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ENVIRONMENTAL MEASUREMENTS LABORATORY

Use of EIChroM TRU RESIN in the determination of Americium, Plutonium and Uranium in air filter and water samples

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ABSTRACT

TRU Resin, an extraction chromatographic material ((octyl (phenyl)-N,Ndiisobutylcarbamoyl-methylphosphene oxide (CMPO) dissolved in tributyl phosphate (TBP)) manufactured by EIChroM Industries, was tested for its actinide sorption and desorption characteristics. A study was initiated to demonstrate the effectiveness of extracting plutonium, americium and uranium from water and air filter samples from the Environmental Measurements Laboratory's Quality Assessment Program (QAP), and the effectiveness of subsequent desorption of one chemical species at a time in order to prepare each of them for α spectrometry. Crossover of plutonium into the americium fraction with the TRU Resin was observed and could not be eliminated while using TRU Resin only. However, prior extraction of plutonium using an anion exchange resin can overcome this problem. A method for the determination of americium is proposed which combines the extraction of plutonium onto Bio-Rad AG 1-X8 anion exchange resin with the extraction of americium using the TRU Resin. This method was tested on three triplicate sets of QAP air filters and two triplicate sets of QAP water samples. The recoveries ranged from 70 to 90 percent, and the results were identical to those obtained by the existing methods. The time required to perform the analysis for americium was shortened from 5 weeks to 1 week.

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INTRODUCTION

Quantitative determination of transuranic elements in environmental matrices presents problems due partly to the nature of their nuclear emissions and partly to chemical similarities. Many isotopes of interest are α emitters and therefore α spectrometry is the most suitable method of analysis, providing both quantitative and qualitative information about the nuclides in the sample. However, a good measurement source for α spectrometry has to satisfy certain specific requirements. First, the α emitter has to be separated from the matrix to prevent self-absorption and energy degradation of the α particles. Second, the α emitter of interest has to be isolated from any other α emitters with similar energy peaks that cannot be resolved by the spectrometry system. For example, the α particles from ^{241}Am cannot be distinguished from those released by ^{238}Pu, since both have energies of approximately 5.45 MeV. Consequently, in order to remove any ambiguity in the interpretation of a spectrum of α energies observed for a given sample we must rely on the effectiveness of the chemical separation of the interfering nuclides from each other.

Once the sample is solubilized and equilibrated with the appropriate tracers, the nuclide of interest can be isolated from the matrix and from nuclides of other elements by a series of coprecipitations, by solvent extractions, or by the use of ion-exchange chromatography. Many schemes have been developed which combine one or more of these techniques (O'Malley, 1994). All of these methods have similar drawbacks in that they are time-consuming, the chemical recovery is never 100% (and use of tracers is therefore necessary), and, in addition, large quantities of hazardous waste are usually generated. Any new material or approach which addresses even one of these major problems is worth investigating.

Reduction in time would increase our capability for analyzing the large number of samples anticipated in restoration and waste management programs. If a method was quantitative, tracers could be eliminated, which would reduce costs and remove sources of uncertainties associated with the calibration and the aliquoting of the tracer solutions. Any significant reduction in the waste stream produced is in compliance with the DOE waste minimization and pollution prevention policy and would be achieved by the most desirable option, namely source reduction.

EIChroM Industries has introduced a number of extraction chromatographic materials which demonstrate quantitative recovery, analysis time reduction and minimization of hazardous waste (Horwitz et al., 1990). It was the objective of this project to evaluate the performance of one such material, TRU Resin, for the determination of americium, plutonium and uranium in air filter and water samples. According to Horwitz et al. (1990) the organophosphorus extractant present in TRU Resin is 100% effective as an adsorber for all actinides present in acidic aqueous solutions. The extraction of all actinides in one step would represent a significant reduction in the time required for analysis. Once the actinides are removed from the sample matrix, they could be selectively desorbed by eluting with appropriate solutions and then prepared for α spectrometry. The stated 100% efficiency of the adsorption and the desorption steps would eliminate the need for tracers. The eluting solutions are in general very dilute and the volumes are much lower then those used in the conventional ion-exchange methods, and, therefore, we should observe a very significant reduction in the waste stream.

In the Phase 1 of this study test solutions containing tracers only and EML Quality Assurance Program (QAP) water samples of known composition (with and without tracers added) were used to evaluate and validate the claims made by EIChroM. Our attention was focused on two factors. The first was the effectiveness of the adsorption and the desorption steps in terms of the chemical recovery. The

second factor dealt with the effectiveness of the chemical separation of one actinide from another, which is necessary for a nonambiguous interpretation of the α spectrogram obtained for each eluate.

The QAP water samples (QAP-Wa) were prepared at EML by adding known quantities of calibrated solutions of the nuclides of interest to a known volume of 1M HCl and mixing them thoroughly. The activities of the nuclides were calculated using appropriate dilution factors. Initial sample homogeneity was tested using gamma-ray spectroscopy. The activities were also confirmed by radiochemical analysis of α and ß emitters using methods found in the EML Procedures Manual (Chieco et al., 1992). The glass fiber air filters (QAP-AF) were prepared by placing 12 10-µL aliquots of a calibrated stock solution on each filter and drying them. The aliquots were dispensed using an automated system to assure quantitative and geometric uniformity. Each filter was counted on a gamma-ray spectrometer and utilized for program needs if the results were within specified acceptance criteria. Several randomly chosen filters were analyzed radiochemically.

As a result of the observations made during Phase 1, a second phase of this study was initiated, consisting of developing and validating a method for the determination of americium in QAP water and air filter samples. This method would be included in a revised edition of the EML Procedures Manual and thus be available to general public. The Phase 1 and 2 results are included in this report.

MATERIALS AND METHODS

TRU Resin

The extractant in the TRU Resin chromatographic material is octyl (phenyl)-NAN-diisobutyl-carbamoylmethylphosphene oxide (CMPO), which is dissolved in tributyl phosphate (TBP) to make a 0.75M solution and then is placed and supported on an inert substrate (Amberlite XAD-7). Combining CMPO with TBP creates a new mixed solvent system with following properties:

1. enhanced distribution ratios of Am^{+3} (D_{Am}) in the range of 0.5 to 6M HNO_3,
2. suppressed D_{Am} at low acidity, and
3. maximum D_{Am} at 2M HNO_3.

