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HIGH-PRECISION ISOTOPIC ANALYSIS OF NANOGRAM QUANTITIES OF PLUTONIUM

by

R. E. Perrin, G. W. Knobeloch, V. M. Armijo, and D. W. Efurd

ABSTRACT

A surface ionization-diffusion-type ionization source that uses a rhenium filament overplated with platinum has been developed and optimized for 0.5- to 2-ng plutonium samples. This source is capable of measuring the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in nuclear-test-debris samples to 0.15% precision and accuracy at the 95% confidence level.

1. INTRODUCTION

Nuclear test diagnostic programs conducted by Los Alamos National Laboratory require accurate and precise analysis of the plutonium that has been separated from debris collected after underground detonations at the Nevada Test Site. Measurements are made on thermal ionization mass spectrometers operating in the pulse-counting mode. Sample sizes are kept small to help minimize the radiation exposure to the separations chemist.

Originally, the separated and purified plutonium samples were loaded from aqueous solutions onto rhenium filaments for analysis by triple-filament techniques. The quality of the results was periodically degraded by scatter from ion beams produced by trace quantities of alkali metals and isobaric interferences from residual hydrocarbons associated with the samples. Electrodeposition of the plutonium onto the side filaments eliminated these interferences; however, a small but consistent scatter background remained. This background was attributed to migration of alkali metals present in ceramic insulators of the ionization filament operating at 1950°C. To eliminate this interference, it was necessary to develop a low-temperature ionization technique that has high precision and accuracy.

Rec et al.¹ developed a single-filament surface ionization-diffusion (SID)-type source for plutonium measurements. The plutonium was evaporated onto a rhenium filament from a weak acid solution. Next, the sample was clad with a film of high-work-function rhenium by radio-frequency diode sputtering techniques. The cladding provided high ionization efficiencies and improved control over the generation of the ion beam. It limited the prompt escape of neutral atoms. It also completely dissociated molecular species so that only atoms appeared in the mass spectrum.

Perrin et al.² modified this SID-type ionization source. They electroplated nanogram quantities of plutonium onto rhenium filaments. Next, a thin layer of rhenium was overplated by electrodeposition. This new SID source lowered the plutonium analysis temperature to 1450°C and eliminated the scatter background caused by heating the filament's ceramics. However, the source suffered from two weaknesses. (1) The conditions for proper rhenium overplating and spectrometer operation were very critical. The rhenium overplate was deposited as a hydride, which was then converted to metal by decomposition in the ionization chamber of the spectrometer. The conditions for both overplating and conversion were very subjective and led to a 5% failure rate. (2) The sample reached maximum count rate before the plutonium ion beam reached maximum stability. Once the beam stabilized, it underwent an appreciable decrease in single intensity. This changing beam intensity forced the analyst to accept a compromise between very precise determination of the major isotopes early in the analysis and poorer precision in later measurements.

Rather than attempt to improve the performance characteristics of the electrodeposited rhenium overplate, we chose to investigate other metals. If a metal is to be useful as an overcoating, it must have a melting point above the desired analysis temperature. The overcoating must also have a high work function and be inert in the atmosphere of the spectrometer's ionization chamber. Platinum and rhodium seemed to offer the most attractive alternatives to rhenium; platinum was selected for study because it has a higher work function.

This report summarizes the development of the SID ionization source using a platinum overplate. The technique was optimized for 1-ng samples, but it is useful for samples ranging from 0.5 to 2 ng. Samples smaller than 0.5 ng do not produce sufficient ion beam intensities to meet the precision and accuracy requirements. Samples larger than 2 ng produce excessive ion currents. Large ion beams will eventually degrade the operational characteristics of the spectrometer's multiplier; therefore, large samples are analyzed at lower temperatures to protect the multiplier. Fractionation patterns and ion beam stabilities for large plutonium samples have not been accurately established.

II. INSTRUMENTATION

The mass spectrometer used in this study is a modified version of the 30.5-cm radius, 90°-deflection, thermal ionization instrument that was developed at the National Bureau of Standards (NBS).³ The spectrometer is designed to operate as an ultrahigh-vacuum instrument. Its pumping system consists of a mercury diffusion pump and a 140-l/s ion pump. Additional pumping is achieved during analysis by filling a cold trap (located in the source housing) with liquid nitrogen.

