NBL-298

THE QUANTITATIVE ION EXCHANGE SEPARATION OF PLUTONIUM FROM IMPURITIES

Research and Development Report

by

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ADDENDUM

The manufacturer of the disposable mini ion exchange columns described on pages 20 and 45 of this report has changed the ordering specifications for this item. Henceforth, do not use the stated catalog number, but order columns as follows: "Polypropylene Econo-Columns with a 70-micron nominal porosity frit; column size 0.7 x 4 cm (not pre-filled); SPECIAL ORDER."

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Carleton D. Bingham, Director

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ABSTRACT

The methods used at the New Brunswick Laboratory for the quantitative ion exchange separation of plutonium from impurities prior to plutonium assay are described. Other ion exchange separation procedures for impurity determination and for isotopic abundance measurements are given. The primary technique used consists of sorption of plutonium(IV) in 8N HNO_3 on Dowex-1 anion exchange resin and elution of the purified plutonium with 0.36N HCl-0.01N HF. Other methods consist of the anion exchange separation of plutonium(IV) in 12N HCl and the cation exchange separation of plutonium(III) in 0.2N HNO_3. The application of these procedures to the subsequent assay of plutonium, isotopic analysis, and impurity determination is described.

INTRODUCTION

Plutonium is efficiently and quantitatively separated from impurities by anion exchange in nitric acid medium. This separation is made possible with a high degree of selectivity by the ability of plutonium(IV), to the exclusion of most elements, to form an anionic hexanitrato complex [$Pu(NO_3)_6^{-2}$] which is readily sorbed on Dowex-1 anion exchange resin. The plutonium must be in the Pu(IV) oxidation state since Pu(III) and Pu(VI) are not quantitatively sorbed on the resin. Plutonium and only a few elements such as Pd, In, Pt, Np(IV), Au, and Th are strongly sorbed on Dowex-1 resin, while other impurities are either not sorbed or weakly sorbed. The unsorbed or weakly sorbed elements are removed from the resin by washing with sufficient quantities of 8N HNO_3 although some impurities, especially uranium, require more washing than others for complete removal. Plutonium is retained on the resin column and quantitatively eluted with 0.36N HCl-0.01N HF solution.

Plutonium can also be separated from impurities by anion exchange in 12N HCl or by cation exchange in 0.2N HNO_3. These separations are either not

sufficiently quantitative or selective to permit subsequent assay of the purified plutonium to better than 0.01%, and are generally used for procedures where impurity or isotopic abundance measurements are required.

This report summarizes ion exchange methods used at the New Brunswick Laboratory for the quantitative separation of plutonium for assay or isotopic analysis, and for the separation of trace elements for impurity determination. The scope of this report covers a broad spectrum of applications such as the separation of plutonium for subsequent determination by constant current potentiometry, controlled-potential coulometry, isotope dilution mass spectrometry, alpha spectrometry, and the separation of impurities prior to determination by emission spectroscopy. The quantity of plutonium used in the various separations schemes varies from multimilligram to sub-microgram amounts.

I. MACRO ION EXCHANGE SEPARATION OF PLUTONIUM FROM IMPURITIES

The slurry-column technique[1] is used for the anion exchange separation of plutonium where quantities up to 250 mg of plutonium are used. This separations procedure is applicable to the determination of plutonium using constant current potentiometry[2,3] and other methods requiring relatively large amounts of plutonium for analysis. Several parameters of this ion exchange separation were studied.[4,5] Conversion of plutonium to the Pu(IV) oxidation state, comparison of the performance of various batches of anion exchange resin, elution of large amounts of uranium from anion exchange resin, and the effect of $NaHSO_4$ on the recovery of plutonium.

EXPERIMENTAL

Apparatus

Ion Exchange Column, with a Teflon stopcock, Figure 1.

Reagents

Anion Exchange Resin, Dowex-1, X-2, 50-100 mesh, nitrate-form. Commercial-grade resin is obtained from Dow Chemical Company, Midland, Michigan, and is graded, screened, and purified prior to use. The adequacy of the resin for the quantitative separation of plutonium is verified by determining the plutonium recovery on each resin lot processed. Procedures for processing the resin are given in Appendix 1.

Hydrogen Peroxide, H_2O_2, 30%.

Nitric Acid, 8N. To a 13-liter polyethylene carboy, add 6 liters of HNO_3 and 6 liters of distilled water. Mix well and cool.

Eluting Solution, 0.36M HCl-0.01N HF. To a 2-liter polyethylene bottle, add 60 ml of HCl, 15 drops of HF, and 1960 ml of distilled water. Mix well and cool.

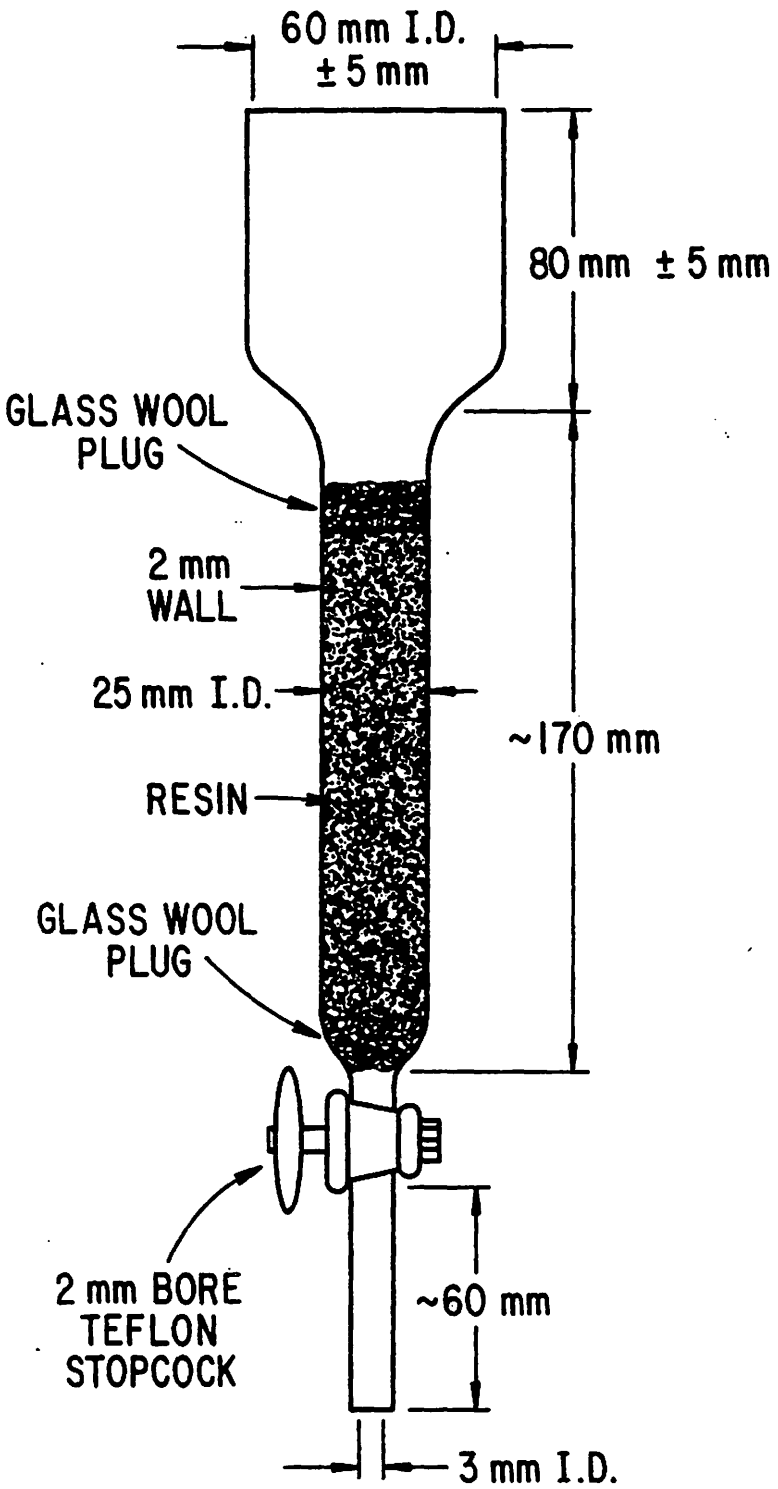

Figure 1. Macro Ion Exchange Column

Procedure

Insert a glass wool plug into the ion exchange column and wet the plug with water. Add a water slurry of resin to a height of 6 cm above the plug. (For samples with fusion salts, increase the resin bed height to 10 cm). Use a fine stream of distilled water and a stirring rod to loosen any resin beads adhering to the column walls. Store the column filled with distilled water until needed. Transfer, quantitatively, the sample aliquot containing 150-250 mg of plutonium to a 250-ml Teflon beaker. Evaporate the solution to incipient dryness. Cool, dissolve the sample in 8N HNO_3 and evaporate again to incipient dryness. Cool and add 100 ml of 8N HNO_3 and redissolve the sample. Add 20 drops of 30% H_2O_2. Stir the solution well with a Teflon stirring rod, rinse the rod with 8N HNO_3 and cover the beaker with a Teflon watchglass. Allow the solution to stand the interval required - usually overnight - to effect reduction of Pu(IV) and (VI) to Pu(III).

(NOTE: Color changes observed in the plutonium reduction process in nitrate medium are olive-green to emerald green to bright blue. When large amounts of uranium are also present in the solution, the yellow uranyl ion offsets the final blue color to a bright yellow-green.) Rinse the Teflon watchglass with 8N HNO_3 and replace it with a glass watchglass. Heat the solution moderately for 30-60 minutes to destroy any excess peroxide and to regenerate Pu(IV). Remove the beaker immediately after formation of the olive-green color. Avoid overheating and boiling the solution! Cool, rinse the beaker and watch glass with 8N HNO_3, then add 20-30 ml of a resin-8N HNO_3 slurry. Mix well by swirling and let the beaker stand until the resin settles and the supernatant appears colorless. If necessary, add more resin. (NOTE: When uranium is present in the sample, the supernatant will be bright yellow in color; high levels of other impurities may color the supernatant also.) Rinse the ion exchange column resin bed with 150 ml of 8N HNO_3. Transfer the entire sample, in two equal portions, to the column and rinse the Teflon beaker several times with 8N HNO_3 to remove all traces of resin. Allow the resin bed to settle and the supernatant to drain to within 3 mm of the bed. Rinse any resin adhering to the column walls with 8N HNO_3 into the resin bed and allow to drain to the same height. Insert a glass wool plug at the top of the resin bed and use a Teflon stirring rod to remove any air pockets by tamping. Add 150-200 ml of

8N HNO_3 to the column and allow to drain at a flow rate of 3-4 ml per minute to within 3 mm of the resin bed. Repeat this washing step twice. Proceed directly to the plutonium elution step below if uranium is not present in the sample. If uranium is present, continue washing using the volume shown in Table 1. Transfer 20 ml of the wash from the third rinse to a 250 ml Teflon beaker and test for residual uranium.[6] Continue to rinse with 150-200 ml portions of 8N HNO_3 until the test indicates less than 10 µg uranium per 20 ml of effluent. Elute the plutonium from the column with 125-150 ml of eluting solution into a 400-ml glass beaker. (NOTE: Fusion samples may require about 200 ml of eluting solution to complete the elution process.) Add 1 ml of conc. H_2SO_4 to the beaker and evaporate to minimal volume. Transfer the solution quantitatively to a 150-ml beaker using 1N H_2SO_4 and evaporate to incipient dryness. Add 20 ml of 1N H_2SO_4 and 1 ml of conc. H_2SO_4. Evaporate to total dryness to remove all traces of fluoride, chloride, nitrate and organic residue. Dissolve the sample in 20 ml of 1N H_2SO_4, cover the beaker with a watchglass, and store in the appropriate container until analysis. Dispose of the used resin and glass wool plugs in an appropriate container.

TABLE 1

Acid Volume Required To Elute Uranium From Plutonium

U, mg/sample	8N HNO_3, ml
200	600
400	800
800	900
1300	1000

RESULTS AND DISCUSSION

Conversion of Plutonium to Plutonium(IV). The Pu(IV) oxidation state required for the ion exchange separation[1] is obtained by treatment with hydrogen peroxide. The peroxide apparently converts the plutonium mostly to

Pu(III) which is then oxidized to Pu(IV) on standing for several hours or by gentle heating. Although the color change from blue to olive is quite distinct, in the presence of amounts of uranium greater than twice the plutonium content, the color change from yellow-green to olive-green may be difficult to detect. In these cases, it is customary to ensure the complete conversion of plutonium to the tetravalent state by heating the solution after the apparent color change for a short period of time. However, prolonged heating in 8N HNO_3 can cause oxidation to Pu(VI).[4,7]

Studies were made of the effect of heating plutonium and plutonium-uranium solutions at about 90°C for 30 minutes after the apparently correct color change had occurred. The solutions were then carried through the ion exchange procedure and titrated, Table 2. The data indicate that the heating period can be as long as 30 minutes beyond the usual attainment of the Pu(IV) oxidation state. This heating step, therefore, is recommended as a precautionary measure to ensure the complete conversion.

TABLE 2

Effect of Heating Solutions 30 Minutes Beyond Color Change

Plutonium, mg		
Added	Found	Recovery, %
198.18	198.34	100.08
204.93	205.05	100.06
201.81	201.93	100.06
196.35	196.33	99.99

Average Value: 100.04

Conversion of Pu(III) or Pu(VI) to Pu(IV) with H_2SO_4. The technique of fuming with H_2SO_4 was studied as an alternative to the usual peroxide treatment since in previous work[8] it was shown that this procedure can convert large amounts of Pu(III) and small amounts of Pu(VI) to Pu(IV).

In an initial study, three sets of plutonium and uranium-plutonium solutions were used. One set was fumed with H_2SO_4 three times to incipient dryness, the solutions were taken up in 8N HNO_3, separated by the column procedure, and titrated. Another set was separated without an oxidation state adjustment and then titrated. The last set was treated conventionally by peroxide, separated and titrated, Table 3. The data confirmed that small amounts (about 0.2%) of Pu(VI) can be readily converted by the H_2SO_4 treatment.

TABLE 3

Conversion of Small Amounts of Pu(VI) to Pu(IV)

Pu Recovery, %				
Pu-Solutions			U-Pu Solutions	
No Treatment	H_2O_2	H_2SO_4	H_2O_2	H_2SO_4
99.78	99.97	100.03	99.94	100.06
99.83	99.97	100.03	100.00	100.00
	100.00	100.03	100.06	99.81
			100.00	99.99
				100.04
Average Values:				
99.80	99.98	100.03	100.00	99.98

In another series of tests designed to produce large amounts of Pu(VI), plutonium solutions were either heated under reflux for 72 hours with 8N HNO_3 or evaporated to incipient dryness after each of two 8-hour reflux periods. The solutions were then passed through the ion exchange columns and titrated to determine the relative quantities of Pu(VI) and Pu(IV), Table 4.

TABLE 4

Formation of Pu(VI) by HNO_3 Treatment

	Treatment	
	Two 8-hour Refluxes Plus Evaporation to Dryness	72-hour Reflux
Pu(IV),%	13	42
Pu(VI),%	87	58
Total Pu, %	100	100

Plutonium solutions treated similarly were then fumed either three or six times with H_2SO_4 before being taken up in 8N HNO_3 for the ion exchange separation and titration, Table 5. The data show that the large amounts of Pu(VI) obtained by the HNO_3 treatments cannot readily be converted to Pu(IV) quantitatively by the H_2SO_4 fuming procedure used.

TABLE 5

Conversion of Large Amounts of Pu(VI) to Pu(IV)

Pu(IV) Recovery, %[a]	
Three H_2SO_4 Fumings	Six H_2SO_4 Fumings
89.43	91.90
75.02	94.72
84.37	93.66

[a]Initial estimated sample composition: 20% Pu(IV), 80% Pu(VI)

Evaluation of Ion Exchange Resin. Bio-Rex 9 resin has been reported to be more stable to radiation and HNO_3 then Bio-Rad AG-1 (Dowex-1).[9] The recovery of plutonium from plutonium nitrate solutions with this resin was tested. The results appeared to be slightly high, averaging 100.06 in four runs. Some characteristics of Bio-Rex 9 as compared to Bio-Rad AG-1 were observed: (1) it settles more rapidly in the column, (2) it does not adhere to glass surfaces as tenaciously, (3) it has faster sorption-elution times, and (4) its darker color makes impossible any visual observation of the green plutonium band during separation. Although Bio-Rad AG-1 had been used for many years at NBL and had given satisfactory recoveries of 99.99 $\pm$ 0.05%, differences have been noted between different batches of resin in plutonium recoveries and elution characteristics. These differences are shown in Table 6 along with the results from two different batches of Bio-Rex 9. Samples of NBS SRM $Pu(SO_4)_2 \cdot 4H_2O$ and plutonium-uranium nitrate solutions were used in the tests. It is clear that the batches vary widely, and each batch received should be tested carefully to determine its acceptability.

