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SEPARATIONS WITH A MICRO MERCURY CATHODE

EXPERIMENTAL

Preparation of the Electrode

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ACKNOWLEDGEMENT

LITERATURE CITED

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SEPARATIONS WITH A MICRO MERCURY CATHODE

by Richard B. Hahn

The conventional mercury cathode⁽¹⁾ used for separations of metals is not very satisfactory with small volumes of solution since the surface of the mercury in contact with the solution is limited. Keeping the solution thoroughly stirred and avoiding spray losses are other difficulties which arise in electrolyzing small volumes.

These difficulties can be eliminated by using a rigid metal cathode plated with liquid mercury. The mercury surface is thus increased two-fold, and stirring is accomplished by the evolution of gases during electrolysis.

EXPERIMENTAL

A description follows of the construction and use of an electrolysis cell employing such an electrode.

Preparation of the Electrode

The cathode is constructed as shown in Figure 1. A 5-mil silver foil is used and is spot welded to a platinum wire. The foil is cleaned by rubbing with fine-gauge steel wool, then bent into a semicircular shape and immersed in 6 N nitric acid for a minute or two to further clean the surface. Mercury is applied to the surface of the electrode by electrolysis of a 10% solution of mercurous nitrate containing a few drops of nitric acid. Electrolysis is continued until the surface of the silver foil is completely covered with liquid mercury and a noticeable deposit of liquid mercury hangs on the bottom of the electrode. The electrode is then removed from the mercurous nitrate solution and washed with water. The electrode is conditioned by placing it in a

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CONSTRUCTION OF CATHODE

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dilute sulfuric acid solution and electrolyzed at a current of 1 ampere for about 15 minutes. It is then ready for use.

Procedure

A 3 to 5 ml volume of the solution to be analyzed (0.5 to 1.0 N in sulfuric acid and free from other anions) is placed in the electrolytic cell, a flat-bottomed tube of dimensions shown in Figure 2.

The prepared cathode is introduced to the bottom of this tube. A platinum wire, approximately 12 gauge, serves as the anode. The mercury-coated cathode should be completely immersed in the solution, otherwise mercury will be lost at the liquid-air interface. The cell is suspended in a water bath at room temperature to effect cooling during the electrolysis. The solution is electrolyzed one hour, the current being 1 ampere during the first 45 minutes and then being reduced to 0.5 ampere during the last 15 minutes. Higher current will cause the loss of mercury from the cathode. The sides of the cell should be washed down at 15-minute intervals with a small amount of water. At the end of one hour and with the current still on, the cathode is lifted from the solution and washed immediately with a small amount of water, the washings going into the electrolysis cell. The solution remaining in the electrolysis cell is now ready for analysis.

Results

The efficiency of the micro mercury cathode was tested by removing iron and/or copper from pure solutions of aluminum(III), uranium(VI) and zirconium(IV) ions. The results are given in Table 1.

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ELECTROLYTIC CELL

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TABLE I

SEPARATIONS EFFECTED WITH A MICRO MERCURY CATHODE

(Sample volume 3 to 5 ml)

Sample	<u>Separable Metals</u>			<u>Nonseparable Metals</u>		
	<u>Identity</u>	<u>Mg Added</u>	<u>Mg Found</u>	<u>Identity</u>	<u>Mg Added</u>	<u>Mg Found</u>
1	Fe(III)	1	None	Al(III)	250	249
2	Cu(II)	10	None	Al(III)	100	100
3	Fe(III)	10	None	Al(III)	0.90	0.89
	Cu(II)	10	None			
4	Fe(III)	10	None	U(VI)	2.53	2.51
5	Cu(II)	10	0.005	U(VI)	2.53	2.55
6	Fe(III)	10	None	U(VI)	0.485	0.470
	Cu(II)	10	0.001			
7	Fe(III)	10	None	Zn(IV)	0.91	0.90
	Cu(II)	10	None			

These data indicate that the micro mercury cathode made separations as effectively as the conventional mercury cathode⁽²⁾, the separable metal ions being completely removed as shown by colorimetric and radio-chemical tests. Iron and copper were determined colorimetrically with 1,10-phenanthroline and diethyldithiocarbamate respectively. The quantitative recovery of the remaining metal ions was shown by precipitation of the aluminum as the hydroxide, and by potentiometric titration of the uranium with ceric sulfate. Zirconium was determined by

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DISCUSSION

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Electrodes of copper, lead, and pure platinum were also used as bases for the mercury coating. These were not as satisfactory as the silver electrode described. The mercury did not adhere well to the platinum, and the lead and copper introduced these ions as impurities in the test solution. The stem of the electrode must be of an inert material since the solution tends to attack the metal at the liquid-air interface.

The silver-mercury electrode prepared as described above holds about 0.3 to 0.5 g of liquid mercury on its surface. Such an electrode has a capacity to remove about 25 mg of iron from solution.

The silver foil base may be prepared for re-use by immersing the electrode in 1 to 2 N nitric acid which slowly dissolves off the mercury coating but does not attack the silver to any great extent. The electrode is then treated as described previously. If only a few milligrams of impurity were deposited on the electrode surface, the same electrode may be re-used after the simple treatment of immersing it in dilute (2 to 4 N) sulfuric acid.

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