LA-5490

Spectrophotometric Measurement of Uranium in Plutonium Dioxide

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $4.00; Microfiche $1.45

LA-5490
UC-4
Reporting Date: December 1973
Issued: April 1974

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

Spectrophotometric Measurement of Uranium in Plutonium Dioxide

by

N. L. Koski
R. D. Gardner
G. R. Waterbury

Work supported by the U.S. Atomic Energy Commission's
Division of Reactor Research and Development.

SPECTROPHOTOMETRIC MEASUREMENT OF URANIUM IN PLUTONIUM DIOXIDE

by

N. L. Koski
R. D. Gardner
G. R. Waterbury

ABSTRACT

Uranium in plutonium dioxide is measured spectrophotometrically as the Arsenazo-I complex after separation by anion exchange resin in a hydrochloric acid medium. The sample is dissolved in 12*M* HCl at 300°C in a sealed tube or, alternatively, by repeated fumings with HNO_3-HF-H_2SO_4 mixtures. A sample size of 70 mg permits the determination of 300 to 1100 ppm of uranium with a relative standard deviation of 10%. At the 1400 to 3000 ppm level the relative standard deviation is 5%. The procedure is normally free from interferences.

INTRODUCTION

Uranium is an expected impurity in recycled plutonium from $(U,Pu)O_2$ or (U,Pu)C fuel elements, and uranium contents greater than a few hundred parts per million in the PuO_2 raw materials must be known for accurate preparation of mixed oxide fuel blends. A well tested method for measuring trace concentrations of uranium in plutonium metal[1] was modified and applied to the analysis of PuO_2 for uranium. The original method used a 3-g sample of metal dissolved in HCl and a double separation of the uranium from the plutonium on anion exchange resin columns. The modified method includes a reduction in the sample size to 70 mg, dissolution in either HNO_3-HF by repeated fumings or in HCl at 300°C by the sealed tube method,[2] and a single pass separation on the anion exchange resin columns. These modifications, which simplify and shorten the method, permit more rapid measurement of uranium contents of 300 ppm or greater in small samples of PuO_2.

EXPERIMENTAL

Separation of Uranium

The success of the method depends upon a clean separation of the small amount of uranium because other actinides and several other metals form highly colored complexes with Arsenazo I. The plutonium(IV) colored complex with Arsenazo I, for example, has a molar absorptivity of 21 000.[3] Ion exchange resin and liquid-liquid extraction methods generally are favored for separating uranium and plutonium. In the anion exchange resin separation method selected for this purpose, uranium(VI) is adsorbed onto strongly basic anion exchange resin from HCl solution containing plutonium reduced to its nonadsorbable (III) oxidation state.

Kraus and Nelson[4] report a distribution coefficient of 1000 for uranium(VI) between Dowex-1 resin and 12*M* HCl, and under the same conditions the distribution coefficient for plutonium(III) is essentially zero.[1] With this large difference in distribution coefficients, there is little difficulty in the separation if the proper oxidation states can be achieved. This is accomplished by reducing the plutonium with $NH_2OH \cdot HCl$ followed by 3 drops of $SnCl_2$ solution to delay air oxidation of the plutonium during ion exchange. The uranium remains in the (VI) oxidation state during the reduction steps and adsorbs on the resin while the plutonium(III) passes through the column. The uranium is subsequently washed from the column with 0.1*M* HCl. The ion exchange separation is more selective than comparable liquid-liquid extraction separations.

Hydriodic acid also was considered as a reducing agent in this separation. Prepared solutions containing known amounts of uranium and plutonium in 11*M* HCl-0.25*M* HI were passed through the Bio-Rad AG 1-x2 anion exchange resin columns. The adsorbed uranium was subsequently eluted and measured spectrophotometrically as described in this method. The results were less precise using HI as the reductant, and the resin had a shorter useful life. The resin selected (Bio-Rad AG 1-x2) has a cross linkage of two for minimal washing. Thirty milliliters proved to be ample for removal of either the plutonium(III) with 12*M* HCl or the uranium (VI) with 0.1*M* HCl. The resin particle size selected was 100-200 mesh; larger resin particles permitted the solution to flow too rapidly for the uranium adsorption. The resin was held conveniently in 10-cm columns with coarse glass frits.

Formation of Colored Complex

A highly colored chelate complex is formed in a ratio of 1 to 1 between UO_2^{2+} and Arsenazo I. The complex is a highly stable, six-membered ring involving the UO_2^{2+} and the cyclic O-C-C-C-O group.[5] The reaction is complete at a pH of 8 to 9, and Beer's law is followed closely. At a wavelength of 600 nm, the molar absorptivity is 23 000.[6]

Dissolution of Sample

Dissolution of PuO_2, especially if it is high-fired, may present a problem. Plutonium oxide is dissolved slowly in 15.6*M* HNO_3 at its boiling point with HF added in very low concentrations. The HF acts catalytically on the PuO_2 and also helps dissolve any SiO_2 contamination. The HNO_3 and HF are then removed by repeated fuming with H_2SO_4; NO_3^{1-} would adversely affect the quantitative reduction of plutonium to its (III) oxidation state. The sealed tube method[2] is recommended for high-fired PuO_2, although prolonged heating with HNO_3-HF and repeated fumings with H_2SO_4 will effect solution.