TABLE 6

Plutonium Recovery With Different Batches of Resin

Bio-Rad AG-1							Bio-Rex 9	
A[a]	B	C[a,b]	D	E[a]	F	G[b]	A	B
98.88	99.99	99.90	99.84	100.01	99.95	99.62	99.91	100.05
98.79	99.97	99.77	99.92	100.01	99.99	99.52	99.94	100.04
98.82	100.06	99.76	99.87	100.05	100.04	99.47	99.86	100.04
	100.01	99.80		99.98	100.02	99.39		
Average values:								
98.93	100.01	99.81	99.88	100.01	100.00	99.50	99.90	100.04

[a]diffuse sorption band, slow sorption-elution

[b]large elution volume

Elution of Large Amounts of Uranium From An Anion Exchange Resin Column. Since little was known of the column behavior when the plutonium content in samples was as low as 15%, and uranium was the major constituent, a study was made of the elution behavior of large amounts of uranium in this slurry-column system.[5] Approximately 200 mg to 1300 mg quantities of uranium in 8N HNO_3 solution were made into a resin slurry and loaded on the resin columns. Uranium was considered to be removed completely when its concentration dropped below 0.01 mg/100 ml of effluent. The conditions needed for complete elution of the uranium are shown in Table 7. Initial runs with 400- and 800-mg quantities of uranium in Table 7 showing 4.3- and 5.3-hour elution times, respectively, were carried out without glass wool plugs on top of the column and indicate the effect of disturbing the resin bed on adding the wash solution. With the other tests the top glass wool plug was used.

TABLE 7

Elution of Uranium on Bio-Rad AG-1 (Dowex-1) Resin with 8N Nitric Acid

Uranium, mg	Wash Volume, ml[a]	Flow Rate, ml/hr	Elution Time, hr
400	1300[b]	300	4.3
800	1600[b]	300	5.3
200	600	350	1.7
400	600	230	2.6
400	800	320	2.5
400	800	320	2.5
1300	900	300	3.0
1300	800	300	2.7
1300	900	300	3.0

[a]Volume required to obtain <0.01 mg U in 100 ml 8N HNO_3 wash.

[b]Resin bed not plugged on top.

Past experience indicated that a flow rate of 300 ml/hr is nearly optimum. Faster rates increase the wash volumes materially. At this rate the increase in quantity of uranium from 400 to 1300 mg only increases the elution volume by 100 ml. In all cases, from 95-99% of the uranium is eluted in the first 500-ml effluent. A typical elution curve exhibiting two maxima is shown in Figure 2. Apparently the non-equilibrium conditions of the slurry column technique cause the unsorbed uranium from the slurry to elute immediately from the column to give rise to the first peak; the sorbed uranium elutes chromatographically to give the second. This slurry column technique was used because in the separation of plutonium from impurities practically all the plutonium is sorbed by the resin slurry. To simulate the removal of plutonium from the column after the elution of the uranium, 100 ml of 0.36N HCl-0.01N HF mixture, the required amount to elute plutonium was passed through the column in another series of elutions. In every test less than 0.01 mg of uranium was found in the effluent. This value of 0.01 mg would yield a negligible error of about 0.003% in the determination of greater than 150 mg of plutonium by constant current potentiometry.

The Effect of $NaHSO_4$ on Plutonium Recovery Using the Slurry-Column Anion Exchange Technique. In the dissolution of refractory plutonium materials, it is often necessary to fuse residues, or even entire samples, with $NaHSO_4$[10] which leads to higher sulfate concentrations in the dissolved sample. Complete recovery of plutonium on samples fused with $NaHSO_4$ was obtained only when the length of the resin bed was increased at least twofold. Apparently the excess sulfate from the fusion salts significantly affects the usual chromatographic separation of plutonium on the anion resin bed when 20 g of $NaHSO_4$ is used for the fusion. Preliminary results also show that the use of 40 g of $NaHSO_4$ may result in a slight loss, Table 8. Furthermore, the use of H_2O_2 to adjust the plutonium to the required (IV) oxidation state was found to be unnecessary since the $NaHSO_4$ apparently performed the conversion during the fusion process.

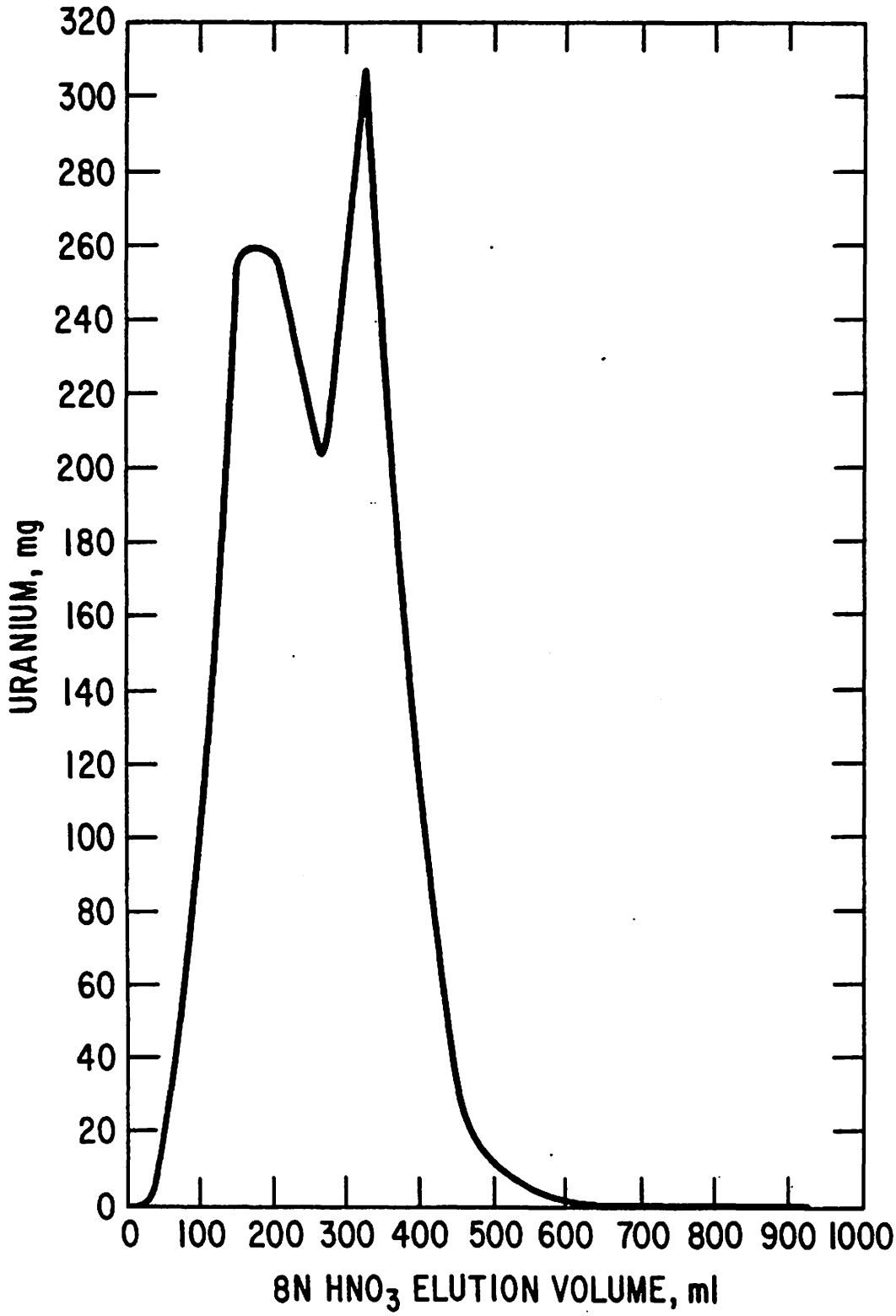

Figure 2. Elution of Uranium from Dowex-1 Anion Resin with 8N Nitric Acid (Slurry-Column Method)

TABLE 8

Dissolution of Refractory Plutonium Dioxide
by Sodium Bisulfate Fusion

Conditions				
$NaHSO_4$, g	Column Length, cm	H_2O_2 Added	Uranium Added	Plutonium Recovery, %
20	4	No	No	99.13
20	4	No	No	99.72
20	8	Yes	No	99.99
20	8	Yes	Yes	100.00
20	8	No	Yes	100.01
40	8	No	Yes	99.90

The accuracy of the $NaHSO_4$ fusion-anion-exchange separation scheme of analysis was verified using NBS SRM 944 $Pu(SO_4)_2 \cdot 4H_2O$ standard reference material. A known amount of NBS SRM U_3O_8 was added to simulate a 1:4 Pu-U oxide mixture. As shown in Table 9, complete recovery of the plutonium was obtained. The $NaHSO_4$ fusion-anion-exchange method appears to be a quantitative and relatively rapid method for dissolving refractory plutonium materials and preparing them for analysis.

TABLE 9

Recovery of Plutonium Using Standard Plutonium
and Uranium Materials

Conditions			
$NaHSO_4$, g	Pu: U	Column Length, cm	Plutonium Recovery, %
20	1:4	8	99.99

Thus, this study indicates that samples fused with $NaHSO_4$ and dissolved in 8N HNO_3 can be separated quantitatively provided the resin column length is increased to 8 cm. The separation is normally carried out 24 hours or less after the fusion. To study the effect of a longer delay time in applying the separation, samples of PuO_2 and U_3O_8-PuO_2 (U:Pu ratio of 4:1) were processed with and without a five-day delay before the separation, Table 10. It is apparent five-day delays can give recoveries low by 0.1 to 0.2%.

TABLE 10

Effect of Five-Day Delay Between Fusion Dissolution and Separation

	Pu Recovery, %			
	Normal Procedure (<24 hour)		Five-Day Delay	
	PuO_2	U_3O_8-PuO_2	PuO_2	U_3O_8-PuO_2
	100.01	99.94	99.82	99.83
	99.97	100.05	99.99	99.80
	100.02	99.99	99.86	99.79
	99.98	99.95	99.80	99.79
Average Values:	100.00	99.98	99.87	99.80

Appendix I

Preparation of Commercial Grade Dowex-1 Resin For Use In Quantitative Separations

The procedure for processing commercial-grade Dowex-1 anion exchange resin consists of a screen analysis, grading into the required particle size range, a determination of sphericity, and chemical purification.[11]

EXPERIMENTAL

Apparatus

U. S. Standard screens, 50-and 100-mesh size, 8-inch diameter
Porcelain pans
Brush, stiff bristles
Graduated cylinder, assorted sizes
Microscope, 10-500X magnification
Ion Exchange column, as shown in Figure 3

Reagents

Resin, Dowex-1, X-2, nominal 50-100 mesh, chloride-form, commercial-grade anion exchange resin.
NaOH, 1N
HNO_3, 1N
$AgNO_3$ solution, 1%

Procedure

Screen Analysis. The screen analysis may be performed on either wet, swollen resin or dry resin. Considerably different results will be obtained and the difference will vary with cross-linkage of the resin and the extent of the drying. (Dry resin usually has a higher proportion of fractured beads than moist resin). Wet screen analysis is more meaningful since the ion

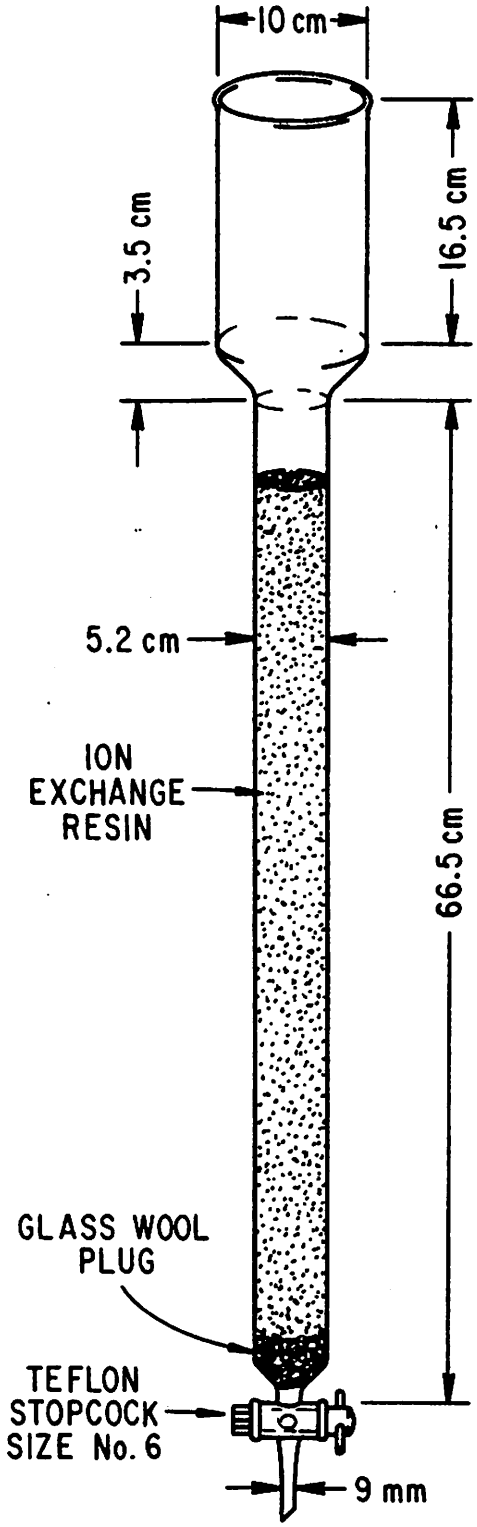

Figure 3. Resin Processing Column

exchange procedures used at this laboratory utilize wet resin. There is evidence that dry resin fragments easily and gives unreliable plutonium recovery. Take three representative samples of approximately 50 ml each of wet, swollen resin from the batch to be processed. Assemble the set of screens to be used and place a sample on the screen of the largest mesh size. Apply a stream of deionized or distilled water to flush the beads smaller than this mesh through the screen. NOTE: If a screen becomes blinded due to a large percentage of material on the screen, perform several screenings and cleanings of the screen. After flushing all fine material through the screen, invert each screen into a porcelain pan and flush the resin from the screen with distilled water. Remove the particles lodged in the screen mesh with a brush. Place the sample from each screen in a graduate of the proper size and determine the tapped and settled volume of material. NOTE: To measure the tapped and settled volume of a sample of resin, slurry the resin into a graduated cylinder, place the cylinder on the table and hold in place with a finger over the top. Tap the side firmly until the resin has completely settled. This volume is normally smaller than the backwashed and drained column volume. Report the screen analysis as the percentage of material on a wet volume basis retained by each screen. Reject the batch of resin if less than 90% of the particles fall within the 50-100 mesh size.

Sphericity. A qualitative determination of sphericity is helpful in determining the amount of physical degradation of the resin during use. Degraded resin (non-spherical fragments of beads) is directly related to resin performance in achieving the quantitative separation of plutonium. Take 3-5 representative samples from the batch to be tested and mount on a microscope slide so that the resin beads are distributed in a monolayer over a small area. Visually determine the amount of breakage (non-spherical particles) and cracking (particles with cleavage planes or lines which have not yet broken). Ideally there should be no breakage or cracking in the resin beads. Reject the batch of resin if more than 1% of the beads are degraded.

Grading and Chemical Purification. Resin beads and fragments outside of the 50-100 mesh size, extraneous matter (including organic substances from the resin fabrication process), and chemical impurities must be removed by grading and chemical treatment. Spread 1-2 kg of moist resin (Cl^- form) on a U. S.

Standard Series 50-mesh screen and wet-sieve it onto a 100-mesh screen. Continue to wash the bulk resin collected until all fines <100-mesh are removed. Transfer the resin to a 4-liter beaker, allow it to settle, and decant the excess water. Add two bed volumes of 1N NaOH to regenerate the resin. Stir the resin well with a plastic stirring rod and allow it to settle 30 minutes before decanting the excess NaOH. Repeat the NaOH treatment. Add two bed volumes of water, stir the resin well and allow it to settle 30 minutes before decanting the excess water. Repeat the washing until the pH of the decanted water matches the pH of fresh distilled water. Add two bed volumes of 1N HNO_3 to convert the resin to the nitrate form. Stir the resin well and allow it to settle before decanting the excess HNO_3. Repeat the HNO_3 treatment. Prepare the ion exchange column by inserting a glass wool plug moistened with 1N HNO_3 and seating it firmly. Tamp the plug with a stirring rod to provide a leak-tight base above the stopcock and to remove any air pockets. Transfer the resin to the column, using 1N HNO_3. Allow the resin to settle, then drain the 1N HNO_3 to within 3 cm of the top of the resin bed. Add two bed volumes of 1N HNO_3 and drain the column to within 3 cm of the resin at a flow rate of about 10-15 ml/minute. Repeat HNO_3 washing until a test on the effluent with 1% silver nitrate solution indicates no detectable chloride. Wash the resin bed with distilled water until the pH of the effluent matches the pH of the influent. Transfer the resin, as a water slurry, to a labelled, clean glass container and store in a cool dark location.

II. MINI ION EXCHANGE SEPARATION OF PLUTONIUM FROM IMPURITIES

Since the macro ion exchange separation of impurities from plutonium involves samples containing from 150-250 mg of plutonium, the separation is slow and somewhat tedious. For increased efficiency of operation, a more rapid technique was studied. Furthermore, it is sometimes appropriate to work with smaller amounts of plutonium using methods such as controlled-potential coulometry which can provide highly accurate and precise results.[12,13] For these reasons the macro separations technique was scaled down to accommodate 5-15 mg plutonium samples.[14] Many studies were performed on this separations technique to determine the effect of various inherent and added impurities. These studies are described in detail, and their effect on the separation is reviewed.

