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UNITED STATES ATOMIC ENERGY COMMISSION

SEMIANNUAL PROGRESS REPORT FOR THE PERIOD JANUARY 1961 THROUGH JULY 1961

C. J. Rodden, Area Manager

NEW BRUNSWICK LABORATORY

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AEC Research and Development Report

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Issuance Date: March 1962

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ABSTRACTS

Spectrophotometric Determination of Tin and Molybdenum with 8-Quinolinol

A procedure is presented for the determination of both molybdenum and tin in a wide variety of samples with 8-quinolinol (oxine). The molybdenum complex is extracted with chloroform from a sulfate solution of the sample at pH 0.85 and determined spectrophotometrically at 385 mμ. The tin complex is then similarly extracted and determined after the addition of chloride to the sample solution.

Pyrohydrolytic Separation of Boron from Boron Minerals for Mass Spectrometric B^{11}/B^{10} Ratio Determination

Boron is separated quantitatively from various boron minerals by pyrohydrolysis. The distillate is passed through a cation-exchange resin column to remove interfering strontium, rubidium, and other cations, after which the effluent is neutralized to pH 9.3 to 9.4 and evaporated to dryness. The residue is suitable for the mass spectrometric determination of the B^{11}/B^{10} ratio.

Design and Construction of a Versatile Mass Spectrometer for the Isotopic Analyses of Gas, Liquid, and Solid Substances

A single-focusing mass spectrometer of 6-inch radius, 60° sector magnetic analyzer has been designed to analyze a wide range of sample materials that require high precision and accuracy in the low-mass range but which offers considerable flexibility to evaluate high-mass materials for comparison purposes. A gas, solid, or liquid type of analysis may be performed. A change-over can be made from one type of analysis to another with minimum loss of instrument time and requiring minimum technical knowledge.

Single peak measurement, or ratio measurement may be made from M/e 6/7 to M/e 238/235, with the use of vibrating reed electrometers or an electron multiplier for measuring the ion beams.

The Stability of Plutonium Sulfate Tetrahydrate and Anhydrous Plutonium Sulfate

The stability of plutonium sulfate tetrahydrate and anhydrous plutonium sulfate has been evaluated. Recent tests disclose no significant change in the plutonium content of the tetrahydrate or the anhydrous salt for periods of at least 18 and 6 months, respectively. Both thermogravimetry and chemical analysis showed the formula of anhydrous plutonium sulfate to be $Pu(SO_4)_{2.000 \pm 0.002}$.

The Stability and Stoichiometry of Dicesium Plutonium Hexachloride

Dicesium plutonium hexachloride has been prepared and its suitability as a primary standard for plutonium evaluated. The composition of the material has been determined by analysis and fits the formula Cs_2PuCl_6. Although the compound is stoichiometric, it is susceptible to changes in relative humidities greater than 17%, and showed a small but significant weight loss during a six-month testing period.

The Cation-Exchange Separation and Spectrographic Determination of Silicon in Plutonium

Silicon is separated from plutonium using a cation-exchange procedure prior to spectrographic determination. Plutonium(III) in 0.2N nitric acid is adsorbed on Dowex-50 cation resin while silicon, as silicate anion or colloid, passes unadsorbed into the effluent. The effluent is evaporated to dryness and the residue is dissolved in dilute nitric acid containing hydrofluoric acid. Aliquots of the solution are dried on graphite electrodes and excited in a D.C. arc. Typical results on synthetic solutions give an estimated overall average deviation of ± 25% and sensitivities from 1 to 5 p.p.m. silicon. This method offers an alternate procedure to the carrier distillation technique which employs large amounts of plutonium dioxide as matrix for the determination of silicon in plutonium.

Spectrographic Determination of Trace Impurities in High-Purity Plutonium

The development of a sensitive method for the spectrographic determination of trace impurities in plutonium is continuing. The method was modified for use with plutonium sulfate samples, and enlarged to include the determination of boron, cadmium, and some alkali elements, and also for the estimation of americium. Plutonium breakthrough during the ion-exchange separation of plutonium from its impurities was found to be $< 0.001\%$. Data from plutonium metal analyzed at this laboratory generally agreed with results obtained on similar material at Hanford Atomic Products Operation. Methods were investigated for preparing high-purity reagents and reducing reference blank values in order to obtain greater sensitivity. At present seventeen elements may be determined in the 1st and 2nd optical orders using only 200 mg. of sample.

SPECTROPHOTOMETRIC DETERMINATION OF TIN AND MOLYBDENUM WITH 8-QUINOLINOL

A. R. Eberle and M. W. Lerner

In the search for a separation procedure capable of separating microgram amounts of tin from uranium, the use of 8-quinolinol (oxine) was investigated. Although Gentry and Sherrington[1] have reported that tin(IV) can be extracted quantitatively by oxine in chloroform at pH 2.5 to 5.5, copper, nickel, iron, molybdenum, and aluminum also give colored complexes coextracting with tin. Wyatt[2] found that by adjusting the pH to slightly below 2.5 some separation of the tin from small amounts of these interferences was possible. However, the procedure was not considered to be satisfactory and it required close pH control.

The present investigation shows that both tin(IV) and molybdenum(VI) can be separated from large amounts of most elements by extraction of the oxine complexes with chloroform at a pH range of 0.70 to 0.90 with a fairly high concentration of oxine. The tin and molybdenum can also be separated from each other and determined separately. This separation is possible because it was found that tin(IV) will only extract in the presence of halide: chloride, bromide, or iodide. Accordingly, the molybdenum is first extracted in the absence of chloride, then chloride is added and the tin is extracted. The procedure is simple, rapid, and, except for the interference of tungsten, niobium, and possibly tantalum, is apparently specific for both tin and molybdenum.

A procedure is described for the analysis of uranium and a variety of other metals. The investigation is continuing and will be given in a final report.

Reagents

Ammonium Chloride, 20%. Dissolve 200 g. in 1 liter of water. Adjust the pH to 0.85 with hydrochloric acid.

Ammonium Chloride Wash Solution. Dilute 200 ml. of the 20% solution to 1 liter. Readjust the pH to 0.85.

Oxine, 4.0%. Add 20 g. to about 480 ml. of water. Stir the mixture and slowly add sulfuric acid while observing the pH. When the oxine is completely dissolved and the pH is 0.85, dilute the solution to 500 ml.

Standard Tin(IV) Solution, 100 μg./ml. Dissolve 0.2 g. of tin metal in 10 ml. of concentrated sulfuric acid by heating. Fume the solution to expel sulfur dioxide. Add 30 ml. of sulfuric acid, cool; add 125 ml. of water and again cool. Dilute the solution to 200 ml. Transfer 100 ml. of this solution to a 1-liter flask, add 300 ml. of sulfuric acid (1+2), and dilute to volume.

Standard Molybdenum(VI) Solution, 100 µg./ml. Dissolve 0.092 g. of $(NH_4)_6Mo_7O_{24}.4H_2O$ in water and dilute to 500 ml.

Procedure

Standard Curve Preparation. To 60 ml. of dilute sulfuric acid solution at pH 0.85 add 0 to 80 µg. of molybdenum and 0 to 140 µg. of tin. Add 25 ml. of the 4.0% oxine solution. Readjust the pH to 0.85 with dilute ammonium hydroxide or dilute sulfuric acid. Extract the molybdenum for 2 minutes with 20.0 ml. of chloroform. Wash the extract with 50 ml. of the 4% ammonium chloride wash solution for 2 minutes. Filter the extract through a dry 11-cm. Whatman No. 41 filter paper. Determine the absorbance at 385 mµ in 5-cm. cells against chloroform as a reference. Wash the aqueous phase with 10 ml. of chloroform and discard the wash. Add 5.0 ml. of the 20% ammonium chloride. Extract the tin for 2 minutes with 20.0 ml. of chloroform. Wash and filter the extract as in the molybdenum extraction and determine the absorbance at 385 mµ in 5-cm. cells against chloroform.

For 50 to 400 µg. of molybdenum and 50 to 500 µg. of tin, repeat the above with the required amounts of standard solution but measure the absorbances in 1-cm. cells.

Analysis of U_3O_8 (0 to 50 µg. of tin or molybdenum.) Mix a 2- to 5-g. sample with potassium persulfate, 2 g. per g. of black oxide, in a platinum dish and fuse over a Meker burner until a clear melt is obtained. Cool the melt and dissolve it with 50 ml. of warm sulfuric acid solution of pH 0.85. Transfer the cooled solution to a separatory funnel. Wash the platinum dish with about 25 ml. of the sulfuric acid solution and add the wash to the separatory funnel. Add 25 ml. of 4.0% oxine solution. Extract the molybdenum and tin as described under the preparation of the standard curve. Measure the absorbances in 5-cm. cells against chloroform.

Analysis of Various Metals. Various metals soluble in sulfuric-nitric acid mixtures are analyzed by the following procedure.

Dissolve a 0.5- to 2-g. sample in 10 ml. of sulfuric acid (1+1) plus 10 ml. of nitric acid (1+1). Evaporate the solution to fumes of sulfur trioxide. (With steel samples, evaporate the solution until ferric salts begin to precipitate.) Add 25 ml. of water, and boil the solution until it is clear. Adjust the volume to about 75 ml. Adjust the pH to 0.85 with dilute ammonium hydroxide. Transfer the solution to a separatory funnel with a maximum of 10 ml. of wash water. Add 25 ml. of 4.0% oxine solution and 20.0 ml. of chloroform. Extract the molybdenum and tin as in the standard curve preparation.

Results

In Table 1 are given the results of analyses on U_3O_8 standards, Zircaloy, various types of brasses, and steels. Agreement between the certified values and the values obtained is seen to be good.

TABLE 1

ANALYSIS OF U_3O_8 AND VARIOUS METALS FOR MOLYBDENUM AND TIN

Sample	Molybdenum, %		Tin, %	
	Present	Found	Present	Found
U_3O_8 NBL 95 (In preparation)	0.0050	0.0048	0.0050	0.0050
	0.0020	0.0020	0.0020	0.0019
	0.0010	0.0010	0.0010	0.0010
	0.0005	0.0005	0.0005	0.0005
	0.0002	0.0002	0.0002	0.0002
	0.0001	0.0001	0.0001	0.0001
Zircaloy, NBS 360	--	--	1.43	1.42
Sheet Brass, NBS 37d	--	--	0.97	0.95
Aluminum Brass, NBS 164	--	--	0.63	0.64
Silicon Brass, NBS 158	--	--	0.97	0.96
Zinc-Base Die Casting Alloy, NBS 94a	--	--	0.005	0.005
Bessemer Steel, NBS 8g	0.003	0.003	0.002	0.002
A.O.H. Steel, NBS 19e	0.012	0.012	0.010	0.010
A.O.H. Steel, NBS 20e	0.017	0.017	0.013	0.013
B.O.H. Steel (Sn Bearing), NBS 152	0.013	0.013	0.036	0.036
Basic Electric Steel, NBS 65c	0.007	0.007	0.008	0.008
A.O.H. Steel (Sn Bearing), NBS 21d	0.035	0.035	0.077	0.075

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2. Wyatt, P. F., Analyst, 80, 368 (1955).

