R0139037

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM(IV) WITH ARSENAZO III

ELIZABETH W. BAUMANN

**E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, SC 29808**

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America

Available from

National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy A03; Microfiche A01

726373✓

DP-1560

Distribution Category: UC-4

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM(IV) WITH ARSENAZO III

ELIZABETH W. BAUMANN

Approved by

M.L. Hyder, Research Manager
Analytical Chemistry Division

Publication Date: July 1980

**Issued by E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, SC 29808**

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-76SR00001

ABSTRACT

A spectrophotometric procedure was developed for determining U(IV) in the presence of U(VI) by forming a colored complex with Arsenazo III in 4M HCl. The results compare satisfactorily with U(IV) determinations by ceric titration. Total uranium can be determined after reduction of U(VI) with metallic zinc. The concentration range for the absorbance cell solution is 0 to 2 μg U(IV)/mL. Other tetravalent ions, such as thorium, zirconium, hafnium, plutonium, and neptunium, will interfere.

CONTENTS

Introduction 5

Background 5

Procedure 7

Results 8

Appendix 11

References 15

INTRODUCTION

Tetravalent uranium [U(IV)] is a reducing agent that has potential application as a holding reductant in nuclear fuel reprocessing. In the presence of U(IV), plutonium is maintained as Pu(III), which is not extractable into the organic phase (tributylphosphate in n-paraffin). Use of U(IV) as the reductant avoids addition of foreign ions into the extraction system, which later will add to the waste volume. Details of the preparation of U(IV) salts by electrolytic reduction¹ and their usage in reprocessing applications² are discussed elsewhere.

The method that is currently in use for determination of U(IV) consists of a redox titration with ceric ammonium sulfate and ferroin indicator.³ This method has the following limitations: 1) relatively large amounts of U(IV), and thus of radioactive sample, are needed; 2) Pu(III) is also oxidized by Ce(IV), so that only the total Pu(III) + U(IV) can be determined; 3) hydrazine, which is added as a stabilizer and nitrite scavenger, makes the end point somewhat indefinite; and 4) titration of U(IV) in the organic phase has a relatively slow end point.

The objective of the present work was to develop a simple procedure for colorimetric determination of U(IV) that would not have the limitations of the ceric titration. The work was prompted by the report⁴ that a highly colored complex is formed by U(IV), but not by U(VI) or Pu(III), with Arsenazo III (Ar) in strong acid solution.

BACKGROUND

Arsenazo III, which has the structure

forms highly colored complexes with many metal ions. Therefore, it finds use in many colorimetric methods. Although relatively non-selective at lower acidities, selectivity of Arsenazo III increases in strongly acid solutions (>4M) for a number of elements in their tetravalent state (U, Th, Zr, Hf, Pu, and Np, for example) that would otherwise be hydrolyzed. Thus, in 4M HCl, determination of U(IV) in the presence of U(VI) becomes feasible.

Figure 1 shows the absorption spectra of the Ar reagent and of the U(IV) complex in the region of the absorption maximum of the complex. Although Ar reagent itself is highly colored (pink), its absorbance is minimal in the region of maximum absorbance (660 to 670 nm) of the green-blue U(IV) complex. The molar extinction coefficient of the complex is about 100,000.

The 1:2 complex has a much higher extinction coefficient than the 1:1 complex.⁵ Therefore, a large (e.g., 10-fold) excess of Arsenazo reagent is needed to ensure formation of the 1:2 complex.

The colored metal complex is relatively stable. However, oxidizing and strong reducing agents attack the reagent and must be absent. In nitric acid systems, for example, addition of urea to scavenge nitrous acid is recommended.⁶

FIGURE 1. Absorption Spectra with Arsenazo III (4M HCl)

PROCEDURE

The essence of the detailed analytical procedure, given in the appendix, is addition of Ar reagent to aqueous U(IV) solution in 4M HCl, followed by determination of the absorbance of the colored complex at 663 nm. Determination of U(IV) in the organic phase (30% tributylphosphate in n-paraffin) involves prior extraction into 4M HCl that contains ascorbic acid. The color is stable more than 30 minutes. Occasional high blank values were encountered, perhaps a matter of technique. Consequently, water, rather than blank reagent, was used as the reference for the spectrophotometric measurement.

Preparation of Ar reagent to ensure complete dissolution of the Ar crystals appears to be important for stable color formation. Initial experiments with freshly prepared solutions and/or solutions stronger than 0.05% Ar resulted in rapidly fading absorbances (within minutes) and in some cases in precipitation of the metal complex. As described in the appendix, a suitable 0.05% reagent was produced by prolonged stirring to dissolve the crystals followed by aging overnight and filtering.