All actinides are extracted from the loading solution, which is usually 2M HNO_3 and 0.5M $Al(NO_3)_3$. $Al(NO_3)_3$ is added to enhance americium sorption. Separation of the actinides is achieved by choosing an appropriate eluting solution.

The resin used for this study has a particle size ranging from 125 to 150 µm. Currently, the manufacturer offers TRU Resin in two particle size ranges, 100-150 µm and 50-100 µm. The smaller average diameter of the particles causes a decrease in the rate of elution and an increase in the breakthrough volume, from 50 free column volumes (FVC) for the medium particles to 65 FVC for the smaller particles. In addition, the elution band width for americium decreases somewhat with the smaller diameter particles which results in a reduction of the total volume needed to strip americium from the column. It is our recommendation that for routine analysis of water and air filters the particle size chosen

is as close as possible to the one used in this study, which would mean the 100-150 µm range.

COLUMN PREPARATION

An 8-mL polyethylene disposable transfer pipette with a fine tip was used to contain the resin. The top of the bulb was removed to create a funnel. A small glass wool plug was inserted through the top all the way to the base of the pipette to support the resin. The barrel dimensions (~ 6.5x100 mm) were such that ~ 0.5 g of dry resin was required to fill it almost to the top. The resin was first placed in a small beaker, covered with deionized water and allowed to equilibrate at least overnight. On the day of the analysis the polyethylene pipette was placed in a holder and filled with the presoaked resin. The column had to be used immediately after assembling since there was no stop cock that could be turned to prevent the solution from running out in case of interruption. If a column was allowed to dry out, it would have to be discarded due to the problems associated with trying to re-wet the resin inside the column. However, with care this problem was easily avoided since the whole procedure of assembling the column, washing the resin, loading the sample and stripping the individual fractions never took more than 2-3 hours.

SPECIAL REAGENTS

1. Column-feed solution, 0.5M $Al(NO_3)_3$ in 2M HNO_3 - place 18.76 g of $Al(NO_3)_3 \cdot 9H_2O$ (certified ACS) in a 100-mL volumetric flask and add 2M HNO_3 to the mark. Shake to mix thoroughly.

2. Bioxalate strip solution, 0.1M $NH_4HC_2O_4$ - combine 50 mL of aqueous solution containing 0.71 g of $(NH_4)_2C_2O_4 \cdot H_2O$ with 50 mL of aqueous solution containing 0.63 g of $H_2C_2O_4 \cdot 2H_2O$ (both certified ACS).

3. 2M HNO_3 - 125 mL HNO_3 diluted to 1 L with H_2O.

4. 1M HNO_3 - 62.5 mL HNO_3 diluted to 1 L with H_2O.

5. 0.025M HNO_3 - 25 mL 1M HNO_3 diluted to 1 L with H_2O.

6. ^{243}Am tracer solution, about 0.2 Bq g^{-1} in a dispensing bottle.

7. ^{242}Pu tracer solution, about 1 Bq g^{-1} in a dispensing bottle.

8. ^{232}U tracer solution, about 0.2 Bq g^{-1} in a dispensing bottle.

CHROMATOGRAPHIC TEST SOLUTIONS

Several times, one or two nuclides were loaded onto the column and eluted with appropriate strip solutions. The objective was to observe the interaction of the nuclide (or nuclides) of interest with the resin without any interference from a sample matrix. Calibrated solutions of plutonium and americium isotopes were introduced onto the column, the eluted fractions were analyzed and the chemical recovery was determined. In an effort to simulate real-life conditions, the very small amount of the calibrated solution

was first treated with HNO_3, evaporated to dryness and the residue was redissolved in 3 mL of the column-feed solution.

SAMPLE PREPARATION

QAP-Water - 100 to 500 mL aliquots of QAP-Wa were transferred to beakers of appropriate sizes. Tracers (known quantities of isotopes of ^{242}Pu or ^{236}Pu, ^{243}Am, and ^{232}U) could be added here at this time. The samples were first slowly reduced in volume and transferred to 50-mL beakers, then evaporated to dryness and wet-ashed with several additions of HNO_3. Finally, the dry residue was redissolved in 3 mL of the column-feed solution.

QAP-Air Filter - The glass fiber air filters were used in Phase 2 only. They were treated according to the procedure Plutonium-01 (Chieco et al., 1992), which was modified in two ways. First, ^{243}Am tracer was added in addition to the plutonium tracer to allow for eventual determination of ^{241}Am in the sample. Second, steps involving the use of HF were omitted. Once the solution containing the ions leached from the air filter was adjusted to 7.5M HNO_3, it was then processed according to the EML procedure Pu-11, in which a Bio-Rad AG 1-X8 anion-exchange resin is used to separate plutonium from all other ions. As the sample solution passes through the column, plutonium is adsorbed on the resin. The eluate, which contains all other ions, including americium, is combined with the 120 mL of 7.5M HNO_3 rinse. That solution was evaporated and redissolved in 3 mL of the column-feed solution.

SEPARATION SCHEME

The following separation scheme was used in Phase 1 of this study. This scheme was evaluated using both the chromatographic test solutions of single nuclides as well as radiochemically characterized QAP water samples.

Step 1: Assemble the adsorption column, as described in **Column Preparation**.

Step 2: Prepare the column by washing with 9 mL of 0.1M $NH_4HC_2O_4$ (**fraction 1**), followed by 15 mL of 2M HNO_3 (**fraction 2**). Let each fraction reach the top of the resin bed before adding the next one. Discard both effluents.

Step 3: Load the column with the sample dissolved in the 3 mL of the column-feed solution, as described in sample preparation. Wash the beaker with 3 mL of the column-feed solution and add to the column. Collect the effluent as **fraction 3**.

Step 4: Rinse the column with 8 mL of 2M HNO_3 and collect the effluent as **fraction 4**.

Step 5: Rinse the column with 8 mL of 1M HNO_3 and collect the effluent as **fraction 5**.

Step 6: Strip the americium with three 3-mL portions of 0.025M HNO_3 and collect this eluate as **fraction 6**.

Step 7: Strip the plutonium and uranium with 15 mL of 0.1M $NH_4HC_2O_4$ and collect this eluate as

fraction 7.