EXPERIMENTAL

Apparatus

Disposable pipet and 1-ml bulb.

Resin, Dowex-1, described in section I.

Columns, disposable polypropylene mini ion exchange columns, Catalog No. 7311110, Bio-Rad Laboratories, Richmond, CA, Figure 4.

Reagents

Ferrous Sulfate, 0.1M; 7.5 g $FeSO_4.7H_2O$ dissolved in 250 ml of distilled water containing approximately 1.5 ml of concentrated H_2SO_4.

Eluting Solution, 0.36N HCl-0.01N HF, described in section I.

Nitric Acid, 1.5N HNO_3

Nitric Acid, 15N HNO_3

Procedure

Resin and Column Preparation. Place a beaker under the column, add enough resin to the column to give a resin height of approximately 5 cm, fill the column reservoir with 8N HNO_3, and stir the resin bed with a glass

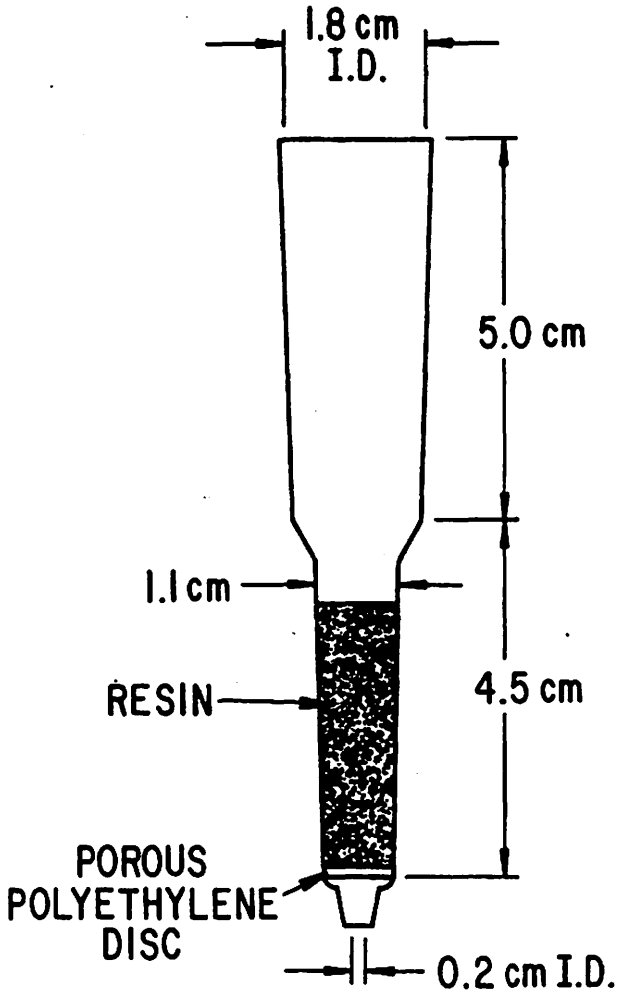

Figure 4. Disposable Polypropylene Mini Ion Exchange Column (Style 1)

stirring rod. Repeat the treatment with 8N HNO_3 until the resin has been washed at least three times.

Sample Preparation and Loading. (NOTE: Aliquoted samples to be separated by ion exchange have been fumed to dryness in 1-2 ml of 6N H_2SO_4.) Remove the parafilm beaker cover and turn inside out. Using the disposable pipet, deliver 1 ml of 1.5N HNO_3 rinsing the inside of the parafilm into the beaker containing the sample. Wash down the sides of the beaker with a second 1-ml portion of 1.5N HNO_3. Swirl gently until the sample dissolves. Pipet 1 ml of 0.1M ferrous sulfate solution into the sample beaker. Swirl gently to mix; note the color change to blue indicative of Pu(III). Pipet and deliver (washing the beaker sides) 3 ml of 15N HNO_3. Swirl gently, until liquid phases disappear, to mix; note the color change to olive-green indicative of Pu(IV). (NOTE: This addition of acid, along with oxidizing the plutonium to Pu(IV), also serves to oxidize the excess ferrous ion and to adjust the final concentration of nitric acid to 8N.) Dilute the sample solution to approximately 25 ml with 8N HNO_3. Add 5 ml of 8N HNO_3 to the column and stir the resin bed with a glass stirring rod. Allow the liquid level to drain to within ~0.5 cm of the resin bed. Slowly pour the sample solution into the column reservoir. NOTE: A glass stirring rod may be used as an aid to pouring to prevent any drops from running down the outside of the beaker. (NOTE: When the liquid in the columns reaches the resin, the column stops dripping and the resin does not go dry immediately. Thus, it is not necessary to add more reagent to the column before flow stops.) Rinse the walls of the sample beaker with about 1-2 ml of 8N HNO_3 and add the washings to the reservoir. Repeat the rinsing step three times. Rinse the outside of the beaker pour spout into the reservoir with a few drops of 8N HNO_3.

Washing. Empty the column effluent into the acid waste container. Wash the sides of the reservoir, adding ~30 ml of 8N HNO_3 in 5-10 ml increments. Allow the liquid level to drain to within ~0.5 cm of the resin bed top before each addition. Once ~30 ml wash have been collected, allow the liquid level to drain to within ~0.5 cm of the resin bed.

Eluting. Place a clean 50-ml beaker (coulometry cell) under the column. Wash the sides of the reservoir, adding ~5 ml of eluting solution and

allow the liquid level to drain to within ~0.5 cm. Continue adding eluting solution in increments of ~5 ml until the green band on the resin has been removed from the column. Continue filling the reservoir with 7-10 ml of eluting solution until 30 ml of eluate has been collected. Allow to drain dry. Remove the column and rinse the tip with a few drops of eluting solution into the cell. Carefully place the cell into the stainless steel cell holder and move to a fume box.

Fuming. Add 1 ml of 6N H_2SO_4 to rinse the side of the cell. Place the sample under the fume hood, set the variac control at no more then 65% of full scale, and evaporate the solution to concentrated H_2SO_4. Turn the variac control to full capacity and fume the concentrated acid solution to complete dryness. Repeat the above steps until three fumings have been completed. Remove sample and allow to cool. Cover the cell with parafilm and store.

RESULTS AND DISCUSSION

In one series of tests, aliquots of a plutonium standard were each treated to adjust the oxidation state and then were separated by ion exchange and analyzed for plutonium. These aliquots contained large amounts of Pu(VI) prepared by heating the aliquots for a long period of time with 2N HNO_3.[14] The data indicate that complete recovery of plutonium occurred and that the reproducibility (relative standard deviation, RSD) was satisfactory, Table 11.

TABLE 11

Recovery of Plutonium Using Mini-Columns

Aliquot	Plutonium, mg Taken[a]	Found	Recovery, %
1	4.659	4.655	99.91
2	4.441	4.442	100.02
3	4.783	4.788	100.10
4	4.624	4.629	100.11
5	4.467	4.465	99.96
6	4.773	4.772	99.98
7	4.661	4.662	100.02
8	4.864	4.868	100.08
9	4.800	4.802	100.04
10	4.767	4.770	100.06
		Average Value:	100.03
		RSD, %:	0.06

[a]Pretreated to generate Pu(VI) in solution prior to adjustment of oxidation state.

To evaluate the adjustment of the oxidation state in the presence of large amounts of impurities, aliquots of a second plutonium standard were spiked with metal impurities at the following concentrations relative to the plutonium:

Fe - 0.5%	Al - 1%
Mn - 0.02%	Ca - 0.1%
Mo - 3%	Cu - 0.02%
Cr - 0.5%	Mg - 0.05%
Ni - 0.2%	U - 400%

idation state of each solution was adjusted and the plutonium was separated and determined as proposed. In addition, aliquots without added impurities were analyzed after the conventional hydrogen peroxide adjustment of the oxidation state used routinely at NBL. The results, shown in Table 12, show a plutonium recovery of 99.94% and a precision (RSD) of 0.02% for the overall procedure involving the ferrous oxidation state adjustment technique. The proposed overall procedure appears to be satisfactory for the determination of plutonium in the presence of the gross impurities tested.

TABLE 12

Recovery of Plutonium in the Presence of Impurities

Pu Found, mg/g Solution	
H_2O_2 Adjustment - No Separation	Proposed Adjustment - Impurities Added
5.013	5.010
5.025	5.011
5.019	5.014
5.014	5.008
5.015	
5.008	
5.005	
5.015	
Average Values: 5.014	5.011
RSD, %: 0.12	0.02
	Recovery, %: 99.94

Several studies have been made on the miniaturized separation to improve reliability, efficiency and usefulness regardless of any pre-ion exchange treatments.

Effect of Liquid Level in the Column. A technique designed to provide greater ease of manipulations for the mini anion exchange separation of plutonium[15] has been investigated. In the mini ion exchange procedure

plutonium[15] has been investigated. In the mini ion exchange procedure described, a fixed minimum level of liquid was maintained in the ion exchange column through all operations including loading, washing and eluting steps; i.e., columns were not allowed to run "dry". However, it was observed that flow of liquid through the plastic columns stopped when the liquid level in the column reached the top of the resin. Thus, the columns can be permitted to run "dry" at any stage without adverse effects (such as channelling and the creation of air pockets) on the separation process. The hypothesis was confirmed with a series of plutonium measurements on aliquots of a standard solution. Seventeen of the aliquots were processed through ion exchange columns. The columns were allowed to run "dry" and to stand for 10 minutes at each phase of the separation (loading, washing, eluting). The plutonium content was then measured using controlled-potential coulometry. Eight of the aliquots were analyzed directly without the ion exchange treatment. The mean recovery of the aliquots processed by ion exchange was 99.97$_0$% (RSD, 0.05%); the mean recovery of the unprocessed samples was 99.99$_6$% (RSD, 0.06%). The results demonstrate that the modified ion exchange technique provides satisfactory purification. The studies also show that 20 samples can be processed in about 4 1/2 hours which is a significant reduction in processing time per sample from the previous 10 samples in 3 1/2 hours.

Effect of Fusion Salts. In section I of this report, results of a study on the effects of $NaHSO_4$ on the macro ion exchange separation of plutonium were shown. The study was repeated to determine the effect of large quantities of fusion salts on the miniaturized ion exchange procedure used to separate impurities from plutonium samples for analysis by controlled-potential coulometry.[16] Standard samples of a solution containing 10-15 mg of plutonium in 1N H_2SO_4 were placed in 50-ml Vycor crucibles and fumed to dryness. Two grams of $NaHSO_4$ were added to each of the crucibles; the crucibles were covered and placed in a cold muffle furnace. The temperature was slowly increased to 600°C while periodically swirling the crucible. After the samples had dissolved (~20 minutes) the crucibles were removed, cooled, and the fusion cakes were dissolved and transferred to 50-ml beakers with 9 ml of 1N HNO_3. The purified plutonium was measured by controlled-potential coulometry. The mean recovery of plutonium from 17 standard samples was 99.98% with an RSD of 0.09%, indicating that the presence of 2 grams of $NaHSO_4$ had no effect on the ion exchange process.

Effect of Zirconium. Zirconium is reported to have an accumulative adverse effect, even in quantities of less than 100 μg, on the controlled-potential coulometric determination of plutonium.[17] A study was made to determine whether an ion exchange technique is effective in reducing zirconium concentration to a level which does not cause interference with controlled-potential coulometry.[18] Zirconium nitrate was added to aliquots of a plutonium standard solution and the resulting solutions processed by the ion exchange procedure. The purified samples were then analyzed by controlled-potential coulometry. Results shown in Table 13 indicate that zirconium interference is effectively eliminated by ion exchange. For measurements, recovery of plutonium, from aliquots containing 9-14 mg of plutonium and 3-5 mg of zirconium, was found to be 100.01% with a precision of 0.05% (RSD).

TABLE 13

Determination of Plutonium Following
Ion Exchange Separation from Zirconium

Aliquot	Zr Added, mg	Plutonium		
		Taken, mg	Found, mg	Recovery,%
1	5.4	11.811	11.804	99.94
2	4.0	14.050	14.043	99.96
3	4.8	9.311	9.317	100.06
4	4.9	10.064	10.070	100.06
5	5.4	9.502	9.508	100.08
6	5.7	9.562	9.560	99.98
7	4.6	9.986	9.989	100.03
8	4.3	14.398	14.401	100.02
9	4.3	11.112	11.115	100.03
10	3.5	10.594	10.600	100.06
11	3.4	9.933	9.932	99.93
12	3.1	12.850	12.856	100.05
13	4.5	14.512	11.500	99.90
14	4.1	10.438	10.443	100.05
15	4.5	9.622	9.622	100.00

Mean, %: 100.01
RSD, %: 0.05
Standard Deviation of the Mean, %: 0.01

III. SEPARATION OF PLUTONIUM FROM IMPURITIES BY A PRESSURIZED FLOW ION EXCHANGE TECHNIQUE

The pressurized flow ion exchange method for the purification of plutonium prior to its determination by controlled-potential coulometry is a modification of the NBL mini anion exchange procedure described in section II.[19] The modified technique involves a higher flow rate through the columns during the wash and elution steps of the separation. These steps constitute the major portion of the time spent in separation, and the use of a higher flow rate significantly decreases the time required for sample purification. While the usual mini anion exchange separation method for ten samples can take three to four hours to perform, the pressurized flow modification reduces this separation time by at least 50%.

EXPERIMENTAL

Reagents and Apparatus

Rubber bulb. A large rubber bulb with an outside diameter greater than that of the column reservoir is used to force solution through the resin bed.

Other reagents and apparatus used have been described previously, sections I and II.

Procedure

The procedure performed prior to loading samples on the columns is similar to that previously described, section II. The technique used to achieve higher flow rates in the wash and elution steps for the improved procedure is as follows: use a rubber bulb to gently force the 8N HNO_3 wash solution through the column at a rate of three drops/second until the solution level is equal to the resin bed height. Repeat this step three to five times. For plutonium elution, add 0.36N HCl-0.01N HF eluting solution to each column until it is half-filled, and apply the bulb technique again; repeat this operation six times. The eluted plutonium solution is fumed three times to dryness in 6N H_2SO_4 yielding solid $Pu(SO_4)_2$ in preparation for controlled-

potential coulometric assay. Alternative procedures may be used to prepare the eluted plutonium solution for other assay methods.

RESULTS AND DISCUSSION

This method was tested for quantitative recovery of plutonium in the presence of the following levels of impurities:

Impurity	Impurity Content, mg/10 mg Pu	% Impurity (Based on Pu)
Uranium	40 mg	400
Nickel	0.4 mg	4
Molybdenum	0.6 mg	6
Chromium	1.0 mg	10
Aluminum	0.5 mg	5
Calcium	0.2 mg	2
Copper	0.4 mg	4
Magnesium	1.0 mg	10
Na_2SO_4	200 mg	2000
$FeSO_4$	30 mg	300

Aliquots of NBS SRM 944 plutonium sulfate tetrahydrate reference solution spiked with the above impurities and from solutions of reference material grade UO_2-PuO_2 were separated by the pressurized flow method. The prepared value of the NBS standard was verified by controlled-potential coulometry to be 99.99_7% with a relative standard deviation (RSD) of 0.04%. Results from these studies are shown in Table 14.

TABLE 14

Recovery of Plutonium Using the Pressurized Flow Ion Exchange Separation Technique

	NBS SRM 944, previous method, Pu Recovery, %	NBS SRM 944, this method, Pu Recovery, %	UO_2-PuO_2, this method, Pu Recovery, %
	100.03_3	99.98_2	100.04_1
	99.88_3	99.95_2	100.02_6
	99.93_5	100.07_8	99.98_8
	100.00_1	100.02_4	99.97_1
	100.03_7	100.02_2	100.05_6
	100.10_4	99.98_1	99.98_3
	100.00_5	99.91_7	99.95_1
	99.97_9	99.91_7	99.95_6
		100.09_3	99.94_0
		100.06_9	100.03_7
		99.88_8	
Mean, %:	99.99_7	100.00_1	99.99_5
RSD, %:	0.03_9	0.06_8	0.04_0

IV. AN AUTOMATED SYSTEM FOR THE SEPARATION OF PLUTONIUM FROM IMPURITIES (AUTOSEP)

The AUTOSEP system[20,21] was designed to automate an existing ion exchange procedure for separating plutonium from interfering impurities prior to analysis. This system, Figure 5, after several design changes and modifications, consists of five modules: an ion exchange separator, a reagent delivery module, a programmer, a controller, and a waste collection system. These modules are shown in Figure 6 and described below. A schematic of the electrical layout is shown in Figure 7.

EXPERIMENTAL

Apparatus and Reagents

The ion exchange columns, resin, and reagents are described in sections I and II.

The ion exchange separator module, designed for glove box operation, is used for separating plutonium from impure samples. The module incorporates ten disposable polypropylene ion exchange columns mounted in a rack. Each column has a removable reservoir at the top for sample loading, reagent addition, and mixing. Mixing is accomplished by means of a stirrer positioned above each reservoir. The flow of effluents through the columns is controlled by motorized three-way stopcocks which turn the stopcocks to the "off", "wash", or "elute" modes of operation. No metallic contamination of the samples occurs, since all components in contact with the samples are made from plastic or glass.