The spectrometer has been equipped with a 17-stage electron multiplier that has copper-beryllium dynodes. The front dynode is flat. The multiplier can be translated along the x axis for proper interception of the ion beam. The gain is set by calibration against a Faraday Cup. The signal from the multiplier passes through a Shidler discriminator-amplifier that is capable of supplying a 1-V, 7-ns-wide output pulse when it is triggered by pulses from 6 MV to 2 V (Ref. 4). Counts are accumulated on a 250-MHz scaler; a voltage divider is placed between the amplifier-discriminator and the scaler to reduce line reflections. The dark current of the counting system is 0.05 cps; its dead time is 11 ± 1 ns. The overall linearity and deadtime of the system is verified by analyzing NBS standards U-100, U-500, and U-900. The data acquisition system has been automated with a Hewlett-Packard 9830B computer.

The mass spectrometer filaments are 0.76 mm wide and 12 mm long. They are fabricated from 0.025-mm-thick zone-refined rhenium. Before the sample is loaded, the filaments are degassed by being heated in a vacuum for 30 min at 2100°C. The pressure in the degasser starts at 1×10^{-6} torr and is reduced to about 5×10^{-8} torr by the end of bakeout. A negative 90-V dc potential is applied to the filament during outgassing.

III. PRODUCTION OF AN SID IONIZATION SOURCE USING PLATINUM OVERCOATINGS

Previous studies had established that plutonium could be plated onto rhenium filaments from hydrochloric acid that contained ammonium chloride. Three platinum solutions were chosen for testing as candidates for production of an overplate. Platinum diammino dinitrite and platinum ammonium chloride solutions were unsatisfactory; both caused dissolution of the previously plated plutonium. Overplates deposited from platinum DNS (dinitrato sulfato platinous acid) diluted with 1.5M HCl produced excellent SID filaments.

Samples were prepared for electrodeposition by adding 1.5M HCl to dilute the plutonium concentration to 1×10^{-10} g/ μ l. Figure 1 shows the apparatus used for the electrodeposition; Figs. 2(a) and (b) show the apparatus in plating and rinsing modes, respectively. A trough is formed by placing 6.4-mm-wide Teflon tape beneath a rhenium mass spectrometer ionization filament and over two support rods. This trough will hold $\approx 150 \mu$ l of solution. The Teflon tape forms a seal and prevents electrodeposition of the plutonium on the bottom of the filament. The platinum anode is

made by spotwelding 0.25-mm-diam platinum wire on a filament pin. A regulated HP-6100 dc power supply furnishes the electrolysis current. The electrode spacing is maintained at 3.2 to 3.6 mm. If an electrode spacing less than 3.2 mm is used, the higher current density will destroy the electrolyte too quickly; spacings greater than 3.6 mm increase the plating time. The method used to produce platinum-overplated SID filaments is detailed below.

Fig. 1. Electrodeposition apparatus.

Fig. 2. Electrodeposition apparatus in (a) plating and (b) rinsing modes.

Pipette 100 μl of electrolyte onto the filament. The ammonium chloride electrolyte is prepared by bubbling ammonia gas through 1.5M HCl until a pH of 2.7 is obtained. **Place 10 μl of the plutonium solution in the electrolyte, and electrolyze for 30 min at 3.5 V.** The pH of the solution at conclusion of electrolysis will be 0.8. These pH and voltage values were determined by experiments to give the best recovery yield and the most adherent coating of plutonium. The plutonium plating efficiency is $\approx 95\%$. New solutions of electrolyte should be prepared on a periodic basis.

Add 5 μl of platinum solution to the electrolyte, reduce the plating voltage to 3 V, and overplate the platinum for 20 min. The platinum solution is platinum DNS dissolved in 1.5M HCl. The platinum concentration is 5 $\mu\text{g}/\mu\text{l}$. The 1.5M HCl is added to the platinum DNS to ensure that the pH of the electrolyte during the overplating remains below 2. If the pH rises above 2, the platinum DNS produces a nonuniform black coating that may degrade the analysis.

