

LA-3247

325
5-25-65

LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS ██████████ of the ██████████ NEW MEXICO
University of California

THE SPECTROPHOTOMETRIC DETERMINATION
OF SILICON IN PLUTONIUM

PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.

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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes 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, trademark, 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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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,
U. S. Department of Commerce,
Springfield, Virginia

LA-3247
UC-4, CHEMISTRY
TID-4500 (38th Ed.)

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

Report written: January 31, 1965

Report distributed: April 7, 1965

**THE SPECTROPHOTOMETRIC DETERMINATION OF
SILICON IN PLUTONIUM**

by

T. K. Marshall
K. S. Bergstresser
G. R. Waterbury

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ABSTRACT

Microgram quantities of silicon are separated from plutonium by selectively precipitating plutonium (III) and (IV) fluoride, and the silicon in the supernatant solution is determined spectrophotometrically as the reduced silicomolybdic acid complex. Boric acid is used to complex and prevent interference caused by the excess fluoride ion during the formation of the blue silicomolybdic acid complex. The absorbance of the complex is measured at a wavelength of 825 $m\mu$. Based upon 14 determinations each of 52, 104, and 152 ppm of silicon in plutonium (10.4, 20.8, or 31.4 μg . of silicon added to 200 mg. of plutonium), the relative standard deviation of the method was found to be 3.7, 1.8, and 2.8%, respectively. The molar absorptivity of 16,600 calculated from these data shows that 10 ppm (2 μg . of silicon in a 200-mg. plutonium sample) can be determined reliably. High concentrations of chromium, germanium, iron, nickel, or potassium interfere in this determination.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance and helpful suggestions of Charles F. Metz under whose supervision this work was performed.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

CONTENTS

	Page
Abstract	3
Acknowledgment	3
Introduction	7
Experimental	8
Apparatus and Reagents	12
Sample Preparation	13
Recommended Procedure	14
Reliability	16
References	17

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

INTRODUCTION

Several years ago, the need for a reliable means of determining microgram quantities of silicon in plutonium led to the development by M. E. Smith⁽³⁾ of a spectrophotometric method for this purpose. In this method hydrofluoric acid is added to the chloride solution of the plutonium sample to precipitate plutonium (III) and (IV) fluorides and to "activate" the silicon. The precipitate is separated by centrifugation, excess fluoride is complexed with aluminum ion, and the silicon, as the reduced silicomolybdate complex, is determined spectrophotometrically at a wavelength of 825 millimicrons. This method was applied satisfactorily to the determination of silicon in many plutonium metals although some uncertainty was introduced by the high absorbances of the reagent blanks (0.200 to 0.300). Therefore, when the need arose recently to determine small concentrations of silicon in plutonium, the method was reinvestigated to find a means of reducing the high blanks. Smith⁽³⁾ suggested that complexing the excess fluoride ion with boric acid in place of the aluminum chloride should reduce the blank. This proved to be the case. However, with the above change, it was found that the pH at which the silicomolybdic acid is formed becomes more critical. The exact pH for maximum absorbance was redetermined, and the proper conditions for obtaining the desired pH were found. This report describes the modifications to Smith's⁽³⁾ method that have reduced the reagent blank and improved the analytical results.

