Distribution of Report

A- 2707

Copies:

To:

1 & 2	C. E. Winters
3 to 10	TRIO Files
11 to 25	A. V. Peterson
26 to 30	Purdue Files

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A-2707

0
Analytical Report

on

A. MODIFIED MERCURY CATHODE CELL FOR THE PURIFICATION
OF URANIUM SOLUTIONS AND THE REDUCTION OF URANIUM

Submitted

Photostat Price \$ 3.30

Microfilm Price \$ 2.40

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

on

March 8, 1966

under

Contract No. W-405-ENG-474

by

Purdue Research Foundation

and

Department of Chemistry, Purdue University

by

E. S. Gantz, W. S. Barnhart, T. DeVries, and M. G. Mellon

Classification changed to Unclassified
Authorized by Cecar Ferrell 12-855
Changed by Hugh Kinon Date 6-7-12

Analytical Report

on

Research at Purdue University

by

Purdue Research Foundation and Department of Chemistry

March 8, 1946

A MODIFIED MERCURY CATHODE CELL FOR THE PURIFICATION
OF URANIUM SOLUTIONS AND THE REDUCTION OF URANIUM

Abstract

A modified mercury cathode cell having a separate anode compartment has been developed for the simultaneous purification of solutions containing uranium and the reduction of the uranium. Solutions containing uranium 0.5 M in sulfuric acid and free of organic matter and nitrates are electrolyzed for 30-60 minutes at 6-12 volts. The time of electrolysis depends upon the amount of iron that must be removed from the sample. The hold up of uranium in this cell is less than 1 part in 5000. A simple procedure for purifying the mercury is given. The rates of removal of various impurities (principally iron and chromium) have been studied under various conditions. A procedure for the satisfactory purification of Purdue pilot plant samples containing cupric, chromic, ferric and nickelous ions has been developed. The use of the mercury cathode diaphragm cell eliminates a separate reduction step in the analysis of uranium solutions,

A MODIFIED MERCURY CATHODE CELL FOR
THE PURIFICATION OF URANIUM SOLUTIONS AND THE REDUCTION OF URANIUM

Introduction

The analysis of uranium samples from the Purdue pilot plant required that such solutions be purified prior to a titrimetric determination of uranium with potassium dichromate. A chloroform extraction of the cupferrides of the metal impurities (principally cupric, chromic, nickelous, and ferric ions) has been used as well as the ethyl ether extraction of uranium in nitric acid solutions saturated with calcium nitrate. Better results have been obtained with a mercury cathode cell in which copper, nickel, iron and some chromium are removed. Since uranium solutions must also be reduced before titration, it occurred to the authors that by shielding the anode from which oxygen is liberated a simultaneous purification and reduction might occur. This modified mercury cathode diaphragm cell has been studied and has proven quite satisfactory.

Discussion

The modified mercury cathode cell was constructed as shown in Fig 1. The anode is an 18 gauge platinum wire, 10 cm of which is rolled into a spiral. The anode is placed inside a 15 x 1.5 cm pyrex tube which has a medium porosity pyrex sintered disk for a bottom. An air driven stirrer, the blades of which push downward, and the anode compartment are held in a rubber stopper that fits rather tightly in the

FIGURE 1 - MERCURY CATHODE DIAPHRAGM CELL

4

44

top of the cell.

In operation mercury is run into the cell from the leveling bulb to a depth of 4-5 mm. The solution to be purified is transferred quantitatively into the cell using 0.5 M sulfuric acid. The anode compartment is filled with enough 0.5 M sulfuric acid so that the level of the solution in the compartment will be 3-5 cm above the level of the solution in the cell. The blades of the stirrer should just touch the surface of the mercury. The solution is electrolysed at a potential of 6-12 volts. The current will vary from 0.6-2 amperes depending upon the voltage used.

Reduction of 0.3-0.5 g of uranium will occur in 5-15 minutes. Part of the uranium will be in the plus 3 state as evidenced by the red color of the solution. If the solutions are rather badly contaminated with iron the electrolysis will have to be run for 30-60 minutes. No samples in connection with the pilot plant work have needed electrolysis for a longer period than 1 hr.

After electrolysis the solution is drained from the cell without turning off the current. The cell is washed twice with 0.5 M sulfuric acid solution. With the first washing the solution in the anode compartment is added to the cell and replaced with fresh sulfuric acid. Each wash solution is electrolysed for 3 minutes. The under side of the rubber stopper should also be washed into the cell during the first washing.

The solution removed from the cell is now ready for the titrimetric determination of uranium. Provision must be made for the determination of

=

the oxidation of uranium (III) to uranium (IV) and uranium (IV) to uranium (VI). The latter determination will denote the total amount of uranium in the sample as only part of the uranium is reduced to the plus 3 state.

Some doubt was expressed concerning the hold-up of uranium in the anode compartment of the mercury cathode cell. Therefore, after several runs, the 0.5 M sulfuric acid in the anode compartment was allowed to drip through the sintered glass diaphragm into the empty cell proper. These anode solutions were analyzed colorimetrically for their uranium content. They contained 0.04 to 0.10 mg of uranium. This amounts to a hold-up of less than 1 part in 5000 when the usual 500 mg samples of uranium are used.

