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CONTROLLED-POTENTIAL COULOMETRIC TITRATION OF URANIUM(VI) IN THE PRESENCE OF NITRATE

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ABSTRACT

A study into the use of sulfamic acid as a nitrite-destroying reagent in the controlled-potential coulometric titration method for uranium(VI) has been made. When nitrites are thus destroyed, the titration is much less subject to error from HNO_3 . The results of titrations of known amounts of uranium(VI) in the presence of various amounts of HNO_3 , $\text{Th}(\text{NO}_3)_4$, $\text{Al}(\text{NO}_3)_4$, and LiNO_3 are given.

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I. Introduction

The controlled-potential coulometric titration of uranium(VI) is generally reported to be subject to interference from small amounts of nitric acid.^(1,5) Accordingly, it is common practice to maintain as low a nitrate ion concentration in the supporting medium as is practical, either by taking a small test portion or by removing nitrate from the sample by fuming with sulfuric or perchloric acid before the titration is made. Fuming and transfer operations are troublesome and may lead to error in the determination, particularly when such operations are done remotely. Thus, a simple means for increasing the tolerance of the controlled-potential coulometric titration method for uranium(VI) toward the nitrate ion is desirable.

Stability studies of uranium(IV) nitrate solutions in HNO_3 ^(2,3) have established that tetravalent uranium is relatively stable when (1) the nitric acid concentration is kept low, ca. 3 M or less, (2) the temperature is maintained at room temperature or less, and (3) a reagent such as sulfamic acid or urea is added to destroy traces of nitrites. It is likely therefore that the errors that are experienced when U(VI) is coulometrically titrated in the presence of HNO_3 are due not to nitrate but rather to the nitrites which are often present in small and varying amounts as a result of decomposition of nitric acid. This being the case, the controlled-potential coulometric titration method for uranium(VI) determination could be made more tolerant to the presence of nitric acid by including a nitrite-destroying reagent in the supporting electrolyte solution. This report presents the results obtained when sulfamic acid was used for that

purpose. Sulfamic acid was chosen because it reacts rapidly and quantitatively with nitrite, because the reaction products (nitrogen and sulfuric acid) are not detrimental to the titration, and because it has been used successfully in a similar application: the controlled-potential coulometric titration of plutonium.^(4,6)

II. Apparatus and Reagents

The ORNL Model Q-2005 electronic controlled-potential coulometric titrator was used for this work. The titration vessel was conventional.

Two uranyl sulfate solutions were used: the first contained 6.19 mg/ml and the second contained 11.16 mg/ml, uranium(VI) in 0.5 M H₂SO₄. The amount of uranium(VI) titrated in all cases was 6.19 mg or 5.58 mg. Total solution volume was constant at 10 ml. Each series of results presented below contains the average result of several titrations of the uranium(VI) standard; subsequent results in a given series should be compared with that value. This is necessary because different instruments, cell assemblies, operators, and standard solutions were used in obtaining these data.

III. Procedure

1. Place approximately 5 ml of 0.5 M H₂SO₄-0.1 M NH₂SO₃H in the titration vessel.
2. Pipet into the solution a test portion that is estimated to contain 5 to 10 mg of uranium.
3. Dilute to ~10 ml with 0.5 M H₂SO₄-0.1 M NH₂SO₃H and swirl the solution to ensure thorough mixing.
4. Place approximately 7 ml of mercury in the titration vessel.

5. Sparge the solution with helium for 5 minutes
6. Prerreduce at +0.075 volt until the current decreases to 50 μ a.
7. Zero the integrator.
8. Reduce at -0.325 volt until the current decreases to 50 μ a.
9. Read and record the readout voltage.

IV. Data

Polarograms were run on 473 μ g of U(VI) in 10 ml of supporting electrolyte solutions that contained various concentrations of sulfuric, sulfamic, and nitric acids. The half-wave potential values taken from these curves are given in Table I (no corrections applied).

