LA-3985

543

MASTER

214
11-27-67

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

Separation and Spectrochemical
Determination of 0.5 to 5 ppm Niobium,
Tantalum, and Titanium in Uranium

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 the United States of America. Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

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

Report written: May 1968

Report distributed: November 1, 1968

**Separation and Spectrochemical
Determination of 0.5 to 5 ppm Niobium,
Tantalum, and Titanium in Uranium**

by

H. M. Burnett
J. V. Pena
C. J. Martell
R. T. Phelps

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.

CONTENTS

	<u>Page</u>
Abstract	3
Introduction	3
Apparatus and Reagents	4
Recommended Procedure	6
Preparation of Sample, Blanks, and Standards	6
Extraction	7
Conversion to Excitation Form	7
Electrode Preparation	8
Excitation and Exposure	8
Photographic Processing	8
Photometric Measurements and Calculations	8
Experimental	9
Standards	9
Sample Weight	9
Evaluation of Excitation and Exposure Parameters	9
Internal Standardization	10
Extraction Behavior of Hafnium and Tantalum	11
Interferences	13
Palladium	13
Vanadium	13
Iron	13
Molybdenum and Zirconium	14
Evaluation of Method	14
Standards	14
Calibration Curves	14
Reliability	15
Evaluation of Uranium Tetrafluoride Samples	16
Acknowledgments	16
References	16

SEPARATION AND SPECTROCHEMICAL DETERMINATION OF 0.5 TO 5 PPM NIOBIUM, TANTALUM, AND TITANIUM IN URANIUM

by

H. M. Burnett, J. V. Pena, C. J. Martell, and R. T. Phelps

ABSTRACT

Microgram quantities of niobium, tantalum, and titanium are separated from uranium and determined by emission spectrochemical analysis. The elements are extracted into chloroform as complexes of N-benzoylphenylhydroxylamine (BPHA) from a 10N hydrochloric acid solution of the uranium. The chloroform extract is treated first with aqueous iron(II) and then with citric acid to remove vanadium and iron interferences. The organic material is removed by evaporation and ignition; the residue is dissolved in a hydrochloric-hydrofluoric acid mixture. The solution of extracted elements is evaporated on the ends of graphite electrodes, then excited by spark discharge. For samples containing 5.0 grams of uranium, the method covers the concentration range of 0.5 to 5.0 ppm. Standards are processed in the same manner as samples. Hafnium and palladium are added to serve as internal standards. More reliable results are obtained with hafnium because it is carried through the entire procedure, whereas palladium is added after the extraction processing. With hafnium, the precision is 15% relative standard deviation using photographic recording and photometry. Results from spiked samples and a statistical evaluation of synthetic samples are presented to indicate the reliability of the method.

INTRODUCTION

Recycle operations involving enriched uranium at the Los Alamos Scientific Laboratory are required to produce a product, either U_3O_8 or UF_4 , that contains not more than 1 ppm each of niobium, tantalum, and titanium.

Since the available carrier-distillation methods do not apply to the determination of these refractory elements in concentrations as low as 1 ppm, development of a method applicable to the product became necessary. Two major considera-

tions were the need for a relatively large sample to compensate for the inherently low sensitivity of the impurity elements and, consequently, for a means to separate the uranium to prevent interference by its multiline spectrum.

Solvent extraction has served as a means for separating impurities from uranium. Scribner and Mullin¹ indicated that hafnium, niobium, tantalum, vanadium, and zirconium could be separated from uranium as their cupferrates. Katz and Carter² reported successful extraction of these cupferrates

in the analysis of impurities in uranium. These techniques were found inapplicable in this case because the cupferron was neither sufficiently selective nor stable at the temperatures required.

Vita³ has described the use of a cupferron analog, N-benzoylphenylhydroxylamine (BPHA), for extracting niobium, tantalum, titanium, vanadium, and zirconium from a 10N hydrochloric acid solution of uranium. This information was used as a basis for developing the method described here.

The method uses solvent extraction with a BPHA solution to separate niobium, tantalum, titanium, and hafnium (added to serve as an extractable internal standard) from uranium. The separated elements are determined by spectrochemical analysis, using graphite-spark excitation to produce the characteristic spectra. The extraction procedure includes treatments to remove vanadium and iron, so they can not cause interference. Precision and accuracy studies were made to evaluate the reliability of the method.

APPARATUS AND REAGENTS

Apparatus:

Balance, keyboard, chain-weight, with 0.05-mg sensitivity, or equivalent.

Fig. 1. Electrode drying apparatus.

Fig. 2. Extraction apparatus.

Electrodes, preformed, SPK grade graphite, 1/4-in. diam, National Carbon Co., No. L 3721 (ASTM C-3).

Electrode drying apparatus. See Fig. 1.

Drying block, graphite or wood, with 24 holes of 1/4-in. diam.

Lamp, infrared, 250-W.

Excitation source, ac spark, 5-kV-amp., National Spectrographic Laboratories, or equivalent.

Extraction apparatus. See Fig. 2.

Funnel, separatory, 300-ml with Teflon stop-cock.

Racks and clamps, assorted, with Krylon coating to minimize corrosion.

Stirrer, electric, 115-V.

Stirring rod, glass, propeller tip.

Timer, stopwatch or clock, for timing extraction steps.

Furnace, muffle, capable of attaining temperatures to 600° C.

Gloves, rubber, surgical.

Graph paper, assorted linear and log-log coordinate.

Microphotometer, recording, Knorr-Albers type, Leeds and Northrup No. 6700-A-1, or equivalent.

Fig. 3. Sample preparation apparatus.

Photographic emulsion, Eastman SA-3, 35-mm film.

Photographic processor, integral with dryer, National Spectrographic Laboratories, or equivalent.

Pipets, disposable plastic, 1-ml serological type with 1/100-ml graduations, Falcon Plastics, Division of B-D Laboratories, Inc.

Platinum ware

Cover, for 100-ml dish.

Dish, evaporating, 100-ml.

Tongs, platinum-tipped.

Polyethylene ware, assorted bottles from 100-ml to 2-liter.

Sample preparation apparatus, See Fig. 3.

Graphite blocks, 3 x 5 in.

Hot plate, Fisher Autemp Heater, 6-in.-square plate.

Lamp, infrared, 250-W.

Timer, electric, automatic "ON-OFF" control.

Spectrograph, 2-m Paschen mounting, with 24,400-groove-per-in. grating, Applied Research Laboratories No. 2100, or equivalent.

Syringes, glass, 1- and 2-ml.

