

LA-3551

Q. 3

CIC-14 REPORT COLLECTION  
**REPRODUCTION  
COPY**

**LOS ALAMOS SCIENTIFIC LABORATORY**  
of the  
**University of California**  
LOS ALAMOS • NEW MEXICO

**The Spectrophotometric Determination  
of Trace Amounts of Uranium in  
High-Purity Plutonium Metal**



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

## LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

This report expresses the opinions of the author or authors and does not necessarily reflect the opinions or views of the Los Alamos Scientific Laboratory.

Printed in USA. Price \$1.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, United States Department of Commerce, Springfield, Virginia

**LOS ALAMOS SCIENTIFIC LABORATORY**  
**of the**  
**University of California**  
LOS ALAMOS • NEW MEXICO

Report written: June 1966

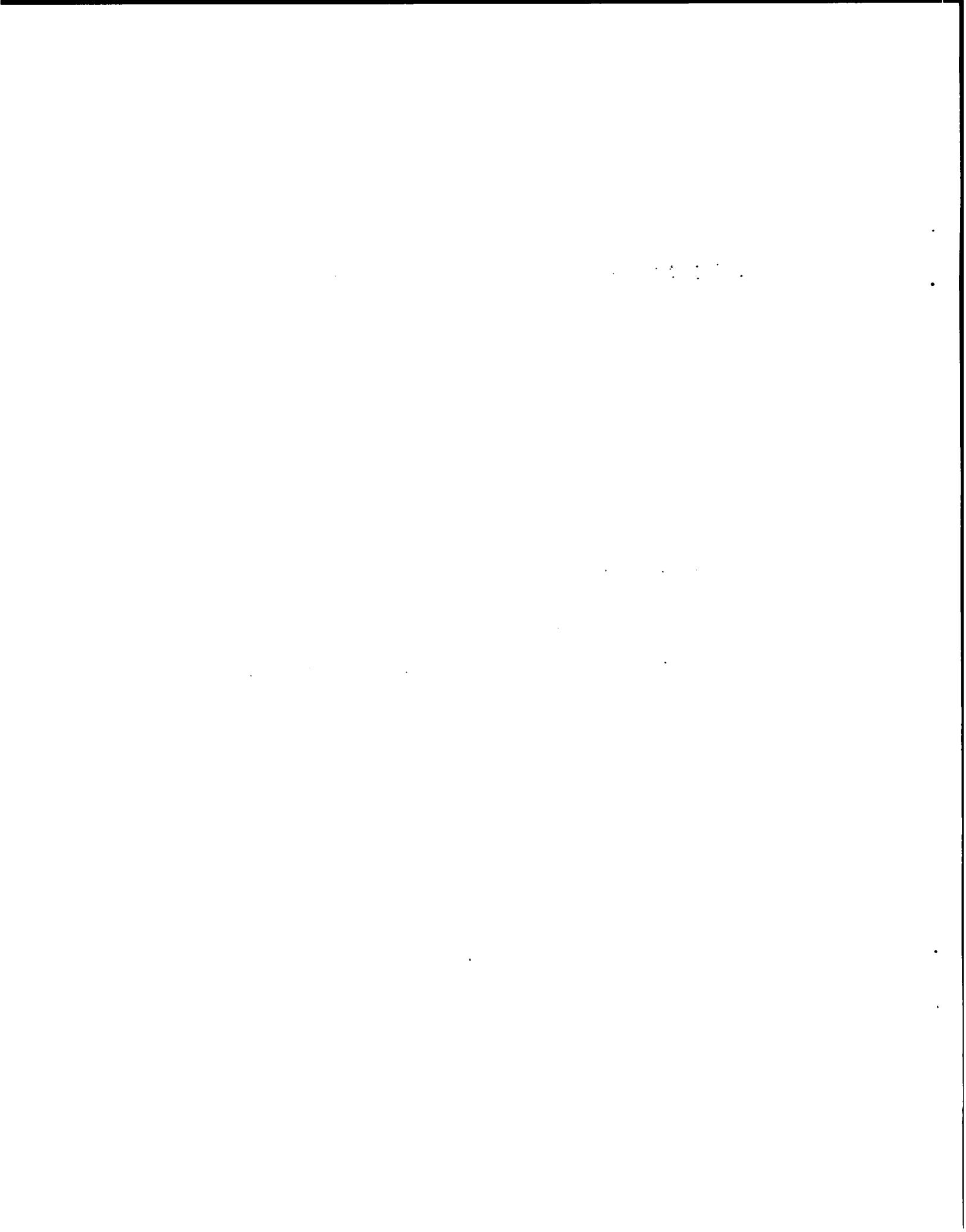
Report distributed: October 19, 1966

**The Spectrophotometric Determination**  
**of Trace Amounts of Uranium in**  
**High-Purity Plutonium Metal**

by

Ross D. Gardner  
William H. Ashley





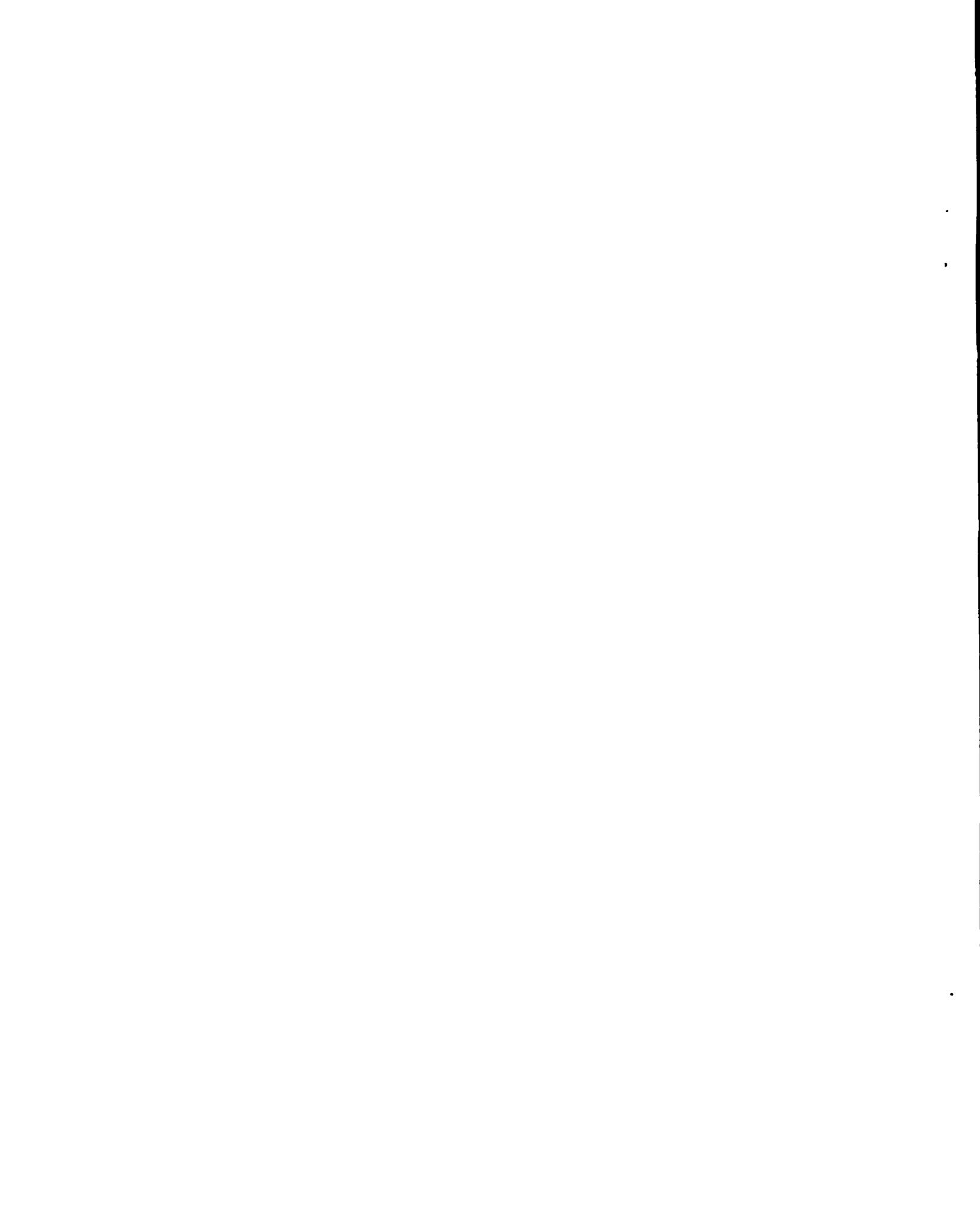
### ABSTRACT

Trace amounts of uranium in high purity plutonium metal are determined spectrophotometrically with Arsenazo after an anion exchange separation in hydrochloric acid. In the procedure described, the dissolution of the metal sample in hydrochloric acid results in a solution in which both uranium and plutonium are present in the (III) oxidation state. The addition of a small amount of bromine water oxidizes all of the uranium to the (VI) state, and any excess oxidizes plutonium to (IV). When this solution is passed through a column of Dowex-1 resin, the uranium(VI) and plutonium(IV) are adsorbed, but