The reagent delivery module is mounted above the glove box. This module provides for the dispensing and delivery of the necessary reagents to each of the columns in the ion exchange separator module. Reagents are delivered from their reservoirs by gravity through two-way solenoid valves controlled by the programmer module. Reagents are delivered through Teflon tubing to calibrated glass reservoirs through five dual three-way rotary valves actuated by a separate motorized gearbox. These calibrated glass reservoirs are used to measure the amount of reagent to be delivered to each column. When these

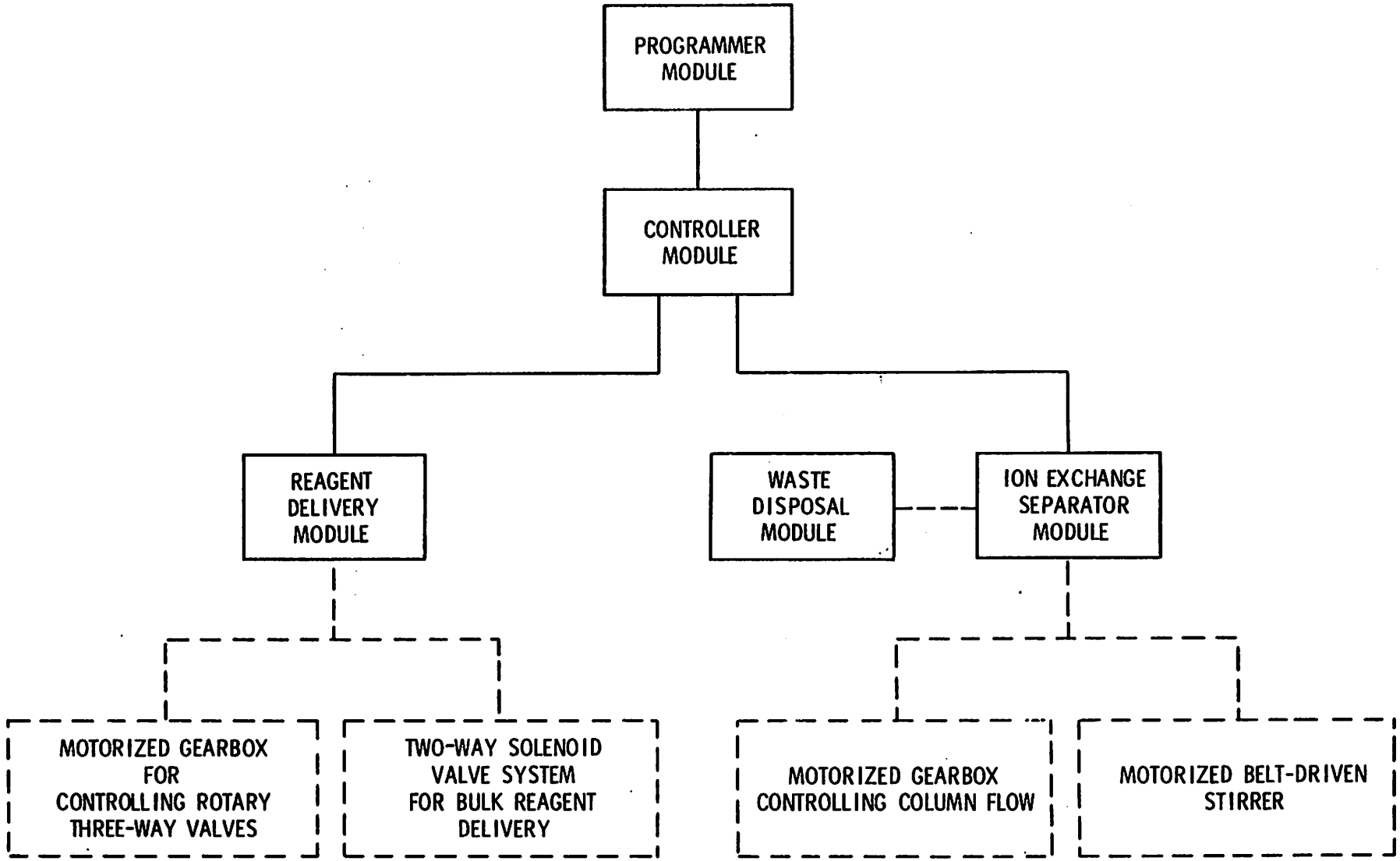

Figure 5. AUTOSEP System

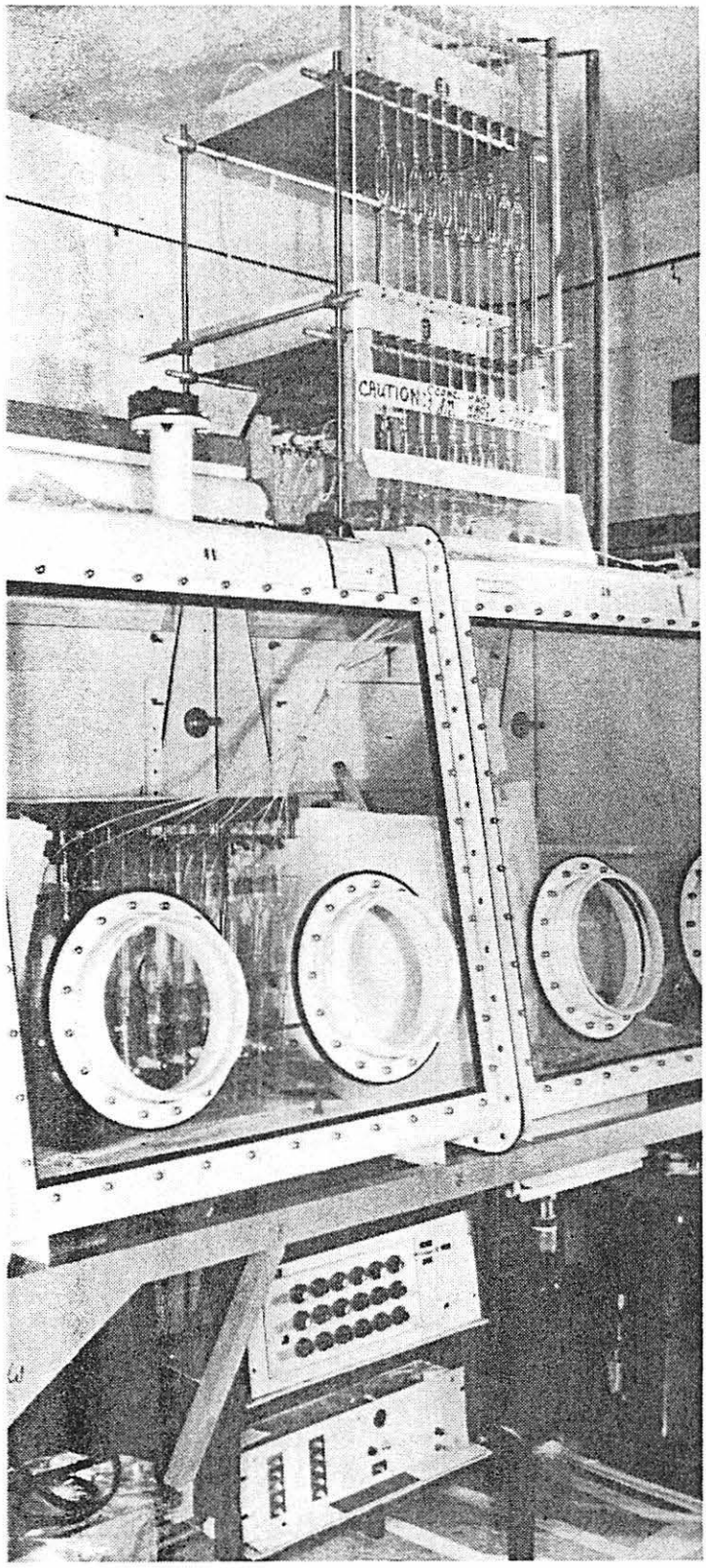

Figure 6. AUTOSEP System for Plutonium Purification

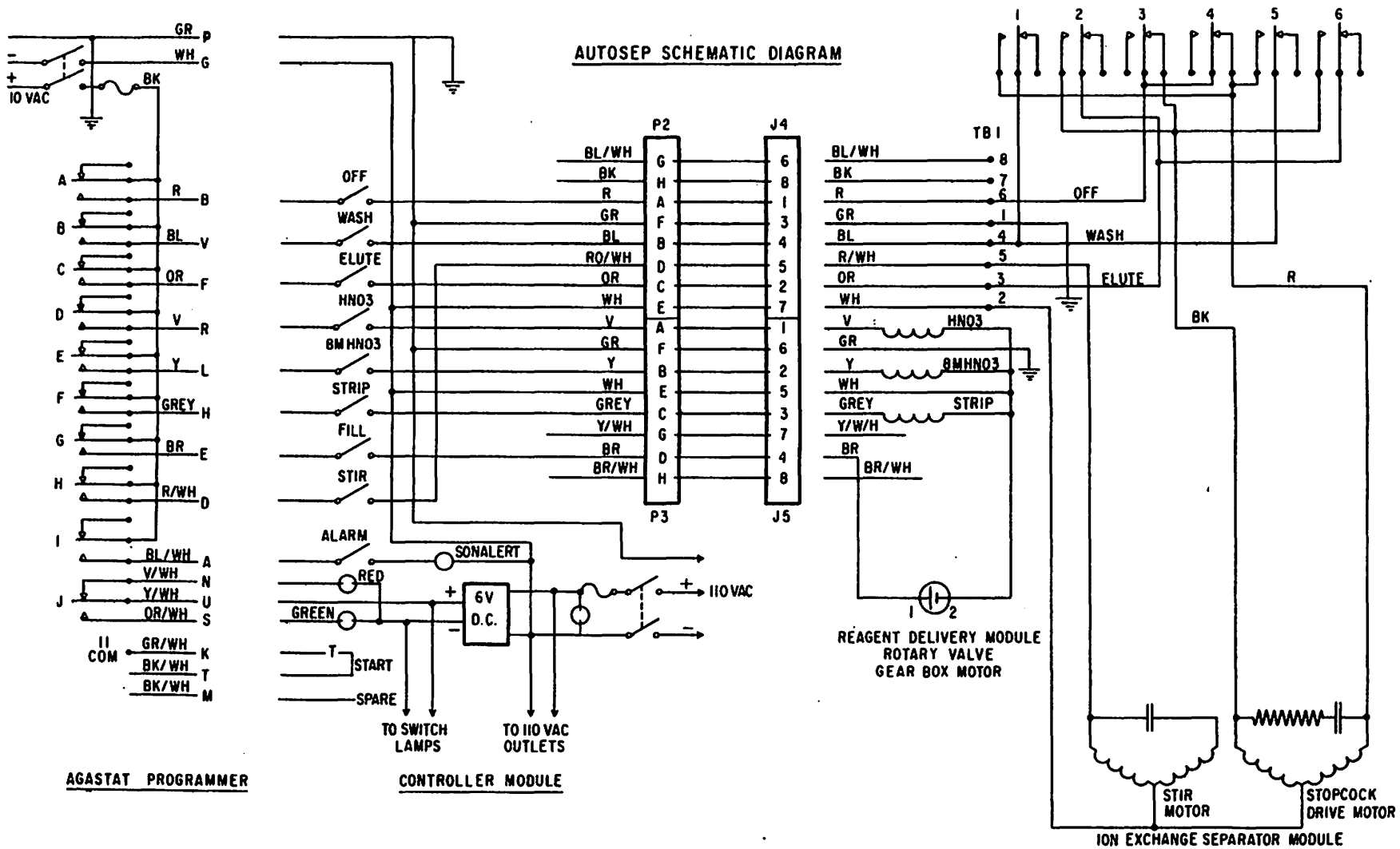

Figure 7. AUTOSEP Schematic Diagram

three-way valves are actuated by the programmer, reagents are delivered to each column reservoir through Teflon tubes. The reagents contact only Teflon, Kel-F, polyethylene, and glass.

The programmer module consists of an 18-step Agastat Programmer, which is used to select reagents and to time the various modes of operation before shifting the sequence to the next mode. At the end of the cycle the programmer shuts AUTOSEP off, and a start switch must be activated before the cycle can be repeated.

The control module contains wiring interfaces for the other three modules. Each function that the AUTOSEP performs (reagent delivery, elution, stirring, etc.) can also be manually controlled by means of switches for each operation. The entire system can be turned on or off from one switch on this module.

The waste collection module consists of ten glass tubes (5 mm ID) bent in the shape of an "S", one end being connected with Tygon tubing to the waste arm of each stopcock in the ion exchange separator module, and the other leading to a polyethylene waste run off tube (25 mm ID). Wash waste flows out the waste arm of the stopcock into the "S"-tube to a point equal in height to the height of the resin bed in each column and subsequently down to the polyethylene waste run-off tube into a holding bottle. The purpose of the "S"-tube is to prevent the columns from going dry prior to the completion of the plutonium elution step.

Procedure

The procedure describes the steps to be taken following the completion of a run by the AUTOSEP. At this point the programmer and control module are "on", the program "off" light is indicating, and the programmer is in the last position. The beakers beneath the columns contain the eluted plutonium solution and each column insert reservoir contains 10 ml of concentrated HNO_3. Remove the beakers beneath the columns, add one drop of H_2SO_4 to each and fume the plutonium solutions. Use vacuum to remove the 10 ml of concentrated HNO_3 from each column insert and transfer the acid to the waste

bottle. Remove the stirrers and column inserts and clean both by successive washings with 8N HNO_3, water and acetone. Check the frits visually for signs of plugging. Fill the Tygon sleeves with distilled water and insert the new or cleaned columns. Fill the columns to the neck with a water slurry of Dowex-1 resin.

Add distilled water from a wash bottle to the columns until the water level is about 2-3 cm above the resin bed. Wipe the exterior of the Tygon sleeves, check for leaks and replace any leaking sleeves. (NOTE: Continued leaking requires the replacement of the column.) Wipe any water or resin from the inside walls of the columns with a tissue in order to insure good seals with the inserts. Lubricate the lower Tygon collars of the column inserts lightly with silicone lubricant and seat them into the columns; avoid greasing the drain tip. Slide the reagent addition tubes through the clips until they touch the inside wall of each column insert reservoir. Put the stirrers in place on the shafts and place clean, labeled beakers beneath each column. Turn all lighted switches to the "off" position. Set the program in step 1 by pushing the start switch and holding for a few seconds until activated: closure of the stopcocks occurs.

Flip the "stir" switch to the "on" position and check the stirring operation. Bend the stirrers manually, if necessary, to achieve proper stirring and to avoid hitting the walls of the insert reservoirs. Flip the "stir" switch back to the "off" position when stirring is satisfactory.

Priming: Jog the programmer to step 5. Activate the switches "8N HNO_3", "wash", and "fill" to allow the reagent delivery reservoirs to fill with 8N HNO_3 and the stopcocks to open to the waste bottles. Fill the lower reservoirs with approximately 10 ml of acid and then jog the programmer to step 6 to allow the acid to be delivered to the column insert reservoirs. Jog the programmer to step 11 after the 8N HNO_3 is delivered to the column insert reservoirs. Insure flowing columns by applying vacuum to the appropriate waste tube of any of those columns requiring it. Drain all column inserts empty and turn all the lighted switches to the "on" position until closure of the stopcocks occurs. (NOTE: Stopcock closure at this point is important to prevent premature loading of the plutonium.) (NOTE: Shrinkage of the resin will occur in 8N HNO_3.)

Oxidation State Adjustment: Inspect stopcocks for closure and add manually one ml of ferrous solution to each column insert. Add by weight from plastic wash bottles the appropriate standards and samples to each column. Dispense the solution well into the column insert and against the wall to avoid splashing. Fill each column insert reservoir to the 10-ml mark with 1N HNO_3 from a small wash bottle. Carefully rinse any droplets of ferrous solution or sample from the column insert reservoir walls.