Teflon ware

Beaker, 100-ml.

Crucibles, 10-ml, machined from 1-in.-diam. rod, 1-3/16-in. high x 1-1/8-in. deep inside.

Reagents:

All solutions containing hydrofluoric acid are stored in polyethylene ware and measured by use of plastic pipets.

Ammonium hydroxide, saturated, prepared by bubbling commercial grade ammonia gas through water after first passing it through a water scrubber.

N-benzoylphenylhydroxylamine, $C_6H_5CON(OH)C_6H_5$ (designated BPHA), Eastman Organic Chemicals, Distillation Products Division, Rochester, New York, Item No. 7297.

BPHA-chloroform, 0.5%, prepared by dissolving 2.5 grams of N-benzoylphenylhydroxylamine in 500 ml of chloroform.

Chloroform, analytical reagent grade.

Citric acid solution, 1.6 mg/ml, prepared by dissolving 1.6 grams of citric acid in 1 liter of 3N hydrochloric acid.

Electrode sealing solution, 20 mg/ml, prepared by dissolving 2 grams of petrolatum in 100 ml of isopropyl ether.

Ferrous ammonium sulfate solution, 12 mg/ml, prepared by dissolving 3.6 grams of Mohr's salt, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in 300 ml of 10N hydrochloric acid. This solution was prepared fresh on the day of use.

Hafnium stock solution, 250 μ g/ml, prepared by dissolving 25 mg of pure hafnium metal in 30 ml of 5:1 hydrochloric-hydrofluoric acid mixture. The dissolved metal was diluted to 100 ml with water so that the final concentration of mixed solvent was 3N hydrochloric-2.5% hydrofluoric acids.

Hafnium internal standard solution, 5 μ g/ml, prepared by diluting 2 ml of hafnium stock solution to 100 ml with 3N hydrochloric-2.5% hydrofluoric acid mixture.

Hydrochloric acid, 12N, analytical reagent grade.

Hydrochloric acid, 3N and 10N, prepared by appro-

prate dilutions of 12N hydrochloric acid.

Hydrochloric-hydrofluoric acid mixture, 5:1, prepared by adding 250 ml of 12N hydrochloric acid to 50 ml of 49% hydrofluoric acid.

Hydrochloric-hydrofluoric acid mixture, 3N - 2.5%, prepared by diluting 30 ml of 5:1 hydrochloric-hydrofluoric acid mixture to 100 ml with water.

Hydrofluoric acid, 49%, "Baker Analyzed" reagent, J. T. Baker Chemical Co., Phillipsburg, N. J. (low in the elements of interest).

Hydrogen peroxide, 30%, analytical reagent grade.

Metals, hafnium, niobium, tantalum, and titanium, good-purity, spectrochemically analyzed, for preparation of standard solutions.

Niobium, tantalum, and titanium stock solution, 250 µg/ml, prepared by separately dissolving 25 mg of each metal in 10 ml of 5:1 hydrochloric-hydrofluoric acid mixture. A small amount of nitric acid was required for the dissolution of niobium and tantalum. The dissolved metals were combined and diluted to 100 ml with water so that the final concentration of mixed solvent was 3N hydrochloric-2.5% hydrofluoric acids.

Niobium, tantalum, and titanium standard solutions, 25 and 5 µg/ml, prepared by successive dilutions of the stock solution with mixed acid solvent (3N hydrochloric-2.5% hydrofluoric acids).

Standard Solution A, 25 µg/ml, prepared by diluting 10 ml of niobium, tantalum, and titanium stock solution to 100 ml with mixed acid solvent.

Standard Solution B, 5 µg/ml, prepared by diluting 20 ml of Standard Solution A to 100 ml with mixed acid solvent.

Nitric acid, 16N, analytical reagent grade.

Nitric acid, 8N, prepared by diluting the 16N nitric acid with water.

Palladium stock solution, 250 µg/ml, prepared by dissolving 0.0416 gram of PdCl₂ in 100 ml of 3N hydrochloric acid.

Palladium internal standard solution, 5 µg/ml, prepared by diluting 2 ml of palladium stock solution to 100 ml with 3N hydrochloric acid.

Potassium permanganate solution, 3 mg/ml, pre-

pared by dissolving 0.3000 gram of KMnO₄ in 100 ml of water.

Sulfuric acid, 36N, analytical reagent grade.

Sulfuric acid, 3.6N, prepared by diluting 36N sulfuric acid with water.

Uranium solution, 0.25 g/ml, prepared by dissolving 527.4 grams of uranyl nitrate hexahydrate, UO₂(NO₃)₂·6H₂O, in 8N nitric acid. Gentle heating was required for dissolution. Solution was cooled and diluted to 1 liter with 8N nitric acid. The uranium material used to prepare this stock solution should be of high purity, free of niobium, tantalum, titanium, and other elements which co-extract with these elements.

Water, purified by distilling in apparatus made of silica. All reagent water was of this quality.

RECOMMENDED PROCEDURE

CAUTIONS: The analyst should use proper precautions in handling potentially hazardous materials and operating high-voltage spectrographic equipment required by this procedure.

Preparation of Sample, Blanks, and Standards

1. Weigh a portion of the sample containing 5.0 grams of uranium into a 100-ml Teflon beaker for each determination.
2. Treat the sample as follows:
 - a. Uranium metal. Add 20 ml of 8N nitric acid and heat gently until the metal is dissolved. A few drops of hydrogen peroxide may be required for complete dissolution.
 - b. Uranium oxide or nitrate. Add 20 ml of 8N nitric acid and heat gently to complete dissolution.
 - c. Uranium tetrafluoride. Add 10 ml of 30% hydrogen peroxide and warm slightly. Add 10 ml of ammonium hydroxide in 1-ml portions with heating after each addition. Evaporate the sample to dryness and heat at 250° C for 1 hr. Add 20 ml of 8N nitric acid.
3. Prepare reagent blanks and a set of standards in 100-ml Teflon beakers by adding the following materials:

<u>Blanks and Standards, ppm^a</u>	<u>Uranium Added, grams^b</u>	<u>Standard Solutions Added</u>
Reagent blank (Residual 1)	0	0
Uranium + Reagent Blank (Residual 2)	5	0
0.5 + Residual 2	5	0.5 ml of B ^c

Blanks and Standards, ppm ^a	Uranium Added, grams ^b	Standard Solutions Added
1.0 + Residual 2	5	1.0 ml of B ^c
2.5 + Residual 2	5	0.5 ml of A ^d
5.0 + Residual 2	5	1.0 ml of A ^d

^aBased on 5 grams of uranium.