While the plating voltage is still applied, rinse the electrolyte from the filament with ethanol. Remove the filament from the plating apparatus, and rinse thoroughly with de-ionized water and then glass-distilled acetone. Failure to completely rinse the electrolyte from the filament will result in a large alkali metal contamination. **Dry the filament at 350°C by placing it under a heat lamp while passing 1.5 A through it for 15 min. Examine the filament to verify that the platinum is deposited as a shiny, nonporous, and uniform layer. Monitor the filament for alpha activity to verify that 0.5 to 2 ng of plutonium are present.**

Scans of the sodium and potassium mass regions at 1450°C indicate that the alkali metal ion beams have been reduced to $\approx 1 \times 10^6$ cps. These beam intensities are consistent with data obtained from degassed filaments before any sample has been loaded. Hydrocarbon interference is also eliminated by the electroplating process. The scatter from the alkali metal ion beams and isobaric hydrocarbon interferences are reduced to 0.05 cps in the plutonium mass regions.

One advantage of the platinum overplate compared to the electrodeposited rhenium overplate was evident from these first experiments. The plutonium ion beam intensity from a platinum-overcoated filament continues to grow after the beam stabilizes. Figure 3 shows typical signal intensities from a 1-ng plutonium sample for both a rhenium- and a platinum-overcoated filament.

The growth rate of the plutonium signal is an inverse function of the thickness of the platinum overplate, which was measured by Rutherford backscattering using 3-MeV alpha particles. The optimum overplate for a 1-ng sample is $110 \pm 10 \text{ \AA}$; the plating procedures detailed above produce a 110-Å overcoat.

Our mass spectrometer obtains maximum stability 30 min after it is switched from the standby mode to the operational mode. Data acquisition for a plutonium sample takes 35 min. Therefore, we conducted experiments to optimize operating parameters for producing the most stable and reproducible ion beam during the data acquisition period. The optimum heating pattern is shown in Table I.

Fig. 3. Typical ion beam intensities for a 1-ng plutonium sample.

**TABLE I. OPTIMUM HEATING
PATTERN FOR SID
FILAMENT**

Time (min)	Heating Pattern (°C)
0	1000
2	1100
4	1200
6	1300
8	1350
10	1400
12	1450
20	Take baseline
30	Begin data acquisition

IV. CHARACTERIZATION OF THE SID IONIZATION SOURCE

To determine the fractionation characteristics of the platinum overplate, seventeen 1-ng aliquots of a 1 to 1 mixture of ^{239}Pu to ^{242}Pu were analyzed using the standard operating procedure described above. The filament fractionation as a function of time is plotted in Fig. 4. The change in fractionation as a function of time is small and linear from 30 to 55 min; the $^{239}\text{Pu}/^{242}\text{Pu}$ ratio only changed by 0.07% during this time. A fractionation factor of 0.27% per mass unit was determined from analysis of the ^{239}Pu - ^{242}Pu mixture.

Next, a series of 1-ng aliquots of NBS-947 were measured. The measurement of the mass fractionation factor that was calculated from the $^{240}\text{Pu}/^{239}\text{Pu}$ observed ratio divided by the certified $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio was also 0.27% per mass. All data were corrected by this fractionation factor, and the results are shown in Table II. The measured isotope ratios were then compared to the certified NBS value. The 95% confidence interval for the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio was 0.072%,* which is within the certified limit for the standard. The excellent agreement for the $^{241}\text{Pu}/^{239}\text{Pu}$ and the $^{242}\text{Pu}/^{239}\text{Pu}$ atom ratios indicates that the fractionation factor of 0.27% per mass is both accurate and linear. No definite cause for the positive bias of the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio has been determined. However, a systematic uranium blank of 2×10^{-14} g would be sufficient to account for this bias. Attempts to demonstrate the existence of a systematic blank at this level were inconclusive.

Samples from the US Department of Energy Isotope Exchange Program were analyzed to verify the long-term stability of the SID source. This program submits a series of blind samples to eight US Department of Energy and Department of Defense related laboratories on a monthly basis. For a 12-month period, the ratio of the $^{239}\text{Pu}/^{240}\text{Pu}$ ratios to the reference values for the samples was 1.00016, with a 95% confidence level of 0.062%.

