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Coulometric Determination of Uranium in the 100-500 μg Range

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ABSTRACT

An endeavor was made to increase the sensitivity of the coulometric determination of uranium to the range of sample concentrations of 100-500 μg uranium per milliliter. This report shows the results of two phases of this work. The first phase which was titrating contamination free uranium samples, was reasonably successful. However, the second phase which was the separation of the uranium from the contaminants to be found in power reactor fuel dissolver solutions, and the subsequent titration of the uranium, was not successful below the range of sample concentration of one milligram uranium per milliliter.

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I. INTRODUCTION

The proposed sampling schedule for the PRFR interim operation for building 4507[1], showed that in the Raw Feed Preparation, samples submitted to the 3019 Pilot Plant Control Laboratory could possibly contain a mixture of 12 M HNO_3, 250 mg/ml Th, 0.5 mg/ml U. Previous work has been done on dissolver solutions with a more favorable uranium concentration[2], and consequently no coulometric procedure existed which would analyze dissolver solutions of this concentration.

It was desired that one coulometric analytical set-up inside the HRLAF would be able to handle any variety and concentration of the power reactor fuel dissolver solutions submitted. It was decided to apply the existing techniques and equipment to the determination of uranium in these proposed samples.

The changes made to the ORNL Mark III Controlled-Potential Coulometer will be enumerated in a later section. However, the coulometer had to be able to integrate a larger amount of cell current, and be more stable than on previous work.

The concentrations of the proposed samples eliminated the possibility of taking an aliquot directly into the coulometric cell. Consequently, a separation technique had to be developed by which the uranium could be introduced into the titration cell in a form so that a quantitative electrolytic reduction of the uranium could take place.

II. INSTRUMENTATION

A. ORNL Mark III Controlled-Potential Coulometer

1. In order to titrate uranium in the range of 100-500 μg, the sensitivity of the ORNL Mark III Controlled-Potential Coulometer

was increased by a factor of ten. This was accomplished by an additional circuit to the integrator in which the input resistor was decreased from 400 K ohms to 40 K ohms. This new circuit could be activated from a switch on the front of the coulometer, and would allow ten times the normal cell current to be integrated.

2. With this higher sensitivity, the grounded leads in all sections of the coulometer had to be re-grounded to a common buss.

3. Preliminary work indicated that the controlled-potential supply circuit did not act satisfactorily, and it was eventually replaced by a standard mercury cell.

After these changes were made, the general performance of the coulometer was good. However, the drift had to be calculated and adjusted each day. Current surge at the beginning of each titration remained a problem, but was reduced by starting the titration at a lower potential and then adjusting the correct potential after cell-current was established.

B. Titration Cell, Extraction Apparatus

The titration cell and extraction apparatus were not changed from that already reported[2].

III. EXPERIMENTAL

As previously mentioned, the titration of contamination free uranium standards was reasonably successful and the data on this phase of work will be presented in the next section.

The larger amount of work was concerned with the separation of the uranium from the samples to be submitted for analysis. The previous

work involved solvent extraction using tri(iso-octyl)amine as the organic solvent. This technique and the techniques of separation by anion resin and hexone extraction were investigated as possible means of separating the uranium in these particular samples.

For clarity, each of the techniques will be discussed individually.

A. Hexone Extraction

As previously reported by Blevins[3], hexone was successfully used as an organic extractant for the separation of uranium from dissolver solutions, and the eventual determination of the uranium by a coulometric method. However, the samples used in developing the method contained uranium in concentrations of at least 5 mg/ml. Also the method called for the complete destruction of a hexone aliquot in order to make the separation compatible to a coulometric determination.

Samples with uranium concentrations of less than 500 μg, however, in order to completely destroy the organic aliquot, the techniques that have to be used are detrimental to the complete containment of the uranium. But the incomplete destruction of the organic aliquot, and insuring the retention of the uranium, results in an incompatible sample that cannot be analyzed by coulometric means. Also, at this low level of uranium concentration, a coulometric reduction is very sensitive to organic interferences.

For these reasons it was decided that a hexone separation together with the coulometric titration was not satisfactory for application to samples containing less than 500 μg u/ml.

B. Resin Separation

Reactor fuel dissolver solutions were successfully analyzed by Blevins using anion exchange separation of the uranium[4]. Here again, however, the samples contained a much more favorable uranium concentration. Several factors prevented a favorable recovery of uranium from the proposed samples under discussion by use of anion exchange resins.

The first factor was the high concentration of HNO_3 (12 M) in the proposed sample itself. An aliquot of the sample not properly diluted with the appropriate medium, could cause improper separation or acid-attack on the resin. By diluting the sample aliquot, large volumes of liquid were involved; and consequently longer periods of time for the separation. Only fine mesh resin could be used to recover the uranium, and the flow rate through the resin was very slow.

Secondly, the mediums from which the uranium could be separated were limited. HCl is the one from which best results are obtained. However, the uranium containing effluent introduced into the coulometric titration cell has to be essentially free of chloride. At these low uranium concentrations, chloride causes a very serious catalytic effect. The removal of chloride to a level which would be compatible to a coulometric reduction, involved a series of acid cook-downs, and more often than not, you either lost some of the uranium, or did not completely rid the sample of chloride. Also involved in using the HCl absorbing medium, was the prospect of always having some thorium present. The NO_3^- content of the sample was enough to

cause some initial absorption of thorium, and to completely free the resin column of this contamination involved large volumes of HCl rinse, and extended times for the separation.

