Automated extraction chromatographic separations of actinides using separation-optimized sequential injection techniques

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A sequential injection (SI) separation system has been developed for automated analytical separations of actinides using an actinide specific extraction chromatographic material (TRU-resin, Eichrom Industries, Inc., USA). On-line liquid scintillation counting was used to observe eluting species during method development, and fraction collection and alpha energy analysis were used for quantification. Several procedures for individual and group actinide elution are demonstrated and discussed, including elution of actinides as a single group; elution as groups based on valence state; selective separation of Pu using on-column redox chemistry; selective separation of Th; and various sequential actinide elution schemes. Eluent solution compositions and reagent chemistries were investigated with regard to elution peak shapes, selectivity, recoveries, carryover, and suitability for rapid automated procedures. The SI separation methods described serve as the basis for an automated actinide separation work station. An automated actinide separation procedure has been applied towards the analysis of Am, Cm, and Pu isotopes in three types of aged nuclear waste samples. Results from automated analytical separations followed by quantification by alpha spectroscopy were in good agreement with results obtained using manual separation techniques.

Introduction

Environmental restoration of the radioactively contaminated sites and processing of stored radioactive wastes require reliable radioanalytical characterization methods.[1] Determination of actinide isotopes in nuclear waste is important due to their long radioactive half-lives, high radiological toxicities, and criticality concerns. In addition, actinide isotope determinations are necessary for waste classification purposes.[2] Actinide analyses typically require preconcentration and separation from excess inactive matrix components and highly radioactive fission products. Group and/or individual actinide separations are required because a number of important actinide isotopes have unresolvable alpha-energies (*e.g.*, ^{241}Am /^{238}Pu) or have mass to charge ratios that are indistinguishable by low resolution mass spectrometric techniques (*e.g.* ^{241}Am/^{241}Pu, ^{238}Pu/^{238}U, *etc*.) Therefore, the development of improved analytical separation methods for actinide elements is of interest.

Recently, various extraction chromatographic methods have been developed by Horwitz and co-workers at the Argonne National Laboratory (USA) to simplify and improve the chemical separations required in radiochemical analyses.[3–8] Impregnation of macroreticular polymer beads with a solution of a neutral bifunctional organophosphorus complexant, octyl-(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in tri-*n*-butyl phosphate (TBP), yielded an actinide specific sorbent material now called TRU-resin (Eichrom Industries, Inc., USA).[3,6,9] Nitrato complexes of tri-, tetra- and hexavalent actinides are strongly and nearly selectively extracted from nitric acid solutions by the CMPO–TBP stationary organic phase on TRU-resin, with retention increasing with greater aqueous phase nitric acid concentration. Chloro complexes of tetravalent and hexavalent actinides, but not trivalent actinides, are extracted from hydrochloric acid solutions. Actinides retained on TRU-resin columns can be recovered, individually or in groups, by eluting with acidic solutions, complexants, or redox reagents.

TRU-resin can be utilized for a number of analytical purposes, including separation of the actinides as a group from a sample matrix; group actinide separations based on the valence state; individual separation of Am/Cm and Pu from each other and other actinides; and possibly the sequential separation of individual actinides on a single TRU-resin column.[1,3,6,9–12] In a number of radiochemical procedures, TRU-resin has been utilized in combination with other extraction chromatographic materials such as Actinide-resin, UTEVA-resin, and TEVA-resin (Eichrom).[5,7,12,13] The use of TRU-resin for analyses of nuclear waste samples, enviromental samples, and biological samples has been described.[1,3,6,7,9,14,15]

In a typical manual extraction chromatographic separation, samples and various eluents are added to the top of an open column operated under gravity flow, and fractions are collected for subsequent radioactivity measurement or additional separations. Vacuum manifolds for solid phase extraction (SPE) are sometimes used to speed up the separation.[7] Despite significant improvement over classical radiochemical separation procedures based on combinations of precipitation, solvent extraction, and ion exchange steps, the extraction chromatographic separation format remains somewhat tedious when performed manually, and the analyst is exposed to the open sources of radioactivity. It would be advantageous to perform these separations in an automated closed-column format.

Though known primarily for automating simple chemical analyses, flow injection (FI) and sequential injection (SI) techniques provide a very versatile fluid handling approach that can be used to automate chemical separations.[16–19] In several recent reports, FI and SI methods have been demonstrated as

useful approaches for automating extraction chromatographic separations of radionuclides prior to detection by inductively coupled plasma mass spectrometry (ICPMS) or radiometric methods.[19–27] In one of our own recent reports, we described the use of a continuous-forward-flow FI instrument with an on-line liquid scintillation detector to investigate the separation of Am and Pu using a TRU-resin column.[25] Particular attention was paid to the on-column redox chemistries involved in adjusting the Pu speciation from the trivalent to the tetravalent and back to the trivalent states. No nuclear waste samples were analyzed in this study.

SI techniques represent a more recent approach to flow analysis[18,28] that has been demonstrated for automated extraction chromatographic separations and analyses of ^{99}Tc and ^{90}Sr in aged nuclear waste samples.[23,26,27] These separations involve loading the sample on an extraction chromatographic column, washing away matrix and interfering species while the desired analyte is retained, and then eluting the analyte with another solution. These procedures are most effectively carried out using a 'separation-optimized' SI methodology for solution handling.[19,23,26] This approach supercedes an initial report where conventional 'stacked-zone' SI methods were used to load the required sample, wash and eluent solutions into a holding coil.[22] In the separation-optimized SI method, each eluent solution is loaded into a wide-bore holding coil at a high flow rate, and then immediately dispensed prior to loading and dispensing the next solution. An air segment between each solution and the carrier fluid prevents dispersion. This method provides rapid manipulation of milliliter quantities of discrete solution compositions for column separation procedures.