Selection of Sample Size

A 70-mg sample size was chosen to accommodate uranium concentrations between 300 and 3000 μg/g. If the 70-mg sample should contain more than 200 μg of uranium, a small aliquot of the final colored solution may be taken into another flask, more buffer and Arsenazo reagent added, and the absorbance measured spectrophotometrically. Being able to measure an aliquot of the colored solution in this manner is a real advantage and eliminates the need to repeat the analysis of a sample with an unusually high uranium content. The theoretical capacity of the resin bed is several hundred milligrams of uranium, thus ensuring quantitative retention of the larger quantities of uranium.

SAFETY PRECAUTIONS

Special care must be taken when handling concentrated acids. At the minimum, rubber gloves should be worn. When preparing dilute H_2SO_4 solutions, always add the acid carefully to the water and not vice versa. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Any operation involving plutonium-containing materials must always be done in laboratories designed for adequate protection of the worker through suitable equipment and protective clothing. Particular care should be used in handling plutonium or any of its compounds in dry, finely divided form. It is the responsibility of the individual worker to thoroughly understand and rigidly follow the health and safety rules pertaining to his work.

OPERATION PROCEDURE

Apparatus

Columns, ion exchange, 1- x 10-cm. Seal a 1-cm-diam filtering tube with a coarse glass frit to the bottom of a 40-ml centrifuge tube, and cut off the tube diagonally just below the frit. Fill the 1- x 10-cm tube with Bio-Rad Ag 1-x2 anion exchange resin, chloride form, 100-200 mesh. Wash the column with 50 ml of 12*M* HCl.

Dishes, platinum, 30-ml.

Infrared lamps, Pyrex, 250-W.

Spectrophotometer, Beckman, Model DU, with 1-cm cells, or equivalent.

Reagents

Ammonium hydroxide, 1*M*.

Arsenazo I, 0.05% aqueous solution. Purify the reagent, 3-(2-arsonophenylazo)-4, 5-dihydroxy-2, 7-naphthalenedisulfonic acid, trisodium salt by reprecipitation from HCl. Add a saturated aqueous solution of the Arsenazo I to an equal volume of 12*M* HCl, filter the orange precipitate, wash with acetonitrile, and dry for 1 h at 100°C.

Hydrochloric acid, 12*M*, 6*M*, and 0.1*M*.

Hydrofluoric acid, 27*M* and 1*M*.

Hydroxylamine hydrochloride, 10% aqueous solution.

Nitric acid, 15.6*M*, 6*M*.

Phenolphthalein solution, 0.025% in 1:1 water-ethanol solution.

Sodium cyanide, 5% aqueous solution.

Sulfuric acid, 6*M*.

Stannous chloride, 7% in 12*M* HCl. Make fresh preparation daily.

Triethanolamine buffer, aqueous. Dissolve 74.5 g of triethanolamine, 72 mg of disodium salt of ethylenediaminetetraacetic acid (EDTA), and 14.0 ml of concentrated HNO_3 in water and dilute to 1 liter. Allow the solution to stand overnight before using.

Sample Analysis

An accurately weighed, 70-mg portion of the PuO_2 sample is dissolved either by repeated fumings with HNO_3-HF-H_2SO_4 mixtures or, preferably, by heating at 300°C with 12*M* HCl in a sealed tube.[2] For the dissolution in the mixed acids, the sample is heated with 10 ml of 15*M* HNO_3 containing a few drops of 27*M* HF and 18*M* H_2SO_4 until fumes of SO_3 are evolved. The solution is cooled and water is added to dissolve the soluble portion, which is then decanted. The acid treatments of the undissolved portion are repeated until solution is complete. The combined solution is evaporated to dryness, and the salts are dissolved in 2 ml of water. Quantitative reduction of the plutonium to the blue (III) oxidation state is achieved by adding 3 ml of 10% $NH_2OH{\cdot}HCl$ solution and warming the solution. Reduction is repeated if the solution is not blue. Three drops of 7% $SnCl_2$ in 12*M* HCl and 13 ml of 12*M* HCl are added, and the solution is transferred to a 1- x 10-cm ion exchange resin column filled with 100-200 mesh Bio-Rad AG 1-x2 anion exchange resin that has been washed with 30 ml of 12*M* HCl. The sample solution is washed onto the column with five 1-ml portions of 12*M* HCl, and the column is washed with six 5-ml portions of this acid. The uranium is eluted with 30 ml of 0.1*M* HCl, added in 5-ml portions, and the eluate solution is evaporated to dryness under heat lamps. Dissolution of the residue in 3 drops of 12*M* HCl and 2 ml of water, addition of 4 drops of 5% aqueous NaCN and 2 drops of 0.025% phenolphthalein solution, and then addition of 1*M* NH_4OH dropwise until the solution is slightly basic prepares the solution for the color development step. This is done by adding 5 ml of triethanolamine buffer and 3.0 ml of Arsenazo I solution. The solution is diluted to 25.0 ml and allowed to stand 1 h before the absorbance is measured at 600 nm in 1-cm matched cells using a solution containing phenolphthalein, NH_4OH, NaCN, triethanolamine buffer, and Arsenazo I as a reference.