Ammonium sulfate was tried as the absorption medium. But 0.01 M $(NH_4)_2SO_4$ as the absorption medium was too easily upset by the strong acid concentration of the sample, and resulted in poor uranium recovery. To mask the acid of the sample would again involve large volumes of liquid and almost prohibitive time periods for the separation.

The third reason for the failure of the anion exchange-resins was that having to use fine mesh resin, there always appeared to be some organic material in the uranium containing effluent as previously mentioned, the coulometric determination was very sensitive to any organic contaminants, and again you were involved with the destruction of the organic material while still retaining the uranium.

C. Tri(iso-octyl)amine Separation

Most of the separation work was done using tri(iso-octyl)amine as a solvent extractant. It became apparent very early that there was some nitrate carry-over into the titration cell, presumably from the $Al(NO_3)_3$ used as the salting agent. The lower the uranium concentration that was being separated and coulometrically titrated, the greater the catalytic effect of this nitrate carry-over. A cook-down of the separated uranium to rid it of nitrate was prevented by the presence of thorium. Other salting techniques had to be investigated.

HCl was the most likely of the other salting mediums. However, it too was carried into the titration cell and gave as serious catalytic effects as the NO_3^-. Cook-down did not give satisfactory recovery, and was practically prohibited by the presence of thorium which was salted into the organic phase by the HNO_3 of the sample aliquot.

$AlCl_3$ was tried, but could not be made into a solution of molar strength concentrated enough to completely salt the uranium into the organic phase.

Aluminum acetate could not be made into a concentrated solution of enough molar strength.

Ammonium sulfate was too easily changed by the addition of the aliquot acid to be effective as a salting agent.

The combination of an $Al(NO_3)_3$ extraction, an ammonium sulfate wash prior to the back-extraction of the uranium into an aqueous phase, proved unsatisfacotry.

Along with the anionic interferences, there was also an organic carry-over involved in this solvent extraction. The combination of all these factors prohibits the coulometric determination of uranium, to any reasonable degree, of less than 500 μg which has been separated by means of TIOA solvent extraction. This, however, does not mean that the uranium cannot be extracted and recovered in essentially an aqueous phase. There is suitable evidence that this can be done. But it cannot be done in a way that a suitable coulometric determination can be made.

IV. DATA

A. To determine the ability to titrate uranium solutions in the range of 100-1000 μg, a standard uranium solution containing 1.003 mg u/ml was used. This standard was essentially free of any contaminants and contained stoichiometric amounts of HNO_3. A total of one hundred fifty-five analysis was done with the precision and accuracy at particular concentrations as follows:

	100λ	200λ	250λ	500λ	750λ	1000λ
Mg contained	0.1003	0.2006	0.2508	0.5015	0.7523	1.003
Mg found	0.1004	0.1998	0.2527	0.5039	0.7503	0.998
Error	+ 0.1 %	- 0.4 %	+ 0.8 %	+ 0.5 %	- 0.3 %	- 0.4 %
Relative S. D.	± 1.9 %	± 0.8 %	± 0.6 %	± 0.3 %	± 0.4 %	± 0.5 %
Limit of error	3.8 %	1.6 %	1.2 %	0.6 %	0.8 %	1.0 %

The procedure for these determinations was to add the particular aliquot of sample to 10 ml 1 N H_2SO_4, and titrate at - 0.300 v vs. S. C. E.

B. An extraction of this same uranium standard was attempted. The procedure consisted briefly of:

1. Addition of sample aliquot to 5 ml 1 N A. D* $Al(NO_3)_3$.
2. Extraction with 5% tri(iso-octyl)amine in xylene.
3. Back extraction of the uranium with 0.05 M $HClO_4$-1 N H_2SO_4.
4. Addition of ascorbic acid.
5. Adjustment of pH to 4.0.
6. Titration of the uranium at -0.400 v vs. S. C.E.

No satisfactory results were obtained. Estimations of errors at different levels of sample concentrations:

* A.D. - acid deficient

	Error	Relative S. D.
100 μg	> 20 %	> 20 %
250 μg	+ 3 %	± 9 %
500 μg	+ 2 %	± 4 %

C. All other data concerning the resin work and the hexone extractions, was unsatisfactory and will not be reported.

V. DISCUSSION

Using the present equipment and techniques for the coulometric determination of uranium in reactor fuel dissolver solutions, it has not been possible to successfully apply these techniques to the determination of uranium in concentrations of less than one milligram/milliliter. This is specifically true of samples of the CONED type, where the uranium to thorium ratio is very low, and the solutions are very high in HNO_3. It is true that the equipment can titrate such quantities of uranium, and such amounts can be successfully separated. But they cannot be separated in a way compatible to a coulometric determination.

It is possible that APPR type dissolver solutions in this range of concentration can be successfully separated and titrated, but this was not investigated.

Perhaps a redesigned cell where smaller volumes of electrolyte can be used, and a more sensitive controlled-potential coulometer would enable a coulometric technique to be developed in the 100-500 μg range of concentration of uranium.

VI. CONCLUSION

For the analysis of the samples to be submitted to the 3019 Pilot Plant Control Laboratory by the 4507 interim operation in which the solutions have the concentrations as previously outlined, I recommend that a spectrophotometric analysis of the uranium be done in preference to a coulometric type of analysis.

VII. REFERENCES

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