PYROHYDROLYTIC SEPARATION OF BORON FROM BORON MINERALS FOR MASS SPECTROMETRIC B^{11}/B^{10} RATIO DETERMINATION

A. R. Eberle

In the determination of the normal boron isotopic ratio, it was required to analyze a variety of boron minerals. Since the minerals themselves are not suitable samples, it was necessary to separate the boron completely from these different minerals and recover the boron in a form suitable for a charge material for the mass spectrometer.

The pyrohydrolysis procedure of Williams, Campbell, and Magliocca[1] developed for the determination of boric oxide in glass was found to be satisfactory for the isolation of the boron from the various minerals. Recovery tests carried out on borax, borosilicate glass sand NBS No. 93, and synthetic calcium and beryllium borate mixtures approximating the composition of the minerals to be analyzed, indicated the boron yield to be essentially 100%. The presence of rubidium and strontium in the product, however, interfered in the mass spectrometric analysis. Accordingly, a second step was incorporated into the procedure involving the passage of the pyrohydrolysis distillate through a cation-exchange resin column. No loss of boron was found to occur in the column. Tests carried out on effluent from boric acid solutions showed that no loss of boron results if the effluent is neutralized to pH 9.3 to 9.4 with dilute sodium hydroxide solution before evaporation to dryness; losses occur if a pH below this range is used. The residue is completely satisfactory for the mass spectrometric analysis when it is dissolved in a few milliliters of water.

Apparatus

The pyrohydrolysis apparatus used is similar to that described by Williams, Campbell and Magliocca[1] except that a Burrell high-temperature tube furnace and an all-platinum boat are used.

The ion-exchange column is made from a 1-1/4" I.D. Teflon tube. A porcelain filter crucible is fitted to the lower end of the tube. A 2" bed of Dowex 50-x8, 50-100 mesh, is placed in the column, converted to the hydrogen form, and washed well. The frit of the filter crucible is selected to give a flow rate of about 10 ml. per minute.

Procedure

Transfer a 0.5-g. sample of the pulverized mineral, 0.1 g. of sodium metasilicate nonahydrate ($Na_2SiO_3.9H_2O$) and 3.0 g. of powdered urano-uranic oxide (U_3O_8) to an agate mortar. Grind the mixture intimately to a fine powder of less than 300 mesh. Transfer the entire mixture to the platinum boat. Place the boat in the reaction tube at room temperature. Connect the reaction tube to the steam generator, and allow the exit end of the condenser to dip into 100 ml. of water held in a 1-liter platinum dish placed in an ice-bath. Begin heating the reaction tube and steam generator simultaneously. Maintain the reaction tube temperature at 400° to 500°C until steam begins to pass through, then rapidly raise the temperature to 1300° to 1350°C. Collect about 500 ml. of distillate over a period of 1 hour.

Pass the distillate through the ion-exchange column. Wash the column with four 25-ml. portions of distilled water. Adjust the pH of the effluent to 9.3 to 9.4 with dilute sodium hydroxide solution.

Evaporate the solution to dryness on a steam bath. Dissolve the residue in 1 to 2 ml. of water; this solution is used for the mass spectrometric analysis.

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DESIGN AND CONSTRUCTION OF A VERSATILE MASS SPECTROMETER FOR THE ISOTOPIC ANALYSES OF GAS, LIQUID, AND SOLID SUBSTANCES

H. O. Finley, R. J. Hemmer, and L. C. Nelson, Jr.

The design and fabrication of a six-inch radius mass spectrometer is now in progress. The instrument is designed in such a way as to do the most work for a laboratory with a wide variety of requests for isotopic analyses with limited instrumentation and personnel. Basically, the instrument is a six-inch radius, 60° sector-shape analyzer. Its primary intended use is for low-mass work for boron and lithium solid analysis, as well as for comparison studies in the isotopic measurement of uranium. The work for high-mass gas samples is limited by the small radius, although the need for a dual collection ratio gas instrument is essential for comparison purpose. The instrument is designed for the analysis of a wide variety of elements by a number of different methods with minimum change in geometry and lens systems.

Design Features

The basic features that make possible the versatility of the instrument include the rigid all-welded construction of the analyzer tube, a solid-machined slit-valve and flange assembly, removal plates at both ends of the tube, and a pump-out between final slit of the ion source and the magnetic analyzer.

The design of the analyzer tube ends permits rapid exchange of ion sources and collectors with a minimum of physical change or loss of instrument time. The ion source and vacuum system valve arrangement permits fast interchange of samples which may be either solid, liquid, or gas. The solid analysis may be performed by thermal analysis with single and triple filament, or by electron bombardment. The gas and liquid samples may be analyzed by electron impact only. Two leak systems are designed, the viscous and molecular systems.

Description of Components.

A salvaged 60° magnet has been remachined, aligned, and welded, instead of bolted. It is capable of a flux of from 8,000 to 9,000 gauss. The gap is 9/16-inch. The magnet carriage is designed to give freedom of movement for beam alignment.

The electrical components have been purchased commercially and are interchangeable, in most instances, with the existing equipment used with a 12-inch radius, SU-3 Nuclide Analysis instrument. The accelerating voltage will be held to 5,000 volts maximum, with components such as the emmission regulator, the ion-source control panel, and the thermal filament control rated at 15,000 volts.

All A.C. circuits are to be controlled by push-button-type switches, with holding coils that are to be used in the interlocking safety circuits.

Special vibrating reed electrometers or electron multiplier counting-type measuring systems are designed into the instrument, along with a dual collection and ratio precision potentiometer, decade-type measuring device.

A 10-liter per second mercury pump is used for fast pumping in the ion source region and gas sample system. An 8-liter per second ion pump is used in the analyzer section. Gold gaskets, fabricated from 0.025-inch diameter gold wire is used throughout, with the exception of the slit valve, in which Teflon is used.

An automatic liquid nitrogen filler has been designed to control the liquid level of the nitrogen in the Dewar flask. These controllers have the advantage that the small monitoring element can be located in the Dewar flask while the switch itself may be placed as far as two feet away, at a more convenient location for calibration and maintenance purposes.

A rotating coil flux indicator is placed in the magnetic field so as to produce a measurable EMF which is used for mass identification.

At the present time the instrument is virtually complete, and will soon be ready for testing.

THE STABILITY OF PLUTONIUM SULFATE TETRAHYDRATE AND ANHYDROUS PLUTONIUM SULFATE

C. E. Pietri

Previous studies were made and the results evaluated for the use of plutonium sulfate tetrahydrate as an analytical standard, and anhydrous plutonium sulfate, prepared from the tetrahydrate, as a supplementary standard.[1-3] Present investigations disclose additional information on the stability of these compounds as determined by chemical and thermogravimetric methods. The composition of anhydrous plutonium sulfate prepared at 325°C has been determined by analysis and the plutonium to sulfate mole ratio has been calculated. The plutonium content of plutonium sulfate tetrahydrate and its anhydrous salt was redetermined after 18-month and 6-month periods, respectively, to detect any change in composition. To date, various lots of $Pu(SO_4)_2 \cdot 4H_2O$ have been under study for 2 years; $Pu(SO_4)_2$ for nearly 18 months.

Reagents and Apparatus

All reagents and apparatus used in this study have been described in previous reports.[1-3]

Procedure

Other reports[1-5] describe the preparation of $Pu(SO_4)_2 \cdot 4H_2O$ from plutonium metal by controlled crystallization from a sulfuric acid solution, the thermogravimetric techniques used to prepare $Pu(SO_4)_2$ from the tetrahydrate at 325°C, and the methods used for chemical and spectrographic analysis of these compounds.

Experimental

Composition and Stability of $Pu(SO_4)_2$. Two samples each from three representative lots of $Pu(SO_4)_2$ were analyzed for plutonium, sulfate, and trace impurities. Methods of analysis were those used for the tetrahydrate previously described. These same materials were again analyzed 6 months later for stability evaluation. In addition, the weight change of a sample of similar material kept in a relative humidity of 17% for 7 months was recorded.

Stability of $Pu(SO_4)_2 \cdot 4H_2O$. An original analysis for plutonium was made in December 1959 on samples from one representative lot of $Pu(SO_4)_2 \cdot 4H_2O$ taken from 5 lots of material prepared at the same time under similar conditions. In May 1961, the plutonium content of this compound was redetermined to note any change in composition during the previous 18 months.

Results

Both $Pu(SO_4)_2$ and $Pu(SO_4)_2 \cdot 4H_2O$ were found by emission spectroscopy to contain less than 100 p.p.m. impurities or only one-third of the analyzed impurities found in the plutonium metal from which these compounds were prepared.

The formula for anhydrous plutonium sulfate was verified by chemical analysis to be $Pu(SO_4)_2$, Table 1. (Previous thermogravimetric work had indicated this composition.) The plutonium and sulfate content found were within 0.02% of theoretical values. The sulfate to plutonium mole ratios calculated from the thermogravimetric weight of $Pu(SO_4)_2$[3] and from chemical analysis of this compound were 2.000 ± 0.002 in both instances. The anhydrous salt was shown to be stable for at least 6 to 7 months; the analytical test results were well within experimental error, Table 2.

TABLE 1

COMPOSITION OF ANHYDROUS PLUTONIUM SULFATE

Constituent	Content % Theoretical	% Experimental Lot No. 5	Lot No. 6	Not No. 8
Pu	55.45	55.50	55.48	55.45
SO_4	44.55	44.54	44.60	44.56

TABLE 2

STABILITY OF $Pu(SO_4)_2$

Test No. 1*	Plutonium, % Found
Original analysis	55.50
Final analysis	55.49
Test No. 2**	**$Pu(SO_4)_2$, g.**
Original weight	0.76979
Final weight	0.76986

* 6-month test period

** 7-month test period; sample maintained at 17% relative humidity.

Plutonium sulfate tetrahydrate continued to indicate stability over a period of at least 18 months; no change in plutonium content was noted during this time, Table 3.

TABLE 3

STABILITY OF $Pu(SO_4)_2 \cdot 4H_2O$

Analysis Period*	Plutonium, % Found**
Original analysis	47.53
Final analysis	47.55

* 18 months

** Theoretical plutonium content, 47.51%

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THE STABILITY AND STOICHIOMETRY OF DICESIUM PLUTONIUM HEXACHLORIDE

C. E. Pietri

Several compounds have been investigated for use as a primary plutonium standard, and out of necessity, some have been used as interim "standards". For example, high-purity plutonium metal is at present in use at some sites but has certain disadvantages.[1] Plutonium sulfate tetrahydrate prepared at the New Brunswick Laboratory has been tested for over 2 years and found to be satisfactory.[1-4] Recently, another compound, dicesium plutonium hexachloride, Cs_2PuCl_6, has been proposed as a plutonium primary standard.[5] In order to determine its suitability, several lots of this material were prepared by slowly adding a solution of cesium chloride in concentrated hydrochloric acid to a plutonium(IV) solution. The composition of the resulting compound was determined by analysis. The stability of Cs_2PuCl_6 was evaluated under both constant and fluctuating controlled humidities. Present data indicate that although dicesium plutonium hexachloride has certain advantages, its suitability for use as a primary standard appears uncertain.