The samples described above were alpha-surveyed before and after analysis. To determine the ionization efficiency of the SID source, the total number of plutonium atoms evaporated from the filament during analysis was compared to the total number of plutonium ions collected during the analysis. The average ionization efficiency at 1450°C was 0.34%.

*The errors reported in this study are the 95% confidence limits of the population. It has been assumed that the data is normally distributed. Therefore, the t-statistic provides a valid estimate of the standard deviation of the population.

Fig. 4. Filament fractionation as a function of time.

V. DETERMINATION OF SID-SOURCE SENSITIVITY TO CHEMICAL IMPURITIES

To determine the sensitivity of the SID source to chemical impurities, microgram quantities of various salts were added to the electrolyte during the plutonium deposition. The plutonium was electroplated and then overplated with platinum by the standard technique. Rare earths such as gadolinium, neodymium, and samarium significantly increased the temperature at which plutonium ions were formed. The plutonium ion signal followed the typical growth pattern for the first 10 to 12 min. At that time, the beam intensity suddenly decreased. Increasing the filament temperature to 1800 to 1850°C reestablished the increasing plutonium ion signal; however, the measured isotope ratio fractionated by an additional 0.2 to 0.3%. This fractionation was erratic and uncontrollable. In addition, a scatter background at the plutonium mass region resulted from the large rare-earth signal.

Zirconium, titanium, and tantalum also significantly increased the temperature at which plutonium ions formed. These metals ionize less efficiently than the rare earths do, and they could not be detected in the mass scans until the filament temperature was raised to 1950°C. Plutonium ions could be formed by increasing the filament temperature, but the beam was erratic and never stabilized. Precise measurements were not possible.

Iron, chromium, nickel, and tin imparted a yellow or brown color to the platinum overplate. Plutonium ions formed. However, the signal began a rapid decay after 10 to 15 min. No high-temperature run was found. An alpha survey of these filaments after they were heated to 1450°C indicated that all the plutonium had been displaced from the filament. No useful measurements could be made.

Lead had a very deleterious effect on SID filaments. Quantities as small as 0.1 µg imparted a black, shiny appearance to the filaments. When the filaments were heated, it became apparent that the platinum overcoat had been poisoned. As the temperature was increased to 1450°C, all normal background spectra as well as the plutonium ion beam were depressed by a factor of 10 to 50. No meaningful measurement could be made.

Picogram quantities of uranium and americium caused isobaric interferences at the ^{238}Pu and ^{241}Pu masses, respectively. The uranium diffused through the platinum overplate and ionized; this biased the ^{238}Pu measurements. The ingrowth of uranium usually was detected by the constantly changing ^{238}Pu ratio. Americium coplated with the plutonium and the platinum. Under these operating conditions, it ionized more efficiently than the plutonium, and it could not be completely burned off the filament. Therefore, it was imperative that an americium separation be performed on the sample before it was analyzed.

Plutonium samples doped with sodium or potassium during the electrodeposition were not affected; the alkali metals were not electroplated. If large alkali beams were observed from the SID filament, it was the result of improper washing after the electrodeposition.

It is obvious from these studies that the SID source requires extremely clean samples; any material that might coplate with the plutonium or the platinum must be eliminated before the sample is electroplated. The following section details the chemistry that was developed to separate plutonium from Nevada Test Site debris. The dissolution procedure was designed to provide suitable samples for a variety of measurements in addition to those for mass spectrometry.⁵ The plutonium-purification procedure was derived from a combined uranium-plutonium procedure that was designed specifically for mass spectrometry.⁶ The procedure has many applications in addition to those for debris analysis described here.

TABLE II. ANALYSIS OF NBS STANDARD SAMPLE 947^a

Analysis Number	²³⁸ Pu/ ²³⁹ Pu	²⁴⁰ Pu/ ²³⁹ Pu	²⁴¹ Pu/ ²³⁹ Pu	²⁴² Pu/ ²³⁹ Pu
1	0.00368	0.24149	0.01582	0.01556
2	0.00367	0.24141	0.01576	0.01560
3	0.00369	0.24133	0.01576	0.01547
4	0.00365	0.24141	0.01582	0.01558
5	0.00367	0.24136	0.01581	0.01562
6	0.00366	0.24143	0.01585	0.01560
7	0.00366	0.24144	0.01582	0.01563
8	0.00364	0.24145	0.01577	0.01567
9	0.00367	0.24144	0.01576	0.01559
$\bar{X} =$	0.00367	0.24142	0.01580	0.01559
Certified value	0.00363	0.24142	0.01580	0.01559

^aAll data has been decay corrected to March 1, 1981.