nearly all of the plutonium, as plutonium (III), remains in solution and is washed through the column with concentrated hydrochloric acid. The adsorbed uranium and plutonium are readily eluted from the resin with dilute hydrochloric acid. When hydroxylamine is added to the eluate, the small amount of plutonium remaining is selectively reduced to plutonium(III), and the passage of the solution through the column a second time results in a quantitative separation of the uranium. The lower limit of detection of the method is 1 ppm, and the precision in the 0- to 10-ppm range is  $\pm 1$  ppm. The precision in the 10- to 100-ppm range is approximately  $\pm 3$  ppm.



## CONTENTS

	<u>Page</u>
Abstract . . . . .	3
Introduction . . . . .	7
Experimental . . . . .	8
Ion Exchange Columns . . . . .	8
Oxidation States . . . . .	8
Re-Use of the Resin . . . . .	10
Sample Size . . . . .	10
Effect of Diverse Ions . . . . .	10
Range . . . . .	11
Blank . . . . .	12
Apparatus and Reagents . . . . .	13
Safety Precautions . . . . .	15
Recommended Procedure . . . . .	15
Reliability . . . . .	16
Summary . . . . .	17
References . . . . .	18



## INTRODUCTION

Since about 1958, uranium in plutonium has been determined in this Laboratory by means of an anion exchange separation followed by either a titrimetric or spectrophotometric measurement of the uranium. In this method uranium(VI) was adsorbed on Dowex-1 resin from a concentrated hydrochloric acid solution while the plutonium, maintained in the (III) oxidation state with hydriodic acid, was not adsorbed. This method was, in general, similar to that of Boase and Foreman (1) except that their final measurement of uranium was fluorimetric while ours, for small amounts, was spectrophotometric with Arsenazo (2). When uranium was present as an impurity in the low concentration range, results were reported to the nearest 10 parts per million, and below 30 parts per million they were regarded as unreliable.

The advent of high purity electrorefined plutonium metal having a uranium content of a few parts per million made it necessary to develop a more sensitive and precise analytical method. No other proposed method of separation or determination appeared to offer more promise than the ones already in use. Attention was therefore focused on refining the present method and developing techniques for handling larger samples of plutonium metal.

## EXPERIMENTAL

### Ion-Exchange Columns

The distribution coefficient for uranium(VI) between Dowex-1 resin and concentrated hydrochloric acid is given by Kraus and Nelson (3) as about  $10^3$ . Experimental work showed that the coefficient for plutonium(III) under the same conditions was substantially zero. With such a sharp difference in adsorptivity, it was felt that considerable emphasis could be put on speed of passage through the column and on low volume of wash solutions. Accordingly, the columns chosen were relatively short (about 10 centimeters) with a coarse glass frit to hold the resin. The resin selected had a cross linkage of two for minimal washing. Twenty milliliters of wash solution proved to be ample for the complete removal of either plutonium(III) with concentrated acid or uranium(VI) with dilute acid. The particle size of the resin selected was 100-200 mesh. Some 50-100 mesh resin was tried, but it permitted the solution to flow too rapidly for complete adsorption of the uranium(VI).