The separation-optimized SI approach is well suited for the automation of more challenging extraction chromatographic separations of actinide elements involving multiple eluent and reagent solutions. In this report we investigate and demonstrate a number of automated group and individual actinide separations on TRU-resin in a SI format. The SI separation methods described can serve as the basis for an automated actinide separation work station. On-line liquid scintillation counting was used during procedure development to observe eluting species. Fraction collection and alpha energy analysis were used for quantification. Alpha spectrometry is a standard method of analyzing separated actinides that provides isotopic information. Isotopic, as opposed to elemental information, is required because different isotopes have different half-lives, specific activities, and fissile properties. Activities of individual alpha-emitting isotopes are required for waste classification, for bioassay purposes, and for assessing criticality issues. In this paper, the SI automated separation method is applied to the determination of Am, Cm, and Pu isotopes in three types of aged nuclear waste samples.

Experimental

Reagents, standards and nuclear waste samples

All reagents used were of analytical grade. Deionized water (18 MΩ cm^{-1}) was obtained from a Barnstead E-Pure (Thermolyne Corporation, Dubuque, IA, USA) water purification system and was used for all dilutions. A 0.02 mol l^{-1} Ti(III) chloride reagent solution in 4 mol l^{-1} HCl was prepared daily by an appropriate dilution of a 20% stabilized solution (EM Science, Gibbstown, NJ, USA). A 0.05 mol l^{-1} Fe(II) sulfamate–ascorbic acid reagent in 4 mol l^{-1} HCl was prepared daily by dissolving required amount of $FeCl_2.4H_20$ (Sigma, St. Louis, MO, USA) in 0.1 mol l^{-1} solution of ascorbic and sulfamic acids in 4 mol l^{-1} HCl. A 0.5 mol l^{-1} solution of sodium nitrite in water, utilized for Pu oxidation, was prepared fresh weekly. The scintillation cocktail used with the flow-through detector was Ultima Flo-M (Packard, Downers Grove, IL, USA). Ultima Gold (Packard) was used in static LS measurements.

Solutions of radionuclide tracers (^{90}Sr,^{137}Cs, ^{241,243}Am, ^{239,242}Pu, ^{230}Th, ^{233}U) were obtained from in-house standards laboratory. Neptunium-239 source was obtained from "milking" ^{243}Am source fixed on a small TRU-resin column.

Nuclear waste samples used in this study included vitrified glass waste, aged irradiated nuclear fuel (K-basin sludge samples, Hanford site, USA), and waste samples derived from the high-level waste storage tanks located at the Hanford site (tank waste supernate). The samples were obtained as dilute processed solutions after the initial sample preparation steps were performed in shielded analytical facilities (hot cells). The initial sample preparation steps and manual analysis procedures have been described previously.[11,22,23,26]

Apparatus

Sequential injection system. An actinide separation instrument, shown schematically in Fig. 1, was configured using a FIALab 3000 (Alitea USA, Medina, WA, USA) sequential injection system equipped with a 24 000 step digital syringe pump (syringe volume 10 ml) and 14 port multiposition valve (Cheminert low-pressure valve, Valco Instruments Co, Inc., Houston, TX, USA). The holding coil was constructed from 1.6 mm id FEP Teflon tubing (Upchurch Scientific, Oak Harbor, WA, USA) of 6 m length (calculated volume 12 ml). All transport and reagent lines were made of 0.76 mm id FEP Teflon tubing (Upchurch Scientific). Sample lines were made of 0.5 mm id FEP Teflon tubing. The size of the columns used in this study was 4 mm id × 50 mm (calculated bed volume 0.63 ml). The columns were constructed of parts from the Omega-Chrom column system (Upchurch Scientific) and frits from the Quick-Snap column system (IsoLab, Inc., Akron, OH, USA). TRU-resin (Eichrom Industries, Inc., Darien, IL, USA) sorbent extraction material of 20–50 μm particle size was slurried in water and packed into the column under slight pressure using a 10 ml syringe. The free column volume (FCV) of the TRU-resin column was 0.42 ml (gravimetric measurement). Separation experiments were performed using freshly packed columns unless indicated otherwise. Dye dispersion measurements were conducted using a SPD10AV UV-Vis detector (Shimadzu) positioned in place of the sorbent column. The SI system was controlled *via* a serial cable using FIALab software (Alitea USA) running on a lap-top PC.

Radioactivity measurements and fraction collection. The on-line flow-through liquid scintillation detector, a Radiomatic™ 515A (Packard Instrument Company, Meriden, CT, USA) was configured with a 0.5 ml flow cell and operated as described previously.[22] The detector integration time (time to

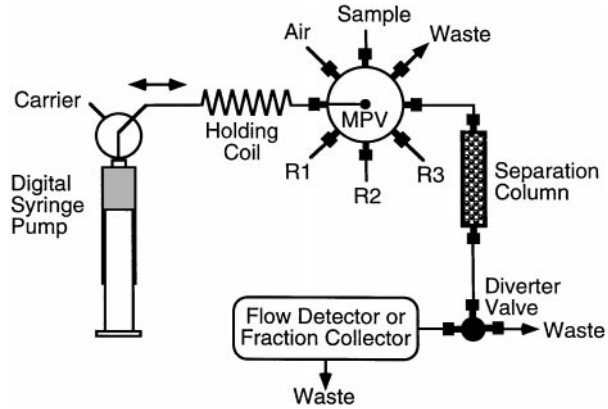

Fig. 1 Schematic diagram of the sequential injection actinide separation instrument. R1, R2, and R3 denote reagents.