Reagents and Apparatus

Cesium Chloride Solution. Dissolve 1.5 g. of CsCl (99.8% pure, obtained from A. D. Mackay, Inc., New York City, N. Y.) in 35 ml. of concentrated hydrochloric acid. Spectrographic analyses of the reagent used at this laboratory indicated only trace impurities.

Hydrochloric Acid, concentrated, reagent-grade.

Hydrochloric Acid, 8N.

Nitric Acid, concentrated, reagent-grade.

Plutonium Metal, high-purity (99.96%), obtained from Hanford Atomic Products Operation.

Plutonium Sulfate Tetrahydrate, $Pu(SO_4)_2 \cdot 4H_2O$, prepared in this laboratory by evaporation of a H_2SO_4 solution of plutonium(IV) made from high-purity plutonium metal.[1]

Ethanol, absolute.

Balance, semi-micro, Model B-6, Mettler Instrument Company, modified for gloved box operations.

Humidistats. Five desiccators, 100-mm. inside diameter, (No. 8-595, Fisher Scientific Company), the base of each filled with H_2SO_4 of a different concentration, Table 1, are used to maintain a different relative humidity in the range of 17 to 96%.

TABLE 1

SULFURIC ACID HUMIDISTATS

Relative Humidity, %	Sulfuric Acid, Weight, %
17	60
36	50
57	40
75	30
96	10

Weighing Bottles, with vent holes, made by drilling a 1/8"-diameter hole in both cap and body of conventional Parr-type, 4-ml. capacity vessels (No. S-9525, E. H. Sargent and Co.) at the ground-glass interface, Figure 1. The bottles are inverted so that the wide cap acts as a base for greater stability in handling.

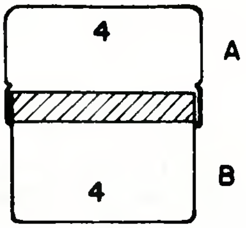
Procedures

Preparation of Cs_2PuCl_6. Dicesium plutonium hexachloride was prepared by the method used at the Rocky Flats Plant.[5]

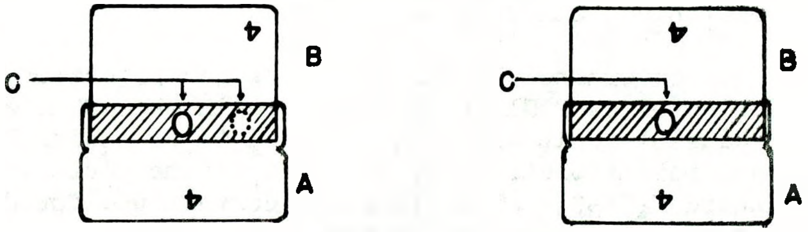
Place 1 g. of bright plutonium metal (99.9+% pure) in a 400-ml. beaker, cover the beaker with a watch glass and add, dropwise, the minimum amount of 8N hydrochloric acid needed to dissolve the metal. After complete dissolution, oxidize the blue plutonium(III) solution to tan plutonium(IV) by adding, dropwise with stirring, a minimum volume of concentrated nitric acid. Slowly pour the prepared cesium chloride solution into the plutonium solution while stirring. The yellow Cs_2PuCl_6 which forms immediately is separated by centrifugation, washed 10 times with ethanol, transferred to a weighing bottle while wet, and dried at 110°C for four hours.

Humidity Testing. A simple, systematic procedure has been standardized for studying the effect of humidity on compounds.

Weigh four clean, dry, vented weighing bottles of the type shown in Figure 1 to constant weight on a semi-micro balance. Place two samples of test material (0.5-3.0 g.) in separate weighing bottles using forceps to handle the bottles at all times. For comparison purposes, place 2 g. of a material of known stability, e. g., potassium dichromate or plutonium sulfate tetrahydrate, in a third weighing bottle, using the remaining vessel as an empty tare. Close the vent hole in each bottle by rotating the top and reweigh the bottles. Reopen the vent hole and place the bottles in a prepared desiccator with a humidistat of known relative humidity in the desired range. To determine the effect of varying relative humidities of 17, 36, 57, 75, and 96% on the test samples, remove one



Conventional Bottle,
Normal Position,
Capped



Vented Bottle
Inverted Position,
Closed

Vented Bottle
Inverted Position
Open

A - Top
B - Bottom
C - 1/8-in. vent-hole

FIGURE 1. WEIGHING BOTTLE

bottle at a time from the desiccator after a 1-week test period, and close the vent hole. Wipe the surface of the bottle thoroughly with absorbent tissue paper, dust with a soft brush, and place the bottle in the balance box to equilibrate for ten minutes. Weigh the bottle to constant weight. Repeat this process for the remaining three bottles, reopen the vent holes and replace all bottles in another desiccator of different relative humidity for further testing. Continue this procedure until at least 12 sets of weighings are obtained. To study the effect of prolonged exposure in a constant humidity, repeat the above procedure but replace the bottles, after weighing, in their original desiccator.

Experimental and Results

Preparation of Cs_2PuCl_6. Two lots of material (4 and 13 g.) were prepared using the outlined procedure. The yellow compound which precipitated was a finely-divided, powdery material and difficult to handle under gloved box conditions because of its free-flowing nature. Its average particle size was estimated to be 1/25th as large as the more easily handled plutonium sulfate tetrahydrate crystals prepared in this laboratory.

Composition of Cs_2PuCl_6. Previous work indicated that the formula for the cesium salt of the complex acid hexachloroplutonium(IV) acid, H_2PuCl_6, was Cs_2PuCl_6.[6] For determination of the composition of the compound prepared at this laboratory, samples from two lots of material were analyzed for plutonium, chloride, and cesium.

The plutonium was determined by the New Brunswick Laboratory method;[7] 300- to 400-mg. samples of Cs_2PuCl_6 were dissolved in 4N H_2SO_4, evaporated to dryness, redissolved in 4N H_2SO_4, reduced to plutonium(III) in a Jones reductor, and potentiometrically titrated to the plutonium(IV) end point with standard $K_2Cr_2O_7$. The plutonium content was found to be within 0.03% maximum of the theoretical value.

The chloride content was determined by the classical Volhard method[8] where the sample (300-400 mg.) was acidified with HNO_3, titrated with an excess of standard $AgNO_3$ solution and back-titrated with a standard solution of KCNS to the end point using ferrous sulfate as indicator. The chloride content of the compound was found to be within 0.04% maximum of the theoretical value.

Cesium was determined gravimetrically by weighing as CsCl: 300- to 400-mg. samples dissolved in 9N HCl were passed through an ion-exchange column containing Dowex-1 anion resin to remove plutonium[9]; the eluted CsCl solution was evaporated to dryness, extracted into absolute ethanol, evaporated to dryness and weighed. Plutonium contamination of the precipitate, as verified by alpha-counting, was negligible ($< 0.01\%$). The cesium content was found to be within 0.1% maximum of the theoretical value.

For comparison purposes the results of these analyses, and the work reported by other investigators, are tabulated in Table 2.

TABLE 2

COMPOSITION OF DICESIUM PLUTONIUM CHLORIDE

Constituent	Theoretical (%)	New Brunswick Laboratory (%) Lot No.		Rocky Flats Plant[5] (%)	Metallurgical* Laboratory[6] (%)
		1A	2A		
Pu	33.31	33.29	33.28	33.32	35.2
Cs	37.03	37.11	37.05	---	35.7***
Cl	29.65	29.63	29.61	**	---

* Now Argonne National Laboratory. A more recent and independent contribution from this site[10] indicates that only the well-known lines of the pure compound were obtained from X-ray powder patterns of Cs_2PuCl_6; no CsCl lines were observed. However, no chemical analyses of the material were made.

** Analysis performed but not reported.

*** Reported as "alkali".

Stability of Cs_2PuCl_6. Two tests were proposed in order to evaluate the stability of Cs_2PuCl_6 over a long period of time: (1) exposure of the compound to controlled varying humidities for several months according to the outlined procedure; and (2) similarly, exposure in a dry constant atmosphere.

Two samples of Cs_2PuCl_6 (2 and 3 g.), one from each of the two lots of stock material, were dried at 110°C for two hours, cooled in a desiccator, and placed in test according to the aforementioned procedure. The samples were exposed to relative humidities varying from 17 to 75% over a period of six months. For comparison purposes, 2 g. of $Pu(SO_4)_2 \cdot 4H_2O$, and an empty weighing bottle, were included in the tests. In another test, the same samples were exposed to a relative humidity of 17% for extended periods of time.

Results of these tests, Figure 2, indicate that $CsPuCl_6$ is susceptible to changes in relative humidity (R.H.) above 17%. Significant weight changes up to 0.03% (0.8-1.0 mg.) per week in the range of 17 to 57% R.H. were found. Above 57% R.H., the material gained excessive weight and testing in this range was discontinued. A statistical analysis of the test results at the 99.9% confidence level shows that, when compared to data from $Pu(SO_4)_2 \cdot 4H_2O$ or the empty tare, the variation in the weights of the two lots of Cs_2PuCl_6 is significant, Table 3.

TABLE 3

EFFECT OF RELATIVE HUMIDITY ON Cs_2PuCl_6: 17 TO 57% RANGE

	Average Net Weight, g.	Standard Deviation, g. *	Relative Standard Deviation, g.*
Cs_2PuCl_6 Lot No. 1A	3.22712	± 0.00053	± 0.018
Cs_2PuCl_6 Lot No. 2A	2.05784	± 0.00052	± 0.026
$Pu(SO_4)_2 \cdot 4H_2O$ Lot No. 3	1.92928	± 0.00010	± 0.005
Tare (empty)	12.44254	----	----

* 13 weighings

Inspection of the data at 17% R.H. in Figure 2 discloses a steady loss in weight of Cs_2PuCl_6 over a six-month period. Table 4 indicates a small but significant total weight loss to date of 0.07 and 0.10% for Lots No. 1A and 2A, respectively.

TABLE 4

LOSS IN WEIGHT OF Cs_2PuCl_6*

	Cs_2PuCl_6 Lot No. 1A, g.	Cs_2PuCl_6 Lot No.2A, g.	$Pu(SO_4)_2 \cdot 4H_2O$ Lot No.3,g.	Tare (empty),g.
January 1961	3.22755	2.05829	1.92915	12.44260
July 1961	3.22550	2.05621	1.92908	12.44259
Total Change**	-0.00205	-0.00208	-0.00007	- 0.00001

* at 17% R.H.

** The standard deviation, at the 95% confidence level, for one set of differential weighings on the semi-micro balance operated under our gloved box conditions is ~± 0.00010 g.