### Oxidation States

The separation of uranium(VI) from plutonium(III) involved no difficulties once the proper oxidation states were achieved, but we were unable to accomplish this by the old method when large amounts of plutonium were present. Plutonium metal dissolves in hydrochloric acid to plutonium(III) which is slowly air oxidized to plutonium(IV). Uranium

also dissolves to uranium(III), but it is oxidized to (IV) more rapidly. Any of a large number of reagents will oxidize uranium to uranium(VI), but any plutonium that is oxidized will not be separated from the uranium. The procedure formerly used was to oxidize everything to the higher oxidation states and then reduce the plutonium selectively to plutonium(III). Hydriodic acid was used for the reduction. It is an effective reducing agent in concentrated hydrochloric acid, but the free iodine produced adheres so strongly to the resin that the column's capacity to adsorb other ions is sharply reduced. With large amounts of plutonium, hydriodic acid was not found to be practical.

It was found that a limited amount of bromine water could be used to ensure complete oxidation of the uranium without affecting very much plutonium. In accordance with the observations of Metz and Waterbury (4), uranium(III) is oxidized preferentially because uranium(IV) reduces plutonium(IV) and (VI) to plutonium(III). The small amount of plutonium that is oxidized and stays with the uranium in the first pass through the column can easily be selectively reduced and separated from the uranium by a second pass through the column. After the plutonium (and any iron present) is completely reduced with hydroxylamine in dilute hydrochloric acid, a single drop of stannous chloride solution is added before increasing the acid concentration. This is not enough to cause significant interference in the uranium determination, and it delays air oxidation of the plutonium and iron after the acid concentration is increased.

### Re-Use of the Resin

Elimination of the use of hydriodic acid had the advantage that the same resin could be used repeatedly with no apparent deterioration. After the uranium was eluted with dilute hydrochloric acid, the resin was washed with concentrated hydrochloric acid and was ready for another sample. If the solution drained below the surface of the resin overnight or over a weekend, letting air into the columns, a reverse flow of water under pressure was used to force the resin up into the reservoir, from which it could settle into the column again.

### Sample Size

Using the double pass through the column, it was found that the sample size could be greatly increased. However, incomplete recovery of uranium was experienced when 5 grams of plutonium was used. It was thought that adsorption of the uranium by the resin might be affected by the high concentration of plutonium ions. For the columns used, 3 grams of sample in a volume of approximately 30 milliliters was found to be most satisfactory.

### Effect of Diverse Ions

The details for the spectrophotometric determination of the uranium with Arsenazo were taken from Hues and Henicksman (2) who made a rather intensive study of the subject. They indicate that, by using sodium cyanide and EDTA as masking agents, essentially all of the impurities

usually found in high purity plutonium metal could be prevented from interfering. The conspicuous exception is iron. Consequently, special attention was given to the elimination of this metal in the ion exchange separation. To check the effectiveness of the procedure, 3-gram portions of plutonium containing 20 parts per million of uranium were spiked with 50, 100, and 200 micrograms of iron. The results for uranium were 20, 21, and 21 parts per million, respectively, indicating satisfactorily complete removal of iron. No further work was done on interfering substances. An indication of the behavior of other metals in the separation step can be found in the work of Kraus and Nelson (3).

#### Range

The procedure was developed primarily for use in the analysis of highly purified plutonium metal, in which the uranium content is usually only a few parts per million. However, metals are occasionally encountered which contain in excess of 100 parts per million. The theoretical capacity of the resin bed is several hundred milligrams of uranium, so the separation is not a limiting factor. The highest concentration for a reliable spectrophotometric measurement is about 200 micrograms or 67 parts per million in a 3-gram sample. If a sample is found to contain more than this it is not necessary to start over. An aliquot of the final solution can be taken into another flask, more buffer and reagent added, and the new solution made to volume and measured as before. The same steps should be applied to the reference solution.

This technique was used with the last set of determinations whose results are shown in Table I.