^bContained in 20 ml of 8N nitric acid.

^cContains 5 µg/ml of niobium, tantalum, and titanium.

^dContains 25 µg/ml of niobium, tantalum, and titanium.

4. Add 1 ml of hafnium internal standard solution to each beaker containing blank, standard, or sample.

5. Add 5 ml of 36N sulfuric acid and 5 ml of hydrofluoric acid to each beaker. Swirl gently to mix contents thoroughly.

6. Evaporate the solutions to dryness by heating the beakers in graphite blocks. Use hot plate below the graphite blocks and infrared lamp above as follows:

a. Use infrared heat from above until nitric acid fumes are removed. Swirl the beakers occasionally to liberate trapped gases and minimize spattering. Six hr is normally allowed for this heating step.

b. While continuing to heat from above, add heat from below using 370° C setting on hot plate. This step takes about 6 hr, but can be done overnight. The use of an automatic "ON-OFF" timer is recommended.

7. Cool the beakers.

Extraction

1. Add 8 ml of water, washing down any material on the sides of the beakers.

2. Add 4 drops of the potassium permanganate solution to ensure the highest oxidation states of hafnium, niobium, tantalum, and titanium. Solution will be pink-brown color.

3. Add 25 ml of 12N hydrochloric acid.

4. Transfer the contents of the beaker (33 ml) to a separatory funnel that contains 25 ml of BPHA-chloroform solution. This funnel is designated No. 1.

5. Rinse the beaker with 17 ml of 12N hydrochloric acid and add to the funnel. The aqueous layer is 10N in hydrochloric acid.

6. Stir with an electric stirrer for 10 min. Stirring should be constant and slow enough to prevent rapid evaporation of chloroform.

7. Lift the glass stirring rod from the contents, allow the phases to separate for 5 min, and drain all but a small portion of the organic layer into funnel No. 2. A purple organic phase indicates the presence of vanadium.

CAUTION: Do not allow any of the aqueous layer containing uranium to be transferred.

8. Repeat the extraction in funnel No. 1 with 15 ml of BPHA-chloroform; stir for 5 min, allow the phases to separate for 5 min, and combine the organic extracts in funnel No. 2. Discard the aqueous layer containing uranium into a suitable salvage container. Take special care to keep the different isotopes of uranium separate.

9. Add 25 ml of freshly prepared ferrous ammonium sulfate solution to the combined organic extracts to remove vanadium from the organic phase.

10. Stir for 5 min. After stirring, use a platinum rod to remove any trapped aqueous phase from the neck of the funnel and allow the phases to separate for 10 min.

11. Pour 25 ml of citric acid solution into funnel No. 3.

12. Drain all but a small portion of the organic phase from funnel No. 2 into funnel No. 3. Add 5 ml of BPHA-chloroform to funnel No. 2 and, without stirring, drain all but a few drops of the organic phase into funnel No. 3.

13. Stir the contents of funnel No. 3 for 2 min. Allow the phases to separate for 10 min.

14. Pour 25 ml of citric acid solution into funnel No. 4.

15. Drain all but a small portion of the organic phase from funnel No. 3 into funnel No. 4. Add 5 ml of BPHA-chloroform to funnel No. 3 and, without stirring, drain all but a few drops of the organic phase into funnel No. 4.

16. Stir the contents of funnel No. 4 for 2 min. Allow the phases to separate for 10 min.

17. Drain all but a small portion of the organic layer into a 100-ml platinum dish. Add 5 ml of BPHA-chloroform to funnel No. 4 and, without stirring, drain all but a few drops of the organic phase into the 100-ml platinum dish.

Conversion to Excitation Form

1. Add 3 ml of 16N nitric acid and 1 ml of 3.6N sulfuric acid.

2. Evaporate to dryness under infrared heat.

3. Heat the dry organic deposit on a hot plate. Start at about 40° C and slowly increase the heat to 370° C.

4. Cover the dish and heat it to 600° C in a muffle furnace. Ignite at 600° for 20 min.

- Remove the lid carefully (the ignited material is light and fluffy) and add about one-half of 5 ml of 5:1 hydrochloric-hydrofluoric acid solution, rinsing down the sides of the platinum dish. Apply low heat to insure dissolution.
- Transfer to a 10-ml Teflon crucible.
- Use the rest of the 5:1 hydrochloric-hydrofluoric acid solution to rinse out the platinum dish. Add to the Teflon crucible.
- Add 1 ml of palladium internal standard solution to the Teflon crucible.
- Place the Teflon crucible on a warm hot plate and evaporate the solution to about 200 μ l. During the evaporating, start preparing the electrodes (see Electrode Preparation). When the final volume of sample is about 200 μ l, remove the crucible from the hot plate. Do not allow the sample to go to dryness.

Electrode Preparation

- In a wood block, arrange a pair of graphite electrodes for each sample, blank, and standard.
- Treat one end of each electrode with two 25- μ l portions of electrode sealing solution and heat under an infrared lamp.
- Using a plastic pipet, place the solution prepared in Step 9 of Conversion to Excitation Form, equally divided, on the treated ends of a pair of electrodes.
- Evaporate the transferred solutions to dryness under an infrared lamp and proceed without delay to the next step.

Excitation and Exposure

Produce and record the spectra according to the conditions listed in Table I.

Photographic Processing

- Develop film in Eastman D-19 developer for 4 min at 20° C with continuous agitation of the film.
- Hold in a 2% acetic acid stop bath for 10 sec.
- Fix in Ansco Liquafix for 5 min.
- Wash for 5 min in flowing tap water, wipe, and dry.

Photometric Measurements and Calculations

- Measure the optical densities of the analytical lines in the spectra of the standards, blanks, and sample by use of a recording microphotometer. The wavelengths of the analytical lines are listed in Table II.
- Convert the optical densities to intensities by use of the appropriate emulsion calibration curves. Emulsion is calibrated by the Two-Step Preliminary Curve Method.⁴

Table I.