Every fraction to be analyzed by α spectrometry was evaporated to dryness and carefully converted to HCl. If the eluate contained oxalate ions, as would be the case with **fraction 7**, that fraction was first wet-ashed with HNO_3 to destroy the oxalate. Once the sample was converted to HCl, it was evaporated slowly to dryness and then transferred to a plastic culture tube with 1M HCl. The G-01 procedure for microprecipitation on NdF_3 (Chieco et al., 1992) was followed with subsequent analysis by α spectrometry. **Fraction 7** containing plutonium and uranium was microprecipitated from HCl solution without adjusting the oxidation state of uranium. Under these conditions, uranium remains in the solution and, therefore, was expected to be found in the filtrate obtained during the microprecipitation procedure. That filtrate was collected, treated with HNO_3 to remove HF and converted to HCL. Uranium was then microprecipitated on NdF_3 in the presence of $TiCl_3$ and analyzed by α spectrometry.

RESULTS AND DISCUSSION

PHASE 1

The separation scheme proposed by EIChroM and utilized in this phase was expected to separate plutonium and uranium from americium. After passing the sample through the TRU Resin column the actinides would be adsorbed on the resin. Americium was expected to desorb with very dilute nitric acid (**fraction 6**), while plutonium and uranium would elute with the bioxalate solution (**fraction 7**). Both fractions would be microprecipitated as described in the separation scheme. Normally uranium is present in a +6 oxidation state, which does not form an insoluble precipitate with a fluoride ion. However, when uranium is reduced to a lower oxidation state with $TiCl_3$, it will microprecipitate on NdF_3. The separation scheme used here was to be evaluated for its ability to separate americium from the other two actinides, namely plutonium and uranium. Separation of natural uranium from plutonium was to be achieved through the microprecipitation process.

Horwitz et al. (1990) used electrodeposition to prepare the actinides for α spectrometry, while at EML microprecipitation with NdF_3 is the method of choice. Before any conclusions could be drawn from the experimental results, it was necessary to evaluate the efficiency of the microprecipitation. Two 10.0-mL aliquots containing ~7 mBq ^{242}Pu mL^{-1} and ~6 mBq ^{236}Pu mL^{-1} were placed in 50-mL beakers, evaporated, converted to HCl and then microprecipitated on NdF_3 according to EML procedure G-03 (Microprecipitation Source Preparation for α Spectrometry, Chieco et al., 1992). The results are summarized in Table 1.

TABLE 1

RECOVERIES OF ^{242}Pu AND ^{236}Pu AFTER MICROPRECIPITATION[a]

	Aliquot 1	Aliquot 2
% recovery of ^{242}Pu	83.0 ± 2.9	85.2 ± 3.0
% recovery of ^{236}Pu	74.1 ± 2.6	82.0 ± 2.9

[a]The error term includes the counting error, the detector efficiency uncertainty and the uncertainty in the activity added, all terms combined according to the accepted methods for propagation of indeterminate errors.

The results shown here tell us that the microprecipitation step is not 100% efficient and that we can expect the sum of activities recovered from all possible fractions (the mass balance calculations) to represent as little as 75% of the activity added.

BEHAVIOR OF AQUEOUS SOLUTIONS OF AMERICIUM, PLUTONIUM, AND URANIUM ON TRU RESIN

First study - QAP-Wa solutions are prepared with acidified deionized water and standardized solutions of radioactive nuclides. Since a sufficient amount of QAP-9009-Wa was available, it represented a ready-made chromatographic test solution, which contained all the actinides of interest and required minimal sample preparation. Three aliquots (200 mL, 300 mL, and 500 mL) of previously analyzed QAP-9009-Wa were evaporated and processed using the separation scheme described here. Initially only **fractions 6** (americium) and **7** (plutonium and uranium) were microprecipitated and counted on an α-spectrometer. No tracers were added and the recoveries were calculated from the known activities of QAP-9009-Wa. The recoveries and identities of the actinides found in fractions 6 and 7 are listed in Table 2. The final microprecipitated sources were counted for a sufficient time so that the Poisson error of a major peak was no more than ±3%. The smaller peaks, if present, would then have Poisson errors as much as ±20%.

The results showed a recovery rate of 65-80% for each of the actinides present (^{239}Pu, ^{241}Am and natural uranium). In addition, there was a crossover between fractions, where 1 to 5% of a given nuclide was found in another fraction. In order to get a more complete picture of the mass balance, the rinse fractions and the resin were analyzed for the missing nuclides. The results are included in Table 2. No actinides were found in any of the rinse fractions. Traces of plutonium and uranium (1% or less) were found on the stationary phase of the resin (after dry-ashing).

TABLE 2

RECOVERIES OF ^{241}Am, ^{239}Pu AND Nat U FROM QAP-9009-Wa USING TRU RESIN

Fraction	Aliquot 1 (200 mL)	Aliquot 2 (300 mL)	Aliquot 3 (500 mL)
Am fraction **(fraction 6)**	65.4% ^{241}Am 2.3% ^{239}Pu	69.7% ^{241}Am 3.1% ^{239}Pu	74.8% ^{241}Am 3.7% ^{239}Pu
Pu fraction (**fraction 7**)	74.7% ^{239}Pu 3.6% ^{241}Am	76.6% ^{239}Pu 1.2% ^{241}Am	72.7% ^{239}Pu 1.4% ^{241}Am
Nat U fraction **(fraction 7)**	70.7% Nat U 3.6% ^{241}Am 4.7% ^{239}Pu	79.7% Nat U - 1.0% ^{239}Pu	49.5% Nat U 0.5% ^{241}Am 0.9% ^{239}Pu
HNO_3 rinse[a]	-	-	-
Filtrate[b]	67% Nat U	4.0% Nat U	28.0% Nat U
Stationary phase[c]	11% ^{239}Pu	1.2% ^{239}Pu 1.0% Nat U	0.7% ^{239}Pu 0.8% Nat U

[a] From Steps 4 and 5.

[b] From natural uranium microprecipitation, wet-ashed and microprecipitated again in the presence of $TiCl_3$.

[c] Resin dissolved in methanol, evaporated and dry-ashed at 700°C.