#### Blank

Plutonium, like uranium, develops a color with Arsenazo under the conditions prescribed in this procedure. Any trace of plutonium remaining with the uranium fraction would therefore cause a high result. Such a condition was thought to exist at one point in the development of this procedure. The blank value was determined by passing the same plutonium solution through several resin columns in succession and subjecting each uranium fraction to the remainder of the procedure. The values obtained after the first pass were relatively constant and were assumed to be due to a trace of plutonium left with the uranium. However, it was found later that this blank was due to the use of an old stannous chloride solution -- hence the caution under Reagents to prepare the solution fresh frequently. Using a fresh stannous chloride solution, the above operation was repeated with plutonium from several different lots, and the blank was found in every case to be less than 0.005 absorbance units.

## APPARATUS AND REAGENTS

### Apparatus

Beakers, pyrex, 50-ml.

Columns, ion-exchange, 1-x 10-cm. with a coarse glass frit. These are made by fusing a sealing tube with a glass frit to the bottom of a 40-ml. centrifuge tube and making a diagonal cut just below the frit. See Figure 1. The column is filled with Dowex-1 x 2 anion exchange resin, chloride form, 100-200 mesh. The resin is added as a water slurry to exclude air.

Flasks, volumetric, 25-ml.; and 50-ml., pyrex.

Hot plate, equipped with a Variac control outside the drybox.

Lamps, infra-red.

Pipets, volumetric, 3-ml. and 5-ml.

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

### Reagents

Ammonium hydroxide, reagent grade, 10% aqueous.

Arsenazo, 3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, disodium salt. To purify the Eastman Organic Chemicals product, prepare a solution of 2 grams of the salt in approximately 750 ml. of water and filter through a No. 42 paper. Catch the filtrate in 750 ml. of concentrated hydrochloric acid, stirred with a magnetic stirrer. Filter the precipitated material on a No. 41-H paper, wash with acetonitrile, scrape off onto a watch glass, and dry at 100° C for 1 hr. Dissolve 0.500 grams of the product in 1 liter of water.

Bromine water, saturated.

Hydrochloric acid, reagent grade, 12N, 6N, and 0.1N.

Hydroxylamine hydrochloride, 10% aqueous solution.

Phenolphthalein solution. Dissolve 25 mg. of the reagent grade material in 100 ml. of 50% ethanol.