Spectrographic and Excitation Parameters

<u>Spectrograph</u>	2-m, Applied Research Laboratories
Slit width	18 μ
Filters, entrance slit	None
Emulsion	Eastman SA-3
Spectral region	2400 to 3600 Å.
<u>Excitation</u>	ac spark source
Capacitance	0.0037 μ F.
Inductance	25 μ H.
Resistance	None added
Spark power setting	10
Primary voltage	180
Auxiliary gap	3 mm between two 1/2-in. diam tungsten rods
Discharge	About 2400 per sec
Radio frequency current	11.5 amp
Analytical gap	2 mm
Pre-exposure	None
Exposure period	90 sec

- Calculate the appropriate intensity ratios of element line to internal standard line, using both hafnium and palladium as internal standards.
- Using the graphical method of Pierce and Nachtrieb,⁵ determine the impurity concentrations introduced by the uranium matrix plus the reagents (Residual 2, see Step 3 of Preparation of Sample and Standards).
- Plot the analytical curves for each element with both internal standards, using intensity ratios vs ppm concentration, on log-log coordinate paper. The element concentrations are corrected by applying the values found in Step 4. Typical curves are shown in Figs. 6, 7, and 8.
- Apply the intensity ratios measured for the sample and for the reagent blank (Residual 1, see step 3 of Preparation of Sample and Standards) to the appropriate analytical curves to obtain element concentrations.
- Correct the element concentration in the samples for the reagent blank and report the result along with an indication of the precision expected with this method.

Table II

Analytical Lines

<u>Element</u>	<u>Wavelength, Å.</u>
Niobium	II 2927.8
Tantalum	II 2635.6
Titanium	II 3168.5
Hafnium (Internal Standard)	II 2820.2
Palladium (Internal Standard)	I 3404.6

EXPERIMENTAL

This method may be divided into three parts, preparation of the standards and sample, extraction processing, and spectrochemical analysis. These are shown in Fig. 4, with the extraction processing given in detail to indicate the several steps involved. Pertinent aspects of the development work are discussed in this section.

Standards

Two sets of standards were used for the development work. They were designated either "Unprocessed" or "Working", and contained the following concentrations of niobium, tantalum, and titanium, expressed as parts per million with reference to a 5-gram uranium sample weight: 0.5, 1.0, 2.5, and 5.0. The Unprocessed standards did not contain uranium, and received no treatment other than the final processing steps consisting of additions of a hydrochloric-hydrofluoric acid mixture and the internal standards, and evaporation to reduce the volume to the electrode sample size. Studies made with these standards provided information by which the spectrographic excitation and exposure conditions were selected to give the desired precision. The studies also included selection of the analytical lines, observance of spectral line interferences, and evaluation of the effects of different quantities of the palladium internal standard on the intensity signal of the elements. The Working standards which included 5 grams of the uranium matrix (added from a stock solution of uranyl nitrate in 8N nitric acid) and the internal standards, hafnium and palladium, were used to establish the appropriate analytical curves. Also processed were blanks of the uranium matrix plus reagents and of the reagents alone for the evaluation of residuals.

Sample Weight

The effect of the quantity of uranium present in the sample was studied by analyzing synthetic samples containing 5.0, 2.5, 1.25, 0.5, and zero grams of uranium and the three impurity elements in quantities of either 5 or 12.5 μg each. These quantities corresponded to 1 and 2.5 ppm for a sample weight of 5 grams. Figure 5 is typical of the results obtained for all three elements. The

Fig. 4. Flow chart of the method.

results are shown in comparison to the solid line representing the average intensity ratios obtained from the evaluation of standards containing 5 grams of uranium. The dotted lines represent $\pm 20\%$ relative standard deviation. Only one point for the three elements was outside the $\pm 20\%$ values. This information indicated that the intensity ratios of niobium, tantalum, or titanium to hafnium are not significantly influenced by variations of the uranium concentration. For samples containing more than 5 ppm (5-gram sample) of niobium, tantalum, or titanium, a smaller sample size may be used with the Recommended Procedure.

Evaluation of Excitation and Exposure Parameters

The excitation technique used by Katz and Carter² and by Vita³ is direct sparking of the solu-

Fig. 5. Evaluation of niobium with varying amounts of uranium

tion sample as it is brought to the spark gap by a rotating graphite electrode. Serious disadvantages are the corrosion of the spark stand and the possibility of cross-contamination to other analyses from fumes produced by sparking the hydrochloric and hydrofluoric acids present in the sample. To avoid these difficulties, the technique of evaporating the solution sample on the ends of a pair of graphite rod electrodes before sparking was selected. This technique has been successfully used to analyze many kinds of samples at this Laboratory.

The excitation and exposure parameters were studied using the direct reader section of a Jarrell-Ash combination spectrograph. An extensive investigation was completed to select the excitation behavior that gave a precision of less than 10% relative standard deviation for the intensity readings.

The desirability of increasing the exposure time from an initially selected 30 sec was shown by the data listed in Table III. These results were obtained with Unprocessed standards containing 2.5

ppm of each element and 50 μ g of the internal standard palladium. Other changes indicated that decreasing the quantity of palladium to 2.5 μ g (see Internal Standardization) and tripling the number of spark discharges per charging cycle further improved the precision. The excitation source parameters given in Table I enhance the spark spectra of the impurity elements and minimize interelement effects.

Internal Standardization

Although use of palladium as an internal standard has been reported by Vita,³ it seems to possess undesirable characteristics. One objection is its failure to yield "spark" lines (spectra originating from ions rather than atoms) to tie in with the spark lines of niobium, tantalum, and titanium; hence, the internal standardization is not likely to be optimum. However, use of palladium as an internal standard was investigated by using 2.5 μ g of palladium per electrode sample in the Unprocessed standards. The results, shown in Table IV, clearly indicate that the quantity of palladium present in the electrode sample affects not only the magnitude but also the variability of the intensities produced by the elements. The results show that 2.5 μ g of palladium gave adequate precision of 10% relative standard deviation using direct reader instrumentation. Using photographic recording, a precision of 15% was obtained over the concentration range of 0.5 to 5 ppm for Unprocessed standards.

Analysis of several samples indicated that the method might be improved if the internal standard had extractive behavior similar to that of the elements being determined, so that it could be carried through the entire procedure. An added

Table III
Excitation Behavior of Niobium, Tantalum, and Titanium

Exposure Number	Cumulative Exposure Time, sec.	Cumulative Percentage of Sample Excited			
		Nb 3225	Ti 3373	Ta 2661	Ta 2714
1	30	66	60	84	82
2	60	79	75	94	92
3	90	87	85	98	97
4	120	93	92	100	99
5	150	97	97	--	100
6	180	< 100	< 100	--	--

Concentration of each element is 2.5 ppm.