VI. DISSOLUTION OF NUCLEAR-TEST DEBRIS

The elemental compositions of Nevada alluvium and tuff formations in which the nuclear detonations take place are similar to the average elemental composition of the earth's crust. Debris is fused crustal material that contains trace quantities of device material, fission products, and activation products. The successful dissolution of debris samples depends on repeated evaporations with concentrated hydrofluoric acid to convert silica and silicates to volatile silicon tetrafluoride. After the sample has been dissolved, it is stored as a 3M HCl solution. Dissolution is performed in an exhaust hood that is equipped with a water wash-down. The step-by-step dissolution procedure is outlined below.

Place the dried and pulverized debris sample in a Teflon beaker. Add 25 ml of fuming HNO₃, 100 ml of 72% HClO₄, and 50 ml of 48% HF. Heat the beaker on a hot plate (at a medium setting to protect the Teflon) until fumes of HClO₄ begin to evolve. Cool the solution and add another 50 ml of 48% HF. Heat until HClO₄ fumes are once again observed. Repeat 50-ml additions until the debris is completely dissolved. Four additions of HF will dissolve 5 to 10 g of debris; six treatments are needed to dissolve 15 g. Additional perchloric acid may be added to the beaker as needed to prevent spattering. Following the final HF addition, the sample should be heated for at least 15 min after HClO₄ fumes are observed.

Cool the Teflon beaker and transfer its contents to an 800-ml Vycor beaker. Vycor is used instead of normal borosilicate glass because it is more durable and more acid resistant. *Wash the Teflon with 3M HCl and add the wash to the Vycor beaker. Add 10 ml of 72% HClO₄ to the Teflon and fume it for 5 min. Cool and add the HClO₄ to the Vycor beaker. Wash the Teflon again with 3M HCl and add the solution to the Vycor beaker. Monitor the Teflon beaker for gamma activity to ensure that quantitative transfer has been achieved.*

Swirl the Vycor beaker's contents well and heat it on a hot plate at a high setting until fumes of HClO₄ are observed. Fume the HClO₄ for at least 30 min, adding more HClO₄ if required to prevent spattering. Flame the walls of the beaker at least once during the fuming period to ensure complete removal of all HF. Failure to remove the last traces of HF may result in a loss of plutonium. Continue heating the Vycor beaker until the volume of the sample is reduced to 50 ml. Cool the beaker's contents. Add 100 ml of 3M HCl and warm the solution to dissolve any solids. Transfer the acid to four Vycor centrifuge tubes and centrifuge at 3500 rpm for 2 min. Decant the supernate from the tubes back into the Teflon beaker that was used in the HF dissolution. Wash the Vycor beaker with

3M HCl and transfer this wash into the centrifuge tubes. Warm the centrifuge tubes to dissolve the solids, centrifuge, and add the supernate to the Teflon beaker. If any precipitate remains, it is

- (a) soluble crystalline salts that may be dissolved in warm HCl,
 - (b) gelatinous precipitate containing F^- salts that can be dissolved by additional fuming in $HClO_4$,
 - (c) grains of inactive SiO_2 that can be discarded at this point, or
 - (d) grains of active debris that were not pulverized enough to be destroyed by the HF treatments.
- These active grains may be dissolved by prolonged fuming with HF in Teflon.

Monitor the Vycor beaker and centrifuge tubes to ensure that there has been quantitative transfer back into the Teflon.

Add 50 ml of $HClO_4$ and 50 ml of HF to the Teflon beaker that contains the plutonium and place it on a hot plate at a medium setting until $HClO_4$ fumes are observed. Cool the Teflon and add 50 ml of HF and heat to strong $HClO_4$ fumes. Heat the Teflon beaker for at least 15 min after the $HClO_4$ fumes appear. Transfer the solution while it is still hot back into the 800 ml Vycor beaker that was used earlier. Cool the beaker. Cool the Teflon, wash it with 3M HCl, and add the wash to the Vycor beaker. Add 10 ml of $HClO_4$ to the Teflon and fume for 5 min. Pour an additional 50 ml of $HClO_4$ into the Teflon and transfer its contents to the Vycor beaker.