EXPERIMENTAL

Effects of Boric Acid and Aluminum Complexing Agents on Absorbance

The effect of substituting boric acid for aluminum chloride as the complexing agent for excess fluoride was investigated by analyzing reagent blanks and known solutions each containing 8.7 micrograms of silicon. These analyses were made as described in the method developed by Smith, ⁽³⁾ except that boric acid was used in place of aluminum chloride in some of the determinations. To each sample solution 0.3 milliliters of 24 percent hydrofluoric acid were added to "activate" the silicon, then the excess fluoride ion was complexed with 330 milligrams of aluminum added as the chloride. When boric acid was the complexing agent, 500 milligrams were used. The silicomolybdic acid complex was formed by adding 1 milliliter of 5 percent ammonium molybdate solution and adjusting the pH to 1.2 to 1.3. This complex was reduced, and the absorbance was measured at a wavelength of 825 millimicrons. The results of these determinations (Table I) show that the reagent blank absorbance is approximately three times larger when aluminum is the complexing agent than when boric acid is used for this purpose. The use of boric acid also improves the precision of the method; in determining 8.7 micrograms of silicon, the relative standard deviation is 3.3 percent as compared to 9.7 percent when aluminum is the complexing agent. However, boric acid causes a decrease in the absorbance per microgram of silicon from 0.0270 to 0.0233, a reduction of about 14 percent. Although the sensitivity is decreased, the use of boric acid as the fluoride complexing agent is warranted because of the lower reagent blanks and the improved precision. (It should be noted that 200 mg. of plutonium is present in each of the determinations; therefore, the absorbances in Table I include any contribution caused by trace silicon contamination in the plutonium. This contribution is about 0.023 and increases the absorbance from the normal blank of 0.064 to 0.087.)

Table I

Comparison of Analytical Results for Silicon Using Aluminum
or Boric Acid as Complexing Agent for Fluoride

Si Added, <u>μg.</u>	Absorbance, 825 mμ*	
	<u>Al Complexing Agent</u>	<u>Boric Acid Complexing Agent</u>
0	0.239	0.078
	0.246	0.080
	0.250	0.092
	0.251	0.084
	0.276	0.094
	0.256	0.088
	0.268	0.092
	0.248	0.084
	0.253	0.093
	Av. 0.254	Av. 0.087
Rel. Std. Dev. 4.3%	Rel. Std. Dev. 6.9%	
8.7	0.481	0.287
	0.479	0.293
	0.480	0.289
	0.499	0.292
	0.492	0.286
	0.500	0.290
	Av. 0.489	Av. 0.290
	Rel. Std. Dev. 9.7%	Rel. Std. Dev. 3.3%

*Absorption cell having 1-cm. light path.

Effect of pH

Following the change in complexing agent, several experimental parameters were investigated to ensure that optimum conditions existed. It was found that small variations in pH have large effects on the color development (Table II). These data were obtained by applying the Recommended Procedure to analysis of solutions each containing 21 micrograms of silicon. The only change made was in the pH at which the silicomolybdic acid was formed. As shown in Table II, the pH of the complex formation was varied from 1.0 to 1.6. These data show that maximum color is developed at a pH of 1.2 when boric acid is used

Table II

Effect of pH on the Absorbance of the Reduced Silicomolybdic Acid Complex
(21 μg . of silicon per 25 ml. of solution in each determination)

<u>pH</u>	<u>Absorbance, 825 $m\mu$*</u>
1.0	0.265
1.1	0.565
1.2	0.580
1.3	0.546
1.4	0.538
1.5	0.527
1.6	0.475

*cell having 1-cm. light path.

to complex excess fluoride ion. This pH agrees with the value of 1.2 to 1.3 recommended by Smith⁽³⁾ when aluminum is the complexing agent. Because of the sensitivity of the method to small variations in pH, especially to decreases, it is advisable to redetermine the optimum pH whenever changes in equipment or solutions are introduced that might affect its measurement.

Effect of Time of Formation on Absorbance of Colored Complex

The optimum length of time for development of the colored complex was investigated using solutions each containing 21.0 micrograms of silicon. The silicon was "activated" by adding hydrofluoric acid. Boric acid was added to complex the excess fluoride ion, and ammonium molybdate solution was added. Then the pH was adjusted to 1.1 to 1.3, and the reducing solution was added. The absorbances of each solution were measured at 825 millimicrons following successive 10-minute time intervals. The results (Table III) show that time for color development within the limits investigated is not critical; a time of 20 minutes was recommended for the color development in the Recommended Procedure.

Table III

Effect of Time and pH on Absorbance of 21.0 μg . Si

pH	Absorbance, Following			
	10 Min.	20 Min.	30 Min.	40 Min.
1.1	0.554	0.558	0.559	0.559
1.1	0.552	0.558	0.558	0.558
1.2	0.575	0.579	0.581	0.580
1.2	0.581	0.584	0.586	0.584
1.3	0.554	0.557	0.559	0.558
1.3	0.554	0.557	0.559	0.560

Effect of Plutonium

Plutonium (III), (IV), and (VI) forms insoluble compounds with molybdate which hinder the reproducible formation of the silicomolybdic acid. Removal of the plutonium as the insoluble (III) and (IV) fluorides prevents this interference. Varying the amounts of plutonium in the sample from 0 to 200 milligrams changed the absorbance of the reduced silicomolybdic acid by less than 2 percent.