accumulate counts for each data point reported) was 6 s. For the off-line radioactivity measurements, the column outlet transport line was connected to a programmable FC205 (Gilson, Middleton WI, USA) fraction collector equipped with a two-way diverter valve. Packard Tri Carb 2550 TR/AB liquid scintillation spectrometer (Packard) was used for off-line liquid scintillation measurements. Alpha spectrometry was performed using 450 mm^2 Ortec semiconductor ion implanted detectors (EG&G Ortec, Oak Ridge, TN, USA) equipped with Canberra electronics and data acquisition system. Samples for alpha spectroscopy were prepared using NdF_3 microprecipitation procedure.[11] Gamma spectroscopy was performed using high-purity germanium detectors (HPGe) detectors (Oxford Instruments, Oak Ridge, TN; and Canberra Industries, Meridien, CT, USA) equipped with Canberra electronics and data acquisition system (Canberra Industries).

Procedures

SI solution handling. The SI separation instrument, shown schematically in Fig. 1, was set up to deliver various sample and eluent solutions to a TRU-resin column and transport the separated species to either an on-line detector during procedure development or to a fraction collector for off-line sample analysis. A wide-bore holding coil (1.6 mm id) facilitated the rapid loading of large solution volumes into the holding coil at 10 ml min^{-1} without outgassing. Dispersion in the wide bore holding coil was eliminated by introducing a 100 μl air segment between the carrier (0.3 mol l^{-1} nitric acid) and the selected solution. This separation-optimized fluid handling approach has been described in detail in previous papers.[19,23,26] Solution delivery for the column conditioning, sample load, column wash, and various actinide elution steps are detailed in Table 1. Aspiration flow rates were 10 ml min^{-1} except for the sample solutions, which were loaded into the holding coil at 1 ml min^{-1}. Solutions were delivered to the column at 2 ml min^{-1}, except for the column conditioning step, which was performed at 3 ml min^{-1}.

Sample load matrix for TRU-resin separations. Prior to the separation, 1 mol l^{-1} $Fe(NO_3)_3$ solution in 2 mol l^{-1} HNO_3, and solid sulfamic and ascorbic acids were added to the sample solution in 2 mol l^{-1} nitric acid to give a resulting solution containing 0.05 mol l^{-1} Fe, 0.1 mol l^{-1}sulfamic acid, and 0.1 mol l^{-1} ascorbic acid. This treatment was used to reduce any Fe(III) species to Fe(II) and ensure that all Np is present as Np(IV) and fix all the Pu in a single oxidation state of +III.

Table 1 Reagent delivery procedures for the automated actinide separations

Condition/Load/Wash Sequences[a]—	
Column conditioning	2 ml 2 mol l^{-1} HNO_3
Sample load	0.1–1 ml
Column wash–Pu oxidation	(1) 2 ml 2 mol l^{-1} HNO_3 (2) 0.15 ml 2 mol l^{-1} HNO_3–0.15 ml 0.5 mol l^{-1} $NaNO_2$–8 ml 2 mol l^{-1} HNO_3
Column wash without Pu oxidation	10 ml 2 mol l^{-1} HNO_3
Actinide Elution Sequences—	
Group actinide elution	7 ml 0.1 mol l^{-1} $NH_4HC_2O_4$
Trivalent actinide elution[b]	5 (10 ml) 4 mol l^{-1} HCl
Pu reduction-elution[c]	7 (10 ml) reductant in 4 mol l^{-1} HCl
Tetravalent actinide elution	7 ml 1 mol l^{-1} HCl–0.05 mol l^{-1} $H_2C_2O_4$
Hexavalent actinides (U) elution	7 ml 0.1 mol l^{-1} $NH_4HC_2O_4$

[a] 4 × 50 mm sorbent column; separation flow rate 2 ml min^{-1}. [b] 5 ml Used with on-line detection; 10 ml used with fraction collection. [c] 7 ml Used with on-line detection; 10 ml used with fraction collection.

On-column Pu oxidation. To perform on-column Pu oxidation during the column wash, acidic nitrite wash solution was prepared fresh on-line by first aspirating the required volume of 2 mol l^{-1}nitric acid column wash (nominally 8 ml), and then aspirating 150 μl of 0.5 mol l^{-1} $NaNO_2$ in water, followed by an additional 150 μl of 2 mol l^{-1} nitric acid. With this sequence, the 2 mol l^{-1} nitric acid column wash solution is never diluted by the aqueous nitrite more than by a factor of 2 (as established in prior dye injection experiments), thus maintaining the nitric acid concentration in the range required to retain actinides on the column during the wash step.[25]

Nuclear waste sample analysis. Each analytical sample batch included quality control samples consisting of two blank samples, and a blank sample spiked with the known amounts of ^{241}Am and ^{239}Pu. Known amounts of ^{243}Am and ^{242}Pu were added to each solution in order to trace the overall recovery of the analysis procedure. The recovery tracer approach using these isotopes is valid because the ^{243}Am and ^{242}Pu activity in these samples is negligibly low relative to that of ^{241}Am and $^{239,240}Pu$ and the activity of the ^{243}Am and ^{242}Pu spikes added. Following the addition of spikes, the samples were evaporated to moist dryness and redissolved in 2 mol l^{-1} HNO_3. Just prior to the separation, the samples were subjected to reductive treatment as described in Experimental.