Significant amounts of natural uranium found in the filtrate could be accounted for by incomplete transfer of natural uranium from the Teflon beaker to the culture tube during the first microprecipitation step.

On a mass balance basis ~20% or more of the actinides were not recovered, but that could be caused by the losses associated with the microprecipitation step.

Second study - Three aliquots (100 mL, 200 mL, and 300 mL) of QAP-9103-Wa were analyzed for ^{241}Am, ^{239}Pu, and Nat U, with addition of known quantities of ^{243}Am, ^{242}Pu and ^{232}U tracers. The ^{232}U tracer also contained detectable quantities of ^{228}Th. In order to eventually develop a method utilizing TRU Resin for the determination of actinides in thorium-containing samples, such as soils, it was important to find out which fraction(s) contained thorium.

TABLE 3

RECOVERIES OF ^{243}Am, ^{242}Pu AND ^{232}U, ADDED AS TRACERS TO QAP-9103-Wa AND EXTRACTED USING TRU RESIN

Fraction	Aliquot 1 (100 mL)	Aliqout 2 (200 mL)	Aliquot 3 (300 mL)	Blank
Am fraction (**fraction 6**)	84.7% ^{243}Am 3.6% ^{242}Pu	81.4% ^{243}Am 7.8% ^{242}Pu	75.0% ^{243}Am 6.4% ^{242}Pu	79.5% ^{243}Am 1.2% ^{242}Pu
Pu fraction (**fraction 7**)	64.1% ^{242}Pu	71.7% ^{242}Pu	64.3% ^{242}Pu	76.8% ^{242}Pu
Nat U fraction (**fraction 7**)	87.8% ^{232}U	86.4% ^{232}U	84.9% ^{232}U	83.0% ^{232}U

The following are some of the comments that can be made about the data presented here:

1. The crossover between fractions persisted to the same extent as observed in the first study, and adjust ments would be needed in the separation scheme in order to isolate the relevant chemical species more thoroughly and provide us with sources suitable for α spectrometry.

2. The presence of ^{242}Pu in the americium fraction implies the presence of ^{239}Pu as well. The reported ^{243}Am recoveries are based on the number of counts observed in the ^{243}Am region of interest, which overlaps with the ^{239}Pu region of interest and cannot be resolved by our α spectrometry system. Since the total activity of each plutonium isotope is known, the number of counts in the ^{243}Am region of interest could be decreased by the estimated contributions made by disintegrations of ^{239}Pu. These corrections would represent on the average a ~5% decrease in the calculated ^{243}Am recoveries.

3. Traces of ^{228}Th and its daughters, such as ^{224}Ra, ^{220}Rn, ^{216}Po, were found in the plutonium fraction only of each aliquot. The existing separation scheme did not provide for the separation of thorium from plutonium, which is necessary for the nonambiguous identification of the peaks observed in the α-spectrogram of the plutonium fraction.

VALENCE ADJUSTMENT OF PLUTONIUM

Plutonium is known to exist in several oxidation states. The most stable states are +3, +4 and +6. It is a well known fact that Pu^{+4} disproportionates to Pu^{+3} and Pu^{+6}, and that the rate of this reaction changes with the pH and the nature and concentration of the anions in the solution. Consequently, under certain conditions, Pu^{+3}, Pu^{+4}, and Pu^{+6} may coexist in comparable concentrations (Milyukova et al., 1969). The

chemical behavior of the various plutonium ions may differ significantly from one ion to another. A hypothesis was formulated that this multiplicity of oxidation states was responsible for the crossover of some of the plutonium into the americium fraction. To test this hypothesis, an attempt was made to determine whether a valence adjustment could eliminate this crossover. An assumption was made that Pu^{+3} followed Am^{+3} because of their identical charges and therefore an oxidizing environment was needed to bring as many plutonium ions to +4 oxidation state as possible.

Three 200-mL aliquots of QAP-9103-Wa were taken to dryness and redissolved in 10 mL deionized (DI) H_2O, followed by addition the of ~0.5 g of $NaNO_2$. After adding 5-10 mL of 7.5M HNO_3 the aliquots were taken to dryness, redissolved in 3 mL of the column-feed solution and loaded onto the prepared column. A standard elution procedure was followed. Each fraction was microprecipitated and counted using α spectrometry. In addition, the resin from each column was placed in a platinum crucible and dry-ashed at 600°C. The residue was redissolved in 7.5M HNO_3, converted to HCl, and microprecipitated on NdF_3 in the presence of $TiCl_3$. The minimal activity (less than 1% of the total) found on each resin aliquot demonstrated that the elution procedure was essentially 100% effective. The results are shown in Table 4. The data in Table 4 (see page 9) shows that the valence adjustment did not eliminate the plutonium crossover into the americium fraction.

DOUBLE TREATMENT OF THE AMERICIUM FRACTION

The fraction of plutonium found in the americium eluate was fairly constant over the range of the activities of plutonium in the samples (0.1 Bq to 0.5 Bq per aliquot). This data indicates that perhaps the partition constant for plutonium between the resin and the 0.025 M HNO_3 is not large enough to achieve good separation of plutonium and americium. However, an additional treatment of the americium fraction on a fresh column might remove the remaining plutonium and render the sample pure enough for α spectrometry. To determine whether this was true, the following steps were taken. Four samples were prepared containing increasing amounts of ^{242}Pu (0.07-0.25 Bq) and ~0.07 Bq ^{243}Am. Each sample was treated with HNO_3 several times, evaporated to dryness and redissolved in 3 mL of the column-feed solution. Each load solution was placed onto a TRU Resin column and a standard procedure for washing and elution of plutonium and americium fractions was followed. The four plutonium fractions (one from each column) were prepared for α spectrometry. The americium fractions were evaporated, redissolved in 3 mL of the column-feed solution and loaded onto fresh TRU Resin columns. The plutonium and americium fractions were eluted according to the same scheme and prepared for α spectrometry. The results are summarized in Table 5.