Running: Push the "start" button to initiate the actual run. All subsequent steps are programmed to occur as described below. (NOTE: The assigned programmer times listed for each step are experimentally determined.)

a. The plutonium, ferrous and 1N HNO_3 mixture in the column insert reservoirs is stirred; collection of 10 ml of HNO_3 occurs in each of the holding reservoirs. (9 minutes)

b. The stirrers are turned off and the 10 ml of HNO_3 in the holding reservoirs drains into the column insert reservoirs to adjust the acidity of the solution to 8N for plutonium sorption. (0.5 minute)

c. Stirring is started to thoroughly mix the acid and to adjust the oxidation state of the plutonium to the Pu(IV) state. (4 minutes)

d. The stopcocks are opened to the waste bottles and the solutions begin flowing dropwise through the columns. This process loads plutonium onto the resin beds which were previously conditioned with 8N HNO_3. The plutonium-free effluents are fed into the waste bottles. The liquid height in the columns should be maintained about 2 mm above the resin beds by adjusting the S-tube height. (25 minutes)

e. The plutonium sorption continues while 30 ml of 8N HNO_3, which acts as a wash, is collected in each of the holding reservoirs. Several minutes before completion of this step the column insert reservoirs should be empty and all the plutonium solution loaded onto the resin. (15 minutes)

f. The 30 ml of 8N HNO_3 drains into each of the column insert reservoirs and begins washing the plutonium sorbed resin free of impurities. The stopcocks remain open to allow collection of the washings into the waste bottles. (25 minutes)

g. Washing continues while 30 ml of 0.36N HCl-0.01N HF eluting solution collects in each of the holding reservoirs. Several minutes before this step ends the column insert reservoirs should be empty signifying that the impurities have been washed from plutonium with the nitric acid. (15 minutes)

h. The stopcocks now reverse to allow plutonium to be eluted into the sample beakers, the 30 ml of eluting solution drains from the holding reservoirs into the column insert reservoirs, and the eluted plutonium drains into the clean beakers provided beneath each column. (30 minutes)

i. During the eluting operation 10 ml of HNO_3 is collected in each holding reservoir. (11 minutes)

j. An alarm signals the end of the program. (0.05 minute)

k. The nitric acid now drains from the holding reservoirs into the column insert reservoirs and in the process washes out the residual eluting solution from the reagent delivery lines. The stopcocks then turn off and the acid is held in the insert reservoirs. (0.05 minute)

Routine Maintenance: Change Tygon sleeves every 6-8 runs or more often as the extent of sleeve degradation dictates. Refill reagent bottles before they are empty. (NOTE: Completely empty bottles allow air to enter the lines causing an air blockage which must be removed by strong suction before normal operations can be resumed.)

Empty waste and vacuum trap bottles into a common waste beaker for disposal. Every 6-8 runs lightly grease the joint with silicone lubricant where the column insert reservoir fits into the column. Failure to do so may result in leakage from the reservoirs and cause undetected air leaks. Prepare

any new ion exchange columns by gently scraping the two burrs or flashing from the delivery tip of each column. Sand the deburred tips lightly with sandpaper until smooth. Test for leaks by placing each column in a Tygon sleeve and filling with water.

RESULTS AND DISCUSSION

The AUTOSEP system has been tested for the quality of its separation. About 99.5% of uranium is separated from plutonium under the present AUTOSEP operating conditions. No attempt has been made to modify the procedure to achieve the quantitative uranium separation common to the manual ion exchange method since moderate amounts of uranium do not interfere in the NBL controlled-potential coulometric determination of plutonium. However, in instances where the uranium would interfere in other plutonium assay methods, the AUTOSEP system can be readily modified to provide complete uranium-plutonium separation.

Results from preliminary plutonium separations using the AUTOSEP system are shown in Table 15. Additional studies gave a mean recovery of 100.00% Pu with an RSD% 0.1%. A more detailed report of the AUTOSEP system has been written.[22]

TABLE 15

Separation of Plutonium from Impurities using the AUTOSEP System

NBS SRM 949e	Pu Recovery, %
1	99.99_1
2	100.06_1
3	100.00_2
4	100.10_7
5	100.12_0
6	100.12_0
7	99.88_5
8	100.11_1
9	99.92_0
10	99.90_0
11	100.11_0
12	100.09_5
13	100.00_3
14	100.06_8
15	100.04_1
16	99.88_6

Mean, %: 100.02_6

RSD, %: 0.08_5

V. ANION EXCHANGE SEPARATION OF MICROGRAM AMOUNTS OF URANIUM AND PLUTONIUM FOR ISOTOPIC ANALYSIS AND ISOTOPE DILUTION MASS SPECTROMETRY

The isotopic analysis and determination of uranium and plutonium by surface ionization mass spectrometry at this laboratory involve the prior separation of the two elements. One such separation is an anion exchange procedure in which plutonium and a small part of the uranium are retained on Dowex-1 resin from 8N nitric acid solution and the remaining uranium is eluted with additional acid washing; americium, fission products, and many metallic impurities are not retained and pass directly into the effluent (uranium fraction). The plutonium is eluted with a 0.36N hydrochloric-0.01N hydrofluoric acid solution. Traces of neptunium (as ^{237}Np) may be found in the plutonium fraction since neptunium has similar sorption-elution characteristics in this procedure. This general method has been used at this laboratory with milligram amounts of sample to separate trace impurities from plutonium[23] and has been modified,[24] using a similar procedure developed elsewhere,[25] for separating 0.1 to 5 μg of plutonium and 20 to 1500 μg of uranium. (These concentration ranges are found in many irradiated reactor fuel element dissolver solutions.) This procedure was applied to the determination of the isotopic composition of the plutonium and the uranium fractions by mass spectrometry. In some instances where the amount of uranium to be separated is large (milligram quantities in the presence of microgram amounts of plutonium), a better separation is obtained: (1) by diluting the sample prior to ion exchange to reduce the uranium content, or (2), where dilution is not appropriate, by removing a portion of the resin containing the sorbed plutonium and transferring it to a fresh resin column for a second separation.[26] Where the quantity and type of impurities (americium, iron, fission products, salts, etc.) in the uranium fraction affect the isotopic abundance measurements, they may be removed by a subsequent separation on Dowex-1 resin with 12N hydrochloric acid followed by 6N hydrochloric acid washing. The purified uranium is desorbed from the resin in 0.5N hydrochloric acid.[27] When thorium, which sorbs on Dowex-1 in 8N nitric acid along with plutonium,[28] is present, the plutonium fraction may be purified by a second separation on Dowex-1 in 12N hydrochloric acid. The plutonium is eluted with the dilute hydrochloric acid - hydrofluoric acid solution. These separation procedures can be applied to a variety of plutonium and/or uranium materials

to achieve sufficiently pure uranium and plutonium for satisfactory measurements by mass spectrometry.

Where the ^{238}Pu content is low (<0.1%) it is usually determined by alpha spectrometry on a separate portion of the plutonium fraction of a uranium-plutonium material since traces of ^{238}U possibly remaining in the plutonium fraction after ion exchange separation give apparent high ^{238}Pu values by mass spectrometric techniques. Any ^{241}Am, which may be present in plutonium as a result of radioactive decay of ^{241}Pu, does not interfere with the determination of ^{241}Pu since americium is quantitatively separated from plutonium in the ion exchange procedure.[29]

For the determination of the concentration of uranium and plutonium, additional modification of the procedure is required. The concentrations of uranium and plutonium are determined by isotope dilution. This technique has been shown to be accurate, precise, and specific.[30,31] The complete preparation consists of adding a known amount of uranium and plutonium tracer to a known amount of sample, equilibrating sample and tracers to ensure chemical and isotopic homogeneity, and performing an anion exchange plutonium-uranium separation prior to the mass spectrometric analysis of the uranium and plutonium fractions. Details of the isotope dilution technique have been published previously.[32,33]

The most critical part of this procedure is the equilibration step prior to ion exchange separation. Losses will occur if the uranium and plutonium, respectively, in both the tracers and in the sample are not completely in the same oxidation state.

EXPERIMENTAL

Reagents and Apparatus

Uranium-233 Tracer. A 100-mg sample of U_3O_8 enriched in ^{233}U obtained from the Oak Ridge National Laboratory is used. The isotopic composition of this material is, in weight percent, ^{233}U, 99.922; ^{234}U, 0.018; ^{235}U, 0.001; ^{236}U, <0.001; and ^{238}U, 0.058. The sample is dissolved in a few milliliters

of 8N nitric acid and the solution is diluted with 2N nitric acid to give a solution containing about 850 μg ^{233}U/g. This solution is standardized by mass spectrometry and assigned a value for the ^{233}U content.

Plutonium-242 Tracer. A sample of about 5 mg of PuO_2 enriched in ^{242}Pu obtained from the Oak Ridge National Laboratory is dissolved in a small amount of 8N nitric acid and the solution is diluted with 2N nitric acid to give a concentration of about 8 μg ^{242}Pu/g. The isotopic composition of this solution, in weight percent, for March 1966, was ^{238}Pu, 0.004; ^{239}Pu, 0.018; ^{240}Pu, 0.033; ^{241}Pu, 0.054; and ^{242}Pu, 99.891. This solution is standardized by mass spectrometry and assigned a value for the ^{242}Pu content. NOTE: ^{244}Pu can be used as an alternative tracer for plutonium. Work at the National Bureau of Standards is in progress to provide a certified plutonium reference tracer, NBS SRM 996.

Uranium Standard. About 100 mg of U_3O_8, National Bureau of Standards SRM U-015, is ignited to constant weight at 850°C (3 hours) and weighed to ± 0.02 mg. Buoyancy corrections are applied to this weight. The oxide is dissolved in a minimum amount of 8N nitric acid and the solution is diluted with 2N nitric acid to give a final concentration of about 850 μg U/g.

Plutonium Standard. About 500 mg of $Pu(SO_4)_2 \cdot 4H_2O$, National Bureau of Standards SRM 948, is weighed to ± 0.02 mg. The weight is corrected for impurities, including the ingrowing ^{241}Am; buoyancy corrections are applied. The salt is dissolved in 2N nitric acid and the solution is diluted to give a final concentration of about 8 μg Pu/g.

Nitric Acid, concentrated, distilled from reagent-grade acid.

Nitric Acid, 1N, 2N, and 8N, prepared from distilled nitric acid.

Hydrochloric Acid (1N)-Hydroxylamine Hydrochloride (0.1%) Solution.

Hydroxylamine Hydrochloride Solution, 20%.

Hydrochloric Acid (0.36N)-Hydrofluoric Acid (0.01N) Solution, stored in a polyethylene bottle.

Hydrochloric acid, 12N, 6N, and 0.5N.

Hydrogen Peroxide, H_2O_2, 30%, reagent grade.

Anion-Exchange Resins. Dowex 1, X-2, 100-200 mesh, chloride-form; Dowex-1, X-2, 100-200 mesh, nitrate-form.

Micro Ion Exchange Column. Two types of columns may be used for the ion exchange separations:

1. Style 1. Disposable polypropylene column, Bio-Rad no. 7311110, Figure 4, described in section II.

2. Style 2. A disposable glass self-leveling column adapted from a larger-capacity unit,[34] is shown in Figure 8 with critical dimensions. NOTE: A column is loaded with wet Dowex-1, nitrate-form, anion resin to make a bed about 2 cm long. The resin is washed with 6 ml of 8N nitric acid prior to use. A column is used once and then discarded. For separations in hydrochloric acid medium, the chloride-form of resin is used and washed with 12N hydrochloric acid. Either column style is satisfactory. Where extended separations times are anticipated, Style 2 is preferred since the liquid level does not drop below the top of the resin bed. Style 1 column has a larger diameter and a greater resin capacity for the same length of resin bed.

Transfer pipets. Made from tubing drawn to a capillary tip; or the commercially available disposable type. They are used once and then discarded.

Glassware. Only new glassware boiled in dilute nitric acid to remove possible contaminants (including organic matter) is used. All glassware is used once and then discarded unless noted otherwise.

Weighing bottles

Balance

Procedure

A. Separations for Isotope Dilution Mass Spectrometry. These procedures are written specifically for samples containing approximately 300 µg U/g and 2 µg Pu/g. Variations from these concentration levels will require adjustment in the ^{233}U and ^{242}Pu tracer concentrations, tracer aliquot sizes, or sample size. The ^{233}U and ^{242}Pu tracers are added in about a 1:1 ratio to the uranium and plutonium isotopes of interest which, in this instance, are ^{238}U and ^{239}Pu.

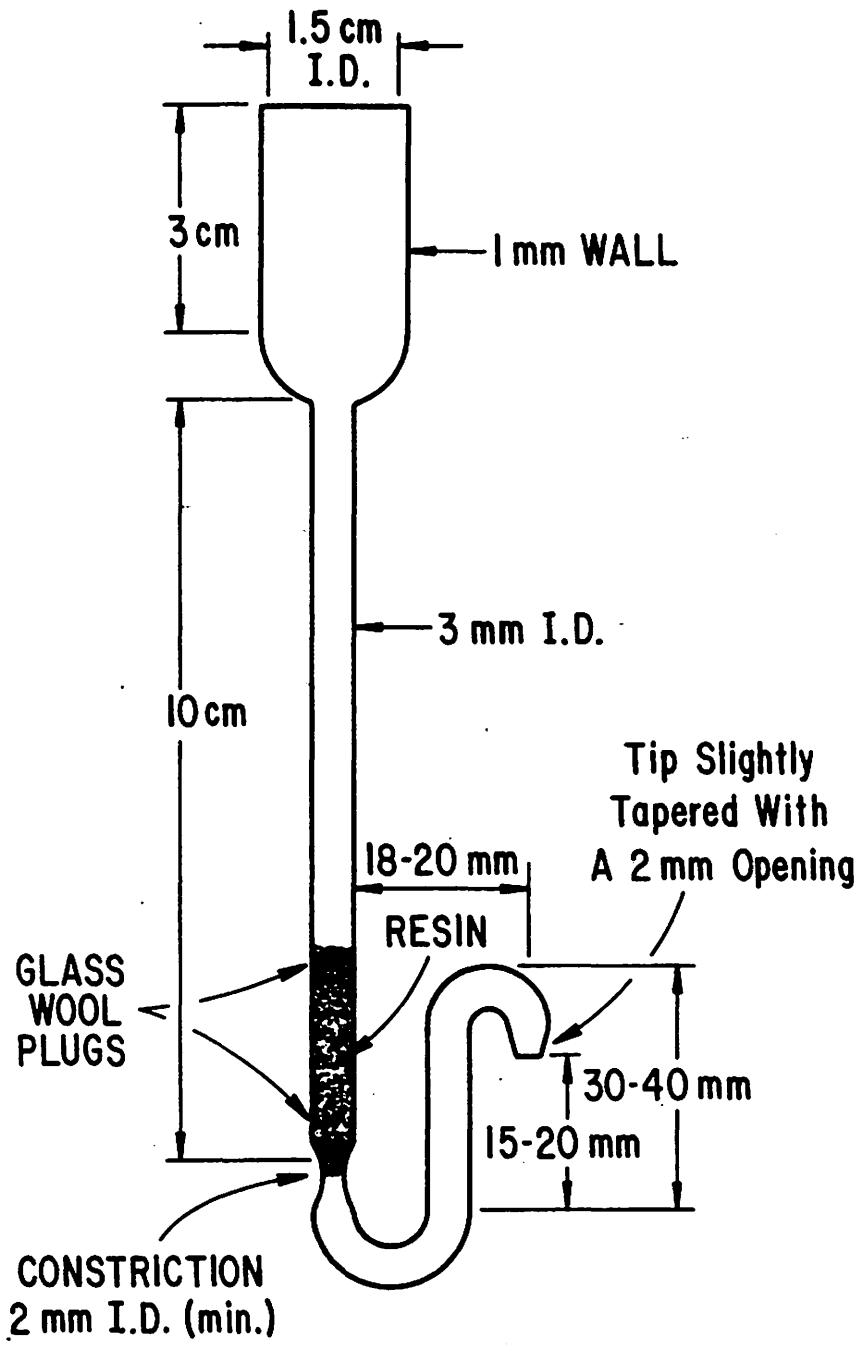

Figure 8. Disposable Glass Micro Ion Exchange Column, Self-Leveling (Style 2)

(1) Isotope-Dilution Mixtures for Mass Spectrometric Standardization of ^{233}U tracer. Prepare all samples in triplicate. Add 500 mg of the uranium standard solution, ~425 µg U, and 500 mg of the ^{233}U tracer solution, ~425 µg ^{233}U, to a 10-ml beaker, by weight. Add 1 ml of concentrated nitric acid, evaporate the solution to dryness, dissolve the residue in 1 or 2 drops of 1N nitric acid, and transfer to a 0.5-ml centrifuge cone for the mass spectrometric measurements. In addition, supply three portions, containing 200 µg each, of the ^{233}U tracer and of the uranium standard for the mass spectrometric isotopic analysis required in this standardization procedure.

(2) Isotope-Dilution Mixtures for Mass Spectrometric Standardization of ^{242}Pu Tracer. Prepare all samples in triplicate. Add 500 mg of the plutonium standard solution, ~4 µg Pu, and 500 mg of the ^{242}Pu tracer solution, ~4 µg ^{242}Pu, to a 30-ml beaker, by weight. Evaporate the solution to incipient dryness, and following the method outlined immediately below equilibrate the standard and tracer, remove any interfering ^{241}Am impurity with the ion exchange separation, and collect the plutonium fraction for mass spectrometric measurements. Discard the 8N nitric acid wash fraction which, in the separation of uranium-plutonium mixtures, would normally contain the uranium. Similarly remove the ^{241}Am from three portions, containing 4-6 µg each, of the ^{242}Pu tracer and of the plutonium standard for the mass spectrometric isotopic analysis required in this standardization procedure.

(3) Isotope-Dilution Solutions for Mass Spectrometric Determination of Plutonium and Uranium Concentration. Prepare all samples in duplicate. Add a 2000 mg aliquot of sample to a 30-ml beaker, by weight. Pipet 500 mg of ^{242}Pu tracer solution into the beaker, by weight. Pipet 750 mg of ^{233}U tracer into the beaker, by weight. Swirl the solution gently to mix.