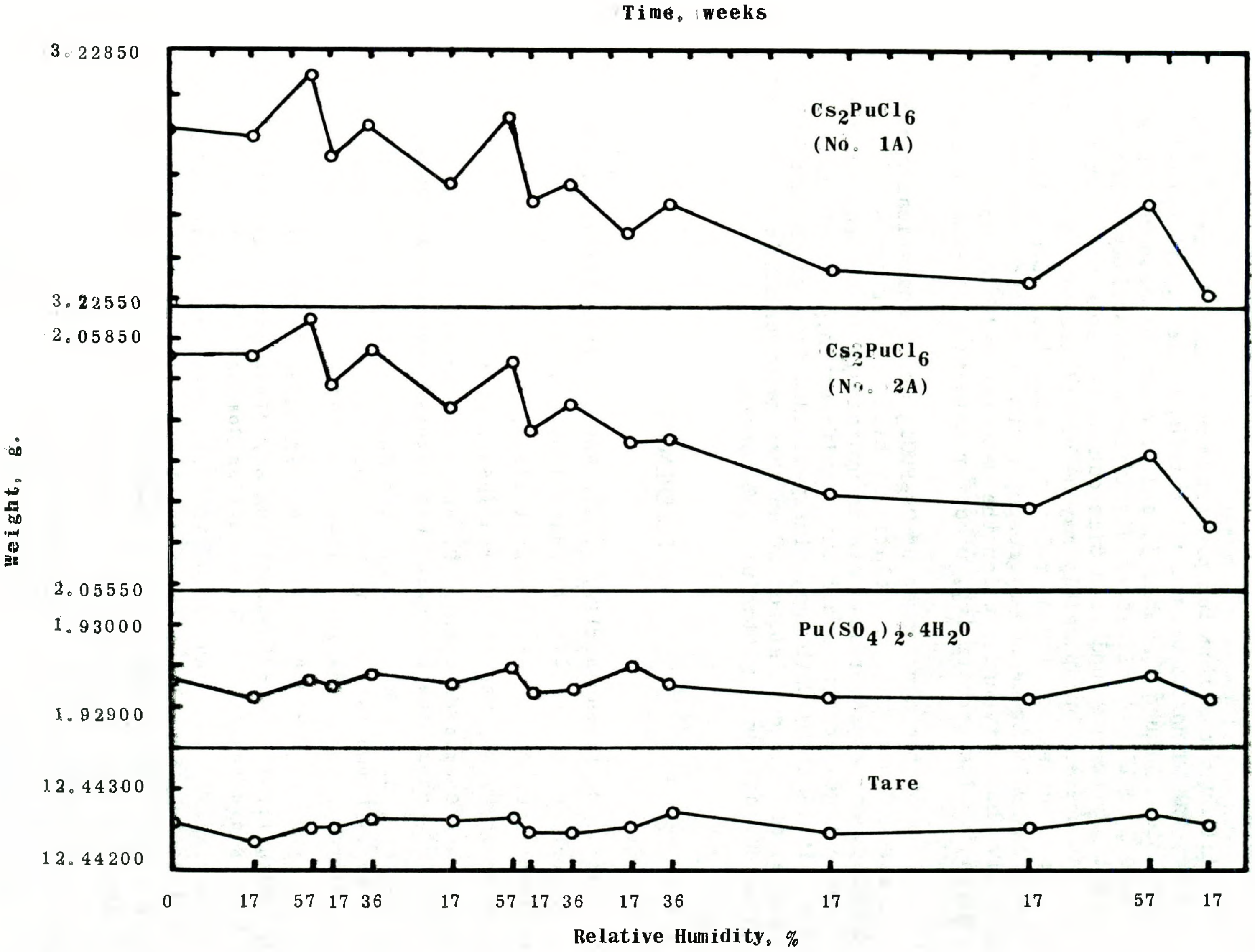


FIGURE 2. VARIATION OF Cs_2PuCl_6 WEIGHT WITH HUMIDITY

Discussion

Although the dicesium plutonium hexachloride prepared in this laboratory was shown to be stoichiometric, Table 2, its behavior in various humidities, Figure 2, Table 3, and in a dry atmosphere for several months, Figure 2, Table 4, discloses significant instability. The overall loss in weight of the compound with time cannot be explained from the data available at present but possibly may be associated with the previous exposure of the material to varying relative humidities. Other investigators have found Cs_2PuCl_6 to be non-hygroscopic but no mention was made of either the relative humidity under which the material had been observed,[10] or the method, or its sensitivity, used for detecting effects of humidity.[5]

Some of the advantages of Cs_2PuCl_6 as an analytical standard are in its ease of preparation, relatively high solubility ($\sim$0.8 mole/liter in 1M HCl), and apparent low rate of hydrolysis in neutral solution. Some disadvantages are its small but significant hygroscopic nature below 57% R.H., instability with age, finely-divided form which is difficult to handle, and the coexistence of another major cationic constituent, cesium (37% content), with plutonium (33% content).

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THE CATION-EXCHANGE SEPARATION AND SPECTROGRAPHIC DETERMINATION OF SILICON IN PLUTONIUM

C. E. Pietri and A. W. Wenzel

There is a potential health hazard from the excitation of large amounts of plutonium dioxide used in the carrier distillation method[1] and in order to reduce this possibility, ion-exchange separations are often used to remove the plutonium. A spectrographic analysis is then made on the separated impurities. Existing anion-exchange methods employing nitric or hydrochloric acid media[2-4] are useful because of the large number of elements that can be separated. Silicon, however, may either precipitate as insoluble gels from negatively-charged colloids, or be adsorbed along with plutonium on anion resins depending upon the nature and concentration of the acid and other conditions. Accordingly, the purpose of this study was to investigate an ion-exchange separation of silicon from plutonium suitable for subsequent spectrographic analysis.

A cation-exchange separation process was chosen since plutonium(III, IV) is adsorbed on strong sulfonic acid-type resins at nitric acid concentrations less than 1M[5] while silicon, either as $SiO_3^=$ or as a colloid, should pass unadsorbed into the effluent.

The procedure under study at this laboratory is to adsorb plutonium(III) in 0.2N nitric acid-0.2N hydroxylamine hydrochloride solution on Dowex-50 cation resin, evaporate the effluent containing the silicon, dissolve the residue in a small volume of dilute HNO_3 containing HF, pipet an aliquot onto graphite electrodes, dry, and excite in a 25-ampere D.C. arc. Synthetic solutions have been used to evaluate the procedure. The method appears to be suitable for the determination of silicon in plutonium and may be useful as a supplementary method in determining other elements not normally separated by anion exchange.

Reagents and Apparatus

Silicon Standard Solutions.

Standard A, 71 μg. Si/ml. Reagent-grade $Na_2SiO_3 \cdot 9H_2O$ (179.3 mg.) is dissolved in 25 ml. of distilled 0.2N HNO_3, diluted to 250 ml. with the acid, and stored in a polyethylene bottle.

Standards B, C, D, E, F, and G are prepared by dilution of Standard A to give concentrations of 40, 20, 10, 4, 2, and 1 μg. Si/ml., respectively.

Plutonium Standard Solution, 5 mg. Pu/ml. High-purity (99.96+%) plutonium metal (250 mg.) is dissolved in a minimum amount of distilled HCl, evaporated just to dryness, diluted with 50 ml. of a 0.2N HNO_3-0.2N $NH_2OH \cdot HCl$ solution and stored in a polyethylene bottle.

Wash Solution, 0.2N HNC_3-0.001N $NH_2OH.HCl$ prepared from distilled HNO_3 and reagent-grade hydroxylamine hydrochloride in deionized water. The solution is stored in a polyethylene bottle.

Nitric Acid, 5N, prepared from distilled reagent-grade acid.

Hydrofluoric Acid, concentrated, reagent-grade.

Ion-Exchange Resin. One hundred (100) grams of wet AG-50W cation resin (a highly purified analytical grade of Dowex-50, X-10, 200-400 mesh, hydrogen-form, obtained from Bio-Rad Laboratories, Richmond, California) is washed free of "fines" with water. The resin is then washed several times with 0.2N HNO_3-0.001N $NH_2OH.HCl$ solution.

Ion-Exchange Column. The design and operation of this column is described in another report.[6] Dowex-50 cation resin is used to load the column and is washed with 30 ml. of 0.2N HNO_3-0.001N $NH_2OH.HCl$ prior to use.

Pipets, polyethylene. One-ml. volumetric pipets are calibrated to contain 50 and 100 μl. and are used with solutions containing hydrofluoric acid.

Spectrograph, Baird-Atomic, Model GX-1, 3-meter concave grating, Eagle mount, and accompanying accessories. The actual arrangement and operation of the unit is described in a previous report.[4]

Step-sector, equipped with a seven-step, step-sector wheel, with an exposure ratio of the steps of 1 to 2, and the first step of which is 100% exposure.

Electrodes, similar to those supplied by United Carbon Products Company, Bay City, Michigan, as follows:

Lower: Anode cap, No. 1991.

Upper: Cathode, No. 1992

Pedestal: To fit above anode cap.

Electrode Sealer, 2 $^{w}/_{o}$. Two grams Kel-F grease (Minnesota Mining and Manufacturing Company) is dissolved in 100 ml. of reagent-grade CCl_4, mixed well, and stored in a dropper bottle. The electrodes are sealed by adding 5 drops of the Kel-F sealer to the electrode cup. The solvent is allowed to penetrate and evaporate. This sealing step is repeated and the electrodes are air-dried.

Photographic Emulsion, Eastman Kodak S.A. 1.

Heat Lamps, 2 standard 500-watt heat lamps connected to a 10-ampere, 115-volt input Variac transformer.

Procedure

Sample Analysis. Prepare a sample blank solution by adding 30 ml. of 0.2N HNO_3-0.001N $NH_2OH.HCl$ wash solution to the prepared ion-exchange column. Collect all the effluent in a 125-ml. platinum dish at the rate of about 0.3 ml./min. Cover the dish with a Teflon watch glass during the collection for protection against contamination. After passage of the blank solution, add the sample solution containing not more than 250 mg. of plutonium and up to 350 µg. of silicon to the column. Collect the effluent in a second platinum dish. A purple band at the top of the resin bed indicates adsorption of plutonium. When the level of the solution in the column reaches about 1 mm. above the resin bed, add 10 ml. of the HNO_3-$NH_2OH.HCl$ wash solution using a 25-ml. polyethylene graduate. Repeat the washing procedure with an additional 20 ml. of the wash solution and collect all the effluent. Remove the adsorbed plutonium on the column by adding 50 ml. of 5N HNO_3 to the column, and collecting the effluent.

Place the covered blank and sample effluent dishes under heat lamps. When all the solution has evaporated, remove the dishes from the heat and allow to cool. With a microliter pipet add 450 µl. of the wash solution to each dish. Swirl the dishes for about a minute, making sure that the sides are washed so as to completely wet the residue. Add 50 µl. of concentrated hydrofluoric acid using a polyethylene pipet. Repeat the swirling step to insure complete dissolution of the residue. With a polyethylene pipet add four 100-µl. aliquots of the sample and of the blank solutions to eight Kel-F-sealed electrodes. Add two 100-µl. aliquots each of Silicon Standard A and G to four sealed electrodes. Carefully place the electrodes under heat lamps adjusted to a temperature of about 80°C and slowly evaporate the solutions for 1 hour. At the end of the drying period, increase the temperature to 100°C and bake the electrodes for about 1 hour.

