UNCLASSIFIED

DP - 161

Chemistry

AEC Research and Development Report

DETERMINATION OF MICROGRAM AMOUNTS OF ZIRCONIUM IN URANYL NITRATE SOLUTIONS

by

E. R. Russell
Analytical Chemistry Division

May 1956

E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

Printed in USA. Price $0.15
Available from the Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

253652

UNCLASSIFIED

DP - 161

CHEMISTRY

DETERMINATION OF MICROGRAM AMOUNTS OF ZIRCONIUM IN URANYL NITRATE SOLUTIONS

by

Edwin R. Russell
Analytical Chemistry Division

May 1956

E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

Printed for
The United States Atomic Energy Commission
Contract AT(07-2)-1

ABSTRACT

A colorimetric method was developed for the determination of one to ten micrograms of zirconium in uranyl nitrate solutions. Samples containing one microgram of zirconium and 400 milligrams of uranium were analyzed successfully.

External Distribution according to
TID-4500 (11th Ed.)

No. of Copies		
(5)	AEC, SROO	Aiken, S. C.
(1)	R. M. Evans - B. H. Mackey	Wilmington AED
(1)	J. E. Cole - M. H. Smith - J. B. Tinker	"
(1)	H. Worthington	"
(1)	V. R. Thayer	"
(1)	"W" File	"
(1)	S. I. Winde	Engineering Department
(1)	D. M. Smith	Polychemicals Dept., Exp. Station, Wilm.
(1)	J. A. Monier	Savannah River Plant
(1)	W. P. Overbeck	"
(1)	R. B. Fenninger	"
(1)	W. R. Tyson	"
(1)	PRD File	"
(1)	M. H. Wahl - C. W. J. Wende - W. M. Heston	Savannah River Laboratory
(1)	J. W. Morris - W. P. Bebbington	"
(1)	J. O. Morrison	"
(1)	H. M. Kelley	"
(1)	C. H. Ice	"
(1)	A. L. Marston	"
(1)	M. O. Fulda - E. R. Russell	"
(15)	TIS File	"
(1)	TIS File Record Copy	"

TABLE OF CONTENTS

	Page
INTRODUCTION	4
SUMMARY	4
DISCUSSION	5
Development of Method	5
Experimental Results	5
BIBLIOGRAPHY	6
APPENDIX	
Determination of Zirconium by the DPB Method	7
Preparation of Reagent Solution	7

DETERMINATION OF MICROGRAM AMOUNTS OF ZIRCONIUM IN URANYL NITRATE SOLUTIONS

INTRODUCTION

An analytical method was needed for the determination of zirconium in solutions containing nitric acid, uranyl nitrate and fission products. The level of radioactivity limited the size of the sample to that which contained one to ten micrograms of zirconium and 400 milligrams of uranium.

Chloranilic acid[1] has been used as a colorimetric reagent for the determination of one to ten micrograms of zirconium in the presence of 6 milligrams of uranium. However, higher ratios of uranium to zirconium interfered in the method and the colored complex was not stable in the presence of nitric acid.

Feigl[2] described a qualitative test in which as little as 0.2 microgram of zirconium was precipitated with p-(p-dimethylaminophenylazo)benzenearsonic acid (DPB) in the presence of 500 micrograms of thorium. The colored precipitate was collected on filter paper and washed free of reagent and interfering elements with hydrochloric acid. Hayes and Jones[3] used this reagent for the quantitative determination of zirconium in steel where as little as 50 micrograms of zirconium was present in the sample. In the steel samples, titanium was the only element present that interfered with this method. Jean[4] extended the method to the analysis of zirconium in aluminum alloys and reported a precision of three per cent.

The procedure described here is similar to that of Hayes and Jones. It was developed for the determination of a few micrograms of zirconium in the presence of as much as several hundred milligrams of uranyl nitrate.

SUMMARY

As little as one microgram of zirconium can be determined by using p-(p-dimethylaminophenylazo)benzenearsonic acid (DPB) in an indirect colorimetric method. Zirconium is precipitated with the colored reagent (DPB), filtered and washed. The precipitate is then redissolved and the amount of DPB released is measured spectrophotometrically.

The method was used successfully for the analysis of zirconium solutions, including those containing uranyl nitrate. The precision was five per cent for the analysis of 50 microliter samples of a 1.7M uranyl nitrate solution that contained 90 micrograms of zirconium per milliliter.

DISCUSSION

DEVELOPMENT OF METHOD

The precipitation of zirconium with p-(p-dimethylaminophenylazo)benzenearsonic acid (DPB) was studied to determine the conditions required for reproducibility. Test solutions were 1.7M in uranyl nitrate, 0.2M in nitric acid, and contained 90, 9 and 0.9 micrograms of zirconium per milliliter. A fourth test solution contained only zirconium in nitric acid solution.

DPB solution was added to 1.0 milliliter of each of the zirconium test solutions in 4.0 milliliters of 1.2M hydrochloric acid. The solutions were filtered and excess reagent was washed from the precipitate and paper with dilute hydrochloric acid. The precipitate was then treated with a mixture of hydrofluoric acid and oxalic acid to release the DPB, and the absorbance of the resulting solution was measured.

To obtain reproducible precipitation of zirconium with DPB it was necessary to heat the mixture at 60 to 70°C in the presence of excess DPB, and to allow the precipitate to digest overnight. The recovery of DPB was invariably erratic when one of these steps was omitted.