Following the TRU-resin column conditioning and sample load steps (injected sample volume 1 ml), the column wash/Pu oxidation sequence was applied (see Table 1). Next trivalent actinides were eluted with 10 ml 4 mol l^{-1} HCl, followed by the selective Pu reduction–elution using 10 ml of the reducing eluent. A 4 mol l^{-1} HCl solution of 0.02 mol l^{-1} Ti(III) chloride was used as Pu eluent in the analysis of K-basin samples; 4 mol l^{-1} HCl solution of 0.05 mol l^{-1} Fe(II) 0.1 mol l^{-1} sulfamic–0.1 mol l^{-1} ascorbic acid was used to elute Pu in the analysis of tank waste and vitrified waste samples. The separations were performed using freshly packed columns, which were replaced after the Pu elution step.

Results and discussion

Removal of the sample matrix

All the actinide separations to be described begin by retaining actinides on the TRU-resin column and removing unretained species in the column wash. Nitric acid solutions are used for these steps. Capacity factors, k', range from ~100 for least retained Am(III) to over 10^4 for the most strongly retained tetravalent actinides at nitric acid concentrations exceeding 1 mol l^{-1}.[3,9] The predominant radioactive species in aged nuclear waste that are removed in the column wash are the gamma and beta emitting fission products, ^{137}Cs and $^{90}Sr/^{90}Y$. Initial elution of these species in the column wash step is shown in Fig. 2.

Sr and Cs ions are unretained on TRU-resin in 2 mol l^{-1} nitric acid. Using fraction collection, we established that a column wash using 4 ml (10 FCV) of 2 mol l^{-1} nitric acid was sufficient to provide decontamination factors exceeding 10^3 for ^{137}Cs and 10^4 for ^{90}Sr. Yttrium showed noticeable retention (see Fig. 2) corresponding to capacity factor k' ~11 in 2 mol l^{-1} nitric acid. Yttrium removal is virtually complete with 24 FCV (10 ml) of 2 mol l^{-1} nitric acid wash. Fraction collection experiments indicated that 99.9% of ^{90}Y originally present in the sample is removed using 10 ml of the 2 mol l^{-1} nitric acid wash.

These fission products account for the majority of the activity of aged high level nuclear waste samples. The removal of the radioactive fission product matrix simplifies subsequent handling and processing of the separated actinide fractions, whose content must be quantified by radiometric or mass spectrometric methods.

Elution of actinides as a single group

Following the sample load and column wash with 2 mol l^{-1} nitric acid, actinides can be eluted as a single group using 0.1 mol l^{-1} ammonium bioxalate complexing eluent.[3,9] Rapid separation of actinides from the sample matrix is useful in a number of analytical applications including the determination of the gross actinide content (actinide screen).[9,11] The detector trace in Fig. 2A illustrates a SI group actinide separation procedure applied to a vitrified nuclear waste sample spiked with ^{241}Am, ^{230}Th, and ^{233}U. These spikes, representative of actinides in trivalent(Am), tetravalent(Th), and hexavalent(U) oxidation states were added to facilitate the observation of elution profiles *via* on-line detection. Following the sample load step, the column was washed with 10 ml (24 FCV) of 2 mol l^{-1} nitric acid in order to remove stable and radioactive sample matrix. The actinides were efficiently eluted using 7 ml of 0.1 mol l^{-1} ammonium bioxalate with nominal recoveries of 85–100%. Recoveries were established in separate experiments with fraction collection and off-line detection). An immediate blank run following the spiked nuclear waste sample indicated carryover of 0.3% of the original alpha activity. The carryover in the second and third blank runs using the same column was 0.04% . The carryover was predominantly due to ^{233}U. Provided that this carryover is acceptable for a given application, columns can be reused multiple times as noted by the previous authors.[20,21]

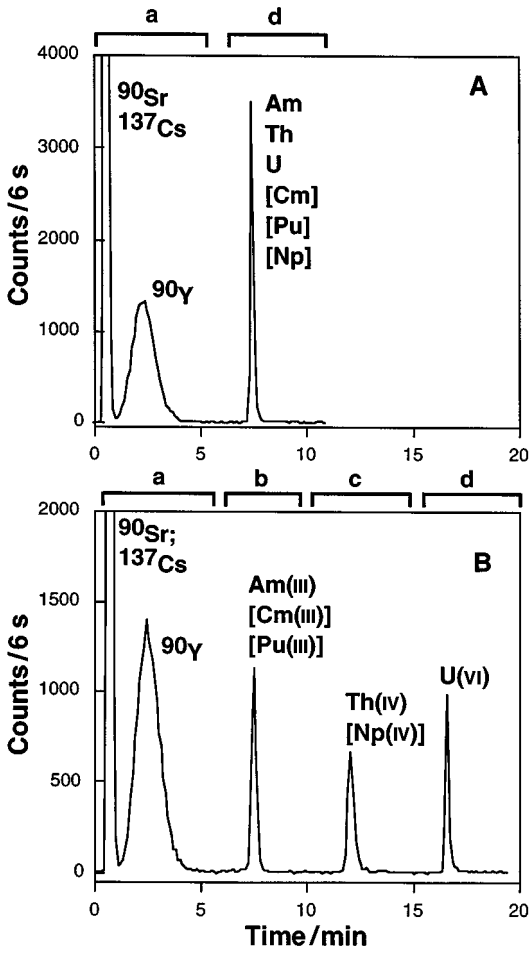

Fig. 2 Detector traces showing separation of the sample matrix and actinide elution in a single group (plot A), and group actinide elution sequence according to the valence state (plot B). The separations shown are applied to 100 μl vitrified glass sample spiked with 1.4 MBq ^{241}Am, 2.0 MBq ^{230}Th, and 2.16 MBq ^{233}U. Actinides shown in brackets indicate other species that elute in the same peak(s) as the spiked elements. Eluents: a, 10 ml 2 mol l^{-1} nitric acid; b, 5 ml 4 mol l^{-1} HCl; c, 7 ml 1 mol l^{-1} HCl–0.05 mol l^{-1} oxalic acid; d, 7 ml 0.1 mol l^{-1} ammonium bioxalate. TRU-resin column 4 × 50 mm; separation flow rate 2 ml min^{-1}. Time zero corresponds to the beginning of 2 mol l^{-1} nitric acid wash.