Divide the samples, standards, and blanks equally into 6-electrode sets and excite under the conditions outlined in Table 1.

TABLE 1

SPECTROGRAPHIC CONDITIONS FOR SILICON DETERMINATION

Electrode Gap:	4-mm.
Entrance Slit:	25-μ.
Exposure:	10-sec.
Source:	25-amp. D.C. arc.
Spectrum:	Photographed in position 3.0 of the 1st order. (Wavelength range 2200-3400 A.)

Process the photographic plates, densitometer the analytical lines, Table 2, determine the relative log intensity ratio of each line, and read the concentration of silicon in the sample directly from the analytical curves.

TABLE 2

WAVELENGTHS OF SPECTRAL LINES FOR SILICON AND LOWER LIMITS OF DETECTION

Wavelength, A.	Lower Limit of Detection, p.p.m. (estimated)
2506.90	5
2516.12	2
2881.578*	1-2

* Preferred analytical line

(A typical curve is shown in Figure 1; the preparation of these curves is described below.)

Calculate the concentration of silicon as expressed on a standard 100-mg. sample basis, as follows:

$$A = B \times \frac{100}{C}$$

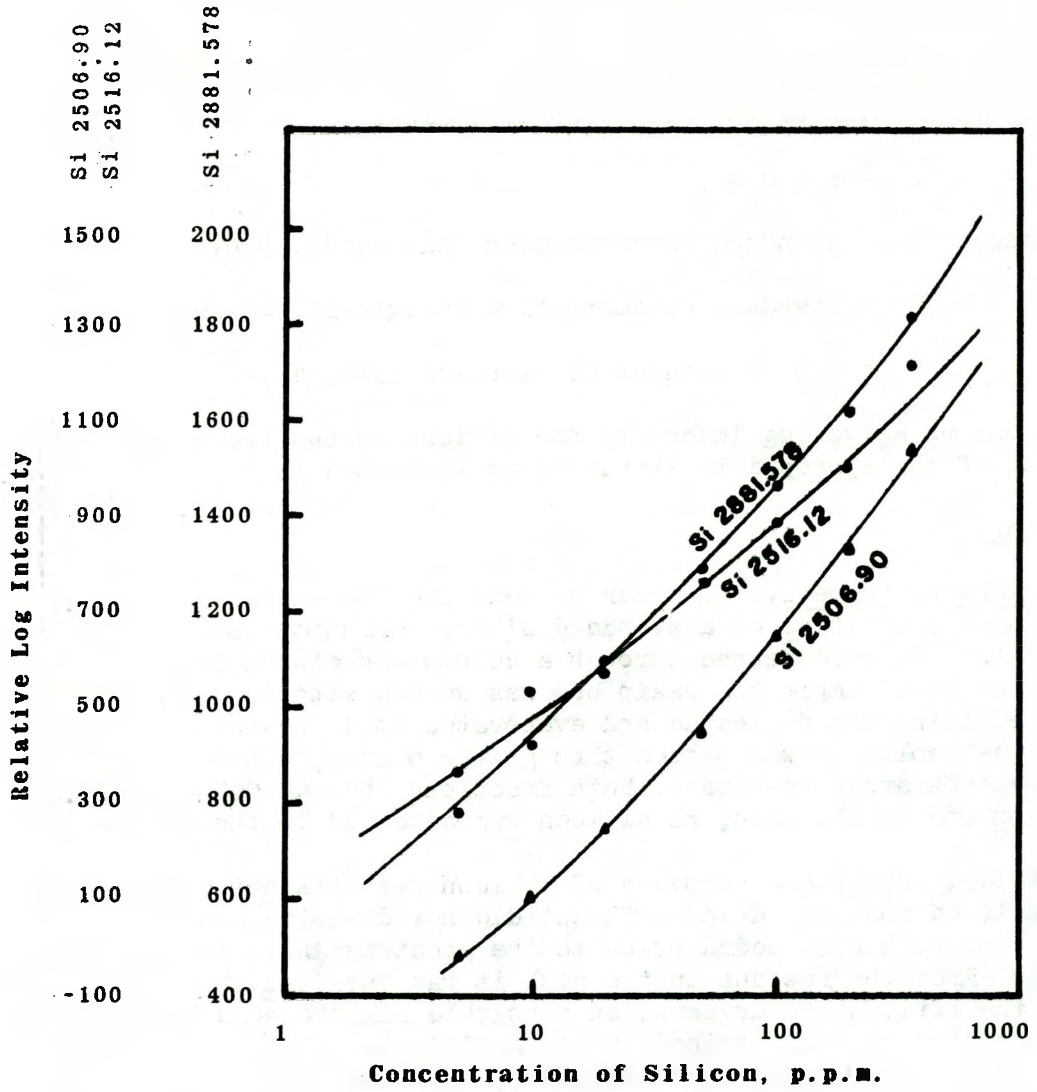

FIGURE 1. ANALYTICAL WORKING CURVES FOR SILICON

Where: A = silicon concentration (100-mg. sample basis), p.p.m.

B = silicon concentration (from graph), p.p.m.

C = sample weight, mg.

Analytical Working Curves. Use 56 electrodes previously sealed with Kel-F sealer, and add, with a microliter pipet, 100 µl. of Standard A to 7 electrodes; repeat, using Standards B, C, D, E, F, and G for a total of 49 electrodes. Use the remaining 7 electrodes as blanks. Dry an excite the electrodes, process the photographic plates, and densitometer the analytical lines, Table 2, according to the procedure outlined above. Determine the relative log intensity of each line. In order to read the silicon concentration from the graph, calculate the adjusted concentration of the standards as follows:

$$A = B \times C \times 5$$

Where: A = standard concentration (adjusted), p.p.m.

B = standard concentration (original), µg./ml.

C = 0.1 = aliquot of standard used, ml.

Plot the relative log intensity for silicon versus the adjusted concentrations of the appropriate standards as indicated in Figure 1.

Experimental

Ion-Exchange Process. In order to test the ion-exchange recovery of silicon, known quantities of a standard silicon solution (Standard A), without plutonium, were passed through a column containing Dowex-50 cation resin. After each sample the resin bed was washed with 30 ml. of 0.2N HNO_3; the effluent was collected and evaporated to dryness. An additional 30 ml. of wash solution was passed through the column, collected, and evaporated. Spectrographic results of both fractions showed 100% recovery of silicon with one 30 ml. wash; no silicon was detected in the second wash.

Initially, incomplete recovery of silicon was obtained. An investigation disclosed that the dried effluent did not dissolve completely in the 500 µl. of 0.2N HNO_3 added prior to the spectrographic determination of silicon. From the residue in the dish it was surmised that upon evaporation of the effluent to dryness, an insoluble silicic acid had formed. Complete dissolution was obtained by the addition of 50 µl. of concentrated hydrofluouric acid to the 0.2N nitric acid, Table 3.

TABLE 3

RECOVERY OF SILICON FROM ION-EXCHANGE EFFLUENT

	Intensity Ratios*		
Wavelength, A.	Control**	HF Added	HF Omitted
Si 2506.90	818	897	664
Si 2516.12	971	1016	521

* Values shown are absolute intensity ratio units based on an arbitrary reference value. A difference of approximately 200 in intensity ratio is equivalent to a 1-step, or a 2-fold, change in intensity.

** Silicon standard added directly to electrodes.

Plutonium adsorption characteristics on the resin in the presence of silicon were studied using 25-ml. portions of the Plutonium Standard Solution spiked with 70 to 150 p.p.m. silicon. Essentially complete plutonium adsorption was obtained using the following techniques: The stock solution was prepared in 0.2N HNO_3 to prevent plutonium hydrolysis and in 0.2N $NH_2OH.HCl$ to stabilize plutonium in the+3 oxidation state for ease in subsequent plutonium removal from the resin. A small amount of $NH_2OH.HCl$ (0.001M) was added to the 0.2N HNO_3 wash solution to maintain this condition during the washing step. Greater concentrations (0.2N, for example) introduced large residues upon evaporation of the effluent causing difficulty in the spectrographic analysis.

Spectrographic Studies. Based on previous experience with light intensity losses in our spectrograph modified for gloved box operations, the effect of matrices on sensitivity was studied. An investigation of In_2O_3 and Ga_2O_3 matrices versus no matrix disclosed that the latter condition was adequate for the determination of silicon, Table 4. Loss of intensity resulted with Ga_2O_3 while In_2O_3 offered no improvement over a matrixless excitation.

Several wavelengths suitable for analytical lines were studied. Although each line had its merit, the 2881.578 A. line was found to be the most reliable and sensitive.

TABLE 4

EFFECT OF MATRICES ON SENSITIVITY

	Intensity Ratios*		
Wavelength, A.	No Matrix	Ga_2O_3	In_2O_3
Si 2506.90	1038	815	1017
Si 2516.12	1200	1120	1248

* Values shown are absolute intensity ratio units based on an arbitrary reference value. A difference of approximately 200 in intensity ratio is equivalent to a 1-step, or 2-fold, change in intensity.

Results

Based on the experimental conditions studied, a quantitative method was developed for the cation-exchange separation of plutonium prior to the spectrographic determination of silicon. Typical analytical curves, Figure 1, give an estimated average deviation of ± 25%. The lower limit of detection for silicon is shown in Table 2.

Discussion

An analysis of the spectrographic data shows that a minimum of 4 exposures per sample is necessary to obtain results precise to ± 25%. Preliminary studies with magnesium as an internal standard show that the precision may be increased to about ± 15%.

Although plutonium(IV) is adsorbed more readily at low acidities on Dowex-50 cation resin than is plutonium(III) (while plutonium(VI) is not adsorbed at all), the former is more difficult to remove. Accordingly, hydroxylamine hydrochloride is used to reduce plutonium to the +3 oxidation state. In order to prevent any leakage of plutonium(VI) into the effluent from oxidation of plutonium(III, IV) during the washing step, a dilute hydroxylamine hydrochloride solution (0.001N) was used.

It is apparent that if this low-acid cation-exchange separation can be applied to other elements, the method may complement existing anion-exchange procedures and offer a complete separation of the elements from plutonium by ion exchange.

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SPECTROGRAPHIC DETERMINATION OF TRACE IMPURITIES IN HIGH-PURITY PLUTONIUM

A. W. Wenzel and C. E. Pietri

The analysis of high-purity plutonium requires the spectrographic determination of traces of more than 15 impurity elements totaling less than 200 p.p.m. in a sample of 100-200 mg. Previous work has produced a quantitative spectrographic method for the determination of impurities in plutonium whereby the plutonium is separated from its impurities by adsorption on Dowex-1 anion-exchange resin in 8N HNO_3, and the impurities in the effluent, after concentration, are then analyzed under special conditions in a D.C. arc using a Ga_2O_3 matrix.[1] Present studies have improved the sensitivity of the method, increased the number of elements determined by including boron, cadmium, barium, sodium, and lithium, modified the method for use with $Pu(SO_4)_2 \cdot 4H_2O$ and $Pu(SO_4)_2$, and investigated methods for preparing high-purity reagents.