A solution of uranyl nitrate that was standardized by a modified Davies-Gray⁷ procedure served as the standard for the calibration curve (Figure 2). The U(VI) was quantitatively reduced to U(IV) in 4M HCl with metallic zinc and ascorbic acid. This reduction procedure can also be used for determination of total uranium.

FIGURE 2. Standard Curve for Determination of U(IV) with Arsenazo III

Because Ar is a non-selective reagent, tetravalent thorium, plutonium, zirconium, hafnium, and neptunium constitute potential interferences. It was beyond the scope of this work to establish procedures to deal with interferences. However, zirconium can be masked with oxalate.⁴ U(IV) could be determined in the presence of thorium as the difference between two determinations: 1) U(IV) + Th, on the untreated sample and 2) Th only, after oxidation of U(IV) to U(VI). Other selective oxidation schemes could be used to distinguish U(IV) from Pu(IV), or to determine U(IV) in the presence of other oxidizable or reducible metal ions.

RESULTS

A typical calibration curve is shown in Figure 2. The concentration is 0 to 20 μg of U(IV) in the 10-mL volume used. Precision diminishes at higher uranium concentrations. A linear least squares fit of the data gives a reagent blank of about 0.03 absorbance units.

The procedure was demonstrated with three solutions of uranium (IV) nitrate prepared by the electrolytic process.¹ These solutions contained about 1M HNO_3 and 0.2M hydrazine. The time between U(IV) preparation and these analyses ranged from less than 3 weeks to 19 months.

Table 1 compares the results from U(IV) determinations by the colorimetric method and by titration with ceric ammonium sulfate.³ The exact end point in the titration was difficult to establish because of fading, probably caused by hydrazine or other reducing agents in the sample solutions. The fading end point was most troublesome in the oldest sample. Because of this problem, the accuracy of the titration values is open to question. Despite this uncertainty, values obtained with the two methods agree satisfactorily.

Table 2 illustrates recovery of U(IV) from the organic phase. The organic solution was prepared by quantitatively extracting U(IV) from an aliquot of Sample 1 (Table 1), through successive extractions with 30% tributylphosphate in n-paraffin. This organic solution was diluted to a known volume; then an aliquot was back-extracted into 4M HCl that contained ascorbic acid to stabilize the U(IV). Table 2 shows that a single extraction of the aliquot with 3 mL of 4M HCl was generally sufficient to remove the U(IV). The absorbance of the second extraction was in the region of the reagent blank. Direct formation of the colored complex in the organic phase was not investigated.

TABLE 1

U(IV) Determinations

Sample	Age	Sample Size, μ L	U(IV) Concentration, M $\pm$ 95% C.L.	
			Arsenazo	Ce Titration
1	<7 weeks	25-100	0.152 $\pm$ 0.010 0.154 $\pm$ 0.008*	0.155 $\pm$ 0.002
2	19 months	25-100	0.141 $\pm$ 0.007	0.131 $\pm$ 0.002
3	<3 weeks	2.5-5	1.24 $\pm$ 0.04	1.15 $\pm$ 0.01

* From organic phase.

TABLE 2

Determination of U(IV) in Organic Phase*
[U(IV) from Sample 1]

Sample Size, μ L	Absorbance after Extraction		Calculated U(IV) Concentration in Sample 1, M
	First	Second	
100	0.329	0.023	0.166
100	0.308	0.032	0.161
100	0.299	0.034	0.155
200	0.604	0.038	0.143
200	0.546	0.031	0.151
200	0.536	0.036	0.150

Average = 0.154 $\pm$ 0.008**

* Extracted into 4M HCl prior to color formation.

** $\pm$ 95% confidence limit.

APPENDIX

PROCEDURE FOR DETERMINATION OF URANIUM(IV) WITH ARSENAZO III

Apparatus

Visible spectrophotometer, with 1-cm cells
10-mL volumetric flasks
0.45-micron filter
Micropipets (10 to 1000 μ L)
Transfer pipets

Reagents and Standards

Hydrochloric acid (HCl, 4M). Add 150 mL concentrated HCl to 300 mL distilled water.

Arsenazo III, Aldrich Chemical Co., Chemical No. A9, 277-5 (0.05%). Weigh 0.05 g Arsenazo III; add about 1 mL 0.1M NaOH to the solid reagent; allow to stand a few minutes. Dilute to 100 mL with water and stir for 1 to 2 hours to ensure that the solid is completely dissolved. Allow the solution to stand overnight. Filter through a 0.45-micron filter. The solution is stable in the absence of oxidizing agents or strong reducing agents.