Table IV
Effect of Palladium Concentration on the Excitation Behavior of Niobium,
Tantalum, and Titanium

Pd Concentration/ Electrode Pair	Intensities (Scaler Readings)			
	Nb 3225.5	Ti 3372.8	Ta 2661.3	Ta 2714.7
50 μ g	988 $\pm$ 273 (28)	2289 $\pm$ 469 (20)	683 $\pm$ 81 (12)	916 $\pm$ 119 (13)
25 μ g	1726 $\pm$ 318 (18)	3672 $\pm$ 469 (13)	943 $\pm$ 105 (11)	1347 $\pm$ 146 (11)
2.5 μ g	2497 $\pm$ 135 (5.4)	4984 $\pm$ 233 (4.7)	1195 $\pm$ 39 (3.3)	1626 $\pm$ 103 (6.3)

Values in parentheses are the percent relative standard deviation of the values shown. Each value is the average from eight exposures.

Concentration of each impurity element is 2.5 ppm.

element having this property could compensate for errors caused by inadvertent loss of sample during processing. In two steps of the Recommended Procedure, the sample requires extra careful handling because it is either a light residue or a small volume of solution.

Hafnium was selected because it should behave similarly to the elements of interest and was not likely to be present in the samples. Tests showed that 5 μ g of hafnium added at the initial acid treatment step were extracted with the niobium, tantalum, and titanium and gave suitable photographic response. Hafnium offered the further advantage of excitation behavior (spark lines) more like those of the elements being determined than that offered by palladium. A least-squares calculation on 15 evaluations of the 5-ppm standard (completely processed), observed on six films, showed a relative standard deviation of 15% with hafnium internal standardization and 25% with palladium.

The possibility that hafnium might be present in samples and thereby affect the internal standardization was not overlooked. This contingency was met by using both elements as internal standards. Results obtained by each internal standard are compared in Table V.

Extraction Behavior of Hafnium and Tantalum

The behavior of hafnium and tantalum in the extraction procedure was studied radiometrically

by following the gamma activity of Hf-181 and Ta-182 added as tracers. Difficulty in resolving the counting of the activities required that the two elements be extracted separately instead of together as desired. Niobium and titanium could not be included because suitable radioactive isotopes were not available.

Table V
Comparison of Results Using
Two Internal Standards

Ti, ppm		Nb, ppm		Ta, ppm	
Hf	Pd	Hf	Pd	Hf	Pd
1.5	2.0	1.8	1.9	0.5	0.7
1.5	1.8	1.5	1.5	0.4	0.6
1.0	1.1	1.5	1.3	0.7	0.7
0.9	1.1	1.2	1.2	0.7	0.9
2.2	2.2	3.0	3.3	2.5	2.9
1.8	2.9	3.6	3.5	1.3	1.3
3.1	3.0	3.3	3.2	1.0	1.3
0.5	0.5	2.4	2.5		
1.0	0.9	1.8	2.0		
1.2	1.3	1.3	1.4		
0.5	0.5	1.0	1.4		
1.0	1.2	0.7	0.9		
0.7	0.9	0.8	1.2		
1.0	1.4	1.2	1.3		

Three extraction steps were considered in the studies, namely:

1. Extraction of the elements into a BPHA-chloroform solution from a 10N hydrochloric acid solution of uranium.
2. Treatment of the extract with iron(II) to remove vanadium.
3. Washing of the extract with citric acid to remove iron.

These steps are indicated on the flow chart (Fig.

4).

The organic phase of each step was decreased to 5 ml and transferred to a suitable test tube which was placed in a deep-well scintillation counter for measurement of the gamma activity. A radiometric interference by the uranium base-material was detected and eliminated. The extracted gamma activity from the uranium, believed to be protactinium with a 7-hr half-life, was avoided by allowing that activity to decay before measuring those of Hf-181 (46-day half-life) and Ta-182 (111-day half-life).

Of particular interest was the extraction behavior of the elements from uranium with the chloroform solution of BPHA. Vita³ investigated the extraction of several elements including niobium, tantalum, and titanium from 10N hydrochloric acid, but gave no information on studies made in the presence of uranium. The results obtained for hafnium and tantalum for the first extraction step are summarized in Tables VI and VII. The extraction efficiency of hafnium was observed to be consistent at 89% in the presence of 5 grams of uranium and 0.5 to 5 ppm of niobium, tantalum, and titanium. With uranium absent, hafnium was 92% extracted. These results indicated that hafnium had satisfactory extractive behavior for use as an internal standard. The results for tantalum, shown in Table VII, indicated 93% extraction for 0.5, 1.0, and 2.5 ppm of the three elements but a somewhat lower, 82%, extraction at 5 ppm. Observations made at the 5-ppm concentration but without extraction processing showed that the decreased extraction of tantalum was not due to the presence of niobium and titanium. The differences shown here -- decreased extraction of tantalum with increasing concentration and less than 100% extraction efficien-

Table VI

Extractive Behavior of Hf-181 from 10N HCl-Uranium Solution with BPHA-Chloroform

Sample Composition ^a		Hf-181	
Ti, Nb, Ta μg each added	Hf, ^b μg added	γ -Counts/ Minute Extracted	Percent Activity Extracted
0	5.0	26,872	92
2.5	5.0	25,535	88
2.5	5.0	25,534	88
5.0	5.0	25,287	87
12.5	5.0	25,784	89
12.5	5.0	25,781	89
25.0	5.0	26,111	90
25.0	5.0	25,981	89

^aAll samples contain 5.0 grams U except that with no added Ti, Nb, or Ta which contains no added uranium.

^bIncludes 0.04 μg of Hf-181 which has a γ -activity of 29,078 counts/min.

cy -- are not detrimental to the method because the standards are processed by the same procedure as the samples. The behavior of Ta-182 was also followed through the second and third extraction steps. As shown by the results in Table VIII, no significant amount of tantalum was removed from the extract by the aqueous phases. The radiometric measurements made with hafnium and tantalum

Table VII

Extractive Behavior of Ta-182 from 10N HCl-Uranium Solution with BPHA-Chloroform

Sample Composition ^a		Ta-182	
Ti, Nb μg each added	Ta, ^b μg added	γ -Counts/ Minute Extracted	Percent Activity Extracted
2.5	2.5	35,852	97
2.5	2.5	34,312	93
5.0	5.0	34,658	94
5.0	5.0	34,207	93
12.5	12.5	34,487	93
12.5	12.5	34,438	93
25.0	25.0	29,809	81
25.0	25.0	31,776	86
25.0	25.0	29,620	80

^aAll samples contain 5.0 grams of U and 5.0 μg of Hf.

^bIncludes 0.02 μg of Ta-182 which has a γ -activity of 36,937 counts/min.