We found that microprecipitation with NdF_3 could be performed directly from 0.1 mol l^{-1} ammonium bioxalate eluent solutions to prepare alpha spectrometry sources for actinide quantification. Actinide precipitation recoveries exceeded 85%. Thus, time consuming digestion of ammonium bioxalate typically done prior to alpha source preparation is unnecessary.

Elution of actinides in valence state groups

The reductive sample pretreatment described in the Experimental section ensures that any iron present is reduced to Fe(II), thus eliminating the suppressing effect of Fe(III) ions on the retention of the trivalent actinides. These conditions reduce all Pu to Pu(III), and also reduce Np(V) to Np(IV), which is important because Np(V) is unretained on TRU-resin.[29–31] Samples loaded on the column after this pretreatment include Pu, Am, and Cm in the trivalent state, Th and Np in the tetravalent state, and U in the hexavalent state.

The chemistry for the separation of actinides in groups according to their valence state was described by Horwitz.[3] Capacity factors for trivalent actinides are less than one in hydrochloric acid solutions of up to approximately 5 mol l^{-1} concentration, while tetravalent actinides and hexavalent U remain strongly retained with $k' > 10^3$ in 4 mol l^{-1} HCl. Therefore, HCl solutions can be used to selectively elute the trivalent actinides. Complexants can then be used to elute the tetra- and hexavalent species. Horwitz used HCl–oxalic acid to elute tetravalent actinides, followed by bioxalate to elute the remaining hexavalent U.[3] Subsequent papers by researchers at Argonne National Laboratory described analytical separations of actinides in valence state groups using tetrahydrofuran 2,3,4,5-tetracarboxilic acid (THFTCA) instead of oxalic acid for selective elution of tetravalent actinides.[1,14,15,21]

We examined the elution of actinides from TRU-resin in valence state groups in an automated SI format. A separation procedure applied to a spiked vitrified glass sample (sample volume 100 μl) is shown in Fig. 2B using on-line detection to monitor the separation process. Sample load and column wash steps were performed just as described above. Trivalent actinides represented by Am were rapidly eluted using 5 ml of 4 mol l^{-1} HCl. Tetravalent actinides represented by Th were eluted using 7 ml of 1 mol l^{-1} HCl–0.05 mol l^{-1} oxalic acid eluent, taking advantage of the preferential complexation of the tetravalent state relative to hexavalent state by the oxalate ion.[3,32] Finally, uranium(VI) was eluted with 7 ml of 0.1 mol l^{-1} ammonium bioxalate solution.

For triplicate runs performed on the same column, Am and U recoveries exceeded 90%, while Th recoveries exceeded 85%. As determined in separate experiments using ^{230}Th tracer, approximately 1–2% of the Th activity was present in the 0.1 mol l^{-1} ammonium bioxalate fraction. When reusing the column, no detectable carryover was evident in the Am and Th fractions (< 1% carryover); U carryover was ~1% (on-line detection data). After 6 runs on a single column there was no visible degradation in peak shape or change in the onset of the elution time for either Am or U. However, the Th elution peak exhibited slight broadening and shift towards longer retention times by the seventh run on the same column. Therefore, in this separation, extended column reuse (for more than 6 runs) may not be feasible.

THFTCA is known to selectively complex tetravalent actinides in preference to hexavalent actinides,[33] and solutions of this reagent have been used in the TRU-resin actinide valence state separations in manual and FI formats.[1,14,15,21] Using our system with on-line detection, we observed that 0.1 mol l^{-1}

THFTCA solutions gave tailed elution peaks for tetravalent actinides (both Th and Pu tracers were tested) with substantial carryover into the subsequent 0.1 mol l^{-1} bioxalate fraction. Aldstadt also reported difficulties with this eluent in a FI format with ICPMS detection and noted the need for further work and better separations.[21] Despite the improved selectivity of THFTCA over oxalate for complexing tetravalent actinides, it does not appear to offer any advantage over HCl–oxalic acid for the elution of tetravalent actinide species from TRU-resin.

The valence state of Pu can be either Pu(III), Pu(IV), or both, depending on the sample load and column wash conditions. If loaded as Pu(III) after reductive sample pretreatment, a reducing agent such as ferrous sulfamate can be included in the column wash solution to maintain Pu in the trivalent state.[7] Alternatively, deliberate inclusion of an oxidizing step in conjunction with the column wash (as described in the Experimental section) can be used to assure that Pu elutes in the tetravalent group along with Th and Np.

One of the potential uses for the sequential elution of actinides according to their valence states is as a sample pretreatment step prior to actinide determination by ICPMS.[1,14,15,21] Using this approach, the actinides are separated from the sample matrix and can be preconcentrated if so desired. The sequential elution of actinides in groups, with Pu in the tetravalent group, addresses a number of potential interferences associated with ICPMS detection, *i.e.* ^{241}Am/^{241}Pu and ^{238}Pu/^{238}U isobaric interferences, ^{239}Pu/^{238}UH and ^{233}U/^{232}ThH polyatomic interferences, and ^{237}Np/ ^{238}U spectral interference. We have successfully developed a SI separation of actinides with on-line ICPMS detection, using a variant of the actinide separation shown in Fig. 2B with HCl–oxalic acid solution for tetravalent actinide elution.[19] Experimental details and application towards analysis of the nuclear waste samples will be described in a subsequent report.

