



Constant Potential Coulometry for the Determination of Uranium in
a Pilot Plant.

Fátima Maria C de Sequeira and Alcidio Abrão

Centro de Engenharia Química, INSTITUTO DE PES
QUISAS ENERGÉTICAS E NUCLEARES (IPEN), Caixa /
Postal 11049, São Paulo, BRASIL.

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INTRODUCTION

Nuclear grade natural or enriched uranium oxide is widely used as a nuclear fuel, either alone or mixed with other oxides, such as thorium and plutonium oxide. In an uranium purification plant it is often necessary to determine the concentration of total uranium present in the yellow-cake, in several solutions, in nuclear grade ammonium diuranate and nuclear grade uranium oxides.

Primary direct coulometric analysis at constant electrode potential and coulometric titrations are of great importance for the determination of uranium at the milli- and microgram-level. Precision and accuracy are excellent, which make this electroanalytical technique of paramount importance for the quantitative uranium analyses. The direct coulometric titration is preferred because it eliminates the need for standard solutions, the use of metal reductors and end-point electrode system, the titration being complete when the background current is attained.

The total uranium, as U(VI), was coulometrically determined according to the procedures described by R.M. Rush /1/ and Mountcastle et alii /2/. A study was made to adapt both procedures to the uranium determination in the streams of the IPEN's Uranium Pilot Plant. Although both methods using 0.5M H_2SO_4 (Rush) and 0.75M NaF (Mountcastle et alii) as supporting electrolyte give equally good results, the first was preferred as advantageous and used more often in our laboratory.

Before the application of the coulometric analysis as a routine basis a study was made of the effects of thorium, copper, cadmium and molybdenum as interferences.

EXPERIMENTAL

Apparatus

All data were obtained with a Princeton Applied Research (PAR) Potentiostat/Galvanostat Model 173 with a Digital Coulometer Model 179. The coulometric cell system Model 377 (PAR) has a 50 ml. capacity and holes through which are inserted a gas inlet tube for bubbling nitrogen over the surface and through the solution; two porous Vycor tubes which contained the platinum counter electrode and a junction salt bridge for insertion of the

S.C.E.; the synchronous stirring motor with a glass stirrer and the mercury pool working electrode. The Vycor tube and the salt bridge were filled with 0.5M H_2SO_4 or 0.75M NaF when the supporting electrolyte was the respective solutions. Water-saturated, high-purity nitrogen was inlet either over the surface of or through the sample solution.

REAGENTS

Mercury - The mercury that was used as the working electrode for the uranium titrations had been treated with 10% HNO_3 , washed with water, dried and distilled once under vacuum. For each analysis an aliquot of 5-7 ml. was filtered through a dry filter paper and then carefully rinsed with 0.5M H_2SO_4 before admission to the coulometric cell.

Nitrogen - High-purity nitrogen gas was used to deaerate all solutions before electrolysis and all electrolyses were made under an oxygen-free atmosphere. For this purpose the nitrogen was further purified before entering the coulometric cell by passage through two scrubbing flasks that contained $CrCl_2$ - solution in contact with 2% Zinc-amalgam and through a third one that contained distilled water.

Uranium standard solutions - Standard uranyl sulfate solutions were prepared to contain U(VI) at the concentration levels of 0.05-0.5 mg. ml^{-1} in 0.5M H_2SO_4 . These solutions were prepared from IPEN's Pilot Plant primary standard U_3O_8 obtained by calcination of nuclear grade ammonium diuranate. The oxide was dissolved with 1:1 HNO_3 and transformed into uranyl sulfate by fuming with sulfuric acid and finally diluted with H_2SO_4 . Uranyl sulfate in 0.5M H_2SO_4 was standardized after its reduction to U(VI) with $SnCl_2$ by titration with dichromate according to the procedure described by Main /3/.

Uranium samples - Ammonium diuranate and sodium diuranate samples were dissolved directly with sulfuric acid and diluted to have a final concentration of 0.5M H_2SO_4 ; aliquots of uranyl nitrate solutions from the Pilot Plant were treated with sulfuric acid to fumes and then appropriately diluted.

Other reagent grade chemicals were used as supplied.

PROCEDURE

(a) With 0.75M NaF supporting electrolyte.

For the coulometric titration using fluoride as supporting electrolyte add to the cell 10 ml of 0.75M NaF and aliquot of uranyl sulfate estimated to contain from 150 to 800 μg U. Adjust the pH to the 6.5 - 7.0 range with 1.0M NaOH or 0.5M H_2SO_4 and with the aid of a pH meter. Wash the electrode with a minimum amount of 0.75M NaF.