Fume the Vycor beaker for at least 30 min after all the HCl has boiled away. Flame the walls once or twice during the fuming. Reduce the $HClO_4$ volume to 50 ml; stop immediately if material begins to salt out or if spattering occurs. Cool the beaker contents. Add 100 ml of 3M HCl and warm slightly to dissolve solids. Transfer the solution to Vycor centrifuge tubes and centrifuge at 3500 rpm for 2 min. Decant the supernate through Whatman 541 filter paper into a storage bottle. If any activity remains in the beaker or the tubes, repeat the 3M HCl wash. If any precipitate remains in the tubes after the 3M HCl washes, add a few ml of $HClO_4$; taking care to avoid spattering, fume over a burner and flame the walls. Do not go to dryness because the oxides formed may stick to the glass and be difficult to remove. Add 20 ml HCl, centrifuge, and decant into the storage bottle through the filter paper. If the $HClO_4$ treatment did not destroy the precipitate, add a few drops of 9M NaOH and warm. Do not boil the NaOH for a prolonged period; it will etch the glass and add silicates to the solution. After treatment with NaOH, any remaining precipitate can be dissolved in 20 ml of 3M HCl, warmed, centrifuged, and passed through the filter paper.

Destroy the filter paper in a Vycor beaker by adding 25 ml of fuming HNO_3 and heating it. After all dry paper disappears, add 50 ml $HClO_4$ and heat to strong fumes. Fume until nearly dry, but avoid spattering. Flame the beaker walls once during fuming. Cool the beaker and wash its contents into a Vycor centrifuge tube with 3M HCl. Centrifuge at 3500 rpm for 2 min. Carefully decant the supernate into the storage bottle. Add enough 3M HCl to dilute the concentration of the ingoing debris to 7.5 mg/ml. Cap the bottle and place in a water bath at 90°C for 12 h.

VII. PLUTONIUM PURIFICATION

For optimum results, the plutonium-purification procedure should be performed in a Class 100 clean area using HCl, HNO_3 , $HClO_4$, and H_2SO_4 acids prepared by subboiling distillation.^{7,8} All glassware and quartz containers are leached in aqua regia and rinsed in distilled water that has been passed through a Milli-Q water de-ionization system.

Place an aliquot of sample containing 5 to 20 ng of plutonium in a 40-ml Vycor centrifuge tube and add ^{242}Pu tracer in approximately the same amount as the ^{239}Pu . * This quantity of plutonium will

*If more than 0.33 g of debris is needed to meet the plutonium requirements, the following fluoride precipitation should be performed after the tracer equilibration step. The sample is dissolved in 3M HCl and enough HF is added to make the solution 3M in F^- concentration. Let the precipitate coagulate for 5 min, centrifuge it, and discard the supernate. Wash the precipitate with a mixture of 3M HCl and 3M HF, centrifuge, and discard the supernate. Dissolve the fluoride precipitate in a minimal amount of concentrated HCl and H_3BO_3 ; add 9M NaOH, boil, cool, and centrifuge the solution. Discard the supernate. Wash the hydroxide precipitate with de-ionized water. Centrifuge and discard the supernate. This hydroxide precipitate is converted to a nitrate salt and dissolved by the addition of 5 ml of 2M HNO_3 .

allow replicate mass spectrometer measurements. *Add 2 ml of concentrated HClO_4 and evaporate to dryness. To equilibrate the sample and spike, add 2 ml more of HClO_4 and flame over a burner at 180°C or higher.* The HClO_4 equilibration step is omitted for untraced samples.

Add 5 ml of 2M HNO_3 , add sufficient solid NH_4NO_3 to saturate the solution, and then warm it to room temperature. Add 10 ml of reagent-grade ethyl acetate, stopper the tube with a plastic top, and shake it for 1 min. Centrifuge to separate the phases, remove the ethyl acetate layer, and transfer it to a clean Vycor tube. Repeat the extraction twice and combine the ethyl acetate phases. Discard the aqueous phase. Wash the combined ethyl acetate phases with 3 ml of 2M HNO_3 that has been saturated with NH_4NO_3 and equilibrated against ethyl acetate. Centrifuge and discard the wash. Wash twice more to remove aqueous entrainments in the ethyl acetate and discard the washes.