Selective Pu elution *via* on-column redox reactions

Plutonium can be selectively separated from the other actinide species by manipulation of its oxidation state. In this approach, Pu(III) is oxidized to Pu(IV) with a reagent included in the column wash, followed by elution of the trivalent actinides with 4 mol l^{-1} HCl. The Pu(IV) retained on the column is then reduced and eluted as Pu(III). [3,11,24,25] The remaining tetra- and hexavalent actinides can be stripped from the column using bioxalate solution,[25] or they can be sequentially eluted using oxalic acid and bioxalate solutions, as described in the valence state separation procedure. The latter elution sequence for actinides in shown in Fig. 3, using a solution of $NaNO_2$ reagent in nitric acid as the oxidant, and Fe(II) sulfamate–ascorbic acid as the reductant. The sample in this example is a K-basin sample spiked with ^{241}Am, ^{239}Pu, ^{230}Th and ^{233}U.

The overall effectiveness of this separation in an automated format is critically dependent on the reliability of the on-column redox reactions. These were investigated previously in a FI system.[25] An excess of $NaNO_2$ in acidic solution, prepared freshly on-line in an FI format, was effective for the on-column Pu(III)–Pu(IV) oxidation step. Fresh preparation of acidic nitrite solutions is necessary because this mixture produces nitrous acid (pK_a = 3.35), an unstable species. However, we also found that nitrous acid is retained by the CMPO–TBP stationary phase on the column, and that there is an irreversible interaction between the polymeric support and nitrous acid or one of its decomposition products. Both processes influence the effectiveness of Pu elution in the subsequent on-column reduction step, requiring strong reductants for rapid, quantitative Pu elution. Hydrochloric acid solutions of titanium(III) chloride and Fe(II) sulfamate–ascorbic acid provided good Pu elution results with the latter reagent performing less reliably when using larger size columns (1.66 ml bed volume). Hydroquinone was not an effective reductant for converting Pu(IV) to Pu(III) on columns previously exposed to nitrous acid solutions.[25]

Issues associated with the redox chemistries were re-examined in the SI format using Pu redox reactions in conjunction with sequential elution of actinide groups by valence state. Because of concerns about nitrite effects arising from our previous studies, we evaluated the IO_3^- ion as a potential alternative Pu oxidizing reagent. This reagent is known to rapidly oxidize Pu(III) to Pu(IV) in aqueous solutions.[29,31] Exploratory experiments demonstrated that IO_3^- ion did oxidize Pu(III) to Pu(IV) on the TRU-resin column but not with the speed and selectivity required. Using 1 ml of 2 mol l^{-1} HNO_3–0.01 mol l^{-1} KIO_3 solution as a part of the 2 mol l^{-1} nitric acid column wash resulted in incomplete oxidation to Pu(IV), with detectable amounts of Pu(III) present in the subsequent 4 mol l^{-1} HCl eluent. Increasing the volume of this solution to 5 ml, and thus increasing the contact time with the oxidizing agent, succeeded in complete oxidation of Pu(III), with none detectable in the 4 mol l^{-1} HCl elution step. However, a small Pu peak appeared in the bioxalate elution, indicating partial oxidation to Pu(VI). We therefore used $NaNO_2$ for on-column Pu oxidation in all further experiments.

It was determined that Pu(III) could be effectively oxidized on the column to Pu(IV) using 150 μl of 0.5 mol l^{-1} $NaNO_2$ in the column wash as described in the Experimental section. This represents a 2.5 fold smaller amount of injected nitrite relative to our previous work.[24,25] In additional experiments, with and without the nitrite oxidation step in place, we observed no effect of the injected nitrite on Np(IV) speciation and elution. Using this revised on-column Pu oxidation procedure, rapid quantitative Pu recovery was possible using 4 mol l^{-1} HCl solutions of either 0.02 mol l^{-1} Ti(III) chloride or 0.05 mol l^{-1} Fe(II)–0.1 mol l^{-1} sulfamic acid–0.1 mol l^{-1} ascorbic acid.

The effect of the reducing eluent on the speciation of U retained on the column was also examined. When using 4 mol l^{-1} HCl–0.02 mol l^{-1} Ti(III) chloride as the reductant, approximately 20% of the U activity eluted with 1 mol l^{-1} HCl–0.05 mol l^{-1} oxalic acid, indicating partial on-column reduction of U(VI) to U(IV). Using 4 mol l^{-1}HCl–0.05 mol l^{-1} Fe(II)–0.1 mol l^{-1} sulfamic–0.1 mol l^{-1} ascorbic acid as the reductant did not result in any detectable U(IV) activity. Based on these results, either reducing agent can be used in the recovery and analysis of Pu, but the 0.05 mol l^{-1} Fe(II) 0.1 mol l^{-1} sulfamic–

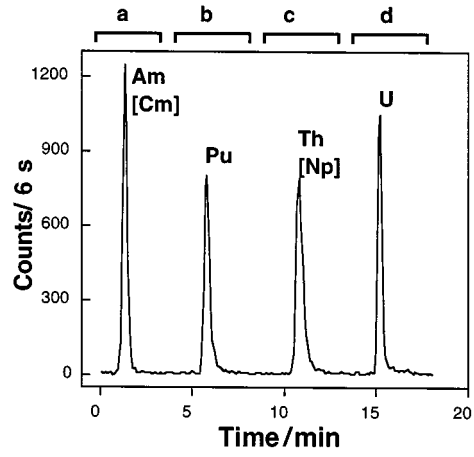

Fig. 3 Detector trace showing a variant of the individual actinide separation sequence. The separation applied to a 100 μl nuclear waste sample (K-basin) spiked with 2.1 MBq ^{241}Am, 2.6 MBq ^{239}Pu, 2.5 MBq ^{230}Th and 2.3 MBq ^{233}U. Am is eluted using 5 ml 4 mol l^{-1} HCl (eluent a); Pu is selectively eluted using 7 ml 4 mol l^{-1} HCl solution of 0.05 mol l^{-1} Fe(II)–0.1 mol l^{-1} sulfamic acid–0.1 mol l^{-1} ascorbic acid (eluent b); Th (Np) are coeluted using 7 ml 1 mol l^{-1} HCl–0.05 mol l^{-1} oxalic acid (eluent c); U is eluted using 7 ml 0.1 mol l^{-1} ammonium bioxalate (eluent d).