Reagents and Apparatus

The modified spectrograph, gloved box arc-stand, step-sector assembly, electrodes, gallium oxide matrix, ion-exchange resin, and other minor reagents and apparatus have been described in detail in a previous report.[1] Only those items which have been added or substantially changed are included below:

Photographic Emulsion, Eastman Kodak, S. A. 1 (for common elements, boron, and cadmium); F-II (for alkali elements).

Electrode Sealer, 2 $^{w}/_{o}$. Two grams of Kel-F grease (Minnesota Mining and Manufacturing Company) is dissolved in 100 ml. of reagent-grade CCl_4, mixed well, and stored in a dropper bottle. The electrodes are sealed by adding 5 drops of the Kel-F sealer to the electrode cup. The solvent is allowed to penetrate and evaporate. This sealing step is repeated and the electrodes are air-dried.

Nitric Acid, Concentrated, distilled from reagent-grade concentrated acid and stored in a polyethylene bottle.

Nitric Acid, 8N, prepared from distilled acid and deionized water and stored in a polyethylene bottle.

Plutonium Sulfate Tetrahydrate,[2] high-purity, prepared from high-purity plutonium metal (99.96%) obtained from Hanford Atomic Products Operation.

Indium Oxide, In_2O_3, spectrographic grade.

Ion-Exchange Column. A self-leveling, glass column, shown in Figure 1, is loaded with 6 cm. of wet Dowex-1 anion-exchange resin. The resin is thoroughly washed five times with 8N HNO_3 before loading by adding the acid to the material, stirring, and decanting the liquid. The liquid in the column will adjust automatically to the level of the tip. The height of liquid remaining above the resin bed may be controlled by the length of auxiliary tip used; it is usually regulated so that not more than 1 mm. of liquid remains. The layout of the apparatus in the gloved box is shown in Figure 2.

Standard Solutions. Reagent-grade chemicals, or better, are dissolved in distilled 8N HNO_3 to make a stock solution of each element to be determined.

Master Standard A is prepared by diluting appropriate aliquots of the individual stock solutions to 200 ml. with distilled 8N HNO_3 in a volumetric flask so that the standard subsequently contains the following concentration of the elements:

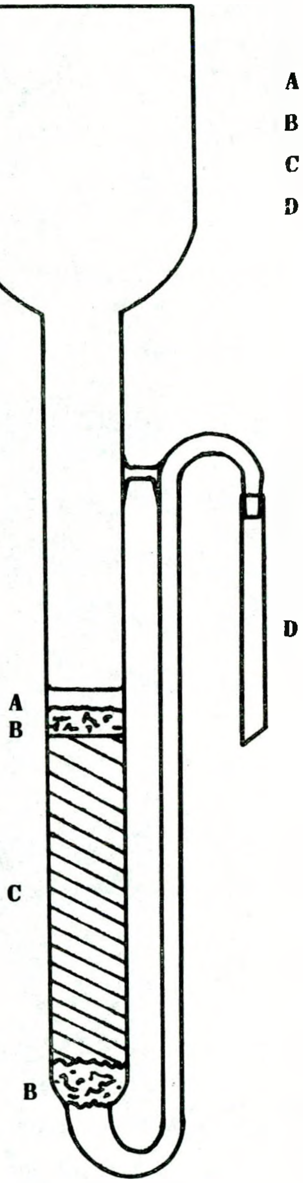
* Co	0.2 mg./ml.
Fe, Al, Zn	0.04 mg./ml.
Cr, Mo, Mg, Mn, Ni	0.008 mg./ml.
Pb, Be, Cd	0.004 mg./ml.
Cu, Ag, B	0.002 mg./ml.

* Internal Standard

Standards B, C, D, and E are prepared by dilution of Standard A as previously reported.[1]

Master Standard F is prepared similar to Standard A and contains the following concentration of the elements:

Na	0.04 mg./ml.
Ba	0.02 mg./ml.
Li	0.002 mg./ml.



A = Liquid Level
B = Glass Wool Plugs
C = Dowex-1 Resin
D = Auxiliary Tip
(Polyethylene Tubing)

FIGURE 1. ION-EXCHANGE COLUMN

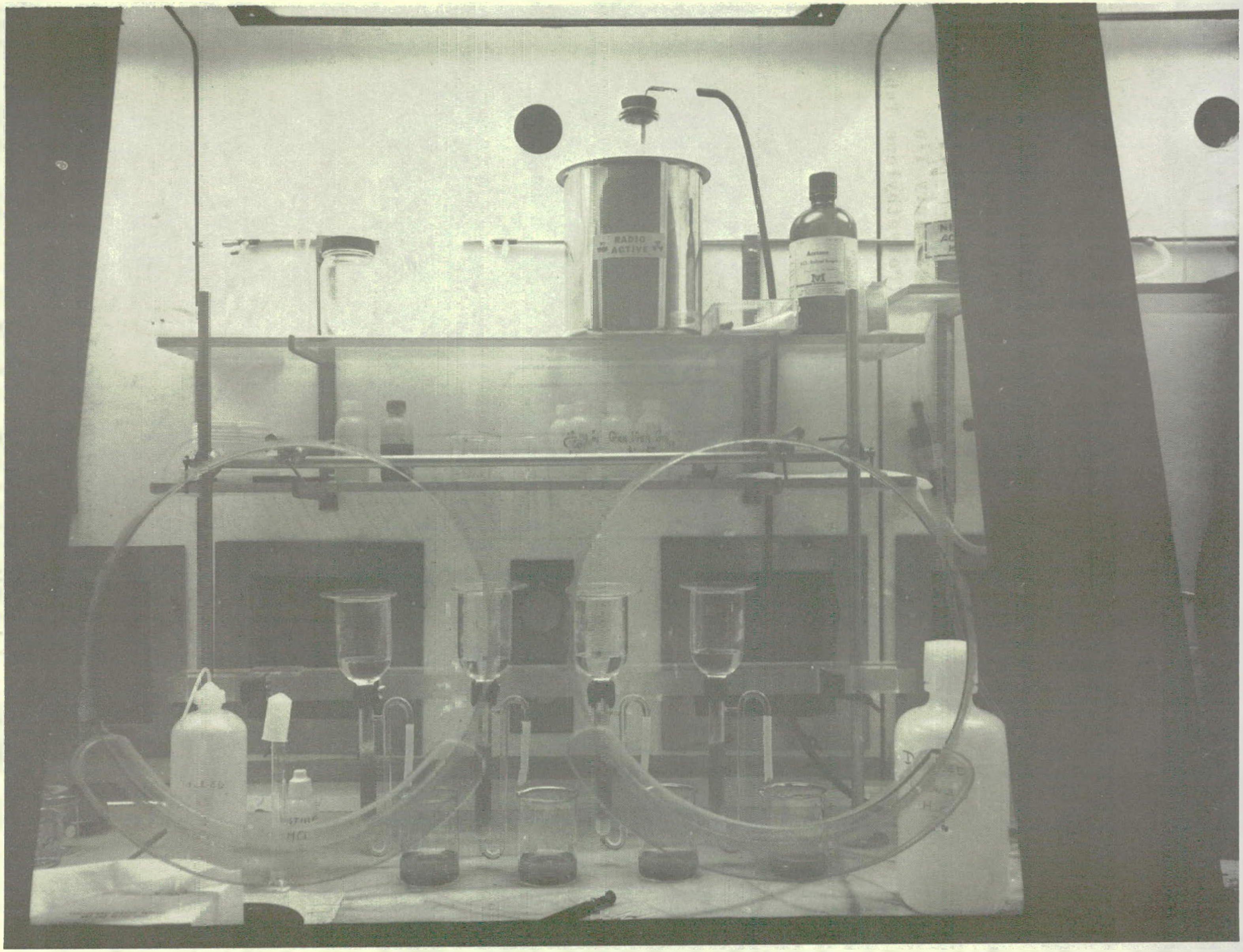


FIGURE 2. GLOVED BOX WITH SELF-LEVELING ION-EXCHANGE COLUMNS

Standards G, H, I, and J are prepared by dilution of Standard F as previously reported for Standards B, C, D, and E.

Procedure

Sample Preparation. Weigh a 100-mg. sample of plutonium metal, or 200 mg. of either $Pu(SO_4)_2 \cdot 4H_2O$ or $Pu(SO_4)_2$. The samples should contain from 200 to 2,000 p.p.m. total impurities. Place the sample in a 100-ml. beaker covered with a watch glass. Follow the sample preparation procedure outlined below for the appropriate material used.

Plutonium Metal. Add 5 to 6 drops of distilled deionized water with a medicine dropper to cover the sample. Make certain that the watch glass is in place to prevent loss of sample from possible spattering, and carefully add, with a dropper, about 1 drop of distilled constant-boiling hydrochloric acid for every 15 mg. of plutonium metal to the beaker at the opening at the pouring spout. The sample reacts vigorously with the acid, forming a purple-green solution. Place the beaker under the heat lamps if the metal does not dissolve rapidly. After the metal has dissolved completely, rinse any material adhering to the underside of the watch glass into the beaker with about 1 ml. water and remove excess HCl by evaporating the solution to a moist residue under heat lamps. Do not allow the sample to bake. When the solution has evaporated, remove the beaker from the heat, cool in air, and add 10 ml. of distilled 8N HNO_3. Swirl the beaker gently to bring all solids into solution.

Plutonium Sulfates. Add 15 ml. of 8N HNO_3 to the sample. Using a stirring rod, pulverize the sample, and stir until dissolved. Place the beaker, with a tight-fitting watch glass, under the heat lamps if the sample does not dissolve rapidly. Do not heat for more than 15 minutes at any one time or some acid may be lost by volatilization. When the sample has dissolved, remove the beaker from the heat, swirl gently, and allow to cool. Add 1 ml. of concentrated HNO_3 to the solution for every 200 mg. of $Pu(SO_4)_2 \cdot 4H_2O$ or $Pu(SO_4)_2$ used, and mix the solution by swirling.

Add the green solution of the dissolved plutonium metal or plutonium sulfate sample to the prepared ion-exchange column. Discard the first 5 ml. of effluent and collect the remaining clear effluent in a 100-ml. beaker at the rate of about 1 ml./3 min. Place the tip of the ion-exchange column against the inside of the pouring spout of the beaker and cover the beaker with a watchglass to afford maximum protection against sample contamination. Wash the sample beaker by adding 10 ml. of 8N HNO_3 and swirl the solution a few times. When the level of the solution in the column reaches about 1 ml. above the bed, add the 10-ml. washing from the sample beaker to the column. Repeat this washing procedure with 30 ml. of 8N HNO_3 and collect all the effluent. At the end of the washing period, add 500 µl. of Cobalt Internal Standard solution to the effluent using a microliter pipet. Exchange the watch glass on the beaker with a ribbed watch glass, and place the effluent beaker under the heat lamps to evaporate the solution.