It was necessary to use pulverized filter paper to retain the precipitate completely on the filter. Losses to the filtrate were proportionately higher for the smaller amounts of zirconium. Excess reagent was completely removed from the paper and the precipitate by careful washing with dilute hydrochloric acid.

The DPB was released from the washed precipitate most efficiently by treatment with a hydrofluoric acid - oxalic acid mixture at 60 to 70°C. Free DPB was then washed from the paper with dilute oxalic acid.

Under these conditions, the recovery of DPB was reproducible and all test solutions showed a linear relation between zirconium concentration and DPB recovered from the precipitate.

EXPERIMENTAL RESULTS

A detailed analytical procedure is given in the Appendix. Aliquots of a 1.7M uranyl nitrate solution that contained 90 micrograms of zirconium per milliliter were analyzed by this procedure to obtain a standard curve for micrograms of zirconium versus absorbance. The absorbance, measured at 490 millimicrons, followed Beer's law, and the apparent molar extinction coefficient for zirconium was 2.9×10^4. Results from the analysis of samples that contained no uranium showed the same molar extinction coefficient for zirconium. The data for the standard curve are given in the following table:

ANALYTICAL RESULTS FOR PREPARATION OF STANDARD CURVE

Zirconium, µg	Average Absorbance	Standard Deviation, %
0.90	0.055	3.6
4.5	0.295	2.7
9.0	0.584	1.2

A 1.7M uranyl nitrate solution that contained 90 micrograms of zirconium per milliliter was analyzed to determine the precision of the method. Results from ten analyses showed a standard deviation of 2.5 per cent with an average recovery of 99.8 per cent.

Zirconium-niobium tracer solutions that were obtained from Oak Ridge were analyzed by the DPB method. The oxalate present in the tracer solution was destroyed prior to analysis by heating the solution with concentrated nitric acid and 30 per cent hydrogen peroxide.

Results from the analysis of these three solutions are given below.

DETERMINATION OF ZIRCONIUM BY DPB METHOD

Sample	Sample Size, ml	Number of Det'ns.	Average Zr Found, µg/ml	Std. Dev., %
1.7M UNH-90 µg/ml Zr	0.050	10	89.2	2.5
Oak Ridge Tracer #1	0.015	6	26	1.8
Oak Ridge Tracer #2	0.010	6	400	2.5

E. R. Russell

E. R. Russell
Analytical Chemistry Division

BIBLIOGRAPHY

1. Menis, O. The Determination of Zirconium by the Chloranilic Acid Method. Oak Ridge National Laboratory, ORNL-1626, April 7, 1954.

2. Feigl, F. Spot Tests. Volume 1, p. 192, Fourth Edition, New York: Elsevier Publishing Co. (1954).

3. Hayes, W. G. and Jones, E. W. "Determination of Zirconium in Steel." Ind. Eng. Chem. Anal. Ed. 13, 603 (1941).

4. Jean, M. "Analysis of Aluminum-base Light Alloys by Spectrophotometric Methods." Anal. Chim. Acta, 7, 523 (1952).

APPENDIX

DETERMINATION OF ZIRCONIUM BY THE DPB METHOD

Preparation of Standard Curve

1. Analyze aliquots of a known zirconium solution by the procedure outlined in the steps given below. Choose aliquots to contain 1, 4, 7 and 10 micrograms of zirconium.
2. Plot the absorbance versus micrograms of zirconium.

Analysis of Samples

1. Add an aliquot of the sample containing 1 to 10 micrograms of Zr, preferably 1.0 milliliter or less, to a 15-milliliter beaker containing 4.0 milliliters of 1.2M hydrochloric acid.
2. Add 1.0 milliliter of DPB solution and heat to 60 to 70°C for 15 minutes. The reddish color of the solution should become brown. If the solution becomes yellow, add DPB dropwise until a brown color appears on heating.
3. Remove from the hot plate and allow to digest overnight at room temperature.
4. Place a wad of shredded Whatman #42 filter paper in the cone of a funnel fitted with Whatman #42 filter paper.
5. Wash the filter with hot (60 to 70°C) 1.2M hydrochloric acid and leave sufficient solution in the funnel to cover the filter mat.
6. Filter the zirconium solution.
7. Wash the beaker with hot (60 to 70°C) 1.2M hydrochloric acid and pour the washings over the filter.
8. Wash the precipitate with hot (60 to 70°C) 1.2M hydrochloric acid until the washings are colorless. Discard the washings.
9. Place a 25-milliliter volumetric flask under the funnel as the receiver and add 2 milliliters of 5M hydrofluoric acid and 5 milliliters of hot (60 to 70°C) 0.4M oxalic acid to the precipitate on the filter.
10. Repeat step 9 and then wash with hot (60 to 70°C) 0.4M oxalic acid until all color is removed from the paper.
11. Dilute to 25 milliliters and mix well.
12. Transfer the solution to a 5-centimeter absorption cell and read the absorbance against a distilled water blank at 490 millimicrons.
13. Determine the micrograms of zirconium from the standard curve.
14. Calculate the zirconium concentration of the sample:

$$\text{Zr, } \mu g/ml = \frac{\mu g \text{ Zr from standard curve}}{\text{sample size, ml}}$$

PREPARATION OF REAGENT SOLUTION

The DPB reagent solution is prepared by dissolving 0.2 gram of p-(p-dimethylaminophenylazo)benzenearsonic acid in 90 milliliters of 95 per cent ethanol that contains 10 milliliters of 2M hydrochloric acid. This solution is filtered and stored in a tightly capped bottle. There is no apparent deterioration during storage for as long as three months.