Table VIII
Extractive Behavior of Ta-182

Sample No.	Extraction Step	Before Extraction	After Extraction	
		Organic Phase	Aqueous Phase	Organic Phase
1	Fe(II) treatment	34,926	0	34,170
2	Fe(II) treatment	35,430	0	34,490
3	Citric acid wash	32,808	0	32,555
4	Citric acid wash	33,985	0	33,336

served to verify the validity of the procedural operations which had been selected previously by spectrographic observations.

Interferences

Interferences either relating to the electrode sample composition or resulting from coincident spectral lines were encountered in the development work. The interferences were reflected by poor precision and erratic analytical curves. Each interference encountered is discussed along with the method used to eliminate it.

Palladium. The data in Table IV show the considerable alteration of the intensities of niobium, tantalum, and titanium resulting from the presence of different quantities of palladium in the electrode sample. Decreasing the quantity of palladium from 50 to 2.5 μg about doubled the intensities and markedly improved the precision. The unreliable observations obtained in the presence of 50 μg of palladium may have two causes. One could be incomplete volatilization of the large quantity of electrode sample; the other could be the considerable difference in electrode sample composition among the standards. In the lowest standard, palladium was the principal constituent (50 μg Pd to 7.5 μg Nb, Ta, and Ti); in the highest standard, it was

one of four major constituents (50 μg Pd to 75 μg Nb, Ta, and Ti). By selecting 2.5 μg of palladium, the composition of the electrode sample as well as the quantity was made such that the influence of palladium was considerably lessened.

Vanadium. Vanadium, often present as an impurity, was extracted with the niobium, tantalum, and titanium. In concentrations exceeding 1 ppm, vanadium yielded lines which interfered with the analytical lines Nb 3094.1 $\text{\AA}$. and Ta 2685.1 $\text{\AA}$. Large concentrations would probably alter the electrode charge composition so as to produce a matrix effect. Interference by vanadium was avoided by treating the organic phase containing the extracted elements with ferrous ammonium sulfate to reduce the vanadium to the (IV) oxidation state. Vanadium (IV) was removed by extraction into the aqueous phase. This treatment was effective in reducing the vanadium concentration to less than 1 ppm. Attempts to reduce the vanadium to the (IV) oxidation state in the presence of the uranium before extraction, as suggested by Vita,³ were unsuccessful.

Iron. Iron was introduced into the organic phase by the treatment used to remove vanadium. Its spectrum interfered with the analytical lines Pd 3404.6 $\text{\AA}$. and Ta 2685.1 $\text{\AA}$. Washing the organic phase with citric acid (200 mg) dissolved in 10N hydrochloric acid reduced the iron sufficiently to eliminate the spectral interferences. Yet, 2 to 20 ppm of iron remained, its concentration being directly related to the combined quantity of niobium, tantalum, and titanium present. Further studies indicated that 5 or more ppm of iron caused low results for niobium and titanium. These findings, summarized in Table IX, showed the need to re-

Table IX
Effect of Iron on the Determination of Niobium, Tantalum, and Titanium

Fe Added, ppm	PPM Found ^a											
	Niobium				Tantalum				Titanium			
	0.5	1.0	2.5	5.0	0.5	1.0	2.5	5.0	0.5	1.0	2.5	5.0
1.0	0.4	0.9	2.6	4.1	0.4	0.9	2.6	4.8	0.4	1.0	2.3	4.0
5.0	0.2	0.6	2.4	5.2	0.4	0.6	2.5	5.3	0.3	0.7	2.0	4.6
20.0	0.4	0.6	1.8	4.9	0.4	0.6	2.1	5.0	0.3	0.6	1.8	4.3

^aEach value represents the average of two results obtained on separate films.

duce the iron concentration to 1 ppm prior to spectrochemical analysis.

The effectiveness of washing the organic phase with citric acid was further investigated by measuring the effects of the following variables: quantity of citric acid, normality of hydrochloric acid, and number of washes. As shown by the data in Table X, less than 1 ppm of iron remained in the organic phase after two washes each with 40 mg of citric acid in 3N hydrochloric acid. This treatment was added to the Recommended Procedure.

Molybdenum and Zirconium. Molybdenum and zirconium were also extracted by BPHA and became part of the electrode sample. Studies were made of their possible interference by analyzing synthetic samples containing 0, 0.5, 1, 2.5, and 5 ppm each of niobium, tantalum, and titanium (plus a constant quantity of hafnium) in the presence of 0, 1, 5, or 20 ppm of molybdenum or zirconium. Since extraction was not a part of the study, uranium was omitted. The results, shown in Table XI, indicated that as much as 20 ppm of either molybdenum or zirconium did not significantly affect the spectrographic determination of niobium, tantalum, or titanium.

EVALUATION OF METHOD

Standards

Standards were prepared for each test or analysis by taking aliquots of appropriate volume

Table X

Iron Remaining in the Extract After Citric Acid Wash, ppm

Number of washes ^b	Normality of HCl Solution ^a						
	0	2	3	4	6	8	10
1	> 50	2.8	3.4	5.0	9.3	8.0	
2	> 50	1.9	0.7	0.8	5.0	7.0	5.4

^aContains 40 mg of citric acid in 25 ml of HCl of the designated normality.

^bWashing time: 2 min per wash.

from two standard solutions. These standard solutions were prepared by successive dilutions of a stock solution made by dissolving weighed quantities of niobium, tantalum, and titanium metals. During the development work, the composition of the original standard solutions was verified by comparing with standard solutions made subsequently from an independently prepared stock solution. Verification was also obtained from standard solutions containing each element separately which were used for recovery studies. There was no evidence of a change in concentration with aging for solutions of the elements in 3N hydrochloric-2.5% hydrofluoric acids.

Calibration Curves

Data for plotting the analytical curves were obtained from the analysis of Working standards and appropriate blank solutions. Each run made to analyze samples included a set of standards. In the early work, standards were repeated at least once in each run in order to accumulate the data needed to adequately calibrate the method.