After a survey of the literature on the purification of mercury, a method by Hillibrand was modified and adopted for cleaning the used mercury from the mercury cathode cell. Impure mercury is covered with 2-3 M nitric acid and air or oxygen is bubbled through the mercury until a fresh nitric acid solution does not become colored after a period of 4-6 hours. The mercury is then dropped through a 4 ft column containing 1 M nitric acid and 0.1 M mercurous nitrate. The mercury in a dropping funnel is rapidly and finely dispersed by passing through a small cloth bag tied to the outlet end of the funnel. A 25 cm crook at the bottom of the column separates the mercury from the solution and delivers dry mercury. A second pass through the column assures pure mercury.

It was ~~advisable~~ to study the removal of iron by mercury cathode electrolysis since 0.1 mg of iron is the maximum allowable amount that can be tolerated in the titration of 400 mg uranium samples with a precision of 1 part in 2000. Pavlish and Sullivan⁽¹⁾ have made a study of voltage and current density on this separation. Various data from the electrolyses of uranium solutions containing iron and chromium are given in Table 1 and Table 2.

A mercury cathode diaphragm cell was made without a leveling bulb attachment. A second stopcock was placed at A, Figure 1. In this cell new mercury can be used for each electrolysis. Only 15 ml of mercury are required. The data in Table 3 are from electrolyses of contaminated solutions.

It is evident that an electrolysis of uranium samples from the Purdue pilot plant for 30 minutes at 12 volts or 45 minutes at 6 volts is sufficient to reduce their iron content below 0.1 mg.

The satisfactory purification and recovery of uranium by mercury cathode electrolysis was established through analysis of uranium (VI)-sulfate solutions followed by analysis of similar samples contaminated with 5 mg of cupric and 5.6 mg of ferric ion. The pure sample contained 289.6 ± 0.2 mg U/g sample while the contaminated samples analyzed to contain 289.5 ± 0.2 mg U/g sample. Thus a recovery of 99.95% was realized when 0.4 g samples of uranium were electrolyzed 45 minutes at 6 volts in the mercury cathode diaphragm cell.

Table 1

ELECTROLYSIS OF URANIUM SOLUTIONS CONTAINING IRON

Sample No.*	Volts	Amp.	U mg	Fe mg	Total time min ^{xx}	Fe left mg	Fe removed g/min	Fe removed %
1	8	0.8-1	250	250	120	0.3	0.0021	99.88
2	8	0.8	250	250	150	0.2	0.0018	99.92
3	8	0.8	200	50	120	0.17	0.00044	99.77
4	8	0.9-1.1	200	50	90	0.18	0.00055	99.96
5	8	0.9-1	200	50	90	0.11	0.00055	99.98
6	8	1.	200	25	120	0.025	0.00021	99.99
7	8	0.8-1	200	25	90	0.035	0.00028	99.99

x All samples 1 N in H_2SO_4

xx Hg surface area, 16 cm²

Table 2

ELECTROLYSIS OF URANIUM SOLUTIONS CONTAINING CHROMIUM

Sample No. x	Volts	Amp.	U mg	Cr mg	Total time, min xx	Cr left, mg	Cr removed g/min	Cr removed %
1	8	0.8-1	200	50	195	1.0	0.00025	98.0
2	8	0.9-1	200	50	120	1.6	0.00040	97.2
3	8	0.8-1	200	25	120	0.28	0.00021	98.9
4	8	0.8-1	200	25	105	2.2	0.00024	91.2

x All samples 1 N in H_2SO_4

xx Hg surface area, 16 cm^2

Table 3
ELECTROLYSIS OF URANIUM SOLUTION

Sample Content,	mg	Sample No.	Volts	Amp	Total time, min **	Fe left, mg
U(VI)	400	1*	5-6	0.6-.8	30	0.27
Cu ⁺²	10.5	2	5-6	0.6-.8	30	0.48
Fe ⁺³	2.0	3	5-6	0.6-.8	45	0.04
Cr ⁺³	0.35	4	5-6	0.6-.8	45	0.02
Ni ⁺²	0.15	5	5-6	0.6-.8	60	0.02
Mg ⁺²	0.15	6	5-6	0.6-.8	60	0.01
Pb ⁺²	0.15	7	10-12	1-2	45	0.08
M ⁺²	0.15	8	10-12	1-2	45	0.06

* All samples 1 N in H_2SO_4

** Hg surface area, 13 cm²

SUMMARY

A modified mercury cathode cell having a separate^a anode compartment has been designed and tested. This cell permits the simultaneous purification and reduction of uranium solutions in preparation for subsequent titration. The rate of removal of various impurities (principally iron and chromium) has been studied and the conditions for the purification of Purdue pilot-plant samples have been established. (anal)

Reference

- (1) Pavlish and Sullivan, Metals and Alloys 11, 56 (1940)

0-10

[illegible]

•

Abstract

Journal of Management Education 30(6)