Blanks and Standards

Two reagent blanks and two standard solutions should be analyzed simultaneously with the sample solutions. The blank solutions are prepared by fuming 1 ml of 6*M* H_2SO_4 to dryness, dissolving any residue in 2 ml of water, and proceeding with the $NH_2OH{\cdot}HCl$ reduction and the following analysis.

Standard solutions are prepared from a solution of PuO_2 containing 7 mg of PuO_2 per milliliter of solution and a solution of U_3O_8 containing 0.030 mg of uranium per milliliter of solution. The plutonium calibration solution is prepared by carefully heating an accurately weighed portion of PuO_2 of known uranium content in 15.6*M* HNO_3 containing a few drops of 27*M* HF and 18*M* H_2SO_4 until fumes of SO_3 are evolved. The solution is cooled and the soluble portion of the sample is dissolved in water and decanted into a volumetric flask. The dissolution process is repeated until the sample is completely dissolved, then the solution in the volumetric flask is made 6*M* in HCl. The uranium calibration solution is prepared by dissolving an accurately weighed portion of pure U_3O_8 in HNO_3, transferring the solution to a volumetric flask, and diluting with water. Each of the standard solutions run with the sample solutions should contain 70 mg of the PuO_2 calibration material and a total of approximately 110 μg of uranium. Each standard solution is fumed to dryness, the residue is dissolved in 2 ml of water, and the analysis is continued with the $NH_2OH{\cdot}HCl$ reduction of the plutonium.

Calculations

A calibration curve is established by analyzing two blank solutions and several standard solutions with uranium concentrations ranging from 20 to 200 μg of uranium. Because the calibration curve is a straight line, a factor can be calculated from the two standard solutions run simultaneously with each set of samples.

DISCUSSION

Applicability

The method is used for the determination of uranium at concentrations between 300 and 3000 μg/g in ceramic grade PuO_2. The recommended quantity for uranium measurement is between 10 and 200 μg, and the specified sample size of 70 mg is optimum for this range. For samples containing larger amounts of uranium, an aliquot having a suitable uranium concentration may be taken in the final color development step.

Reliability

The reliability of the method was established by the repeated analysis of standard solutions. The relative standard deviation in the range between 300 and 1100 ppm of uranium is 10%; between 1400 and 3000 ppm of uranium it is 5% (Table I).

There are practically no interferences in this spectrophotometric measurement because of the effectiveness of the ion exchange separation. Of the several other metals that form highly colored complexes with Arsenazo I, some, when present at low concentration, are effectively masked by EDTA or NaCN without adversely affecting the uranium-Arsenazo I color development. The concentrations at which selected elements will cause interference in the method were established by performing the color development procedure on solutions of those elements (Table II). The interfering element most likely to be present is iron, which interferes at concentrations greater than 500 ppm. Most other elements generally are at concentrations well within the tolerance of the method.

TABLE I

PRECISION OF THE MEASUREMENT OF URANIUM

Uranium Concentration (ppm)	Number of Determinations	Relative Standard Deviation
326	16	10.3
651	18	10.6
1109	14	10.5
1302	17	6.4
1737	15	2.9
2218	10	5.0
2605	15	2.1
3256	10	5.5

TABLE II

NET ABSORBANCES OF URANIUM AND SELECTED ELEMENTS

Element	Amount of Element Present (μg)	Net Absorbances
U	77.58	0.247
Fe	200	0.000
Fe	500	0.020
Fe	1000	0.136
Np	69	0.180
Np	207	0.400
Np	480	0.586
V	1000	0.022
Cu	1000	0.029
Cr	1000	0.026

REFERENCES

1. R. D. Gardner and W. H. Ashley, "The Spectrophotometric Determination of Trace Amounts of Uranium in High Purity Plutonium Metal," Los Alamos Scientific Laboratory report LA-3551 (June 1966).
2. C. F. Metz and G. R. Waterbury, "Sealed-Tube Dissolution Method with Applications to Plutonium-Containing Materials," Los Alamos Scientific Laboratory report LA-3554 (July 1966).
3. C. F. Metz and G. R. Waterbury, *Treatise on Analytical Chemistry*, Part II, Kolthoff, Elving and Sandell, Eds. (Interscience, New York, 1962), Vol. 9, p. 309.
4. K. A. Kraus and F. Nelson, Proc. U. N. Intern. Conf. on Peaceful Uses of At. Energy, 2nd, Geneva, 1956, Vol. 7, p. 118.
5. H. P. Holcomb and J. H. Yoe, "Spectrophotometric Determination of Uranium with 3-(2-Arsonophenylazo)-4, 5-dihydroxy-2, 7-naphthalenedisulfonic Acid (Trisodium Salt)," Anal. Chem. 32, 612-617 (1960).
6. A. D. Hues and A. L. Henicksman, "The Spectrophotometric Determination of Uranium in Mixtures of Uranium and Molybdenum," Los Alamos Scientific Laboratory report LA-3226 (January 1965).