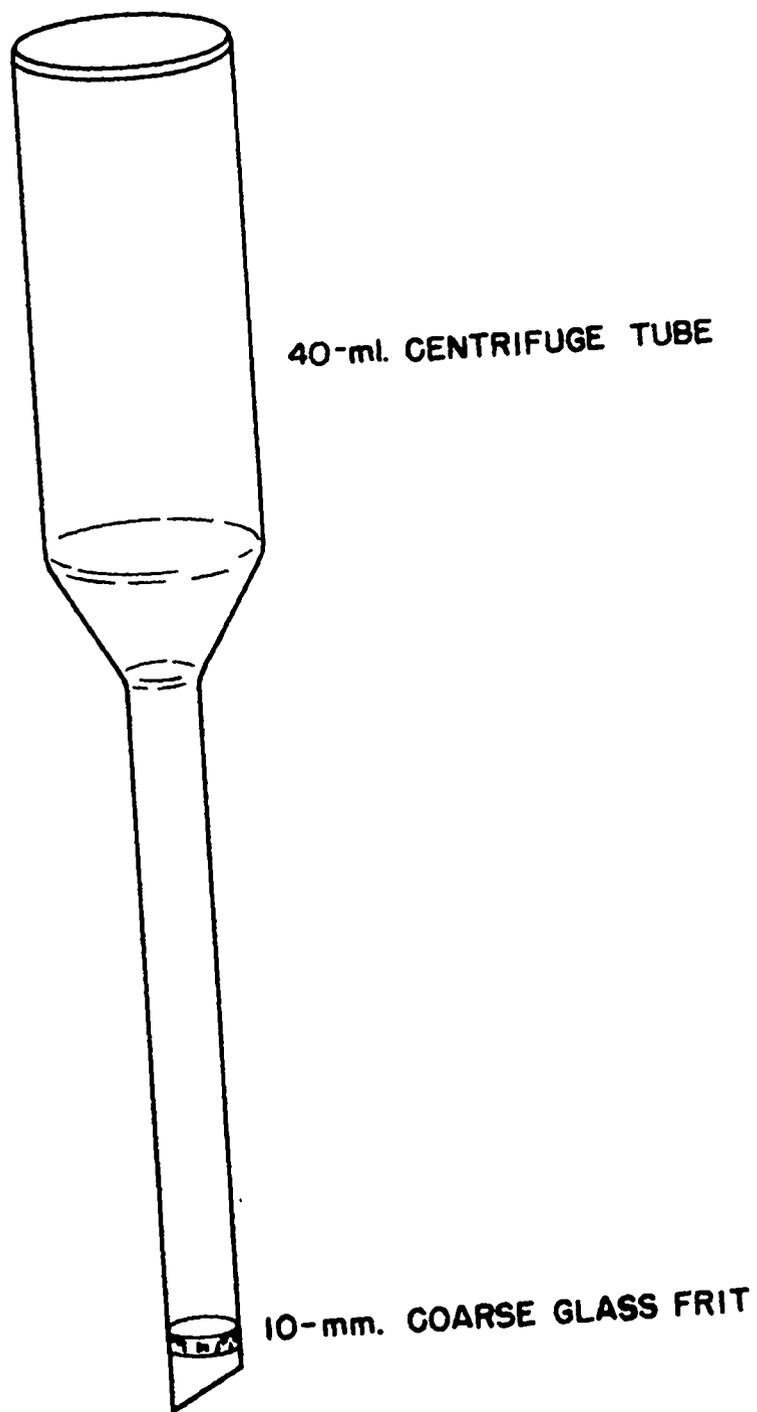


Fig. 1. Ion-Exchange Column

Sodium cyanide, reagent grade, 5% aqueous solution.

Stannous chloride solution. Dissolve 7 grams of the dihydrate salt in 100 ml. of 12N hydrochloric acid. Prepare fresh solution frequently.

Triethanolamine buffer. Dissolve 74.5 grams of triethanolamine and 72 mg. of disodium versenate in water. Add 14.0 ml. of concentrated nitric acid and dilute with water to 1 liter. Allow the solution to stand overnight before using.

Uranium standard solution. Dissolve about 125 mg. (carefully weighed) of ignited Bureau of Standards Sample No. 950 in a little nitric acid and dilute to 1 liter.

#### SAFETY PRECAUTIONS

Any operation involving the handling of plutonium-containing materials must always be done in laboratories designed for adequate protection of the worker, and only under approved conditions. It is the responsibility of the individual worker to thoroughly understand and rigidly follow the health and safety rules pertaining to his work. You are specifically cautioned to use particular care in the handling of plutonium or any of its compounds in dry, finely divided form. It is well to remember that the average particle size of room temperature oxide is less than 5 microns, and the lifetime body burden of plutonium is 0.6 microgram.

#### RECOMMENDED PROCEDURE

Dissolve a 3-gram weighed portion of the plutonium metal in concentrated hydrochloric acid. This step should be accomplished in a 50-ml. pyrex volumetric flask, and the additions of acid must be slow and cautious. Make the solution to about 30 ml., about 9N in hydrochloric acid. Add with stirring 3 drops of saturated bromine water.

Prepare an ion-exchange column by washing it with about 10 ml. of concentrated hydrochloric acid. Transfer the sample solution to the column, using 5 ml. of concentrated hydrochloric acid in small portions to rinse the beaker. When the solution has drained through the resin, wash the column with just enough concentrated hydrochloric acid to remove the obvious blue color of plutonium(III) from the resin. Replace the receiver with a 50-ml. beaker and elute with 20 ml. of 0.1N hydrochloric acid, using small portions at first to wash down the sides of

the reservoir above the resin. Evaporate the eluate to dryness on the hot plate with the aid of heat lamps, keeping the temperature below the boiling point. Meanwhile, wash the resin column with 10 ml. of concentrated hydrochloric acid.