Prepare a reference blank solution by adding 45 ml. of 8N HNO_3 with 500 µl. of Cobalt Internal Standard solution to a 100-ml. beaker. Blanks for plutonium sulfate samples should contain about 1 drop of H_2SO_4. Cover the beaker with a ribbed watch glass and evaporate the solution under heat lamps.

Remove the adsorbed plutonium on the column by adding 10 ml. of 0.35N HNO_3 to the column, collect the effluent, and repeat the procedure several times with the dilute acid.

Continue to evaporate the effluent and blank solutions to dryness but do not bake under the heat lamps. Solutions containing H_2SO_4 may require additional prolonged heating periods. Cool the vessels to room temperature. Using a microliter pipet, add 500 µl. of 8N HNO_3, dropwise, to the beakers making sure that the sides of the vessels are washed with the acid. Swirl the beakers for a few minutes to insure complete mixing of the solutions.

Spectrographic Procedures. With a microliter pipet, add four 100-µl. aliquots of the sample solution, two 100-µl. aliquots of the blank solution, and 100-µl. aliquots each of Standards A and E to prepared electrodes. (Prepare 8 electrodes by adding 2.5 mg. of gallium oxide to each anode cup previously sealed with Kel-F sealer.) Carefully place the electrodes under heat lamps adjusted to a temperature of about 80°C and slowly evaporate, but do not boil, the solutions for 1 hour. At the end of this drying period, increase the temperature to about 100°C and bake the electrodes for an additional hour. Excite the electrodes under the conditions shown in Table 1.

TABLE 1

SPECTROGRAPHIC CONDITIONS FOR THE DETERMINATION OF THE COMMON ELEMENTS, BORON, AND CADMIUM

Electrode Gap:		4 mm.
Entrance Slit:		25 µ.
Exposure:		10 sec.
Source:		25-amp. D.C. arc.
Spectrum:	(1)	Common elements photographed in position 3.0 of the 1st order. (Wavelength range 2200-3450 A.)
	(2)	Boron and cadmium photographed in position 6.0 of the 2nd order. (Wavelength range 2300-2900 A.)

Process the photographic plates according to the manufacturer's instructions. Densitometer the analytical lines shown in Table 2, determine the log intensity ratio of each line relative to the Cobalt Internal Standard, and read the concentration of the impurities in the sample directly from the analytical curves. Typical curves are shown in Figure 3.

TABLE 2

WAVELENGTHS OF SPECTRAL LINES AND LOWER LIMITS OF DETECTION

Element	Wavelength	Lower Limit of Detection, p.p.m. (estimated)
Fe	3020.640	2
	2599.396	15
Mn	2798.27	0.5
Mg	2852.129	0.05
	2802.695	0.2
Pb	2833.069	3
Cr	2835.63	5
Ni	3050.819	2
Co	3072.34	-
Al	3082.15	1
Ag	3280.683	0.05
Zn	3345.020	15
Mo	3132.594	0.5
Cu	3273.962	0.2
Be	2650.47	1
	3130.42	0.2

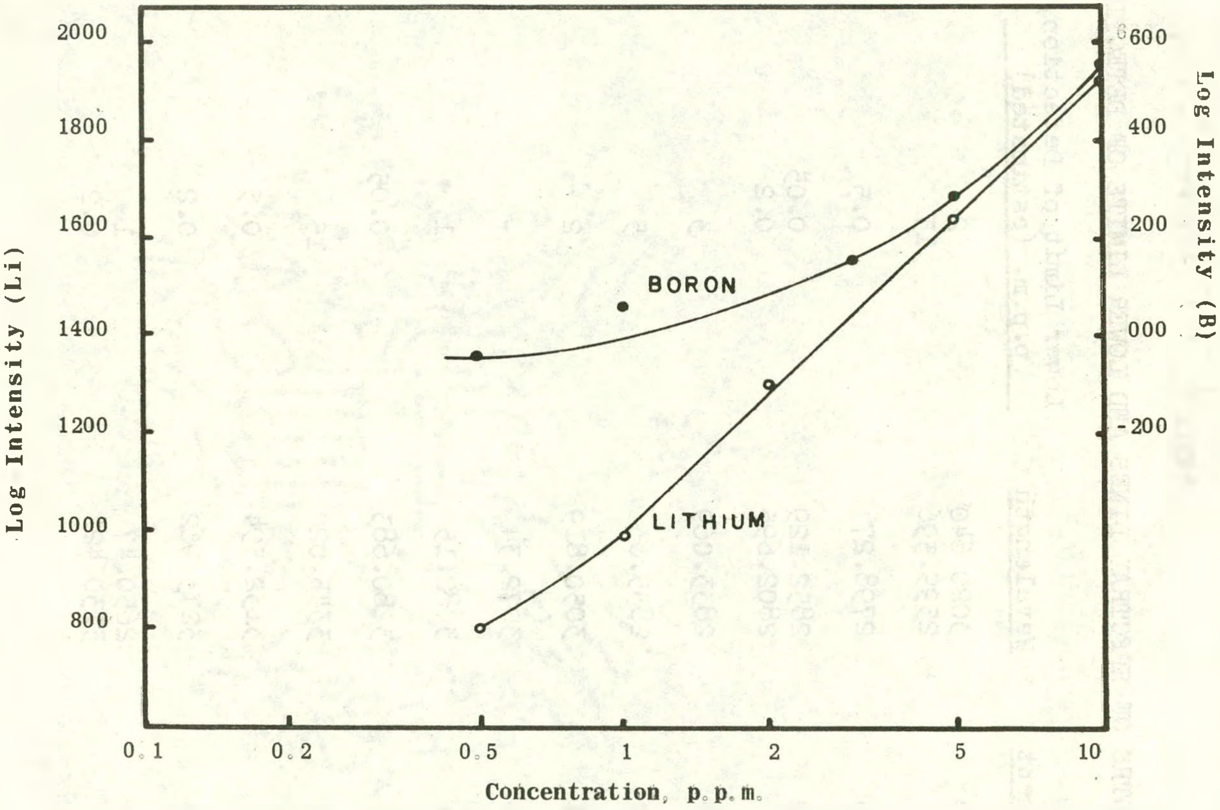


FIGURE 3. TYPICAL ANALYTICAL CURVES FOR THE SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN PLUTONIUM

Calculate the concentration of impurities as expressed on a standard 100-mg. sample basis as follows:

$$A = B \times \frac{100}{C}$$

Where: A = impurity concentration (100-mg. sample basis), p.p.m.

B = impurity concentration (from graph), p.p.m.

C = sample weight, mg.

For the determination of boron and cadmium impurities follow the outlined procedure, but eliminate the Cobalt Internal Standard, and substitute In_2O_3 for Ga_2O_3 as the matrix. Excite the 4 samples, 2 standards, and 2 blanks under the conditions shown in Table 1. Calculate the concentration of impurities in the sample as in the outlined procedure above using the analytical lines shown in Table 3.

TABLE 3

WAVELENGTHS OF SPECTRAL LINES AND LOWER LIMITS OF DETECTION

Element	Wavelength, A.	Lower Limits of Detection, p.p.m.
B	2497.733	1
Cd	2288.018	a10

a = approximate

For the determination of the alkali elements, sodium, barium, and lithium, follow the outlined procedure, but eliminate the Cobalt Internal Standard and the Ga_2O_3 matrix. Substitute Standards F and J for Standards A and E, respectively. Excite the electrodes under the conditions shown in Table 4. Calculate the concentration of impurities in the sample as in the outlined procedure above using the analytical lines shown in Table 5.

TABLE 4

SPECTROGRAPHIC CONDITIONS FOR THE DETERMINATION OF SODIUM, BARIUM, AND LITHIUM

Electrode gap:	4 mm.
Entrance slit:	10 μ.
Filter:	Yellow (To cut out light below 4000 A.)
Exposure:	6 sec.
Source:	25-amp. D.C. arc.
Spectrum:	Photographed in position 8.5 of the 1st order (Wavelength range 5700-6900 A.)

TABLE 5

WAVELENGTHS OF SPECTRAL LINES AND LOWER LIMITS OF DETECTION

Element	Wavelength, A.	Lower Limits of Detection, p.p.m.
Na	5889.95	*
Ba	6141.76	10
Li	6707.844	a0.2

a = approximate

* cannot be estimated reliably at this time because of high blank levels.

Analytical Working Curves. Prepare analytical curves for the analysis of the common elements as follows: Add 2.5 mg. of Ga_2O_3 to each of 40 electrodes previously sealed with Kel-F sealer; using a microliter pipet, add 100 μl. of Standard A to 7 electrodes; repeat, using Standards B, C, D, and E for a total of 35 electrodes. Prepare blank electrodes by adding 100 μl. of the Cobalt Internal Standard to the remaining 5 electrodes. For boron and cadmium, use In_2O_3 instead of Ga_2O_3 and omit the Cobalt Internal Standard. For the alkali elements, omit the matrix and the Cobalt Internal Standard; substitute Standards F, G, H, I, and J for Standards A, B, C, D, and E, respectively.

Using the conditions outlined in the appropriate sample procedure above, dry and excite the electrodes, process the photographic plates, and densitometer the analytical lines, Tables 2, 3, and 5.

For the common elements, determine the log intensity of each line relative to the Cobalt Internal Standard; determine the relative log intensity of each line for the alkali elements, boron, and cadmium. In order to read the sample impurity concentrations directly from the graph, calculate the adjusted concentration of the standards as follows:

$$A = B \times C \times 5$$

Where: A = standard concentrations (adjusted), p.p.m.

B = standard concentrations (original), μg./ml.

C = 0.1 = aliquot of standard used, ml.

Plot the relative log intensity of the lines versus the adjusted concentrations of the appropriate standards, as indicated in Figure 3.

Experimental

Spectrographic Studies. Interfering background lines and high blank values resulted in limiting the sensitivity obtainable for some alkali elements. Several experiments varying slit width, grating mask, excitation variables, and photographic plates, reduced background at the expense of a loss in intensity. In addition, it was necessary to eliminate the matrix with a subsequent loss in some sensitivity since the otherwise pure Ga_2O_3 was found to have a high sodium content. Acceptable results were obtained with a modified procedure although spectral line reversal was found at the 200-p.p.m. level for sodium.

A preliminary investigation of boron and cadmium showed that these elements could not be determined in the 1st order because of lack of sensitivity. Tests in the 2nd order showed an increase in sensitivity of about 1 step (100%). In_2O_3 was substituted for the Ga_2O_3 matrix since lines from the latter material interfered with the boron line. Although acceptable results were obtained, the lower limits of detection for boron and cadmium still need improvement. Cadmium was especially troublesome because of background line interference.

Reduction of Blank Impurities. In order to increase the lower limit of detection for the elements, the impurity content of the reference blanks was lowered by reducing the amount of reagent or material used in the procedure and by preparing high-purity materials. The experimental details are presented here as an aid to others in determining the approach to be taken towards their own specific problems.