Absorption Spectra

Smith found that the absorption curves of the silicomolybdic acid and of its reduced form were comparable to the absorption spectra reported by Carlson and Banks.⁽¹⁾ To ensure that the reduced silicomolybdic acid has an absorption maximum at 825 millimicrons under the present conditions, the absorption spectrum was redetermined for the wavelength region from 815 to 835 millimicrons. This was done by preparing the reduced silicomolybdic acid complex using 21.0 micrograms of silicon and a final volume of 25 milliliters as described in the Recommended Procedure. Absorbances were measured at 5-millimicron wavelength intervals using a Beckman Model DU spectrophotometer. The absorbance maximum was found at 825 millimicrons, indicating that the changes in complexing agent and in pH did not affect the absorption spectrum in the wavelength region examined.

APPARATUS AND REAGENTS

Apparatus

Centrifuge, International Clinical Centrifuge, Model CL.

Centrifuge tubes, 15-ml., polyethylene.

pH meter, Beckman Zeromatic equipped with a calomel electrode, Beckman No. 39170, and a glass electrode, Beckman No. 40498.

Pipets, polyethylene or polystyrene, 1-ml., with 0.1-ml. graduations. These graduated pipets were made from polyethylene or polystyrene tubing having an inside diameter of approximately 3 mm.

Spectrophotometer, Beckman Model DU, with glass or quartz cells having 1-cm. light paths.

Miscellaneous equipment. Normal laboratory volumetric glassware, polyethylene storage bottles for reagents, and other miscellaneous standard laboratory equipment, including No. 10 polyethylene beaker stoppers.

Reagents

Note: All solutions were stored in polyethylene bottles and were prepared from freshly distilled water which had not contacted glass. Smith⁽³⁾ reported some difficulty with silicon contamination of reagents especially of hydrofluoric acid. However, none of the reagents included in the following list were found to require purification; the absorbance of the reagent blank generally was 0.064 without purifying the reagents. It is recommended that each reagent be tested for silicon contamination whenever the reagent blank absorbance exceeds 0.100.

1-amino-2-naphthol-4-sulfonic acid, reagent grade.

Ammonium borate solution. Add 50 grams of boric acid and 40 ml. of 11 N ammonium hydroxide to 400 ml. of distilled water, mix well, and dilute to 500 ml. with distilled water.

Ammonium hydroxide, approximately 11 N. Prepare a silicon-free solution by saturating distilled water contained in a polyethylene bottle with ammonia gas.

Ammonium molybdate solution, 5%. Dissolve 5 grams of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ in a final volume of 100 ml. of distilled water.

Boric acid, reagent grade.

Bromine water. Saturate 50 ml. of distilled water with liquid bromine.

Hydrochloric acid, 12 N, reagent grade.

Hydrochloric acid, 2 N. Dilute 16.7 ml. of 12 N hydrochloric acid to 100 ml. with water.

Hydrofluoric acid, 48%, reagent grade.

Hydrofluoric acid, 24%. Dilute a known volume of 48% hydrofluoric acid with an equal volume of distilled water.

Hydrofluoric acid wash solution. Add 5 ml. of 48% hydrofluoric acid to 250 ml. of 1 N hydrochloric acid.

Hydroxylamine hydrochloride solution, 15%. Dissolve 15 grams of reagent grade hydroxylamine hydrochloride in distilled water and dilute to 100 ml.

Potassium permanganate solution, 0.06%. Dissolve 60 mg. of reagent grade potassium permanganate in a final volume of 100 ml. of distilled water.

Reducing solution. Dissolve 0.5 grams of sodium hydroxide and 6.8 grams of sodium bisulfite in 100 ml. of distilled water. Add 0.125 grams of 1-amino-2-naphthol-4-sulfonic acid, stir until dissolved, and dilute to 250 ml. with distilled water. The solution is stable for at least one month.