(4) Ion Exchange Separation. Evaporate the solution to incipient dryness, equilibrate the sample and tracers, and separate the plutonium from the uranium, fission products, and ^{241}Am as follows:

Dissolve the residue from the evaporation in about 2 ml of hydrochloric acid-hydroxylamine hydrochloride solution, add 3 drops of 20% hydroxylamine hydrochloride, and mix. Evaporate the solution again, dissolve the residue in 2 ml of concentrated nitric acid, and evaporate again. Dissolve the residue in 2 ml of 8N nitric acid and transfer to a prepared anion-exchange column. Wash out the beaker with an additional 1 ml of 8N nitric acid, add to the column and allow the liquid to drain completely into a 30-ml beaker. Fill the column to the top of the reservoir with 8N nitric acid (approximately 6-8 ml) and allow the liquid to drain completely. Wash down the inside of the reservoir with 2 ml of 8N nitric acid using a dropper. Fill the column again to the top of the reservoir with 8N nitric acid and allow the liquid to drain completely; the combined effluent is the uranium fraction. If the removal of americium and fission products from this fraction is necessary, treat the uranium effluent at this point as described below in section (6). Otherwise, evaporate the effluent to incipient dryness, add 1 ml of concentrated nitric acid, and evaporate. Repeat this treatment, then add about 0.2 ml of 1N nitric acid to the beaker and dissolve the residue. Transfer the solution to a 0.5-ml centrifuge cone with a transfer pipet for the mass spectrometric work.

Elute the plutonium fraction from the column with 5 ml of hydrochloric acid-hydrofluoric acid solution. Collect the effluent in a 10-ml beaker, add 1 ml of concentrated nitric acid, and evaporate to incipient dryness. Repeat the evaporation with 2 ml of concentrated nitric acid. Add about 0.2 ml of 8N nitric acid to the beaker and dissolve the residue. Transfer the solution to a 0.5-ml centrifuge cone with a transfer pipet for the mass spectrometric work. Alternative Procedure: Hydrogen peroxide can be used instead of hydroxylamine hydrochloride in the oxidation state adjustment for plutonium during the equilibration step. Evaporate the solution to incipient dryness, dissolve the residue with 5 ml of 8N HNO_3, add about 4 drops of fresh H_2O_2, cover the beaker with a watchglass, and heat the solution for 1.5 hours. A light blue to green solution (depending on the amount of uranium present) should result after a

period of effervescence. When the effervescence ceases, cool the solution, and add it to a prepared Dowex-1 nitrate-form resin column. Wash the resin bed and continue the separation as described above.

(5) Solutions for Mass Spectrometric Isotopic Analysis of Plutonium and Uranium and Alpha Spectrometric Determination of ^{238}Pu. Prepare only a single sample. Add 2-4 ml of the sample to a 10-ml beaker. Add 1 ml of concentrated nitric acid and evaporate to incipient dryness. Add 1 ml of 8N nitric acid to dissolve the residue and transfer the solution to a prepared anion exchange column. Continue the ion exchange separation and collection of the individual uranium and plutonium fractions as described in section (4).

For the determination of ^{238}Pu, add about 5 ml of 8N nitric acid to the unwashed beaker which previously contained the plutonium fraction from the ion exchange separation, swirl the beaker to wash down traces of plutonium solution remaining on the sides of the beaker and pipet about 25 µl onto an electropolished stainless steel planchet. [Experience has shown that this technique provides sufficient sample (~50,000 counts per minute) for analysis.] Dry the planchet under a heat lamp for the alpha spectrometric analysis.

(6) Removal of Fission Products from Uranium Fraction. If it is necessary to remove fission products, which appear in the uranium fraction in the ion exchange separation procedure, evaporate the uranium fraction to incipient dryness. Dissolve the residue in about 5 drops of 12N hydrochloric acid and evaporate again.

Dissolve the residue in 1 ml of 12N HCl. Rinse a prepared ion exchange column with 2 ml of 1N HCl followed by 2 ml of 12N HCl and transfer the solution to the column. Rinse the beaker with an additional 1 ml of 12N HCl and add to the column. Allow the column to drain until the reservoir is empty and fill with 6N HCl. Collect washings in a 30-ml beaker and refill the reservoir with 6N HCl. Rinse the inside of column prior to each filling using a dropper

containing 2 ml of 6N HCl, collect the washings in the beaker, and discard. Elute the uranium with 5 ml of 0.5N HCl into a clean 10-ml beaker. Evaporate the solution, dissolve the residue in 2 ml of 8N HNO_3 and evaporate again. Repeat this process, add 5 drops of 8N HNO_3 to the beaker, dissolve the residue, and transfer the solution to a clean 5-ml beaker.

B. Separation of Plutonium and Thorium. Since thorium sorbs along with plutonium in 8N HNO_3 on Dowex-1 anion resin, it is separated from the plutonium by a second ion exchange purification in 12N HCl. Thorium is removed since it interferes with the stability of the signal upon thermal ionization during the mass spectrometric determination of plutonium.

Transfer the sample containing up to 1 mg of plutonium into a 10-ml beaker containing 5 ml 8N HNO_3 and mix. Add four drops of the sample solution to an ion exchange column containing Dowex-1 nitrate-form resin containing 5 ml of 8N HNO_3 solution. Wash the resin with successive portions of 8N HNO_3 up to 75-100 ml; collect and discard the wash. Plutonium and thorium should appear as a light green band in the resin bed. When the last portion of 8N HNO_3 wash solution drains to 1 mm above the resin bed, add 5 ml of the 0.36N HCl-0.01N HF eluting solution. Collect the eluted plutonium and thorium in a clean 10-ml beaker. (NOTE: The light green band on the column should disappear.) Evaporate the solution to dryness, and dissolve the dry salts with 5 ml of 12N HCl. Add 1-3 ml of this solution to an ion exchange column with chloride form Dowex-1 resin containing 5 ml of 12N HCl solution. Wash the column with successive portions of 12N HCl until 75-100 ml has been added. Collect and discard the washings which should contain the thorium fraction. Elute the plutonium from the resin using 5 ml of 0.36N HCl-0.01N HF eluting solution added when the last 12N HCl wash is 1 mm above the resin bed. Collect the eluted plutonium solution in a clean 10-ml beaker, and evaporate to dryness. Dissolve the plutonium salt with 5 ml of concentrated HNO_3 and evaporate the solution to dryness.

C. Separation of Plutonium From Large Amounts of Uranium. When milligram amounts of uranium are present, the separation of microgram amounts of plutonium using the Dowex-1 8N HNO_3 system may require extended washing to satisfactorily remove traces of uranium. An improved scheme has been used in which a second ion exchange separation is made on a portion of the plutonium-sorbed resin removed from the first separation.

Adjust the sample to a volume of 15-20 ml with 8N HNO_3. Add the sample solution to the resin column (Dowex-1, nitrate-form) in 1-2 ml increments allowing the solution level to drop to within a few millimeters of the resin between increments. After the fifth increment, collect 3-4 ml of the column effluent for uranium analysis. After all the sample has been added to the column, wash the resin with 100 ml of 8N HNO_3, in 6-8 ml increments as described above. (NOTE: During this wash step, prepare another column with resin.) The plutonium fraction will be evident as a 1-2 mm green band at the top of the column. Remove most of this resin band with a spatula and transfer it to the second column. Wash the second column with 100 ml 8N HNO_3 in 6-8 ml increments as described above. Elute the Pu fraction using six 1-ml increments of 0.36N HCl-0.01N HF into a 10-ml beaker containing two drops of concentrated nitric acid. Fume eluate to incipient dryness. Dissolve the plutonium nitrate in 2 ml of 8N HNO_3 and remove approximately 0.1 ml of solution for the preparation of planchets for ^{238}Pu determination by alpha spectroscopy. Fume the remaining sample solution to incipient dryness for mass spectrometric analysis.

RESULTS AND DISCUSSION

Separation of Uranium and Plutonium. The uranium-plutonium separation was evaluated by using a mixture of ^{233}U tracer solution containing 800 µg of ^{233}U and plutonium standard solution containing 8 µg of plutonium in the ion exchange separation. The uranium and plutonium fractions were analyzed by alpha spectrometry. The ^{233}U tracer, which is an alpha emitter, was used instead of the uranium standard so that a positive identification of uranium in the plutonium fraction could be made by alpha spectrometry. The results are shown in Table 16.

TABLE 16

Efficiency of the Separation of Uranium from Plutonium and Plutonium from Uranium by Ion Exchange

Fraction	Purity of Fraction, %
Pu	87.5
	88.0
	87.5
	88.1
U	>99.9
	>99.9
	>99.9
	>99.9

With initial quantities of 800 μg of uranium and 8 μg of plutonium, about 0.02 to 0.06 μg of plutonium equivalent to 0.2 to 0.8% loss is found in the uranium fraction, and about 1 μg of uranium equivalent to 0.1% loss is found in the plutonium fraction. Two different resin types were used to obtain the data in Table 16: X-2, 100-200 mesh; X-10, 200-400 mesh.

These separations may be satisfactory for ordinary chemical manipulations at these concentration levels, but the amount of uranium remaining in the plutonium fraction may seriously affect the mass spectrometric determination of ^{238}Pu. It is for this reason that the ^{238}Pu must be measured by alpha spectrometry. It should be noted that any ^{241}Am remaining in the plutonium fraction after the separation will affect the ^{238}Pu value obtained by alpha spectrometry. However, as is shown by the data on the efficiency of the ^{241}Am-Pu separation, less than 0.002% ^{241}Am remains in the plutonium fraction. This quantity of ^{241}Am will give an apparent ^{238}Pu value high by less than 3% relative at a ^{238}Pu level of 0.01%. The effect is much less at higher ^{238}Pu concentrations.

It is of interest to note that traces of a mass 237 which is assumed to be ^{237}Np is occasionally found in the mass spectrometric analysis of the uranium fraction although neptunium is presumably retained along with plutonium on the resin. Apparently the retention is less than that for plutonium and traces are eluted on the washing step used to remove the uranium.

The recoveries of uranium and plutonium were checked by mixing a solution of the uranium standard containing 1600 µg of uranium with a solution of the plutonium standard containing 8 µg of plutonium and treating the mixture by the ion exchange separation with the two resins. After the fractions were collected, ^{233}U and ^{242}Pu tracers were added to the appropriate fraction for the mass spectrometric analyses. The data are shown in Table 17. The recoveries are satisfactory and are independent of the resin mesh-sizes and cross-linkages used.

TABLE 17

Recovery of Plutonium and Uranium from the Ion Exchange Separation

Element	Recovery, %
Pu	99.3
	--
	99.4
	99.1
U	99.1
	101.0
	100.3
	100.5

Separation of Plutonium and ^{241}Am. Samples of the plutonium standard with no tracer added were analyzed for total ^{238}Pu-^{241}Am alpha activity by alpha spectrometry before and after the ion exchange separation described in

the procedure. The amount of ^{241}Am remaining in the plutonium fractions was calculated by difference using the mass spectrometric value for ^{238}Pu.

Duplicate results indicate that a plutonium product with about 0.0013% americium is obtained from starting material containing about 0.18% americium. The separations with both resin types were nearly identical. The small amount of ^{241}Am remaining in the plutonium does not seriously affect the mass spectrometric determination of ^{241}Pu. Many other impurities are eluted in the 8N nitric acid wash along with the ^{241}Am.

General Comments. The hydrochloric-hydrofluoric acid solution was used as the eluting agent for plutonium because it has been shown that this mixture quantitatively elutes plutonium from Dowex-1 resins.[1] Although strictly quantitative recovery is not required, losses in plutonium reduce the versatility of the method in those cases in which only 0.1 to 0.2 μg is available. Insufficient uranium for analysis is rarely a problem.

It may be possible to increase the efficiency of the separation of uranium from plutonium in the plutonium fraction, Table 16, by additional washing of the resin column. However, this modification may prove to be too time-consuming for the increase in plutonium purity achieved. Similarly, the separations efficiency for americium from plutonium may be increased with further washing.

Although the two resins with different mesh-sizes and cross-linkages apparently are equally as efficient, the 100-200 mesh, 2% cross-linked resin is used in the described procedure because the washing time is decreased and because it is used in this laboratory for other separations.

Traces of resin may persist in the separated fractions in the ion exchange separation even after several treatments with nitric acid. To remove these traces, which may give interfering peaks in the mass spectrometry, the fractions are treated with perchloric and nitric acids.

The amount of uranium and plutonium needed for total element concentration and isotopic composition determinations are about the same. Quantities

of plutonium as low as 0.1 to 0.2 μg have been analyzed. However, in the total element concentration determination, additional uranium and plutonium are provided by the tracers used. If sufficient sample is available, the isotopic composition determination can be facilitated by increasing the sample aliquot taken.

The errors in the total element determination contributed by the weighing, diluting, equilibration operations were estimated to give an uncertainty (defined as the 95% confidence limits for a single determination) of 0.024% in the plutonium and 0.021% in the uranium value. The standardizations of the tracers also contributes to the uncertainties. The uncertainty in the preparation of the standards used in the standardization process is estimated to be about 0.064% for plutonium and about 0.026% for uranium. Because of the unknown factors of purity and stoichiometry of the ^{233}U and ^{242}Pu oxides used for the tracers, it was not possible to prepare these solutions by taking a known weight of oxide. Instead, it was felt that better reliability could be obtained for mass spectrometric measurements if the tracer solutions were standardized by isotope dilution with NBS reference materials. However, no meaningful estimation of the uncertainty in the tracer solution values can be made at this time since these values are derived from the mass spectrometric measurements.

Fission product radioactivity is undesirable because it is a health hazard and because the fission products may affect the efficiency of the mass spectrometric ionization processes. The separation procedure used is adequate to remove these fission products from the uranium and plutonium. Other separations techniques, namely solvent extraction processes using methyl isobutyl ketone or tetrapropylammonium nitrate, may be used.

In cases in which analyses of highly radioactive fuel element solutions are required, it may be more satisfactory to remove the fission products prior to the separation of the uranium and plutonium. For the total element determination, this modification would require the addition of the ^{233}U and ^{242}Pu tracer solutions to the sample before the fission product removal to circumvent the problem of unequal losses of the uranium and plutonium in the extraction. After decontamination, the uranium and plutonium would be separated into the respective fractions as before.

VI. SEPARATION OF SUB-MICROGRAM QUANTITIES OF PLUTONIUM IN HIGH SALT SOLUTIONS

An effective scrubber system can absorb and neutralize HNO_3-H_2SO_4-HCl-HF exhaust fumes from plutonium glove box operations with NaOH solution. The sodium salts of these acids are retained in a holding tank along with any entrained plutonium. It is necessary to reliably determine the amount of plutonium in the scrubber wash solution on a regular basis for purposes of radiation safety, contamination control, and containment. Simple alpha radiocounting procedures require a relatively "solids-free" deposit on the counting planchet for highest reliability. (The presence of solids cause "masking" or low results due to absorption of alpha particles.) In order to determine the concentration of plutonium in the holding tank, it is necessary to purify the plutonium and convert it to a form which can readily be assayed. Since the level of plutonium detected in the holding tank is typically about 5,000-50,000 d/m/ml, it is also necessary to modify existing analytical ion exchange separation procedures to accommodate such trace levels. A procedure is described for the anion exchange separation of sub-microgram quantities of plutonium and the removal of solids for the subsequent alpha counting of scrubber solutions.

EXPERIMENTAL

Reagents and Apparatus

Plutonium Standard Solution, NBS SRM 944, Plutonium Sulfate Tetrahydrate, $Pu(SO_4)_2 \cdot 4H_2O$, diluted to a concentration of about 3000 d/m/ml in 8N HNO_3. Alternatively, NBS SRM 949 plutonium metal can be used.

Nitric Acid, 8N, 1N, and concentrated solutions

Sulfuric Acid, concentrated

Polished stainless steel planchets, 2" diameter, flat

Salt solution, 100 g/l $NaNO_3$, 20 g/l Na_2SO_4, 5 g/l NaCl, and 1 g/l NaF in 8N HNO_3

Variable temperature hotplate

Burner, propane gas

Other reagents, resin, and ion exchange columns are described in sections I and II.

Procedure

Sample Analysis Digest 200 ml of the scrubber solution sample containing approximately 100-200 mg of undissolved material in an equal volume of concentrated HNO_3 for several hours until it is free of all undissolved matter. This digestion will convert existing plutonium as $Pu(OH)_x$ to $Pu(NO_3)_x$, a form which can be readily separated from interfering salts by ion exchange purification. If necessary, dilute a portion of the digested scrubber solution with 8N HNO_3 such that a level of 3,000-5,000 d/m/ml is achieved. Prepare several 1-ml aliquots of the solution, add 3 drops of concentrated H_2SO_4, and fume each aliquot to incipient dryness on a hotplate. This fuming removes volatile interferences such as HF and HCl. Na_2SO_4 is not removed by this procedure, but it has been determined that the ion exchange separation of plutonium is satisfactory even when relatively high concentrations of this salt are present.

Process these aliquots through the ion exchange procedure described in sections II with the following changes:

1. Triple the volume of each reagent added to each aliquot in the Pu oxidation state adjustment phase of the separation, and dilute each aliquot to 100 ml with 8N HNO_3.

2. Use a 2.5-cm resin bed length in each column.

3. Wash the resin bed with 60 ml of 8N HNO_3.

After the separation is completed, evaporate the eluates to approximately 1 ml, quantitatively transfer each solution to a planchet using 1 N HNO_3 and dry on a hot plate. Flame each planchet over a gas burner to red heat, cool, and store.