Add a measured amount of (5 to 7 ml.) of mercury to the coulometric cell. Bubble a nitrogen stream to the solution during 5 minutes and maintain a nitrogen atmosphere over the analyte solution during the electrolysis. Prerreduce the solution at - 0.300 volt vs S.C.E. until the current again decreases to 50 μA . Reduce the U(VI) at -1.000 volt vs S.C.E. until the current again decreases to 50 μA .

(b) With 0.5M H_2SO_4 supporting electrolyte.

Previously wash the mercury with 0.5M H_2SO_4 . Add 5-7 ml. of mercury to the coulometric cell. Add 10 ml. of 0.5M H_2SO_4 . Pipet an uranium aliquot estimated to contain from 300 to 800 μg U. Remove the oxygen from the solution with nitrogen as described above. Prerreduce the solution at + 0.085 volt until the current decreases to 50 μA , then zero the integrator. Reduce the hexavalent uranium at - 0.325 volt vs S.C.E. until the current reaches again 50 μA .

In both cases the solution is agitated with the stirrer placed at the mercury-solution interface and located to give maximum agitation of the solution and mercury surface without splashing. All analyses were done at room temperature ($25 \pm 2^\circ\text{C}$).

RESULTS

Three series of uranium titrations was run at the 0.150, 0.300, and 0.780 mg U level, using 0.75M NaF as the supporting electrolyte. Total electrolysis time varied from 25 to 70 minutes. The results are in table I.

TABLE I

Coulometric determination of uranium (VI) using 0.75M NaF as supporting electrolyte.

Nr of titrations	U(VI), μg		Std. dev.	Average time/ titration min.
	taken	found		
7	772,24	778,19	0,22	75
5	309,00	311,64	0,24	48
5	154,45	151,06	0,50	28

Three series of uranium titration was run at the 0.380, 0.580 and 0.770 mg U as well. Total electrolysis time / varied from 42 to 68 minutes. The results are in Table II.

TABLE II

Coulometric determination of uranium (VI) using 0.5M H_2SO_4 as supporting electrolyte.

Nr of titrations	U(VI), μg		Std. dev.	Average time/ titration min.
	taken	found		
7	772,40	772,54	0,025	63
7	575,92	578,57	0,25	53
7	386,20	386,46	0,018	50

Results obtained in the present study indicate that the reasonable workable uranium range is 150-800 μg U. For lower amounts than 150 μg the results are erratic and for levels / higher than 800 μg the total electrolysis time is disadvantageously long.

Copper, cadmium, molybdenum and thorium were studied as the main interferences in the coulometric determination of uranium (VI). For copper, the results allowed to conclude that this element does not interfere until the maximum of 14 ppm Cu/U, beyond this level the presence of copper give lower uranium results.

Cadmium gave good results at the maximum concentration of 35 ppm Cd/U, lower results for uranium being encountered at higher level of cadmium.

Good results for the determination of uranium in the presence of thorium were attained until 168 ppm Th/U. Higher level of thorium is still being studied.

Molybdenum as interference was studied at, 8, 16, 26 ppm Mo/U. level. Good results were found until the maximum level

of 15 ppm NO₂/U, beyond this ratio high results for uranium were found.

DISCUSSION AND CONCLUSION

Results obtained in the present work indicate that the use of NaF as supporting electrolyte is less convenient although allowed to determine uranium at a lower level than in the H₂SO₄ system. On the other hand the use of fluoride has the inconvenience of that the coulometric cell is attacked and the Vycor tubes don't last for long and, still worse, the fritted glass disks of the bridges are damaged quite frequently.

Although no interference from low level of thorium was observed, in the fluoride medium it is precipitated. Besides that, working at high pH, the uranium itself is precipitated.

Coulometric titration of uranium in sulfuric acid proved to be most convenient and easier if a great number of samples must be run, avoiding the pH adjustment.

Titration of uranium in high-purity samples presented no problem. Probably most metallic interference at very low level, as it is the case of nuclear grade uranium, are nullified during the prereduction, avoiding previous chemical separation.

The first results obtained for the titration of uranium in a yellow cake produced from monazite sand shown that it is not possible to analyse uranium without a previous chemical purification. Further studies are scheduled to attain the coulometric determination of uranium in this uranium concentrate and other impure uranyl solutions.

In conclusion it can be said that the direct coulometric titration of uranium at controlled-potential is feasible and very useful for nuclear grade uranium (solutions, DUA and oxides) but for raw materials, like yellow-cake and crude uranyl solutions previous chemical purification seems to be unavoidable.

LITERATURE CITED

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