Table I

Polarographic Half-Wave Potentials—Reduction of
U(VI) in H₂SO₄, NH₂SO₃H, and HNO₃ Mixtures

<u>Composition of Medium</u>			<u>E_{1/2}</u>
<u>H₂SO₄, M</u>	<u>NH₂SO₃H, M</u>	<u>HNO₃, M</u>	<u>Volt vs S.C.E.</u>
0.5	-	-	-0.24
0.5	0.1	-	-0.24
0.5	0.5	-	-0.24
-	1.0	-	-0.24
0.5	0.1	1.0	-0.24
0.5	0.1	3.4	-0.19

The presence of sulfamic acid thus does not alter the potential at which uranium(VI) is reduced. This is supported also by the data in Table II, the results obtained when known quantities of uranium(VI) were titrated coulometrically in the presence of various concentrations of NH₂SO₃H and H₂SO₄.

Table II

Results of Coulometric Titration of
U(VI) in H₂SO₄, NH₂SO₃H Media

Composition of Medium		U(VI), mg	
<u>H₂SO₄, M</u>	<u>NH₂SO₃H, M</u>	<u>Taken</u>	<u>Found</u>
0.5	-	6.19	6.17
0.5	0.05	6.19	6.17
0.5	0.1	6.19	6.17
0.5	0.2	6.19	6.17
0.5	-	5.58	5.59
0.5	1.0	5.58	5.60
-	1.0	5.58	5.61

Table III

Results of Coulometric Titration of U(VI)
in Presence of HNO₃

(Electrolyte = 0.5 M H₂SO₄, 0.1 M NH₂SO₃H.
Volume = 10 ml)

<u>HNO₃ Present,</u>	<u>U(VI) Found,</u>	<u>Error,</u>
<u>M</u>	<u>mg</u>	<u>%</u>
0	6.16	
1.2	6.16	0.0
1.6	6.15	-0.16
2.4	6.15	-0.16
3.2	6.18	+0.32
4.8	6.15	-0.16
6.4	6.23	+1.1

Table IV

Results of Coulometric Titration of U(VI)
in Presence of $\text{Th}(\text{NO}_3)_4$

(Electrolyte = 0.5 M H_2SO_4 , 0.1 M $\text{NH}_2\text{SO}_3\text{H}$.
Volume = 10 ml.)

<u>Th(NO₃)₄ Present,</u> <u>M</u>	<u>U(VI) Found,</u> <u>mg</u>	<u>Error,</u> <u>%</u>
0	5.60	
0.1	5.60	0.0
0.2	5.61	+ 0.18
0.4	5.60	0.0
0.6	5.60	0.0
0.8	5.62*	+ 0.35
1.8	5.60*	0.0

* $\text{Th}(\text{SO}_4)_2$ precipitates.

Table V

Results of Coulometric Titration of U(VI)
in Presence of LiNO_3

(Electrolyte = 0.5 M H_2SO_4 , 0.1 M $\text{NH}_2\text{SO}_3\text{H}$.
Volume = 10 ml.)

<u>LiNO₃ Present,</u> <u>M</u>	<u>U(VI) Found,</u> <u>mg</u>	<u>Error,</u> <u>%</u>
0	6.16	
0.13	6.17	+ 0.16
0.25	6.19	+ 0.48
0.5	6.20	+ 0.64
1.0	6.23	+ 1.1

Table VI

Results of Coulometric Titration of U(VI)
in Presence of $\text{Al}(\text{NO}_3)_3$

(Electrolyte was 0.1 M $\text{NH}_2\text{SO}_3\text{H}$ and the indicated
concentration of H_2SO_4 . Volume = 10 ml.)

<u>$\text{Al}(\text{NO}_3)_3$</u> <u>Present, M</u>	<u>Uranium(VI) Found, mg</u>		
	<u>0.5 M H_2SO_4</u>	<u>2.5 M H_2SO_4</u>	<u>5.0 M H_2SO_4</u>
0	6.17	6.17	5.60
0.05	6.19	6.18	5.60
0.1	6.18	6.18	5.61
0.15	-	-	5.62
0.2	6.26	6.24	5.62
0.4	6.53	6.34	5.66
0.6	-	-	5.68

Tables III-VI present the results obtained when uranium(VI) was titrated in the presence of various amounts of HNO_3 , $\text{Th}(\text{NO}_3)_4$, LiNO_3 , and $\text{Al}(\text{NO}_3)_3$. Each result is the average of three to six titrations. Table VI also contains the results obtained when U(VI) was titrated in the presence of various amounts of $\text{Al}(\text{NO}_3)_3$ in media containing increased concentrations of H_2SO_4 , viz., 2.5 and 5.0 M.