Characterization of the $Pu(SO_4)_2 \cdot 4H_2O$ Standard Solution: Process the standard solution aliquots for ion exchange separation in the same manner as mentioned in the Sample Analysis section above. Count each standard planchet for 10 minutes according to an accepted procedure and correct this standard for ^{241}Am content.

Analysis of Synthetic Scrubber Solutions: Synthetic scrubber solutions were processed and counted according to the above procedures.

RESULTS AND DISCUSSION

Initially the ion exchange procedure was tested at a low level of plutonium (approximately 3,000 d/m/ml) using a plutonium standard solution. The plutonium level was chosen to approximate the concentration expected in diluted scrubber solutions. After ion exchange separation, the eluted plutonium was alpha counted and the recovery was calculated, Table 20.

TABLE 20

Recovery of Plutonium After Ion Exchange Separation

Aliquot No.	Plutonium Recovery, %*
1	98.6
2	96.8
3	97.4
4	99.3
5	99.1
Mean, %:	98.2
RSD, %:	1.1

*Corrected for Am-241 which is separated by ion exchange

In order to simulate the salts in the acid-digested scrubber solution, a salt solution was added to the plutonium standard. The plutonium was separated by ion exchange and alpha counted. The results are shown in Table 21.

TABLE 21

Recovery of Plutonium from a Synthetic Scrubber Solution

Aliquot No.	Plutonium Recovery, %*
1	99.0
2	100.9
3	101.7
4	98.3

Mean, %: 99.7
RSD, %: 1.9

*Relative to the plutonium recovery for standards, Table 20.

Thus, at the low levels of plutonium studied (approximately 3,000 d/m/ml), satisfactory recovery was achieved by the ion exchange procedure. In standards spiked with salts to simulate actual scrubber solutions, the plutonium was satisfactorily separated.

VII. THE ION EXCHANGE SEPARATION OF TRACE ELEMENTS FROM PLUTONIUM FOR IMPURITY DETERMINATION

The spectrographic determination of impurities in plutonium is complicated by its complex spectrum,[35] while the radiological health hazard would dictate the use of minimal amounts of plutonium during the analysis. Chemical separations are used to remove plutonium from its impurities in order to increase the sensitivity of spectrographic detection and to minimize the health hazard. Two such methods are: (1) solvent extraction with cupferron,[36,37] hexone, and thenoyltrifluoroacetone (TTA)[38]; and (2) ion exchange with anion exchange resin.[39,40] Ion exchange separations are used at this laboratory because of their inherent simplicity. The anion exchange procedure described in section I for use with assay methods was modified for the quantitative separation of impurities in plutonium. Two important impurity elements, however, silicon and boron, cannot be adequately determined by this method. Silicon may either precipitate or be partially sorbed with plutonium on anion resins depending upon the nature and concentration of the acid as well as other conditions. Boron is volatilized during the evaporation of the 8N HNO_3 anion exchange effluent unless impractical amounts of mannitol are used for complexing. Accordingly, to complement the anion exchange separation, a cation exchange method was investigated in which plutonium(III/IV) is quantitatively sorbed from a 0.2N HNO_3 solution[41] while the boron and silicon impurities as anions pass unsorbed into the effluent. The spectrographic procedure for the determination of separated impurities is given elsewhere.[42]

EXPERIMENTAL

Apparatus and Reagents

Heat Lamps, 2 standard 500-watt heat lamps connected to a 10-ampere, 115-volt input Variac transformer. (Regulation of the heat lamp temperature is achieved by adjusting the Variac setting.)

Acids. All acids are stored in polyethylene bottles except where noted.

Nitric Acid, concentrated, 8N, and 1N, distilled from reagent-grade acid and diluted with deionized water where required.

Hydrochloric Acid, concentrated, reagent-grade.

Hydrochloric Acid, constant boiling, and 6N, distilled from reagent-grade acid and diluted with deionized water where required.

Hydrofluoric Acid, concentrated, reagent-grade.

Hydriodic Acid, distilled. Reagent-grade HI is distilled in an inert atmosphere in quartz apparatus using standard procedures.

Sulfuric Acid, concentrated, distilled from reagent-grade acid and stored in a Teflon bottle.

Sodium Carbonate Solution. Approximately 15 mg of Na_2CO_3/ml in 100 ml of deionized distilled water stored in a polyethylene bottle.

Cation Exchange Resin. Two hundred grams of wet AG-50W cation resin (a highly purified analytical grade of Dowex-50W, X-10; 200-400 mesh, hydrogen-form, obtained from Bio-Rad Laboratories, Richmond, CA) is washed free of "fines" and residual color, and stored in deionized distilled water in a wide-mouth polyethylene bottle.

Anion Exchange Resin (Chloride Form). A 200-gram quantity of wet AG-1 anion resin (a highly purified analytical grade of Dowex-1, X-10, 200-400 mesh, chloride-form) is obtained, processed, and stored as above.

Anion Exchange Resin (Nitrate Form). Half of the above-prepared chloride-form resin is converted to the nitrate form by washing with 8N HNO_3 until the effluent is free of chloride when tested with dilute $AgNO_3$ solution. The resin is washed with water to remove the excess acid and is stored in water, as above.

Ion Exchange Column. A self-leveling glass column (1 cm I. D.), shown in Figure 9, is loaded with 9 cm of fresh, wet Dowex-1 anion exchange resin or Dowex-50W cation exchange resin, as required. The anion resin is thoroughly washed five times with 8N HNO_3 (nitrate-form for use with plutonium samples) or with concentrated HCl (chloride-form for use with plutonium-uranium samples) before loading by adding the acid to the material, stirring, and decanting the liquid. The cation resin is washed with 150 ml of 0.2N HNO_3 immediately before use if boron is to be separated. (An initial 30-ml wash is adequate if only silicon is to be separated.) The liquid in the column will adjust automatically to the level of the column tip. The height of the liquid remaining above the resin bed may be controlled by the length of auxiliary tip used; it is usually regulated so that less than 1 mm of liquid remains. The flow rate may be adjusted by means of a small hosecock clamp on the auxiliary

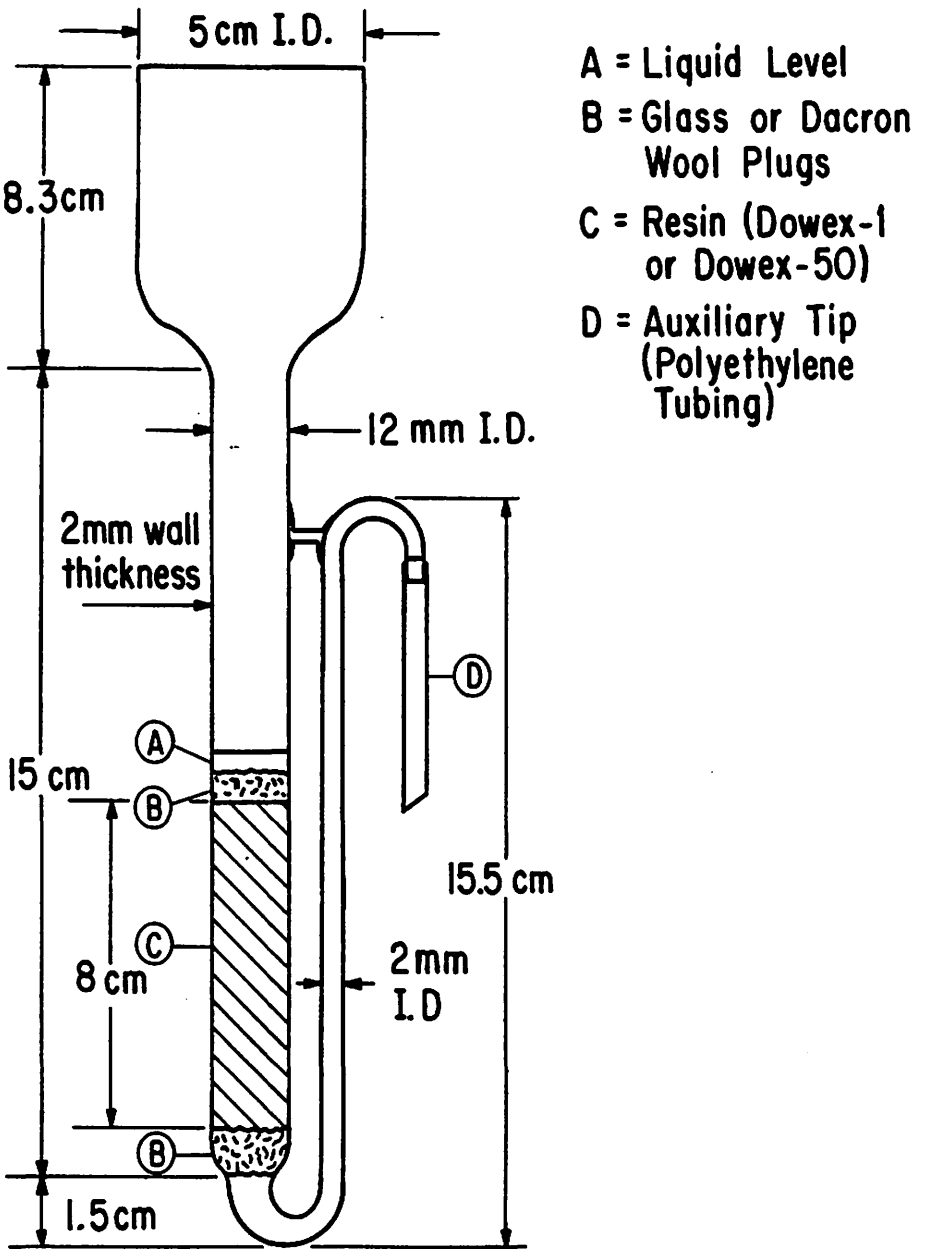

Figure 9. Ion Exchange Column for the Separation of Impurities, Self-Leveling

tip. Glass wool plugs are used to support the resin bed for the anion-exchange separation of the common elements; Dacron wool is used for the cation-exchange separation of boron and silicon. A typical layout of the apparatus in a glove box is shown in Figure 10.

Standard Solutions. Reagent-grade chemicals, or better, are dissolved in distilled HNO_3 and diluted with distilled, deionized water to make a stock solution in 1N HNO_3 of each element to be determined.

Internal Standard (for common elements), 0.020 mg Co/ml and 0.100 mg Eu/ml in 300 ml of 1N HNO_3.

Internal Standard (for boron), 4 mg Zn/ml in 100 ml of 0.2N HNO_3.

Master Standard A is prepared by diluting appropriate aliquots of the individual stock solutions and of the internal standard to 200 ml with 1N HNO_3 in a volumetric flask so that the standard subsequently contains the following concentration of the elements in 1N HNO_3:

Eu*, Am	0.100 mg/ml
Fe, Al, Zn* Ca	0.040 mg/ml
Co*, V	0.020 mg/ml
Cr, Mo, Mg, Mn, Ni	0.008 mg/ml
Pb, Be, Cd	0.004 mg/ml
Cu, Ag	0.002 mg/ml

*Internal Standard

Solutions of these elements are prepared from the following materials: oxide (Am, Eu, Ca, Zn), metal (Fe, Co, Mg, Mn, Ni, Pb, Be, Cd, Cu, Ag), nitrate (Al), sodium vanadate (V), potassium dichromate (Cr), and ammonium molybdate (Mo).

Standards B, C, D, and E are prepared to contain 1/2, 1/4, 1/10, and 1/20, respectively, of the concentration of the elements found in Master Standard A by dilution.

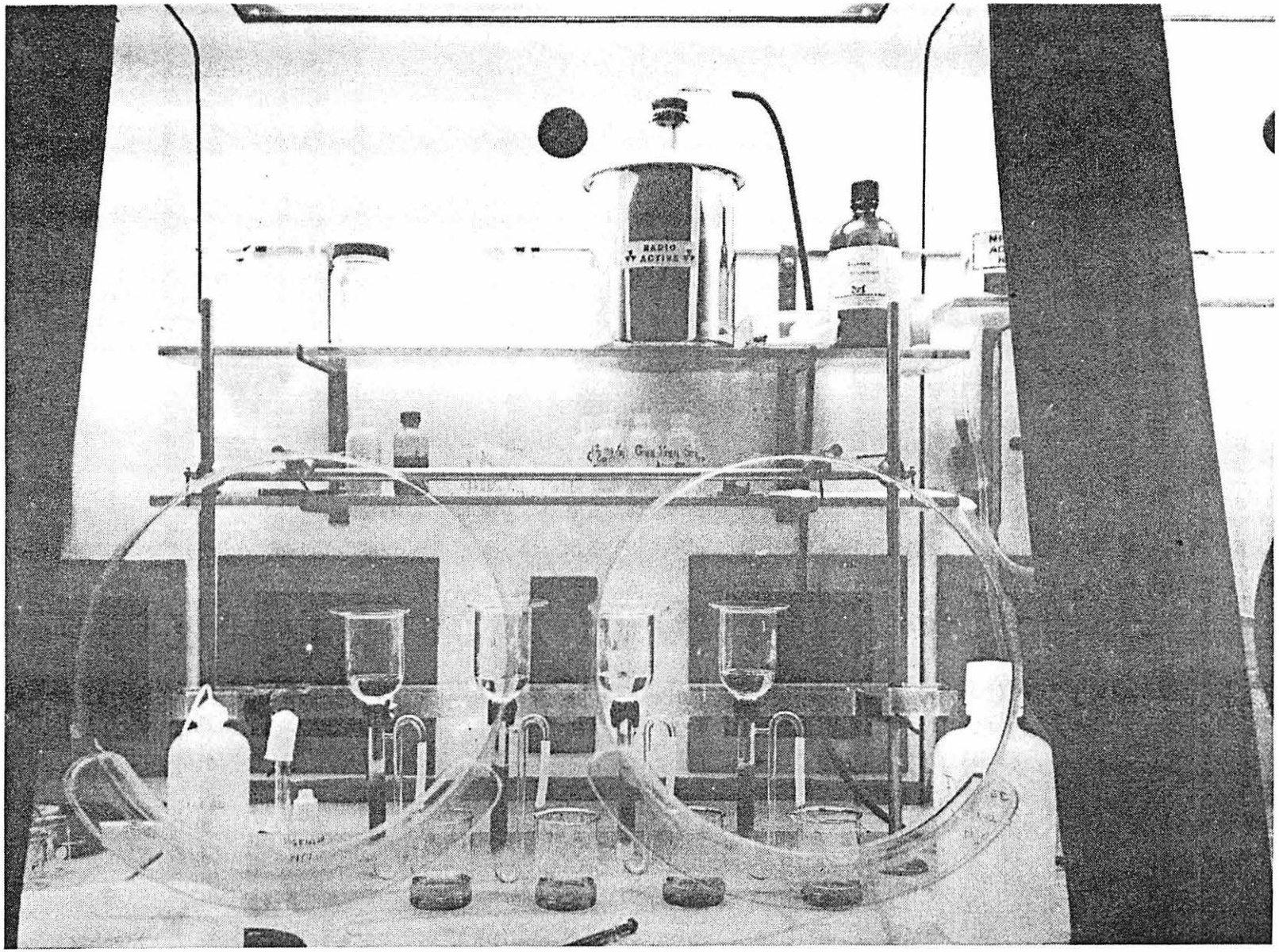

Figure 10. Ion Exchange Columns for Impurities Separation

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

Na, K, Rb	0.040 mg/ml
Ba, Cs	0.020 mg/ml
Li	0.002 mg/ml

Solutions of these elements are prepared from the nitrate (Na, K, Ba), the chloride (Cs, Rb), and the carbonate (Li).

Standards G, H, I, and J are prepared by successive dilution with 1N HNO_3 of Standard F as indicated above for Standards B, C, D, and E. All alkali standard solutions are stored in polyethylene bottles.

Boron Standard. Reagent-grade H_3BO_3 is used to prepare a series of standard solutions in 0.2N HNO_3 with concentrations of 20, 6, 2, 0.6, 0.2, and 0.1 µg B/ml. The solutions are stored in polyethylene bottles.

Silicon Standard. Reagent-grade $Na_2SiO_3 \cdot 9H_2O$ is used to prepare standard solutions in 0.2N HNO_3 by successive dilution to give concentrations of 70, 40, 20, 10, 4, 2, and 1 µg Si/ml. The solutions are stored in polyethylene bottles.

Anion Exchange Separation Procedure

Sample Preparation. Weigh to the nearest milligram a sample containing about 100-400 mg of plutonium or plutonium-uranium in solution, pipet an aliquot containing the appropriate amounts of trace elements. Place the sample in a 100-ml Teflon beaker covered with a watch glass. Follow the sample preparation procedure outlined below for the appropriate material used.

Plutonium Metal. Make certain that the watch glass is in place to prevent loss of sample from possible spattering, and rapidly add about 1 drop of distilled constant-boiling HCl for every 5 mg of plutonium metal to the beaker at the opening at the pouring spout. The sample reacts vigorously with the acid, forming a bluish 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 5 ml of distilled concentrated HNO_3 and remove excess HCl by

evaporating the solution to a moist residue under heat lamps. (NOTE: Do not allow the sample to bake). Repeat the evaporation step with an additional 5 ml of HNO_3. When the solution has evaporated, remove the beaker from under the heat lamp, cool, 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, covered with a watch glass, under the heat lamps if the sample does not dissolve rapidly. When the sample has dissolved, remove the beaker from under the heat lamp, swirl gently, and allow to cool.