TABLE 4

RECOVERIES OF ^{241}AMERICIUM, ^{239}Pu AND Nat U FROM QAP-9103-Wa WITH $NaNO_2$ PRETREATMENT

Fraction	Aliquot 1 (200 mL)	Aliquot 2 (200 mL)	Aliquot 3 (200 mL)
Am fraction (**fraction 6**)	83.8% ^{241}Am 2.4% ^{239}Pu	82.2% ^{241}Am 3.6% ^{239}Pu	80.0% ^{241}Am 5.8% ^{239}Pu
Pu fraction (**fraction 7**)	74.7% ^{239}Pu 2.3% ^{241}Am	54.9% ^{239}Pu 1.2% ^{241}Am	65.9% ^{239}Pu 1.9% ^{241}Am
Nat U fraction (**fraction 7**)	76.4% Nat U 0.5% ^{239}Pu	65.5% Nat U 0.1% ^{239}Pu	80.4% Nat U 0.6% ^{239}Pu
Resin ashed at~600° C	0.60% of total activity*	0.58% of total activity*	0.69% of total activity*

*Total activity is equal to the sum of activities of ^{241}Am, ^{239}Pu, and Nat U expected to be present in 200 mL of QAP-9103-Wa.

It can be seen that the americium fraction contains much less plutonium (anywhere from 0.04% to 0.16% of the added amount) than when a single column separation was used. However, the double treatment of the americium fraction is not 100% effective in removing plutonium. If a sample's plutonium activity is significantly greater than that due to the presence of americium, as is often the case, even a very small fraction of plutonium activity would interfere with the energy spectrum of the americium isotopes.

It is important to note that while the amount of plutonium in the americium fraction has been decreased, the recovery of americium does not seem to be diminished by this double treatment and still ranges from 70 to 80%. Consequently, the double treatment of the americium fraction has some merit, but more work needs to be done on the limitations and the applicability of this approach to the various types of samples encountered at EML.

In conclusion, the sequential determination of plutonium (with natural uranium) and americium using TRU Resin cannot be accomplished with the separation scheme proposed in this study. The main problem is the persistent appearance of traces of plutonium in the americium fraction and vice versa.

TABLE 5

RECOVERIES OF ^{242}Pu AND ^{243}Am AFTER DOUBLE TREATMENT OF THE AMERICIUM FRACTION

Aliquot No.	Tracer added	First Pu fraction	Second Pu fraction	Am fraction
1	0.0675 Bq ^{242}Pu 0.0649 Bq ^{243}Am	not available	0.36% ^{242}Pu 0.96% ^{243}Am	**0.16% ^{242}Pu** 83.75% ^{243}Am
2	0.131 Bq ^{242}Pu 0.0747 Bq ^{243}Am	75.37% ^{242}Pu 11.59% ^{243}Am	none detected 1.52% ^{243}Am	**0.03% ^{242}Pu** 68.64% ^{243}Am
3	0.216 Bq ^{242}Pu 0.0637 Bq ^{243}Am	62.04% ^{242}Pu 0.45% ^{243}Am	0.54% ^{242}Pu 1.37% ^{243}Am	**0.12% ^{242}Pu** 74.06% ^{243}Am
4	0.255 Bq ^{242}Pu 0.0779 Bq ^{243}Am	79.37% ^{242}Pu 1.91% ^{243}Am	0.56% ^{242}Pu 0.38% ^{243}Am	**0.04% ^{242}Pu** 75.95% ^{243}Am

PHASE 2

Determination of Americium in QAP-AF and QAP-Wa - In this Laboratory, the separation and isolation scheme for plutonium is relatively simple and short compared to the scheme for americium. Therefore, a procedure is proposed for plutonium/americium determination which would simplify and shorten the existing method and that can be applied to both water and air filters. For each matrix, the existing plutonium procedure, such as Pu-01 for air filters and Pu-10 for water (Chieco et al., 1992), each combined with Pu-11 (ion-exchange purification) would be followed. The eluate from the ion-exchange column containing americium and all other ions except plutonium is then processed for loading onto a TRU Resin extraction column. The details of the procedure can be found in Appendix A.

The first test of this procedure was conducted using QAP-9303R-AF air filters. Three filters and a blank were analyzed for plutonium using the standard procedure (Pu-01 combined with Pu-11) and the americium determination was accomplished using the TRU Resin. At the same time, three additional air filters were analyzed using the accepted sequential plutonium/americium method, where the eluate from the ion-exchange purification column (method Pu-11) containing americium was processed for americium using an adaptation of method Am-01 (Chieco et al.,1992). The details of that adaptation can be found in Appendix B. The results of the ^{241}Am determination using both methods are summarized in Table 6. Recoveries of known quantities of ^{243}Am tracers added to each sample and each blank are listed as well. The error term for each calculated activity includes the Poisson error for the ^{243}Am tracer and for the ^{241}Am analyte. Other sources of uncertainties, such as that of the detector efficiency and another one of the activity of the tracer, are much smaller and therefore insignificant in comparison with the counting errors.

TABLE 6

COMPARISON OF ^{241}Am DETERMINATION IN QAP-9303R-AF USING STANDARD EML METHOD AND THE TRU RESIN METHOD

Sample No.	Activity (Bq)	% recovery of ^{243}Am tracer
EML method		
QAP-9303R-AF-BLK-1	0.0002 ± 0.0025	68.6 ± 4.0
QAP-9303R-AF-51	0.0434 ± 0.0025	71.3 ± 4.1
QAP-9303R-AF-141	0.0394 ± 0.0024	73.5 ± 4.5
QAP-9303R-AF-191	0.0434 ± 0.0025	70.7 ± 4.1
TRU Resin method		
QAP-9303R-AF-BLK-2	0.0002 ± 0.0001	80.0 ± 3.2
QAP-9303R-AF-81	0.0395 ± 0.0021	86.7 ± 3.5
QAP-9303R-AF-101	0.0399 ± 0.0021	83.5 ± 3.3
QAP-9303R-AF-161	0.0425 ± 0.0022	79.6 ± 3.2

The average value of ^{241}Am activity per filter using the standard method was 0.0421±0.023 Bq ^{241}Am, while the modified procedure resulted in the average value equal to 0.0406 ± 0.0016 Bq ^{241}Am per filter. These two values differ from each other by 3.6%, which is within 1 σ of either result.