V. Discussion

A. Order of Addition. Any nitrites present in the test portion should be destroyed before the cathode material (mercury) is added, thus the order in which reagents are added is important. A saturated solution (~ 2 M) of sulfamic acid can be added dropwise to the test portion in 0.5 M H_2SO_4 or the test portion can be added to an electrolyte solution which has been prepared to contain sulfamic acid of the desired concentration, e.g., 0.1 M. The electrolyte solution should then be

mixed thoroughly before mercury is added; no further delay is necessary because the reaction between nitrite and sulfamate is quite rapid.

B. Concentration of Sulfamic Acid. A sulfamic acid concentration of 0.1 M (in the solution being electrolyzed) was used in this study. However, sulfamic acid concentration is not critical (Table II) so long as enough is added to completely destroy the amount of nitrite that is present. Furthermore, the presence of sulfamic acid is not deleterious when nitrite or nitrate is absent.

C. Titration in the Presence of HNO₃. An old, slightly discolored solution of concentrated HNO₃ (reagent grade) was used to prepare the supporting electrolyte solutions listed in Table III because it should be more representative of sample solutions in general. It was possible to titrate 6.19 mg U(VI) in the presence of as much as 0.6 M of this HNO₃ with no NH₂SO₃H present. When sulfamic acid was present to the extent of 0.1 M, it was possible to titrate uranium(VI) in the presence of as much as 5 M of this HNO₃. Mercury was attacked when the HNO₃ concentration exceeded 5 M and resulted in extended titration times and high answers.

The effectiveness of sulfamic acid against nitrite interference was also checked by titrating uranium(VI) in the presence of NaNO₂ and in the absence of HNO₃. Uranium(VI) could not be titrated in the presence of as little as 2.5×10^{-4} M NaNO₂ in the absence of NH₂SO₃H, but could be titrated normally in the presence of 0.005 M NaNO₂ if the supporting electrolyte solution was made 0.1 M in NH₂SO₃H.

D. Titration in the Presence of Nitrate Salts. Tables IV through VI present the results obtained when U(VI) was titrated in the presence of the nitrates of Th, Li, and Al. The electrolysis medium used for all of

these titrations was 0.5 M H₂SO₄-0.1 M NH₂SO₃H, except where noted.

Thorium nitrate does not interfere below 0.6 M. Greater concentrations of Th(NO₃)₄ are permissible but not recommended because the titration is complicated by precipitation of slightly soluble Th(SO₄)₂. Lithium nitrate does not interfere when its concentration is 0.5 M or less, but larger concentrations cause high results. Similarly, high results were obtained when the Al(NO₃)₃ concentration exceeded 0.1 M in a medium containing 0.5 M H₂SO₄-0.1 M NH₂SO₃H.

These latter two limits are surprising in view of the larger amounts of nitrate that can be present as HNO₃ or Th(NO₃)₄. Similar errors were caused by Al(NO₃)₃ in the absence of sulfamic acid and by Al₂(SO₄)₃, yet blank titrations were not significantly different when Al(NO₃)₃ was present or absent. Consequently, the errors are not attributable to impurities in the Al(NO₃)₃ or to the presence of nitrate. More probably, error is the result of slower disproportionation of UO₂⁺ when large amounts of aluminum are present. This effect would be minimized by increased acidity in the supporting electrolyte solution. The series of titrations (Table VI) in which 2.5 M and 5 M H₂SO₄ were the supporting media show some improvement, i.e., more Al(NO₃)₃ can be tolerated without error, at higher acidities. Accordingly, the use of 5 M H₂SO₄-0.1 M NH₂SO₃H medium for analysis of samples containing Al(NO₃)₃ is recommended.

VI. Conclusion

Addition of sulfamic acid to the supporting electrolyte used for controlled-potential coulometric titration of uranium(VI) is an effective means of destroying small amounts of nitrite. With nitrites thus removed,

the titration is much less subject to interference from nitric acid and solutions containing nitrates.

VII. References

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