Take up the residue, which consists mostly of plutonium(IV), in a few drops of concentrated hydrochloric acid and dilute to 3 ml. with 0.1N hydrochloric acid. Add 10 drops of hydroxylamine solution and return the beaker to the hot plate for 5 min. to reduce the plutonium to plutonium(III). Cool the solution, add 1 drop of stannous chloride solution and 5 ml. of concentrated hydrochloric acid, and again transfer it to the column, using 5 ml. of concentrated acid to rinse the beaker. Wash the column more thoroughly this time, using about 20 ml. of concentrated hydrochloric acid to remove all of the plutonium(III) and any iron(II). Again elute the uranium with 20 ml. of 0.1N hydrochloric acid and evaporate to dryness.

Take up the residue in 3 drops of concentrated hydrochloric acid and wash down the sides of the beaker with water. Add 4 drops of sodium cyanide solution and adjust the pH to the phenolphthalein end point with dilute ammonium hydroxide. Add 5 ml. of triethanolamine buffer solution and 3 ml. of Arsenazo reagent solution. Transfer the solution to a 25-ml. volumetric flask and make to volume with water. After 1 hr. measure the absorbance at 600 m $\mu$  in a 1-cm. cell, using a carefully prepared reagent blank in the reference cell.

The calibration curve is a straight line through the origin to at least 200  $\mu$ g. of uranium, so a standard at one concentration may be analyzed simultaneously with the sample and a factor calculated. A convenient amount for the standards is 100  $\mu$ g. of uranium, which will give an absorbance reading of about 0.400.

#### RELIABILITY

To determine the reliability of the method, a series of determinations was made on "known" materials. The plutonium used was high purity electrorefined metal. For concentrations in the 0-to 10-parts per million range, any uranium in the metal was removed by the method described in the first part of the Recommended Procedure. Known amounts of uranium were then added to the purified plutonium to get the desired

concentrations. For higher concentrations, the uranium content of the metal was carefully determined, and the amount was included in the calculated total. The additional uranium needed was added as a measured amount of standard uranium solution. This was placed in a beaker, and the plutonium was dissolved in contact with it in order to duplicate as nearly as possible the oxidation-reduction conditions that would be encountered in actual samples. The results of these determinations are summarized in Table I.

Table I

The Recovery of Uranium from Known Solutions

<u>No. of detns.</u>	<u>U present, ppm</u>	<u>U found, ppm ave.</u>	<u>Standard deviation, ppm</u>
21	0 <sup>a</sup>	0	1
15	4 <sup>b</sup>	4	1
15	9 <sup>c</sup>	9	1
15	31 <sup>d</sup>	32	2
16	49 <sup>d</sup>	48	3
8	120 <sup>d</sup>	119	3

<sup>a</sup> purified plutonium

<sup>b</sup> purified plutonium plus spike

<sup>c</sup> plutonium metal as received

<sup>d</sup> plutonium as received plus spike.

SUMMARY

A procedure is described whereby trace amounts of uranium can be determined in high purity plutonium metal by an ion exchange separation followed by a spectrophotometric measurement of the uranium with Arsenazo.

The sample, in concentrated hydrochloric acid, is passed through a column of Dowex-1 x 2 anion exchange resin, which adsorbs uranium(VI) but not plutonium(III). The uranium is then eluted with 0.1N hydrochloric acid. Large samples are handled by means of a two-step procedure with all the uranium and some plutonium being oxidized with bromine water prior to the first passage through the column. The remaining plutonium, but not the uranium, is then reduced with hydroxylamine and stannous chloride before the second passage through the column.

An average standard deviation for the method of 2 parts per million was shown by 90 determinations on samples containing 0 to 120 parts per million of uranium. In the 0-to 10-parts per million range the standard deviation was 1 part per million.

#### REFERENCES

1. Boase, D. G., and Foreman, J. K., *Talanta*, 8, 187 (1961).
2. Hues, A. D., and Henicksman, A. L., Los Alamos Scientific Laboratory Report, LA-3226 (1965).
3. Kraus, K. A., and Nelson, F., *Proc. U.N. Intern. Conf. Peaceful Uses At. Energy*, 2nd, Geneva, 7, 118 (1956).
4. Metz, C. F., and Waterbury, G. R., in "Treatise on Analytical Chemistry," Part II, Kolthoff, Elving, and Sandell, Eds., Vol. 9, p. 240, Interscience, New York, 1962.