The second test of this procedure was conducted using QAP-9309-AF and QAP-9309-Wa samples. The overall sequence of steps was slightly altered in order to save time without compromising the integrity of the test. Only three air filters and only three aliquots of QAP-Wa (150 mL, 100 mL, and 200 mL) were analyzed for plutonium. Each eluate from the ion-exchange column was brought to ~100 mL and placed in a preweighed flask with a ground-glass stopper. About half of each solution was transferred to another flask and the first flask was weighed again. Aliquot A was then analyzed for americium using the standard method, and aliquot B was analyzed for americium using the TRU Resin. The results obtained from α spectrometry had only to be multiplied by an appropriate gravimetric factor to give results in terms of activity per filter or per 1 L of water. The individual results of the americium determination using both methods are presented in Table 7 for air filters and Table 8 for water.

The lowest recovery of the added tracer for the standard method approached 70%, while for the TRU Resin method it never went below 80%.

In the third test of this procedure, samples of QAP-8305-AF and QAP-9303-Wa were analyzed and compared with the results available from previous determinations. Both sets of results are included in

Table 9. The results for QAP-9303-Wa using the Am-01 procedure were obtained by two analysts. The overall agreement between the two methods is excellent.

In the next stage of the validation process, other analysts in the laboratory were asked to use the new procedure and their results were compared with the standard method results. Two water samples (QAP-9409 and QAP-9503) and one set of air filter samples (QAP-9409) were analyzed. These results are also included in Table 9. The reported result with its associated standard deviation is the average of triplicate analysis. As was the case with a single analyst performing both sets of determinations (see QAP-9303R-AF, QAP-9309-AF and QAP-9309-Wa), no significant bias was observed.

This procedure represents tremendous savings in time and in the type and volume of the generated waste. While the existing americium procedure can take several weeks (minimum of 15 working days), the use of TRU Resin shortens this time to no more than 5 working days. The generated waste per column is limited to 23 mL of the 1M HNO_3 and 8 mL of the 2M HNO_3 solutions used to rinse the TRU Resin.

It is important to note that this procedure cannot be used on matrices with lanthanides present. The lanthanides will follow americium (and curium, which typically stays with americium) all the way through the microprecipitation and will seriously affect the resolution of the α spectrograph.

TABLE 7

COMPARISON OF ^{241}Am DETERMINATION IN QAP-9309-AF USING STANDARD EML METHOD AND THE TRU RESIN METHOD

Sample No.	Activity (Bq)	% recovery of ^{243}Am tracer
EML method - AliquotA		
Q93-AF-BLK	0.0001 ± 0.0002	30.2 ± 4.7
Q93-AF-062	0.0726 ± 0.0041	83.2 ± 4.7
Q93-AF-063	0.0618 ± 0.0036	91.2 ± 5.3
Q93-AF-064	0.0722 ± 0.0042	80.2 ± 4.7
TRU·Resin method - B		
Q93-AF-062	0.064 ± 0.003	92.5 ± 3.0
Q93-AF-063	0.068 ± 0.004	86.0 ± 2.8
Q93-AF-064	0.067 ± 0.004	81.6 ± 2.4

TABLE 8

COMPARISON OF ^{241}Am DETERMINATION IN QAP-9309-Wa USING STANDARD EML METHOD AND THE TRU RESIN METHOD

Sample No.	Activity (Bq L^{-1})	% recovery of ^{243}Am tracer
EML method - aliquot A		
Q93-Wa-BLK	0.0003 ± 0.0002	72.2 ± 1.5
Q93-Wa-043	1.44 ± 0.04	86.3 ± 1.7
Q93-Wa-044	1.20 ± 0.06	81.1 ± 2.1
Q93-Wa-045	1.33 ± 0.04	74.1 ± 1.4
TRU Resin method - aliquot B		
Q93-Wa-BLK	0.0002 ± 0.0002	81.6 ± 2.0
Q93-Wa-043	1.43 ± 0.04	94.4 ± 1.7
Q93-Wa-044	1.39 ± 0.06	89.2 ± 2.3
Q93-Wa-045	1.33 ± 0.04	89.9 ± 2.0

TABLE 9

COMPARISON OF THE RESULTS OF ^{241}Am DETERMINATION IN WATER AND AIR FILTERS USING TWO METHODS

Sample description	Am-01 procedure (modified)	TRU Resin procedure	EML value
Air filter (mBq filter^{-1})			
8305	130.0 ± 8.00	137.4 ± 1.4	130.0 ± 8.0
9303R	42.1 ± 2.3	40.6 ± 1.6	41.4 ± 2.0
9309	65.4 ± 6.0	66.3 ± 2.1	65.4 ± 6.0
9409	209.0 ± 6.00	214.0 ± 0.9	212.0 ± 9.0
Water (Bq L^{-1})			
9303	0.460 ± 0.100	0.501 ± 0.015	0.460 ± 0.10
9309	1.388 ± 0.057	1.383 ± 0.050	1.390 ± 0.06
9409	1.040 ± 0.060	1.010 ± 0.060	1.010 ± 0.06
9503	1.350 ± 0.010	1.320 ± 0.110	N/A

[a]Sanderson et al., (1995)

SUMMARY AND CONCLUSIONS

When CMPO was first introduced (Horwitz et al., 1990) as an extraction material specific for actinides, its use was limited to gross determinations of all actinides present in a sample. Because the recoveries were believed to be consistently above 90%, no tracers were needed and the actinides could be eluted from the extraction column and electroplated in preparation for gross α counting or α spectrometry. Since the whole process, when applied to urine samples, could be easily completed in 3 days, this method was offered as a reliable and inexpensive way of monitoring workers for exposure to actinide elements (Nelson and Fairman, 1990). EIChroM Industries further developed this approach further and introduced a commercially available extraction chromatographic material with CMPO as the active component. This material, called TRU Resin, was expected to have two characteristics that could be of importance to EML. First, the overall efficiency of extraction of actinides from the sample, followed by desorption and electroplating in order to prepare the sample for α spectrometry, should be very close to 100% so that tracers would not have to be used. Second, different eluting solutions could be used to selectively strip the column of the actinides present and thus achieve their separation from each other with the use of a single column. An extraction and separation scheme for determination of plutonium, americium, and natural uranium in QAP-Wa was proposed, which would allow us to test the validity of both of these claims.

