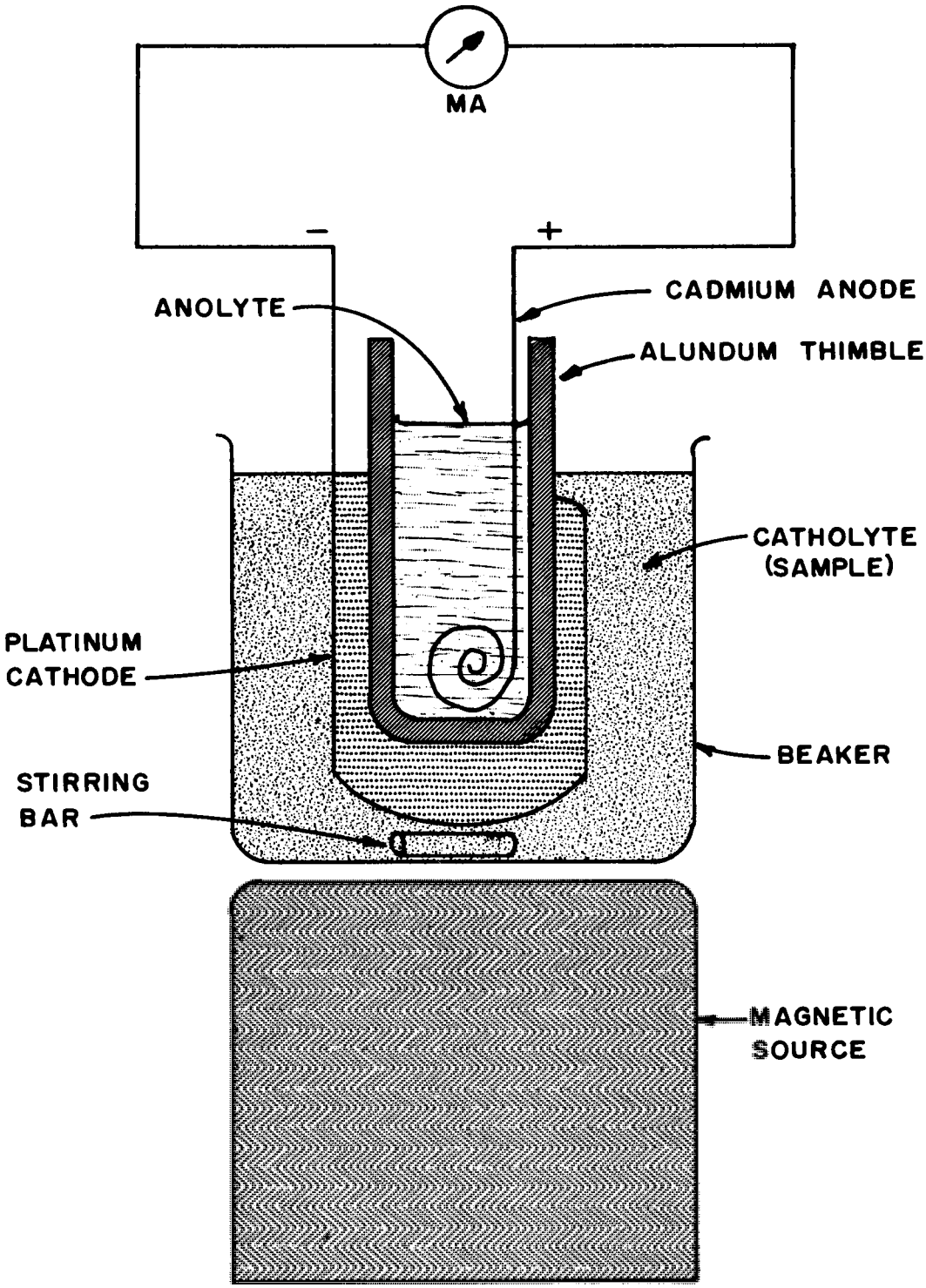

FIGURE 1. APPARATUS FOR THE DETERMINATION OF COPPER BY INTERNAL ELECTROLYSIS