Back-extract the plutonium with 10 ml of de-ionized water, centrifuge it, and transfer the aqueous layer to a clean Vycor tube. Repeat the back-extraction twice and combine the aqueous layers. Discard the ethyl acetate layer. At this point, the macro soil constituents sodium, potassium, magnesium, calcium, aluminum, iron, and most of the fission products have been greatly reduced. The remaining elements are $\approx 95\%$ of the uranium; $\approx 80\%$ of the plutonium; $\approx 50\%$ of the neptunium; 60 to 80% of the zirconium; and traces of niobium, technetium, ruthenium, tellurium, and the macro soil constituents. The ethyl acetate extraction separates americium and curium from plutonium.

To prepare the sample for loading on an anion column, add 1 ml of 0.1M H_2SO_4 and warm the solution. Care must be taken to avoid concentrating the H_2SO_4 by evaporation while the plutonium is being dissolved. If the H_2SO_4 concentration increases to 0.5M, 100% of the plutonium can be eluted from the column. This loss is reduced to approximately 5% if the H_2SO_4 concentration is maintained at 0.1M.

The Bio-Rad AG 1-X8 anion exchange resin, 100 to 200-mesh column was prepared as follows. The resin was warmed overnight in a mixture of 4M HCl and 1% HF. Then it was washed successively with 4M and 0.1M HCl. The resin was packed in a quartz tube 4.5 cm in total length. The lower 2.5 cm of the column, which contains the resin, consists of quartz tubing of 2-mm i.d. by 4-mm o.d.; the tubing's drawn tip was plugged with quartz wool that had been leached in dilute acid and soaked in reagent-grade water. Quartz wool must be used; glass wool contains too many leachable impurities. Quartz tubing that is flared to form a funnel 2 cm long by 2.8 cm in diameter at the top was fused to the top of the column. The column was conditioned by three 1-ml washes with reagent-grade water and a 1-ml 0.1M H_2SO_4 wash.

Load the 0.1M H_2SO_4 containing the plutonium onto the anion column. Wash the tube that contained the plutonium with 1 ml 0.1M H_2SO_4 and add the wash to the resin column. Discard the elute. The 0.1M H_2SO_4 separates the trace quantities of iron from the plutonium; it also elutes some of the alkali metals. *Add 1 ml of 10M HCl containing a trace of HNO_3 (10 ml of HCl + one drop of concentrated HNO_3) to the column. Rinse the tip of the column with de-ionized water.* This step separates plutonium from the remaining neptunium. The amount of solution passed through the anion column is kept large compared to its free column volume. The HCl- HNO_3 wash elutes more of the alkali metals and converts the column to the chloride form for subsequent plutonium removal.

Reduce the plutonium to the +3 valence state and elute it into a Vycor tube by three successive additions of nine drops of HI-HCl mixture. Prepare a fresh HI-HCl reagent mixture that is 1 to 9 by volume, ultrapure, nonstabilized $\sim 48\%$ HI and 10M HCl. Ultrapure, nonstabilized HI must be used; the H_3PO_3 stabilizer and impurities in reagent-grade HI would contaminate the sample. *To destroy residual I^- , add one drop of concentrated HNO_3 to the plutonium and evaporate to dryness. Repeat the evaporation using one drop of 10M HCl.* Gamma-spectral analysis indicates that the major contaminant is zirconium and that only trace quantities of ^{99}Tc and ^{95}Nb are present. Emission spectral analysis shows <1 ppm sodium, potassium, calcium, aluminum, and iron. There is also some uranium contaminant in the plutonium.

It is necessary to use a macroporous, anion-exchange resin column and electrodeposition to achieve the additional levels of purity required for pulse-counting mass spectroscopy. *To prepare the sample for treatment on the macroporous anion-exchange column, dissolve it in 1 ml of H_2O_2 -HCl reagent that was freshly prepared by mixing one drop of 30% H_2O_2 in 10 ml of 10M HCl.* If the H_2O_2 concentration is too high, bubbles will form in the resin and may cause plugging or channeling in the column.