The first study was directed at determining conditions under which fractions eluted from the column would be chemically pure, that is, with a single actinide element present in a given fraction. The crossover

of plutonium into the americium fraction was persistent and none of the steps tried were sufficiently successful. Adjustment of the plutonium oxidation state was tried on the assumption that the oxidation state of plutonium was affecting the extent of the crossover. Horwitz et al., (1990) made a single attempt to eliminate the crossover of plutonium into the americium fraction and did not succeed. We conclude that the crossover is primarily a function of something other than the oxidation state of plutonium. A different separation scheme could be tried, but that is beyond the scope of this study. One approach was tested, that took advantage of the fairly constant fraction of plutonium appearing in the americium fraction. This so called "double treatment" of the americium fraction resulted in a definite reduction of the extent of the crossover (from ~5% to less than 0.2%), but this approach is of limited use and its scope would have to be investigated further.

The new procedure for determination of americium in QAP-Wa and QAP-AF, which combined removal (and possible determination) of plutonium using an anion-exchange column with the use of TRU resin for extraction and isolation of americium has been shown to be very promising. Once all the techniques necessary were mastered and optimized, the recoveries for americium were always greater than 80% (Tables 6, 7, and 8). If this method were to be used for screening purposes only, addition of a tracer could be eliminated. However, when the acceptable error of the determination is less than 5%, a tracer has to be introduced in order to correct for chemical losses. The accuracy of the new method is within 1 σ of the results obtained by the routine method used at EML (see Table 9).

This procedure allows for sequential determination of very low levels of plutonium and americium in water and air filters, which are matrices prepared in EML's QAP. The LLD for americium calculated using the approach described in the EML Procedures Manual (Chieco et al., 1992) (assuming the counter efficiency of ~30%, the detector background in the region of interest (ROI) for americium of 1.6×10^{-5} counts sec^{-1}, and the expected chemical recovery of 80%) is equal to 0.1 mBq for a 5000 min count. Real aqueous samples, such as sea water, might behave somewhat differently due to a higher concentration of inorganic ions. Because this method represents tremendous savings both in time needed as well as in waste generated, it should be tested on as broad a range of real samples as possible.

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APPENDIX A

Am-04
AMERICIUM IN QAP WATER AND AIR FILTERS - EICHROM'S TRU RESIN

APPLICATION

The following procedure has been applied to the preparation, separation, and analysis of spiked water and air filter samples that contain americium but not lanthanides (Berne, 1995). Lanthanides, if present, will not be removed by this method and will significantly reduce the resolution of the α-spectrograph. Combined with Procedure Pu-11,* this procedure allows for the sequential determination of plutonium and americium. Other researchers have applied TRU Resin methods to other matrices (Horowitz et al., 1990). The procedure is used in the EML Quality Assessment Program (QAP) (Sanderson et al., 1995).

The water and air filters are equilibrated with ^{243}Am and processed through the plutonium separation steps using ion exchange resin according to Procedure Pu-11.* If determination of plutonium is desired, an appropriate plutonium tracer should be added along with the ^{243}Am tracer. The eluate from the ion exchange column containing americium (and all other ions, except plutonium) is evaporated, redissolved, and loaded onto a TRU Resin extraction column. The americium (and curium, if present) is separated and purified on the column and finally stripped with dilute nitric acid stripping solution. Microprecipitation is used to prepare for α spectrometry.

SPECIAL REAGENTS

1. EICHROM'S TRU Resin, ion extraction resin, particle size 100-150 µm, Eichrom Industries, Inc., Darien, IL 60561.

2. Column feed solution, 0.5M $Al(NO_3)_3$ in 2M HNO_3 - place 18.76 g of $Al(NO_3)_3 \cdot 9H_2O$ in a 100-mL volumetric flask and add 2M HNO_3 to the mark. Shake to mix thoroughly.

3. 2M HNO_3 - 125 mL HNO_3 diluted to 1 L with H_2O.

4. 1M HNO_3 - 62.5 mL HNO_3 diluted to 1 L with H_2O.

5. 0.025M HNO_3 - 25 mL 1M HNO_3 diluted to 1 L with H_2O.

6. Eichrom's TRU Resin column or equivalent - 2 mL columns from Eichrom Industries or can be prepared from TRU Resin. Place a plug of glass wool in the bottom of polyethylene transfer pipette such as a 3.2 mL bulb draw transfer pipette ((Cat. No. 224, manufactured by Saint - Amand Mfg. Co., Inc. (SAMCO®) San Fernando, CA 91340 U.S.A.)). Add slurried TRU Resin (0.5 g). Assemble immediately before use.

* EML Procedures Manual, HASL-300, 27th Edition, February (1992)

DETERMINATION

See Plutonium Purification - Ion Exchange Technique, Procedure Plutonium-11.*

ION EXTRACTION SEPARATION

1. Collect the sample and the wash effluent from Step 4, Ion Exchange Separation, Procedure Pu-11,* and evaporate almost to dryness. If necessary, sometime during the evaporation process transfer the solution to a smaller beaker. The final residue should be contained in a beaker not larger than 50 mL. Add 3 mL of 0.5M $Al(NO_3)_3$ in 2M HNO_3 to each residue and heat very gently to dissolve.

2. Prepare ion extraction column.

3. Wash the resin with 15 mL of 2M HNO_3, and discard the effluent.

4. Load the column with the sample solution from Step 1. Wash the beaker with 3 mL of column-feed solution and add to the column. Discard the effluent.

5. Rinse the column with 8 mL of 2M HNO_3, followed by 8 mL of 1M HNO_3, and discard the effluent.

6. Elute the americium fraction with three 3-mL aliquots of 0.025M HNO_3 and collect the eluate in a 50-mL beaker.

7. Evaporate the eluate to dryness. Convert the residue to the chloride form by adding 5 mL of HCl three times and evaporating to dryness at a low temperature.

8. Prepare the sample for α spectrometry by microprecipitation (see Procedure G-03).*

DATA PROCESSING AND ANALYSIS

For α spectrometry, see Alpha Radioassay, Procedure 4.5.2.1.*

LOWER LIMIT OF DETECTION (LLD)[+]

The LLD is calculated according to procedures found in the EML Procedure Manual, Section 4.5.3.2.*

Counter Efficiency	(%)	30
Counter Background	(cps)	$1.6x10^{-5}$
Recovery	(%)	80
Blank	(cps)	-
LLD (400 min)	(mBq)	0.5
LLD (1000 min)	(mBq)	0.3
LLD (5000 min)	(mBq)	0.1

[+] Reagent blanks must be analyzed with each set of samples.