Table XI

Effect of Molybdenum and Zirconium on the Determination of Niobium, Tantalum, and Titanium

Amount of Element Added, ppm		PPM Found ^a											
		Niobium				Tantalum				Titanium			
		0.5	1.0	2.5	5.0	0.5	1.0	2.5	5.0	0.5	1.0	2.5	5.0
Mo	1.0	0.5	0.8	2.5	4.6	0.6	0.8	2.2	4.4	0.6	1.0	2.8	4.7
	5.0	0.4	0.8	2.1	4.6	0.4	0.8	2.2	4.6	0.4	0.8	2.6	4.6
	20.0	0.4	0.8	2.0	3.9	0.6	0.8	2.1	4.3	0.4	0.8	2.2	4.1
Zr	1.0	0.5	1.0	2.8	5.2	0.6	1.0	2.8	5.0	0.6	1.1	3.0	5.3
	5.0	0.4	1.0	2.6	5.2	0.4	1.0	2.5	5.0	0.4	1.0	2.6	4.9
	20.0	0.6	1.0	2.4	5.6	0.4	0.9	2.4	5.5	0.4	1.0	2.8	5.9

^aEach value represents the average of two results obtained on separate films.

After each run, analytical curves were plotted using the accumulated results. Because several reagents were used in large amounts, it was necessary to evaluate the residual quantities of the three elements in the uranium matrix. The graphical method of Pierce and Nachtrieb⁵ was used to determine the residuals. In general, the residuals were 0.2 ± 0.1 ppm based on a 5-gram sample of uranium. The corrections for residuals were applied when plotting the analytical curves. The curves obtained for each element, using hafnium internal standardization, are shown in Figs. 6 through 8. The curves represent the least-squares fit of the accumulated data to the following equation:

$$\log (\text{Intensity Ratio}) = \log K + m \log (\text{Concentration}).$$

Reliability

The unavailability of standard uranium samples containing niobium, tantalum, and titanium required that other means be used to assess the reliability of the method. The precision was estimated by evaluating the data used to construct the analytical curves (Figs. 6 through 8). This was done by plotting the deviations of the experimental intensity ratios from the least-squares-averaged intensity ratios vs concentration for about 100 individually processed standards. Figure 9 shows a typical plot of the data with lines indicating ± 10 , ± 15 , and $\pm 20\%$ relative standard deviation.

Fig. 6. Analytical curve for niobium in uranium.

Fig. 7. Analytical curve for tantalum in uranium.

By considering the number of observations within a given percent relative standard deviation, a precision of 15% was established for the concentration range of 0.5 to 5.0 ppm of each element. Because the Working standards were analyzed in the same manner as samples, an assessment of the precision here provides a reasonable evaluation of precision for the analysis of samples.

During the investigation, estimates of accuracy were obtained by the analysis of spiked samples. Portions of samples were analyzed before and

Fig. 8. Analytical curve for titanium in uranium.

after the addition of known amounts of the impurity elements. These results are given in Tables XII through XIV. The results show an average 2% negative relative error for the three elements evaluated, within the range of the method.

Another assessment of precision and accuracy was made by analyzing eight synthetic samples containing different concentrations of niobium, tantalum, and titanium. These samples were prepared by adding selected quantities of newly made stock solutions of the elements to solutions of uranyl nitrate containing 5 grams of uranium. Each sample was analyzed as an unknown four times, two times apiece by two analysts working independently. Table XV shows the results. The values listed under the Added headings include the amounts of niobium, tantalum, and titanium found as residual impurities in the uranyl nitrate and reagents. Each result listed under the Found headings represents a single determination for the indicated element. The results from all eight synthetic samples were statistically evaluated to determine precision and accuracy. The results are shown in Table XVI. The precision is given in terms of relative standard deviation. Accuracy is given in terms of relative error (mean error of a series of test results expressed as a percentage of the

Fig. 9. Deviation plot for tantalum intensity ratios.

expected result). This evaluation of synthetic samples shows an average 8% positive relative error at the two concentrations tested.

All evaluations of precision support a 15% relative standard deviation for a single determination in the concentration range 0.5 to 5.0 ppm using hafnium as an internal standard.

Evaluation of Uranium Tetrafluoride Samples

The analysis of several uranium tetrafluoride samples showed the impurities to be below the lower limit established for this method, that is, less than 0.5 ppm. Because the dissolution procedure for fluorides involves heating with hydrogen peroxide and ammonium hydroxide prior to the acid treatments, tests were made to determine if niobium, tantalum, or titanium might be lost. Duplicate portions of a uranium tetrafluoride sample were analyzed before and after additions of 1, 2, and 4 ppm each of niobium, tantalum, and titanium. The results are shown in Table XVII. There are no indications of a loss of niobium, tantalum, titanium, or hafnium during the processing steps.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the helpful suggestions and assistance of C. F. Metz, under whose supervision this work was performed. Joseph Bubernak, Group CMB-1, gave valuable advice in making the radiometric measurements. Gary Tietjen, Group T-13, provided valuable assistance in the statistical evaluation of the results from synthetic samples.

REFERENCES

1. B. F. Scribner and H. R. Mullin, National Bureau of Standards Report A-2907, 1945.
2. S. Katz and T. A. Carter, USAEC Report TID-7029, 1963, compiled and edited by R. J. Jones.
3. O. A. Vita, Goodyear Atomic Corporation Report GAT-524, 1966.
4. Methods for Emission Spectrochemical Analysis, 4th Ed., ASTM, 1964.
5. W. C. Pierce and N. H. Nachtrieb, Ind. Eng. Chem., Anal. Ed., 13, 774 (1941).

Table XII
Analysis of U_3O_8 Samples Containing Added Niobium

Sample No.	Nb in U, ^a ppm	Nb Added to U, ppm	Total Nb in U, ppm	Nb Found, ^b ppm	Error, ppm	Rel. Error, %
977 A	3.3	1.0	4.3	4.8	+0.5	+ 12
B	9.2 ^c	1.5	10.7	8.0 ^c		
C	4.6	2.0	6.6	5.8 ^c		
D	13.5 ^c	2.5	16.0	16.0 ^c		
968 A	0 ^c	0	0	0 ^c		
B	0 ^c	2.0	2.0	2.1	+0.1	+ 3
C	3.2	2.5	5.7	4.7	-1.0	- 17
D	1.5	3.0	4.5	4.2	-0.3	- 7
944 A	13 ^c	0.7	13.7	14 ^c		
B	20 ^c	1.7	21.7	20 ^c		
C	10.7 ^c	2.0	12.7	13 ^c		
D	2.9	3.5	6.4	7.0 ^c		
939 A	1.5	2.0	3.5	4.4	+0.9	+ 26
B	1.4	3.0	4.4	5.6 ^c		
931 A	1.8	3.5	5.3	4.9	-0.4	- 8
B	1.5	0.5	2.0	2.0	0	0
C	1.5	2.5	4.0	4.0	0	0
D	1.2	4.5	5.7	5.0	-0.7	- 12

^aFrom a single analysis of the sample.