The Bio-Rad macroporous anion-exchange resin AGMP-1, 50 to 100 mesh, was prepared by warming it overnight in 5M HCl. It was washed 20 times with de-ionized water and stored as an aqueous slurry. The resin column was prepared in a disposable automatic pipette tip 7 cm long and 5-mm i.d. (Fig. 5). These tips were leached in dilute acid and soaked in de-ionized water. A plug of prewashed quartz wool was placed in the tip and resin was added to a depth of 2 cm. The column was conditioned with 1 ml of the H_2O_2 -HCl reagent.

Load the plutonium solution on the macroporous anion column. Wash with 1 ml of H_2O_2 -HCl reagent. Elute the last traces of uranium and zirconium with 40 drops of 8M HNO_3 . Variances in the uranium, plutonium, and zirconium ratios in the starting samples, as well as slight variances in column preparation, may result in slight differences in the amount of 8M HNO_3 that is needed. The relative amounts of ^{95}Zr (724 and 756 KeV gammas) and ^{237}U (208 KeV gammas) should be measured to allow adjustment of the 8M HNO_3 wash and obtain the best level of decontamination.

Wash the tip of the column with de-ionized water and elute the plutonium with three 1-ml portions of ultrapure, nonstabilized 47% HBr into a clean quartz test tube. Ultrapure, nonstabilized HBr must be used: the H_3PO_3 stabilizer and impurities in reagent-grade stabilized HBr would contaminate the sample. **Remove an aliquot for alpha assay to ascertain the amount of plutonium available for electrodeposition.** Typical chemical yield for the chemical purification procedure is $\approx 50\%$.

Evaporate the HBr solution to dryness in a heating block. Destroy the traces of HBr and organic material eluted from the resin by adding three drops of concentrated HNO_3 and three drops of concentrated HClO_4 . Heat at 130°C for 1 h. Raise the temperature of the heating block to 180°C and evaporate the sample to dryness. The sample is now ready for analysis.

Fig. 5. Macroporous anion-exchange column.

**TABLE III. ANALYSIS OF PLUTONIUM
SEPARATED FROM TEST
DEBRIS**

Run No.	Ratio of Ratios
1	0.99987
2	1.00031
3	0.99969
4	1.00062
5	0.99920
6	0.99961
7	1.00056
8	0.99814
9	0.99891
10	1.00052
11	0.99996
12	1.00122
13	1.00066
14	1.00031
15	1.00031
16	1.00022
17	0.99970
18	0.99948
19	1.00044
20	1.00022
$\bar{X} = 0.99999$	

VIII. ANALYSIS OF TEST DEBRIS USING THE SID SOURCE

The plutonium in test debris is contained in a much more complex matrix than are the standards that are used to develop the SID source. No two samples of test debris are identical in chemical composition. Therefore, one would expect that extraneous material occasionally "leaks" through the separation and purification chemistry. These impurities increase the uncertainty of the mass spectrometric measurements.

To determine the suitability of the SID source and the chemical separation for debris samples, a series of replicate analyses were performed. Twenty samples were prepared from debris that originated from five separate nuclear tests. Table III presents analysis results for replicate 1-ng aliquots.

Because there is no certified value for these samples, we must examine their precision to determine the suitability of the SID source and chemistry for debris analysis. The mean $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio was determined for each nuclear test. Each individual measurement was divided by the appropriate mean to produce a ratio of ratios. The uncertainty of the ratios of ratios is 0.15% at the 95% confidence level.

IX. OTHER APPLICATIONS FOR THE SID FILAMENT

The platinum-overcoated SID filaments have been used to measure plutonium samples ranging from 200 to 400 ng. Large plutonium samples are coplated with 10 μ g of platinum; a second layer of platinum is then overplated. The large ion beams produced by these samples are measured on a Faraday cup.

Small quantities of plutonium isolated from environmental samples have also been measured using the SID ionization source. Plutonium has been isolated and measured in oceanic sediment samples and in soil samples contaminated by global fallout. Detection limits of 2×10^5 atoms of plutonium have been obtained routinely.

The platinum-overcoated filament can be used to analyze a variety of elements. Thus far, we have used this technique to measure neptunium, americium, uranium, and ruthenium.

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