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Anion Exchange Separation of Uranium From Reactor Dissolver Solutions

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ABSTRACT

Uranium was separated from synthetic stainless steel type dissolver solutions by use of an anion-exchange resin column. The uranium was then titrated coulometrically in sulfate media. Relative standard deviations of 0.69% for samples containing 0.8 mg. and 0.15% for 8 mg. of uranium were found by precision studies.

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ANION EXCHANGE SEPARATION OF URANIUM FROM REACTOR DISSOLVER SOLUTIONS

E. L. Blevins

I. PURPOSE

To develop a method for the determination of uranium in certain reactor dissolver solutions which is accurate, precise, practical for use with highly radioactive materials, and which can be easily run with remote facilities.

II. EXPERIMENTAL

A. Instrumentation

The "Mark I" Controlled-Potential Coulometric Titrator was used for these tests. The titration cell is composed of a 50 ml. beaker from which the top part has been cut until it is approximately 1 1/2" tall. This is covered with a Teflon cap through which the electrodes were fitted.

B. Preparation of Resin Column

Dowex A1 x 8 (200-400 mesh) resin was used in these experiments. Prior to use the resin was treated by washing consecutively with the following reagents:

1. H_2O
2. Acetone
3. Alcohol
4. 6 M HCl
5. 5 M KOH or NaOH
6. 6 M HCl
7. H_2O

However, if analytical grade resin can be obtained, the treatment step may be eliminated. Next, the columns were prepared using approximately 3 ml. of resin for each.

C. Procedure

1. Take an aliquot of the sample (1-5 ml depending on concentration of U) and evaporate to dryness. Do not bake.

2. Take up in 10 ml. of 0.1 M H_2SO_4 and evaporate to dryness again.

3. Take up in approximately 15 ml. H_2O, and add 20 drops of a 5% $NH_2OH \cdot HCl$ solution.

4. Wash the column with 20 ml. of 1.0 M H_2SO_4 solution and 15 ml of 0.01 M H_2SO_4 solution.

5. Transfer the sample to the column. Wash with 30 ml. of 0.01 M H_2SO_4 solution.

6. Add 10 ml. of 10 M HCl solution to the column, then 10 ml. of 6 M HCl solution.

7. Elute into the titration cell with 35 ml H_2O containing 1 drop of conc. HCl.

8. Evaporate to dryness, then take up in 10 ml. of 0.5 M H_2SO_4 solution.

9. Titrate coulometrically at +0.085* v vs SCE and at -0.325 v vs SCE.

10. Note the readout voltage for the reduction electrolysis at -0.325 v and calculate the amount of uranium titrated.

* Note: This titration (at + 0.085 v vs SCE) reduces any traces of Fe+3 that might have carried through the separation.

III. DISCUSSION AND RESULTS

The tests run during the course of this experiment were to determine whether U(VI) can be successfully separated from the other components of stainless steel type reactor dissolver solutions by an anion exchange column and, subsequently, titrated coulometrically. For this purpose, a synthetic stainless steel dissolver solution was obtained from B. J. Ginocchio of the following composition in dilute aqua regia:

18-20% Cr
8-10% Ni
2% max. Mg
1% max. Sr
0.08% max. C
0.8% max. Co
60-61% Fe
6-7% U

According to the data of Kraus and Nelson (1) the HCl system appeared to be the most convenient to use since U(VI) is both quantatively adsorbed and easily eluted from this medium. However, the use of anion resin in the chloride form presented some problems as the study progressed. The first problem was due to the fact that the concentration of chloride in the eluent could not be tolerated in the coulometric titration. An anodic current was noted during the pretitration when an overtolerence of chloride ion was present. Therefore, a series of standards was run containing varying amounts of chloride with the following results:

TABLE I

Effect of Chloride Concentration on the Coulometric Titration of Uranium*

HCl Added (microliters)	Pretitration Potential (volts)	Mg. U Found	% Error
—	+0.125	11.91	0.00
200(0.23 M)	+0.075	11.91	0.00
300(0.35 M)	none	12.01	0.91
500(0.58 M)	none	12.04	1.08
1000(1.2 M)	none	12.05	1.17

* A one ml. sample containing 11.93 mg U/ml in 10 ml. of 0.5 M H_2SO_4 was titrated.

The data in this table indicate that the error increases as the chloride concentration becomes greater and only about 0.25 M chloride in the cell can be tolerated. After unsuccessful attempts to separate the chloride by precipitation, it was decided to evaporate the eluent and redissolve the residue in 0.5 M H_2SO_4.

The work of Kraus and Nelson also indicated that U(VI) and Fe(III) cannot be separated with anion resin in an HCl medium. This is a necessary step since Fe(III) constitutes an interference when present in any considerable amount ($>$200 μg) during a coulometric titration. Therefore, the U(VI) is converted from the sulfate form to the chloride after it has been adsorbed on the column, since the Fe(III) does not adsorb from the sulfate medium. Cr(VI) which presented another interference was eliminated by reduction with $NH_2OH \cdot HCl$ before passing the sample through the column.

The results of this study are shown in the following table:

TABLE II

Precision of Resin Separation - Coulometric Titration of Uranium

Sample	Mg. U Taken	Mg. U Found	No. of Titrations	Relative Standard Deviation, %
U Std.	11.93	11.89	9	0.3
U Std.	2.65	2.64	7	0.5
Syn. Dissolver	8.88	8.92	12	0.2
Syn. Dissolver	0.854	0.855	14	0.7

IV. CONCLUSION

Uranium can be successfully separated from stainless steel type dissolver solutions with anion resin. The method presented here appears to be accurate and precise for concentration ranges of 0.8 - 12 mg. U/ml.

References

1. Kraus, K. A. and Nelson, F., Symposium on Ion Exchange and Chromatography in Analytical Chemistry, Special Technical Publication No. 195.

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