^bFrom a single analysis of the "spiked" sample.

^cExtrapolated value.

Table XIII
Analysis of U_3O_8 Samples Containing Added Tantalum

Sample No.	Ta in U, ^a ppm	Ta Added to U, ppm	Total Ta in U, ppm	Ta Found, ^b ppm	Error, ppm	Rel. Error, %
977 A	0.3 ^c	1.0	1.3	1.5	+ 0.2	+ 15
B	0.2 ^c	1.5	1.7	1.5	- 0.2	- 12
C	0.4 ^c	2.0	2.4	2.6	+ 0.2	+ 8
D	0.8	2.5	3.3	3.1	- 0.2	- 6
968 A	2.9	0	2.9	3.3	+ 0.4	+ 14
B	2.1	2.0	4.1	3.9	- 0.2	- 5
C	1.4	2.5	3.9	2.5	- 1.4	- 36
D	1.5	3.0	4.5	3.9	- 0.6	- 13
944 A	0.6	0.7	1.3	1.0	- 0.3	- 23
B	0.6	1.7	2.3	2.0	- 0.3	- 13
C	0.6	2.0	2.6	2.4	- 0.2	- 8
D	0.7	3.5	4.2	3.7	- 0.5	- 12
939 A	1.0	2.0	3.0	3.6	+ 0.6	+ 20
B	0.6	3.0	3.6	4.0	+ 0.4	+ 11
C	1.0	3.5	4.5	3.5	- 1.0	- 22
D	0.9	2.5	3.4	2.8	- 0.6	- 18
931 A	0.5	3.5	4.0	3.2	- 0.8	- 20
B	0.4 ^c	0.5	0.9	0.8	- 0.1	- 11
C	0.7	2.5	3.2	3.5	+ 0.3	+ 10
D	0.7	4.5	5.2	4.2	- 1.0	- 19

^aFrom a single analysis of the sample.

^bFrom a single analysis of the "spiked" sample.

^cExtrapolated value.

Table XIV
Analysis of U₃O₈ Samples Containing Added Titanium

Sample No.	Ti in U, ^a ppm	Ti Added to U, ppm	Total Ti in U, ppm	Ti Found, ^b ppm	Error, ppm	Rel. Error, %
977 A	0.3 ^c	1.0	1.3	1.6	+ 0.3	+ 23
B	< 0.2 ^c	1.5	1.5	1.4	- 0.1	- 7
C	0.3 ^c	2.0	2.3	2.7	+ 0.4	+ 17
D	0.7	2.5	3.2	2.8	- 0.4	- 13
968 A	2.2	0	2.2	2.2	0	0
B	2.7	2.0	4.7	4.6	- 0.1	- 2
C	3.1	2.5	5.6	4.4	- 1.2	- 21
D	3.4	3.0	6.4	6.2 ^c		
944 A	1.6	0.7	2.3	2.6	+ 0.3	+ 13
B	0.4	1.7	2.1	2.3	+ 0.2	+ 10
C	0.2 ^c	2.0	2.2	2.7	+ 0.5	+ 23
D	0.6	3.5	4.1	4.4	+ 0.3	+ 7
939 A	2.0	2.0	4.0	4.7	+ 0.7	+ 18
B	1.5	3.0	4.5	5.5 ^c		
C	1.0	3.5	4.5	3.8	- 0.7	- 15
D	0.3	2.5	2.8	2.7	- 0.1	- 4
931 A	1.5	3.5	5.0	4.6	- 0.4	- 8
B	1.5	0.5	2.0	1.9	- 0.1	- 5
C	1.0	2.5	3.5	4.3	+ 0.8	+ 23
D	0.9	4.5	5.4	5.4 ^c		

^aFrom a single analysis of the sample.

^bFrom a single analysis of the "spiked" sample.

^cExtrapolated value.

Table XV
Analysis of Synthetic Samples

Sample	Nb, ppm		Ta, ppm		Ti, ppm	
	Added ^a	Found	Added ^a	Found	Added ^a	Found
A	1.2	1.2 1.3	5.2	6.0 5.8	5.2	5.5 5.0
		1.2 1.4		6.0 7.0		6.2 6.8
B	1.2	1.5 1.1	1.2	1.4 1.1	5.2	5.2 5.0
		1.6 1.3		1.5 1.5		7.4 5.9
C	5.2	5.6 5.2	5.2	5.3 5.0	5.2	5.5 5.2
		4.8 5.4		3.8 5.2		5.3 5.0
D	5.2	5.6 5.9	1.2	1.3 1.3	5.2	5.2 5.5
		5.3 7.0		1.0 1.4		5.1 6.0
E	5.2	5.5 6.1	1.2	1.3 1.3	1.2	1.2 1.5
		6.0 7.2		1.0 1.4		1.3 1.6
F	1.2	1.4 1.1	1.2	1.3 1.7	1.2	1.3 1.4
		1.4 1.4		1.3 1.3		1.7 1.5
G	5.2	5.7 5.6	5.2	5.3 5.4	1.2	1.3 1.4
		4.3 7.4		3.8 5.6		1.1 1.4
H	1.2	1.2 1.5	5.2	4.9 5.3	1.2	1.2 1.4
		0.8 1.2		3.4 5.5		1.1 1.3

^aIncludes residual impurities from uranium and reagents, evaluated to be 0.2 ± 0.1 using the graphical method of Pierce and Nachtrieb.⁵

Table XVI

Statistical Evaluation of Eight Synthetic Samples

Precision Data			
Relative Standard Deviation, % ^a			
PPM	Nb	Ta	Ti
5.2	16	15	14
1.2	17	15	13
Accuracy Data			
Relative Error, % ^b			
PPM	Nb	Ta	Ti
5.2	+10	0	+ 8
1.2	+ 7	+10	+13

^aEach estimate made with 12 degrees of freedom.^bEach estimate made from 16 observations.

Table XVII

Analysis of UF₄ Samples Containing
Added Impurities

Sample	Nb	Ta	Ti
867 as received	< 0.5	< 0.5	< 0.5
	< 0.5	< 0.5	< 0.5
867 + 1.0 ppm Nb, Ta, Ti	1.4	1.2	0.9
	1.5	1.4	1.0
867 + 2.0 ppm Nb, Ta, Ti	2.7	2.0	2.2
	2.3	2.3	1.7
867 + 4.0 ppm Nb, Ta, Ti	4.6	4.2	4.0
	4.9	3.9	4.1