Several lots of Ga_2O_3 prepared at the New Brunswick Laboratory were analyzed and the material of highest purity ($\sim 99.99^+\%$) was used as the matrix. The amount of matrix was reduced 50% from the former 5-mg. charge without appreciably changing line intensity, Table 6. Various lots of Kel-F grease and its CCl_4 solvent used as electrode sealer were tested and a purer preparation was found; the amount was reduced from 15 to 10 drops of solution per electrode. Smaller amounts of sealer resulted in incomplete sealing with subsequent loss of precision. Reagent-grade nitric acid, usually the major contributor of impurities, was purified either by distillation from a quartz still, a 50-plate Oldershaw distilling column, or by fractional crystallization below -10°C. No difference in results was noted between either of the three purification methods although it was felt that the 50-plate Oldershaw column was not operated under optimum conditions and that better results with the apparatus might be obtainable. The degree of purification obtained was insufficient, and repeated redistillation or recrystallization of the material gave only slight improvement. Similar results had been obtained in a previous study at this laboratory.[3] Accordingly, the amount of nitric acid used to wash the ion-exchange column completely was reduced from 100 ml. to 40 ml. by reducing the length of the resin bed from 10 cm. to 6 cm.

In general, a significant overall reduction of impurities in the blank values was made by the above purifications and reductions in material quantities used in the analysis.

Analysis of Impurities in Plutonium Metal. The analysis of trace impurities in plutonium metal had been plagued by high blank values. For example, Table 7 shows that one sample (No. 3-1) was analyzed using large amounts of slightly impure Ga_2O_3, Kel-F sealer, and nitric acid. In a later determination, a second sample (No. 3-5) was analyzed using a reduced quantity of higher-purity chemicals and showed improved results which are more in line with Hanford's values.

TABLE 6

EFFECT OF Ga_2O_3 MATRIX ON LINE INTENSITY

	Intensity Ratio*											
Ga_2O_3, mg.	Mn	Mg	Pb	Cr	Fe	Ni	Al	Be	Mo	Cu	Ag	Zn
0	-306	269	-865	-484	045	-186	138	892	056	300	287	271
2.5	-109	-54	-680	-705	140	-281	448	622	211	274	385	039
5.0	-048	085	-641	-709	169	-288	458	490	249	252	411	-044
7.5	-008	042	-542	-709	195	-290	486	348	346	310	498	-049

* Values shown are absolute intensity ratio units based on an arbitrary reference value. A difference of approximately 200 in intensity ratio is equivalent to a 1-step, or a 2-fold, change in intensity; the more positive the intensity ratio unit the greater the intensity.

TABLE 7

EFFECT OF HIGH BLANK VALUES ON PLUTONIUM IMPURITY ANALYSIS

Element	Hanford Values, p.p.m.	NBL Values,* (No. 3-1), p.p.m.	NBL Values,** (No. 3-5), p.p.m.
Mn	20	25	18
Mg	20	20	23
Pb	10	25	4
Cr	10	27	24
Ag	< 1	10	0.8
Fe	<50	110	94
Ni	10	17	15
Al	8	68	10
Cu	2	7	4
Be	--	--	N.D.
Mo	--	--	< 1
Zn	--	--	<50

N.D. = not detected
< = less than
* = high blank values
** = low blank values

The values obtained at this laboratory may not correspond exactly with those of Hanford for reasons explained elsewhere (see Discussion).

Analysis of Impurities in $Pu(SO_4)_2 \cdot 4H_2O$. The impurities were determined in $Pu(SO_4)_2 \cdot 4H_2O$ prepared from high-purity plutonium metal. Four samples of the compound were treated according to the outlined procedure. In all cases, about 1 drop (30-50 µl.) of H_2SO_4 remained in the "dried" effluent after adsorption of plutonium on the anion-exchange column. Suspecting that this H_2SO_4 might interfere with results, a study was made of the effect of the presence of this acid in the sample and its removal by prolonged heating. The data in Table 8 show that the presence of H_2SO_4 on the electrode generally causes erratic results.

TABLE 8

EFFECT OF SULFURIC ACID IN SAMPLE EFFLUENT

Element	Control,* p.p.m.	Unfumed Sample,** p.p.m.	Fumed Sample,*** p.p.m.
Mn	44	39	46
Mg	41	56	45
Pb	24	27	24
Cr	37	56	38
Fe	210	215	250
Ni	48	54	47
Al	245	175	290
Be	16	20	19
Mo	50	23	62
Cu	9	13	8
Ag	7	14	15
Zn	185	270	200
Co****	1.161	0.939	1.078

* = No H_2SO_4 present.

** = Sample contained a total of about 50 µl. of H_2SO_4 or 10 µl. per electrode.

*** = Sample fumed to dryness to remove H_2SO_4.

**** = Cobalt Internal Standard; results expressed in intensity ratio.

It was noted that upon excitation of the samples the acid produced voluminous clouds of vapor in the arc and that electrodes sometimes were knocked from their pedestals during this period. When the effluent from the $Pu(SO_4)_2 \cdot 4H_2O$ samples was evaporated to complete dryness according to the prescribed method, acceptable results were obtained.

Ion-Exchange Separation. A major reason for removing plutonium from its impurities prior to spectrographic analysis is to reduce the potential safety hazard caused by the spread of this material upon excitation of the sample.[4,5] Accordingly, the amount of plutonium found in the effluent from the ion-exchange separation is of interest. One separation gave relatively high plutonium values estimated at $< 0.07\%$ using a 100-mg. plutonium sample. These results were attributed to incomplete preparation of the resin which was in less than the required 8N HNO_3;[6] the adsorbed plutonium band required half the length of the 10-cm.-long resin bed. When the resin was rinsed thoroughly several times with 8N HNO_3 before loading in the column, the plutonium breakthrough was reduced to $< 0.001\%$ per 100-mg. sample; the green plutonium band on a 6-cm.-long column was now only about 1 to 1.5-cm. long. Another investigator attributes high plutonium breakthrough to the formation, on heating the sample, of the less strongly adsorbed plutonium(VI) species.[7] In our tests, a plutonium(IV) solution was heated prior to separation and no increase in breakthrough occurred, Table 9. As indicated in Table 9, americium-241 (from beta-decay of the small amount of plutonium-241 in the sample) was found in the effluent as it is not adsorbed on Dowex-1 anion resin in 8N HNO_3. The amount of americium-241 found was in accordance with the calculated values based on the age and plutonium-241 content of the samples.

TABLE 9

PLUTONIUM BREAKTHROUGH IN DOWEX-1 ANION RESIN EFFLUENT

Condition	Plutonium Found,*,** %	Americium-241 Found,**,*** %
Resin bed contained < 8N HNO_3	< 0.07	0.03
Resin bed adjusted to 8N HNO_3	< 0.001	0.05
Pu(IV) solution heated prior to separation	< 0.001	0.05
Pu(IV) solution unheated prior to separation	< 0.001	0.05

* = Plutonium estimated in the presence of americium-241 by alpha spectrometry.
** = Based on a 100-mg. sample.
*** = Variation in americium-241 content due to different sample ages.

Results

An improved method was developed for the quantitative determination of trace impurities in high-purity plutonium. The method was modified for applicability to plutonium sulfates; the analysis of this material and of plutonium metal is shown in Table 10.

TABLE 10

DETERMINATION OF IMPURITIES IN PLUTONIUM METAL
AND IN PLUTONIUM SULFATE TETRAHYDRATE

Element	Plutonium Metal Hanford Values, p.p.m.	Plutonium Metal New Brunswick Laboratory Values, p.p.m.	$Pu(SO_4)_2 \cdot 4H_2O$* New Brunswick Laboratory Values, p.p.m.
Mn	20	22	< 0.5
Mg	20	26	7
Pb	10	7	2
Cr	10	30	< 5.(a 2)
Fe	< 50	115	18
Be	--	N.D.	N.D.
Ni	10	17	5
Al	8	12	< 40
Mo	--	< 1	N.D.
Cu	2	6	2
Ag	< 1	1.3	0.5
Zn	--	< 50	a 20

< = less than
N.D. = not detected
a = approximately
* = prepared from the plutonium metal quoted

A comparison of values obtained shows that the $Pu(SO_4)_2 \cdot 4H_2O$ contains almost two-thirds less of the analyzed impurities found in the plutonium metal from which it was prepared. Typical analytical curves are shown for the alkali elements (Na, Ba, Li) and for the boron and cadmium determinations, Figure 3. The lower limits of detection for these elements are shown in Tables 3 and 5.

Discussion

In the course of experiments to determine the plutonium content in the effluent from the ion-exchange separation, americium-241 was detected. On the basis of the radiometric determination of the americium content of the samples it was found that the lower limit of detection for this isotope is about 1 p.p.m.

A complete analysis of impurities in plutonium requires three or more separate determinations, e. g., elements in the 1st and 2nd orders, and the alkali elements. The procedures presented herein are for these separate group determinations but may be combined using only one sample and one ion-exchange separation. Accordingly, the amount of sample taken, and the volume of acid used after evaporating the effluent must be doubled in order to increase the number of charges available for excitation. Major advantages of the method are found in its use of only 200-300 mg. of sample for a complete analysis with adequate sensitivity, and the elimination of gross plutonium contamination problems during sample excitation.

Results from several analyses of plutonium metal show good precision but values for all impurity elements do not correspond exactly to those of Hanford. A significant cause of this apparent discrepancy may be attributed to sampling and impurity segregation. The metal analyzed at the New Brunswick Laboratory was from only one portion of one pin taken from a larger batch of material produced at Hanford. Their analysis was made on similar but not the same material. In fact, it has been shown,[8] Table 11, that there is considerable variation in impurities from pin (or button) to pin in the same batch, and even some variation from one segment to another in the same pin.

The problem of determining trace impurities in small samples using chemicals and other materials with the same impurity level, or greater, has been studied at this laboratory for several years.[3] This contamination problem, in combination with the loss in light intensity caused by modifying the spectrograph for gloved box operations has prompted the development of a spectrographic method which shows promise of even greater sensitivity with further modification.

TABLE 11

VARIATION OF IMPURITY CONCENTRATIONS IN PLUTONIUM METAL[8]

	Analysis of Plutonium Buttons, p.p.m.								
Element	1	2	3	4	5	6	7	8	9
Ca	< 3	30	80	25	20	15	40	40	50
Al	< 5	< 5	< 5	< 5	5	< 5	< 5	< 5	10
La	< 10	< 10	< 10	< 10	< 10	< 10	< 10	10	< 10
Si	10	8	10	30	20	12	6	7	6
Pb	3	4	25	30	1	< 1	2	1	1
Cu	15	10	25	50	8	6	< 1	10	50
Ni	3	10	8	30	2	< 1	1	3	10
Cr	< 5	< 5	< 5	3	< 5	< 5	< 5	< 5	< 5
Mg	15	40	25	30	30	30	25	30	25
Sn	3	1	< 1	< 1	< 1	< 1	< 1	< 1	4
Fe	25	25	8	10	80	80	100	80	< 10
Cd	< 1	< 1	< 1	< 1	< 1	5	< 1	< 1	< 1
Zn	< 20	40	50	< 20	< 20	< 20	< 20	< 20	< 20

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