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APPENDIX B

ADAPTATION OF THE Am-01 PROCEDURE* TO WATER AND AIR FILTERS

APPLICATION

This procedure is applicable to water and air filters.

Americium and plutonium tracers are added to the sample and a procedure for plutonium, appropriate to the matrix, is followed. The last step in each procedure will be the ion-exchange technique for the purification of plutonium (see Procedure Pu-11).* The eluate from Step 4 is combined with the eluate from Step 8. Americium is coprecipitated with calcium oxalate, followed by coprecipitation with iron hydroxide. The acidified iron hydroxide solution is loaded onto an ion-exchange column to assure a complete removal of any traces of plutonium, followed by another ion-exchange column designed to remove iron. The eluate from the last column is evaporated, converted to HCl and microprecipitated on NDF_3 and the ^{241}Am plus the ^{243}Am tracer are resolved by α spectrometry.

SPECIAL APPARATUS

1. Ion-exchange columns - see Specification 7.5.*

SPECIAL REAGENTS

1. ^{243}Am tracer solution, about 0.20 Bq g^{-1}, in a dispensing bottle.

2. Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4.*

3. Bio-Rad AG 1-X8 resin (50-100 mesh) - see Specification 7.4.*

4. Calcium carrier solution, 100 mg Ca mL^{-1} - dissolve 25 g $CaCO_3$ in a minimum of HNO_3 and dilute to 100 mL.

5. Iron carrier solution, 100 mg Fe mL^{-1} - slowly heat 100 g of iron powder in 500 mL HCl until reaction ceases. Carefully and slowly add 100 mL HNO_3 while stirring. Cool and dilute to 1 L.

6. Oxalate wash solution - dissolve 10 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) to make 1 L of solution (~ 1% solution).

*EML Procedures Manual, HASL-300, 27th Edition, February (1992)

PROCEDURE

1. Combine eluates from Steps 4 and 8 from Plutonium-11* in a beaker. Evaporate to dryness. Dissolve the residue in 5 mL 7.5M HNO_3, add 45 mL H_2O and stir.

2. Add 1 mL of Ca carrier solution (100 mg Ca) and 2.5 g (50 g L^{-1}) oxalic acid to the sample while stirring with a magnetic stirrer.

3. Adjust the pH of the solution to 2.5-3.5 with NH_4OH using pH paper as an indicator and continue to stir for 30 min. Remove magnetic stirrer.

4. Cool and let stand overnight or for more than 6 h. Check for completeness of precipitation using a drop of saturated oxalic acid solution.

5. Aspirate (or decant) as much liquid as possible without disturbing the precipitate. Transfer precipitate to a 250-mL centrifuge bottle using oxalate wash solution. Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Decant and discard the supernate.

6. Break up the precipitate with a stirring rod and wash the precipitate with the oxalate wash solution. Centrifuge, decant and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount of HNO_3 and transfer the solution quantitatively to a beaker. Heat to destroy the oxalate ion.

7. Dissolve the wet-ashed residue in 5 mL of 7.5M HNO_3 and transfer to a 40-mL centrifuge tube, using H_2O to complete transfer and dilute to 25 mL of solution. Warm the solution in a 90° hot water bath and add 0.1 mL iron carrier solution (10 mg Fe).

8. With the centrifuge tube in the hot water bath adjacent to a hood, adjust the pH of the solution to 8-9 with NH_4OH while stirring with a glass rod. Allow solution to digest in hot water bath for 20 min.

9. Cool in a cold water bath, rinse and remove the glass rod. Centrifuge for 10 min at 2000 rpm.

10. Decant (or aspirate) and discard the supernate. Add 5 drops HCl to dissolve the $Fe(OH)_3$ pellet followed by 25 mL H_2O. Heat the solution in a hot water bath.

11. Repeat Steps 8,9 and 10 three times. Redissolve the final precipitate in 7.5M HNO_3.

12. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL 7.5M HNO_3 and evaporate to dryness again.

13. Dissolve the dry residue immediately in 40 mL 7.5M HNO_3. Cool in an ice-water bath. Add 0.6-1.0 g $NH_2OH{\cdot}HCl$, dissolve and let react for 15 min. Heat on low temperature hot plate to decompose unreacted $NH_2OH{\cdot}HCl$, then bring to gentle boil for 1-2 min. Cool and pass the solution through a 7.5M HNO_3 ion-exchange column (see Note 1). Adjust the rate of elution to ~0.5 mL min^{-1}. Collect the effluent in a 400-mL beaker. Wash with 150 mL 7.5M HNO_3 and collect the effluent in the 400-mL beaker.

14. Evaporate the sample to dryness and treat several times with small volumes of HCl. Dissolve the final residue in 30 mL of HCl. Pass this solution through a 12M HCl ion-exchange column (see Note 2). Collect the effluent in a 250-mL beaker. Wash with 100 mL of HCl, and collect in the 250-mL beaker.

15. Evaporate to dryness. Dissolve the residue in 1-2 mL 1M HCl.

16. See Procedure G-03* for microprecipitation source preparation for α spectrometry.

17. Submit the sample for α spectrometry measurement.

Notes:

1. Preparation of 7.5M HNO_3 Column. Position a plug of glass wool at the base of a small column (i.d. 11 mm). Transfer 10 mL of wet settled Bio-Rad AG-X8 resin (50-100 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the H_2O to reach the level of the upper plug. Wash the column with 40 mL of H_2O, followed by 300 mL of 7.5M HNO_3, passed through the resin bed in 50-mL portions. Allow the level of each portion to reach the top of the upper plug. The conversion of the resin is complete if the effluent from the column tests negative for Cl^- using a dilute silver nitrate solution.

2. Preparation of HCl Column. Position a plug of glass wool at the base of a small column (i.d. 11 mm). Transfer 10 mL of wet settled Bio-Rad AG-X4 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the H_2O level to reach the level of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass plug. Make sure to run this column in a vented hood.

DATA PROCESSING AND ANALYSIS

For α spectrometry measurements, see Procedure 4.5.2.*