Silicon standard solution, 10 μ g. Si/ml. Dilute 10 ml. of the silicon stock solution to 500 ml. with distilled water.

Silicon stock solution, about 500 μ g. Si/ml. Dissolve 5.1 grams of sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) in distilled water and dilute to 1 liter. The silicon concentration was determined gravimetrically as described by Hillebrand, Lundell, Bright, and Hoffman. (2)

Sodium bisulfite, reagent grade.

Sodium hydroxide pellets, reagent grade.

Sodium silicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, reagent grade.

Tartaric acid solution, 20%. Dissolve 20 grams of reagent grade tartaric acid and dilute to 100 ml. with distilled water.

SAMPLE PREPARATION

Plutonium Metal or Alloys

Accurately weigh a quantity of the metal not in excess of 200 mg, that is estimated to contain from 2.5 to 40 μ g. of silicon. Transfer the sample to a 15-ml. centrifuge tube and add 2 to 3 drops of bromine water, to prevent loss of silicon as silane gas, and 6 ml. of 2 N hydrochloric acid to dissolve the sample. Take the entire solution for analysis. For samples containing larger concentrations of silicon, dissolve 200 mg. of

the metal in the described manner, dilute the solution with 2 N hydrochloric acid to a known volume selected so that the final silicon concentration is between 5 and 20 $\mu\text{g.}/\text{ml.}$ Take an aliquot containing 2.5 to 40 $\mu\text{g.}$ of silicon and dilute to 6 ml. with 2 N hydrochloric acid prior to analysis.

Plutonium Solutions

For hydrochloric acid solutions, transfer a measured aliquot containing 2.5 to 40 $\mu\text{g.}$ of silicon and not greater than 200 mg. of plutonium to a 15-ml. polyethylene centrifuge tube and dilute to 6 ml. with water and 12 N hydrochloric acid to adjust the acidity to 2 N. For other solutions, transfer an aliquot containing 2.5 to 40 $\mu\text{g.}$ of silicon and not greater than 200 mg. of plutonium to a platinum or Teflon dish, depending upon the acids present in the solution, and evaporate to incipient dryness under an infra red heat lamp. Add 1 ml. of 12 N hydrochloric acid and repeat the evaporation. Dissolve the residue in a minimum volume of distilled water. Transfer the solution to a 15-ml. polyethylene centrifuge tube rinsing the dish with 1 ml. of 15% hydroxylamine hydrochloride solution and 1 ml. of 12 N hydrochloric acid. Dilute the solution to 6 ml. with water and warm in a steam bath for 15 to 30 min. to ensure reduction of plutonium (VI). Proceed with the Recommended Procedure except in Step 3 use 5% potassium permanganate solution in place of a 0.06% solution.

RECOMMENDED PROCEDURE

CAUTION: Health safety rules for the handling of plutonium must be rigidly followed, and adequate protection for the operator must be ensured by the use of suitable dryboxes and protective clothing.

1. To the solution of the sample in the polyethylene centrifuge tube add 0.1 ml. of 24% hydrofluoric acid for each 100 mg. of plutonium plus an additional 0.1 ml. Swirl the tube gently to stir the solution and allow 10 min. for the silicon to be converted to a reactive form and the plutonium fluoride to precipitate.
2. Centrifuge the solution for 5 min. and carefully decant the supernatant solution into a number 10 polyethylene beaker stopper. Add 3 ml. of the hydrofluoric acid wash solution to the centrifuge tube, mix the precipitate and wash solution intimately using a platinum rod, and as the rod is removed, wash off the tip with a few drops of distilled water. Centrifuge the slurry for 5 min.
3. Carefully decant the supernatant solution into the beaker containing the first supernatant solution and add 5 ml. of ammonium borate solution. Insert a plastic-covered stirring bar, and while stirring the

solution, add 0.06% potassium permanganate solution dropwise until a faint pink color persists. (This is necessary to oxidize any reducing material that would hinder the formation of the silicomolybdic acid.) For plutonium solutions to which hydroxylamine hydrochloride was added, use a 5% solution of potassium permanganate in place of the 0.06% solution.