Plutonium Chlorides. Add 15 ml of 8N HNO_3 to the sample. Swirl the mixture until dissolved, or place the beaker under the heat lamps if the sample does not dissolve rapidly. When the sample has dissolved, remove the beaker from under the heat lamp and allow to cool.

Plutonium Oxide and Plutonium-Uranium Oxide. Add 15 ml of concentrated HNO_3 plus 2-3 drops of HF to the sample and gently heat if necessary to speed dissolution. (NOTE: Difficult-to-dissolve samples may require a modified method of dissolution employing HNO_3-HF under reflux conditions reported elsewhere.[43]) Evaporate the solution to incipient dryness and redissolve the residue in 10 ml of concentrated HCl. Add the green solution of the dissolved sample to the appropriately prepared ion exchange column. Note that the separation of plutonium-uranium solutions from impurities requires the use of a hydrochloric acid media and chloride-form resin instead of the usual 8N nitric acid system and nitrate-form resin used for plutonium samples alone.

Anion Exchange Separation. Adjust the plutonium to the (IV) oxidation state by adding 1 ml of 30% H_2O_2 for every 200 mg of plutonium to the sample solution. Swirl and heat to remove excess peroxide. When the color of the solution turns green and the effervescence from the peroxide ceases, cool the solution to room temperature. Add the green solution to the prepared anion exchange column. Discard the first 5 ml of effluent and collect the remaining clear effluent in a 125-ml Teflon dish at the rate of about 0.3 ml/min. (Platinum ware should not be used in the presence of chlorides or the

spectrographic results may be affected by excessive amounts of rhodium leached from the vessels.) Place the tip of the ion exchange column against the inside of the pouring spout of the dish and cover the dish with a watch glass to afford maximum protection against sample contamination. For samples containing plutonium alone, 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 the bed, add the 10-ml washing from the sample beaker to the column. Repeat with an additional 35-ml wash and collect all the effluent. For samples containing both plutonium and uranium, repeat the above procedure using the appropriate ion exchange column in concentrated HCl but replace the two HNO_3 washes with 10-ml of concentrated HCl followed by 20 ml of 6N HCl.

Prepare a reference blank solution by adding 45 ml of 8N HNO_3 (for plutonium samples) or 40 ml of 9N HCl (for plutonium-uranium samples) to a 125-ml Teflon dish. Blanks for plutonium sulfate samples should contain about 1 drop of H_2SO_4 for every 100 mg of sample used. Cover the dish with a ribbed watch glass and evaporate the solution under heat lamps.

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 1000 µl of the internal standard solution, dropwise, to the dishes, making sure that the sides of the vessels are washed with the solution. Swirl the dishes for a few minutes to insure complete mixing of the solutions. The solutions are ready for spectrographic analysis.[42]

Remove the sorbed plutonium (and uranium) on the column by adding 10 ml of 0.36N HCl-0.01N HF to the column, collect the effluent, and repeat the procedure several times with the dilute acid. Dispose of the plutonium (and uranium) in an appropriate manner. Use the resin once and discard.

Cation Exchange Separation Procedure

Sample Preparation. Pipet an aliquot of sample containing about 100-400 mg of plutonium or plutonium-uranium and approximately 2 to 150 µg/g

of silicon and 2-50 µg/g of boron impurity. (NOTE: Where solid samples are used, weigh the above quantity of sample to the nearest milligram.) (NOTE: Where boron is to be determined in solid samples and standard acid dissolution procedures are employed, the processing must be made under reflux using all quartzware. In addition, where standard fusion techniques are required to solubilize solid samples containing silicon, a minimum amount of flux must be used.)

Cation Exchange Separation. Adjust the acidity of the sample solution to about 0.2N either by addition of sufficient HNO_3 followed by 10 ml of 0.05N $NH_2OH \cdot HCl$ solution, or by dilution with water to which the hydroxylamine has been added. Warm the solution for about 20 minutes at 60-70°C, cool, and add it to the prepared cation exchange column. Maintain the flow rate at about 0.3-0.5 ml per minute. When the level of the solution reaches the top of the resin bed, wash the silicon and boron through with 50 ml of 0.2N HNO_3. Collect the effluent in a Teflon dish and when the washing is complete, transfer one-half of the effluent to another Teflon dish. The solution is now ready for spectrographic analysis.[42]

Remove the sorbed plutonium and uranium on the column by adding 10-ml portions of 5.5N HNO_3 to the column several times. Dispose of the plutonium, uranium, and used resin as before.

RESULTS AND DISCUSSION

Efficiency of the Ion Exchange Separation. One 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. Accordingly, the amount of plutonium found in the effluent from the ion exchange separation and the degree of separation of impurities from plutonium is of interest.

Anion Exchange Separation. One separation gave relatively high plutonium values in the effluent estimated at about 0.07% of a 100-mg plutonium sample. These results were attributed to incomplete preparation of the resin which was conditioned in less than the required 8N HNO_3; 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 the loading on the column, the plutonium in the effluent was reduced to <0.001% per 100-mg sample; the green plutonium band on a 6-cm-long column was now only about 1-1.5-cm long. Another investigator attributes the high plutonium content in the effluent to the formation, on heating the sample, of the less strongly adsorbed plutonium(VI) species.[44] In tests at this laboratory, a plutonium(IV) solution in 8N HNO_3 was heated prior to separation and no increase in the plutonium level in the effluent occurred, Table 22. 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 22

Plutonium Level in Dowex-1 Anion Resin Effluent

Condition	Plutonium Found,[a,b] %	Americium-241 Found,[b,c] %
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

[a]Plutonium estimated in the presence of americium-241 by alpha spectrometry.

[b]Based on a 100-mg sample.

[c]Variation in americium-241 content due to different sample ages.

Tests were made in order to determine the overall efficiency of the recovery of impurities from the anion exchange separation. Master Standard A was analyzed before and after passing through the anion exchange column. The recovery obtained in the anion exchange separation was 100% within the precision of the spectrographic determination, Table 23. Similar results were obtained with Standards B through E, and F through J.

TABLE 23

Recovery of Impurities from Anion Exchange Separation

Element	Recovery, %
Ag	95
Al	101
Be	100
Cr	100
Cu	101
Fe	103
Mg	102
Mn	110
Mo	97
Ni	94
Zn	105

Cation Exchange Separation. Although plutonium(IV) is sorbed more readily than plutonium(III) at low acidities on Dowex-50 cation resin, it is more difficult to remove.[41] Accordingly hydroxylamine hydrochloride was used to reduce plutonium to the +3 oxidation state in the sample. The addition of hydroxylamine to the dilute nitric acid elutriant was unnecessary in maintaining plutonium(III) on the resin bed during the washing step when plutonium was initially adsorbed at the rate of 100 mg per day for at least four days. Plutonium elution was accomplished without difficulty and resulted in 99.9% recovery. Radiometric analysis of the effluent after the column had been loaded in excess of 400 mg of plutonium showed <0.05% plutonium in the effluent for the final 100-mg sample. Under these extreme conditions each electrode would contain no more than 10 μg of plutonium. Other studies with plutonium-uranium samples indicated that the total alpha activity in the effluent did not exceed 0.001% when the amount of plutonium on the column was about 100 mg.[43]

Again, semi-quantitative tests made in order to determine the degree of retention of impurity elements on the resin during the cation exchange separation. Master Standard A, to which the Boron Standards and the Silicon Standards were added, was analyzed before and after passing through the cation exchange column. The summary presented in Table 24 discloses that only B, Si, and Mo were not retained on the resin and were the only elements recovered in any appreciable amounts.

TABLE 24

Recovery of Impurities from Cation Exchange Separation

Element	Recovery, %
Ag	~2
Al	~2
B	85-95[a]
Be	0
Cr	0
Cu	~3
Fe	~2
Mn	0
Mo	99
Ni	~2
Pb	0
Si	70-85[b]
V	0
Zn	~0-3

[a]Mannitol-complexing not used to prevent loss of boron by volatilization during evaporation of ion exchange effluent.

[b]Sodium carbonate fusion not used to dissolve partially insoluble silicon residue after evaporation of effluent.

The low recovery of silicon obtained in this study was expected since no fusion of the dried effluent residue was made; these results are consistent

with those previously reported.[45] Using a sodium carborate fusion technique,[38] quantitative recovery of silicon was obtained, Table 25.

TABLE 25

Determination of Silicon in Plutonium

Silicon, prepared value, µg/g	Silicon Found, µg/g			
	Standards[a,b]		Plutonium Samples[b]	
	Colorimetric	Spectrographic	Colorimetric	Spectrographic
36	36	40	44	36
	38	38	38	34
		36		39
				38
				36
				42
				38
				36
68	63	63	63	67
	63	68	62	69
		64		70
				69
				63
				72
				64
				68
167	165	160	160	163
	162	170	165	160
		163		170
				160
				169
				160
				162

[a]Standards not run through ion exchange separation.
[b]Averages of four determinations.

The slightly low results obtained for boron, Table 24, using 0.2N HNO_3 to dissolve the dried effluent residue is indicative of boron loss due to volatilization during evaporation of the ion exchange effluent.[46]

Using a mannitol-complexing technique during the evaporation step, uranium and plutonium solutions spiked with varying amounts of boron were passed through a Dowex-50 cation exchange column in 0.2N HNO_3 and the boron in the processed effluent was determined spectrographically, Table 26.

TABLE 26

Determination of Boron in Plutonium and Uranium

Boron, µg/g			
Prepared Value	Standards[a,b]	Plutonium[b]	Uranium[b]
3	3	2	3
	3	2	3
	3	3	3
	3	3	3
10	10	10	11
	10	12	10
	12	9	10
	10	11	8
			8
			9
33	33	34	35
	29	33	37
	34	34	36
	32	36	30
			28
			33

[a]Standards not run through ion exchange separation

[b]Averages of four determinations

Conclusion. The anion exchange separations procedure has been shown to be suitable for the impurity analysis of plutonium metal (or plutonium nitrate solution), Table 27, plutonium sulfate tetrahydrate and anhydrous plutonium sulfate, Tables 28 and 29, dicesium plutonium hexachloride (or other alkali salts), Table 30, and with modification, uranium-plutonium oxide mixtures (or uranium-plutonium carbides), Table 31. The cation exchange separation procedure has been applied to plutonium, and plutonium-uranium solutions, Tables 25 and 26. Additional details of this work have been published.[47,49]

TABLE 27

Determination of Impurities in Plutonium Metal

Element	Plutonium Metal, Hanford Values, µg/g	Plutonium Metal, New Brunswick Laboratory Values, µg/g
Ag	<1	1.3
Al	8	12
Be	N.R.	N.D.
Cu	2	6
Cr	10	30
Fe	<50	115
Mg	20	26
Mn	20	22
Mo	N.R.	<1
Ni	10	17
Pb	10	7
Zn	N.R.	<50

N.D. = not detected

N.R. = not reported

TABLE 28

Determination of Impurities in Plutonium Sulfate Tetrahydrate

Element	Impurities, µg/g[a]	
Ag	<0.2	<0.2
Al	48	46
Am	N.R.	N.R.
Ba	N.D.	N.D.
Be	N.D.	N.D.
Ca	42	35
Cr	4	3
Cs	N.D.	N.D.
Cu	2	2
Fe	24	31
K	5	3
L	N.D.	N.D.
Mg	30	32
Mn	0.8	0.5
Mo	0.6	0.8
Na	6	8
Ni	7	4
Pb	5	14
Rb	N.D.	N.D.
V	N.D.	N.D.
Zn	27	22

[a]Duplicate samples; averages of four determinations

TABLE 29

Determination of Impurities in Anhydrous Plutonium Sulfate

Element	Impurities, μg/g[a]	
Ag	0.4	0.4
Al	7	4
Am	N.R.	N.R.
Ba	N.D.	N.D.
Be	N.D.	N.D.
Ca	22	15
Cr	N.D.	N.D.
Cs	N.D.	N.D.
Cu	0.7	0.4
Fe	22	15
K	5	5
Li	N.D.	N.D.
Mg	15	15
Mn	0.4	0.4
Mo	0.4	0.2
Na	6	7
Ni	≤2	≤2
Pb	2	≤2
Rb	N.D.	N.D.
V	N.D.	N.D.
Zn	N.D.	N.D.

[a]Duplicate samples; averages of four determinations

TABLE 30

Determination of Impurities in Cs_2PuCl_6

Element	Impurities, μg/g[a]
Ag	<0.5
Al	10
Be	N.D.
Cr	10
Cu	1
Fe	75
Mg	40
Mn	2
Mo	N.D.
Ni	30
Pb	2
Zn	<100

[a]based on plutonium metal; averages of four determinations

TABLE 31

Determination of Impurities in PuO_2-UO_2-C Mixture

Element	Impurity, μg/g[a]
Ag	50
Al	800
Be	N.D.
Cr	50
Cu	5, 75
Mg	700
Mn	20
Pb	50

[a]approximate values; duplicate determinations run in quadruplicate

A complete emission spectrographic analysis for impurities in plutonium requires three or more separate determinations, e.g., elements determined in the first and second orders, and the alkali elements. The procedure presented herein is for a general impurity determination using only one sample for one anion exchange separation and an additional sample for a cation exchange separation. Accordingly, if only one group of elements is desired, the type of ion exchange separation may be chosen and the amount of sample taken and the volume of acid used to dissolve the residue after evaporating the effluent may be reduced. A distinct advantage of the method is the use of 200-400 mg of plutonium for a complete analysis of 24 trace impurity elements with adequate sensitivity, and the reduction of gross plutonium contamination during sample excitation.

Results from several analyses of production-grade plutonium metal show good precision but values for all impurity elements differ slightly from those of the supplier. A significant cause of this apparent discrepancy may be attributed to sampling problems 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 the production site. Their analysis was made on similar (but not the same) material. In fact, it has been shown 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.[50]

The use of hydrochloric acid is valuable as an alternative to the nitric acid system to permit the anion exchange separation of both plutonium and uranium from impurities. The number of elements separated in the hydrochloric acid system is less than the number separated in the nitric acid system. For example, in the 6N to 12N hydrochloric acid range used Fe, Cr, Mo, Zn, and some other elements are either completely sorbed on the resin or are not quantitatively separated from uranium and plutonium. In addition, the oxidation state of the impurity element is of importance since Cu(II) is completely sorbed while Cu(I) is only slightly retained on the column; Cr(III) and Cr(VI) exhibit similar behavior. (The variability in the reported values for Cu, Table 31, may indicate a discrepancy caused by oxidation state.) A list of elements which are separated by anion exchange in HNO_3 and HCl media is tabulated in Tables 32 and 33, respectively.

TABLE 32

Sorption Behavior of Elements on Dowex-1 Anion Exchange Resin in Nitric Acid Media[51]

Elements Not Sorbed	Acid Conc., N	Elements Partially Sorbed	Acid Conc., N	Elements Completely Sorbed	Acid Conc., N
Al, Am(III), B, Ba, Be, Ca, Cm(III), Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Pu(III), Rb, Rh, Ru, Sc, Sm, Sr, Tb, Te, Ti, Tm, V, Y, Yb	0.1 to 15	Pu(IV)	1 to 3	Ag	1 to 2
		As	1 to 5	Re	1 to 3
		Nb, Pt, Sn, Tl, Zn, Zr	1 to 14	Hg	1 to 4
		Np(IV)	2 to 4	Pd	1 to 8
		Ag	2 to 14	Bi	1 to 11
		Re, Th	3 to 4	Au	1 to 14
		Ce	4 to 8	Pu(IV)	3 to 14
		Hg, U	4 to 14	Np(IV), Th(IV)	4 to 14
		Pd	8 to 14		
		Bi	11 to 14		

TABLE 33

Sorption Behavior of Elements on Dowex-1 Anion Exchange Resin in Hydrochloric Acid Media[52]

Elements Not Sorbed	Acid Conc., N	Elements Partially Sorbed	Acid Conc., N	Elements Completely Sorbed	Acid Conc., N
Ac, Al, Am(III), Be, Ca, Ce, Cs, Eu, Fr, K, La, Li, Mg, Mn(II), Na, Ni, Pu(III), Ra, Rb, Re(III), Sr, Th, Y	0.1 to 12	Fe(III), Mo, Pu(IV)	0.1 to 3	Ag, Nb	1 to 8
		Ge	1 to 12	Cu(I), Tc(VII)	2 to 10
		Pa, Np(IV)	1 to 5	Cu(II), Fe(III), Ga, In, Mo(VI), Os, Pd, Pu(IV), Re(VII), Rh, Ru(IV), Zn	3 to 12
		U	2 to 12		
		Zr	3 to 8	Np(IV), Pa, Ta	5 to 12
		Cd, Co	5 to 12	Fe(II), Zr	8 to 12
		Ca, Cr(III),Mn(IV), Pb, Sc(III),Ti(III), V(IV)	12	Cr(VI), Hf, Sb, Sn, Te(IV), Ti(IV)	10 to 12
				Cd, Co, U	12

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