Zinc metal (Zn, Reagent-Grade, 10-mesh). Clean a batch of zinc each day before use by adding a few mL of 4M HCl to the zinc metal (hydrogen gas is evolved). After about 1 minute, rinse the zinc with water. ~

Ascorbic acid, solid.

Standard U(VI) solution - for example, $\text{UO}_2(\text{NO}_3)_2$ solution that has been standardized by the Davies-Gray titration.⁷

PREPARATION OF STANDARD CURVE/OR DETERMINATION OF TOTAL URANIUM

Procedure	Comment
1. Place aliquots of uranium solution in vials containing about 1 mL 4M HCL.	1. The range of uranium should be 0 to 20 μ g.
2. Add 10 to 15 granules of 10-mesh zinc.	2. Hydrogen gas is evolved.
3. Allow the reaction to proceed for 10 minutes.	3. If gas evolution diminishes or ceases, add more Zn.
4. Add 5 to 10 mg ascorbic acid.	4. The ascorbic acid maintains a reducing environment for the U(IV).
5. Quantitatively transfer the solution to a 10-mL volumetric flask, leaving the Zn granules behind.	5. Use a transfer pipet; rinse the vial twice with 4M HCL. (Gas evolution will increase when fresh acid is added.)
6. Dilute to about 8 mL with 4M HCL. Mix.	
7. Add 1 mL Arsenazo III reagent. Mix.	
8. Dilute to volume with 4M HCL. Mix.	
9. Determine absorbance at 663 nm in a 1-cm cell, with H ₂ O in the reference cell.	9. Color is stable for >30 minutes.
10. a. For standard curve, plot data (absorbance vs. uranium content).	10. A reasonably straight line should be obtained: typical calibration curve is shown in Figure 2.
b. For total uranium, determine uranium content from standard curve.	

COLORIMETRIC DETERMINATION OF U(IV) IN AQUEOUS PHASE

<u>Procedure</u>	<u>Comment</u>
1. Place suitable sample aliquot in 10-mL volumetric flask.	1. Sample should contain 0 to 20 μg U(IV). Volume generally expected to be <250 μL .
2. Dilute to a volume of about 8 mL with 4M HCl that contains a little ascorbic acid. Mix.	
3. Add 1 mL Arsenazo III solution. Mix.	
4. Dilute to volume with 4M HCl. Mix.	
5. Measure absorbance at 663 nm in 1-cm cell, with H_2O as reference.	5. Color is stable for >30 minutes.
6. Determine uranium(IV) content from standard curve.	

COLORIMETRIC DETERMINATION OF U(IV) IN ORGANIC PHASE

<u>Procedure</u>	<u>Comment</u>
1. Place suitable sample aliquot in extraction vial.	1. Sample should contain 0 to 20 μ g U(IV).
2. Add about 3 mL 4M HCl. Mix on vortex mixer for about 1 minute.	
3. When phases have separated, transfer aqueous phase to 10-mL volumetric flask.	3. Centrifugation is recommended for a clean phase separation.
4. Repeat Steps 2 and 3.	
5. Add 1 mL Arsenazo III solution. Mix.	
6. Dilute to volume with 4M HCl. Mix.	
7. Measure absorbance at 663 nm in 1-cm cell, with H ₂ O in the reference cell.	7. Color is stable for >30 minutes.
8. Determine uranium content from standard curve.	

REFERENCES

1. E. G. Orebaugh and R. C. Propst. Electrolytic Production of Uranous Nitrate. USDOE Report DP-1549, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (1980).
2. Gunter Koch. "Existing and Projected Reprocessing Plants: General Review." Atomkernenergie Kerntechnik 33 (4), 241 (1979).
3. Handbook of Analytical Chemistry. First edition, L. Meites, ed., p. 3-73, McGraw-Hill Book Company, New York (1963).
4. S. B. Savvin. "Analytical Use of Arsenazo III - Determination of Thorium, Zirconium, Uranium and Rare Earth Elements." Talanta 8, 673 (1961).
5. S. B. Savvin. "Analytical Applications of Arsenazo III - III. The Mechanism of Complex Formation between Arsenazo III and Certain Elements." Talanta 11, 7 (1964).
6. A. A. Nemodruk and N. E. Kochetkova. "A Study of the Reaction of Tetravalent Plutonium with Arsenazo III." Zhur. Anal. Khim. 18 333 (1963).
7. W. Davies and W. Gray. "A Rapid and Specific Method for the Precise Determination of Uranium Using Iron(II) Sulphate as Reductant." Talanta 11, 1203 (1964).