0.1 mol l^{-1} ascorbic acid reagent is preferred if subsequent actinide groups are to be recovered for analysis.

For quantification of the separated Pu by alpha spectroscopy, we established that NdF_3 microprecipitation can be carried out directly from either of the reducing Pu eluent solutions. The Pu precipitation recoveries were quantitative.

Selective Th elution and sequential actinide separations

Removal of trivalent actinides and Pu as described in the previous sections leaves Np(IV), Th(IV) and U(VI) species remaining on the TRU-resin column. Elution of these actinides with complexants leads to an actinide elution sequence of Am/Cm, Pu, Np/Th, and U, as illustrated in Fig. 3. We were interested in the possibility that Th(IV) could be rapidly and selectively eluted before Np(IV), yielding a method for eluting the actinides in the sequence Am/Cm, Pu, Th, Np and U. Horwitz *et al.* described selective Th elution with a reduced concentration of HCl after eluting trivalent species in 4 mol l^{-1} HCl solutions. Subsequent Np elution was accomplished using 1 mol l^{-1} HCl–0.03 mol l^{-1} oxalic acid and uranium was eluted with 0.1 mol l^{-1} ammonium bioxalate .[3] It was noted, however, that Th must be eluted slowly to achieve good reproducibility due to slow kinetics, and that the procedure 'is probably too tedious for routine analytical use'.[3] Using on-line detection, we observed that Th elution using 1.5 mol l^{-1} HCl at a flow rate of 1 ml min^{-1} yielded broad tailed peaks with significant quantities of Th carried over into a subsequent ammonium bioxalate fraction. This approach was not satisfactory for rapid automated separations.

Dramatically improved Th elution profiles were observed when HF was incorporated into HCl eluent solutions. We selected this approach on the basis of preferential complexation of Th(IV) by fluoride relative to Np(IV) and U(VI).[3,2] By adjusting the concentrations of HCl and HF, a solution composition was found that rapidly and selectively eluted Th from the TRU-resin column in the presence of Np and U, which remained on the column. Detector traces in Fig. 4 illustrate elution profiles for separate standards of Th and Np using 10 ml 4 mol l^{-1} HCl–0.05 mol l^{-1} HF solution for Th elution and 0.1 mol l^{-1} ammonium bioxalate solution to strip remaining actinides from the column. This selective Th elution method leads to a separation sequence of Am/Cm, Pu, Th, and Np/U.

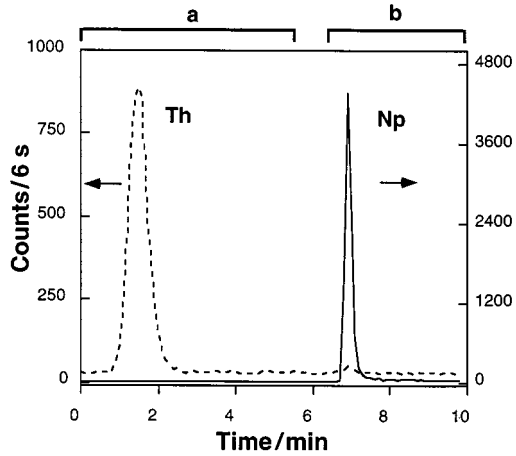

Fig. 4 Detector traces illustrating the feasibility of Th–Np separation using HCl–HF eluent for Th elution. The elution sequence shown was applied to Th (dashed trace, left y-axis) and Np (solid line, right y-axis) standards. Th trace is offset 30 counts for clarity. Eluents: a, 10 ml 4 mol l^{-1} HCl–0.05 mol l^{-1} HF; b, 7 ml 0.1 mol l^{-1} ammonium bioxalate. TRU-resin column 4 × 50 mm; separation flow rate 2 ml min^{-1}. Time zero corresponds to the beginning of 4 mol l^{-1} HCl–0.05 mol l^{-1} HF elution.

Given selective Th elution with HCL–HF eluent, we then attempted to sequentially elute Np and U using HCl–oxalic acid and bioxalate eluents, respectively, exactly as done in separations based on valence state (see Fig 2B for example). However, Np recovery using 1 mol l^{-1} HCl–0.05 mol l^{-1} oxalic acid after Th elution with 10 ml 4 mol l^{-1} HCl–0.05 mol l^{-1} HF was low and unreproducible, with over 70% of Np activity recovered in a subsequent bioxalate elution. Inclusion of a 4 mol l^{-1} HCl wash step between the Th eluent and the Np eluent offered slight but still unsatisfactory improvement in Np elution. The detailed chemistry underlying these results is unclear, but the results suggest that HF solution either alters the speciation of Np(IV) retained on TRU-resin column, or that the separation material itself is affected when using the HF–HCl eluent. Consequently, the use of an HCl–HF eluent for selective Th elution did not lead to an effective scheme for sequential separation sequence of Am/Cm, Pu, Th, Np, and U. Rapid sequential separation of individual actinides on a single TRU resin column, with fast kinetics, sharp peaks, and minimal carryover of one radionuclide into another, remains a challenge.

