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SUBJECT: Hexone Extraction-Coulometric Titration of Uranium

TO: See Distribution

FROM: E. L. Blevins

ELB-3

ABSTRACT

Samples containing 5 to 10 mg of uranium were extracted with hexone (methyl isobutyl ketone) and titrated coulometrically in sulphate media. Relative standard deviations of 0.43% for samples containing 5 mg and 0.56% for 10 mg were determined by precision studies.

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HEXONE EXTRACTION-COULOMETRIC TITRATION OF URANIUM

E. L. Blevins

I. PURPOSE

To develop a method for the determination of uranium in reactor dissolver solutions which is specific, relatively free from interferences, practical for use with highly radioactive materials, and which can be run in a reasonably short length of time.

II. EXPERIMENTAL

A. Instrumentation

The "Mark I" Controlled Potential Coulometer was used for these tests. The extraction cell is composed of a 25 mm test tube with a glass rod mounted on a mechanical stirrer entering through the top. The titration cell has been described previously.(1)

B. Reagents

1. Aluminum Nitrate Salting Solution. This acid deficient solution was prepared according to the directions given by Booman, et al.(2)

2. Hexone (methyl isobutyl ketone). This reagent (Matheson Coleman and Bell 56M) was obtained from ORNL stores, washed with 1 M HCl, and pre-equilibrated with the acid deficient aluminum nitrate prior to use in order to allow for volume change.

C. Procedure

1. Transfer 5 ml $Al(NO_3)_3$ salting solution, 5.0 ml pre-equilibrated hexone, and 1.0 ml aliquot of the U sample to extraction cell.

2. Stir mechanically for 5 min (10 min for a 10 mg U sample). Allow phases to separate and remove a 4.0 ml aliquot from organic phase to the titration cell.

3. Evaporate to dryness under an infra-red heat lamp and "Flame" over a Mecker burner for 5 min to destroy last traces of organic material.

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4. Dissolve residue in 20 drops 1:2 HNO_3 and evaporate to dryness. Cool and add 10 more drops HNO_3. Evaporate to dryness again to be sure that all the oxide has been converted to nitrate.

5. Take up in 4 drops conc. H_2SO_4, and add 4 drops conc. HCl to eliminate nitrate interference. Evaporate to H_2SO_4 fumes.

6. Cool, add 5 ml 1 N H_2SO_4, and heat until hot but not boiling.

7. Cool, add Hg for the cathode, and deaerate for 5 min.

8. Pretitrate at +0.125 v vs. Ag-AgCl electrode and titrate the uranium at -0.3 v vs. Ag-AgCl electrode.

III. DISCUSSION AND RESULTS

At the present time much work is being done toward developing methods for the determination of uranium in highly radioactive dissolver solutions. One such method developed by Booman and Holbrook(3) is based on the fact that uranium may be almost specifically and quantitatively extracted from such solutions with methyl isobutyl ketone. The uranium was then titrated coulometrically in a citrate medium.

The purpose of the tests run during the course of this experiment was to modify that method so that the titration could be done in a sulphate medium and to shorten the time involved. The data in Table 1 indicate that this modified method has good possibilities as a means of determining uranium in nuclear fuel solutions. To date, no work has been done along this line, but this will be the next consideration.

Samples containing up to 10 mg of uranium may be successfully extracted and titrated by the method presented in approximately one hour. Approximately 5 mg of uranium seems to be the optimum amount to run since the $Al(NO_3)_3$ salting solution was made up for samples of this size. Larger amounts may be extracted by increasing the tetrapropylammonium hydroxide concentration in the salting solution, but this also increases the fission product extraction. There is also the possibility that one may be nearing the saturation point of the organic phase. Also, the precision of this method could probably be improved by making improvements in the titration cell and by decreasing the variation in the temperature at which the samples are run. The data obtained by use of a conventional titration cell support these latter statements.

Table 1

Results of Precision Studies

mg U Taken	Ext'd	Cell	N	o , %	Error, %
5.44	No	Vycor	14	0.18	none
5.44	Yes	Vycor	17	0.43	-0.8
10.31	No	Vycor	9	0.16	none
10.26	Yes	Vycor	14	0.56	-0.5
10.54	No	Conventional	9	0.17	none
10.53	Yes	Conventional*	13	0.38	none

N Number of samples
* The solution was transferred to this cell for titration.

IV. CONCLUSION

The original hexone extraction-coulometric titration for uranium can be shortened considerably by the procedure given herein. It should prove to be a useful supplement to other uranium methods which are being studied as part of the dissolver program because this method is reported to be almost specific for uranium. However, it is felt that the procedure can be further improved, and this is planned before application to actual dissolver solution samples is undertaken.

References

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