4. Add 1 ml. of 5% ammonium molybdate solution and adjust the pH to 1.2 to 1.3. (An excess of alkali should be avoided because a high salt concentration tends to cause low recoveries. Also at this point, it is a good practice to minimize the exposure of the electrodes to the solution because of possible silicon contamination from the glass.)

5. Allow the solution to stand for 10 min. for the formation of the silicomolybdic acid, then, while stirring, add 1 ml. of 20% tartaric acid solution immediately followed by 1 ml. of reducing solution. Wash the solution into a 25-ml. volumetric flask with distilled water, dilute to volume, and thoroughly mix the solution.

6. Allow the solution to stand 20 min. to permit full color development, then transfer a portion of the solution to a spectrophotometer cell having a 1-cm. light path and measure the absorbance at a wavelength of 825 $m\mu$ using water as a reference liquid.

7. For plutonium metal or alloy samples, prepare a reagent blank solution by adding 6 ml. of 2 N hydrochloric acid and a volume of hydrofluoric acid equal to that added to the sample to a 15-ml. polyethylene centrifuge tube and proceed as described in Steps 1 through 6. To prepare a reagent blank for samples submitted as solutions, add 4 ml. distilled water, 1 ml. of 12 N hydrochloric acid, 1 ml. of 15% hydroxylamine hydrochloride solution, and a volume of hydrofluoric acid equal to that added to the sample to a 15-ml. polyethylene centrifuge tube and proceed with Steps 1 through 6 above. Measure the absorbance of the reagent blank solution at a wavelength of 825 $m\mu$ using water as a reference solution. (If the absorbance of the reagent blank solution is greater than 0.100, each reagent should be investigated for excessive silicon contamination.)

8. Calculate the silicon concentration in the sample using a standard curve previously prepared by plotting data obtained by treating known aliquots, containing 2.5 to 40 $\mu g.$ of silicon, of the standard silicon solution according to the Recommended Procedure. (Centrifugation of the standards and blanks is unnecessary as no fluoride precipitate is formed; however the same amount of hydrofluoric acid that is used in the actual analysis must be added.)

RELIABILITY

To estimate the precision of the method, fourteen determinations at each of three silicon concentrations were made in the presence of 200 milligrams of plutonium. The known solutions were prepared by adding measured aliquots of the known silicon solution to 6-milliliter aliquots of the known plutonium (III) solution. Each solution was analyzed as described in the Recommended Procedure. The results (Table IV) indicate that 10.4 to 31.4 micrograms of silicon are determined with a

Table IV
Results for Silicon Determination
(200 mg. of plutonium in each solution)

<u>Si Taken,</u> <u>μg.</u>	<u>Av. Net</u> <u>Absorbance</u>	<u>Relative Standard</u> <u>Deviation, %</u>
0	0.023	8.0
10.4	0.242	3.7
20.8	0.490	1.8
31.4	0.744	2.8

relative standard deviation not greater than 3.7 percent. From the average absorbance per microgram of silicon of 0.0236, a molar absorptivity of 16,600 was calculated. These data show that greater than 2 micrograms of silicon (10 ppm) in a 200-milligram sample can be determined reliably by this method.

The effects of various ions on the method were determined by adding known quantities of each ion to solutions containing known concentrations of silicon. These were analyzed according to the Recommended Procedure. Arsenic and phosphorus in amounts equal to the silicon did not interfere in the spectrophotometric determination, but an equal quantity of germanium increased the absorbance readings by

about 10 percent. Nickel gave erratic results when present in concentrations 20 times that of the silicon. Iron or chromium present in concentrations more than 30 times that of the silicon also could not be tolerated. No interference was observed from sodium, magnesium, or manganese present in concentrations up to 80 times that of the silicon. Solutions containing high concentrations of potassium ions (0.4 N) were found to produce low results.

REFERENCES

- (1) Carlson, A. B., and Banks, C. V., *Anal. Chem.*, 24, 472 (1952).
- (2) Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., p. 671, John Wiley and Sons, Inc., New York, 1953.
- (3) Smith, M. E., TID-6071 (1957).