Nevertheless, the elution sequences described above are potentially useful in the radiochemical analysis of individual actinides. The sequence of Am/Cm, Pu, Th/Np, and U provides a fraction with Th and Np separated from the sample matrix and other actinides. Individual separation of Th and Np may then be accomplished using TEVA-resin extraction chromatographic material, which strongly retains Np(IV) but not Th(IV) from the HCl solutions.[5]

Alternatively, the new separation sequence of Am/Cm, Pu, Th, and Np/U provides selective recoveries of Pu and Th. Np can then be selectively precipitated from the Np/U fraction using a NdF_3 microprecipitation procedure for alpha source preparation. Using this approach, Np(IV) is separated from U(VI) which does not coprecipitate with NdF_3.

Determination of Am, Cm and Pu in nuclear waste samples

Radiometric determination of Am (Cm) and Pu is routinely performed in radiochemical laboratories at the Hanford site. Because of the safety considerations associated with relatively high abundance of these isotopes in aged nuclear wastes, this assay represents one of the most frequently performed radiochemical procedures. Therefore, we were interested in the application of the automated SI separation system towards the analysis of these radionuclides in nuclear waste samples. Three different nuclear waste types (see Experimental) were examined. These included sludge from the aged irradiated nuclear fuel (K-basin samples), tank waste supernate, and vitrified nuclear waste. Nuclear waste and quality control samples were processed as described in the Experimental section, using a procedure consisting of TRU-resin column conditioning, sample load, column wash/Pu oxidation, trivalent actinides elution in 4 mol l^{-1} HCl, and selective Pu reduction–elution using a reducing eluent. The separations were performed using freshly packed columns, which were replaced after the Pu elution step. The separation time including the column conditioning step was 25 min.

The Am/Cm and Pu fractions were collected with a fraction collector and analyzed by alpha spectroscopy. Fig. 5 shows the instrumental alpha spectra of the separated Am/Cm (plot A) and Pu (plot B) fractions for the analysis of vitrified waste sample, illustrating excellent separation obtained using automated SI procedure. Counting source preparation using microprecipitation with NdF_3 was carried out directly from the eluent matrixes. Using the SI procedure, nominal radiochemical yields were 85% for Pu and 86% for Am. High decontamination factors were typically observed with no detectable cross-contamination of Am/Cm and Pu fractions (individual decon-

tamination factors > 100). The analysis results obtained by the standard manual separation method and our automated SI separation procedure are compared in Table 2 and are in good agreement. Trivalent lanthanides, which may also be present in the fraction containing Am and Cm, do not interfere. They are not alpha emitters and are not present in sufficient quantities in the alpha source to cause energy resolution deterioration when analyzing aged nuclear waste.

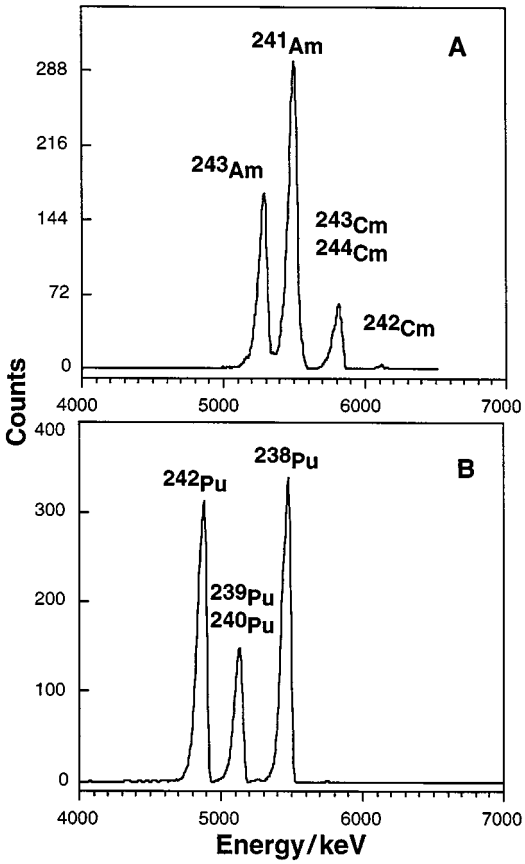

Fig. 5 Alpha energy spectra for the analysis of vitrified nuclear waste sample using automated Am/Cm–Pu separation procedure. Plot A corresponds to the trivalent actinide fraction; plot B corresponds to the plutonium fraction.

Conclusions

This work demonstrates that a separation-optimized fluid handling technique represents a versatile platform for the automation and detailed elucidation of chemically challenging extraction–chromatographic actinide separations. Chemistries for a variety of actinide separation procedures have now been developed that work reliably, reproducibly, and rapidly for unattended automated procedures. The SI separation system can also serve as the basis for an automated radiochemical separation workstation. With an appropriate set of solutions around the multiposition valve, several actinide separation procedures can be selected through software.

All the separations described above were carried out with fixed TRU-resin columns that were periodically replaced. As demonstrated previously for a SI ^{90}Sr separation system, column switching techniques can be used to provide new columns for each sample. Alternatively, we have recently described the ability to pack extraction chromatographic columns on-line, creating a new column for each analysis and disposing of each such column prior to the next analysis.[19,27] In this approach, carryover associated with the separation material is eliminated, and it is not necessary to elute the most strongly retained species on the column if they are not going to be analyzed. Either column switching or the renewable column technique could be incorporated as part of an automated actinide separation workstation.

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Table 2 Determination of the Am, Cm, and Pu isotopes in nuclear waste samples

	SI procedure, manual procedure/kBq g^{-1} or kBq ml^{-1}[a,b,c]				
Sample ID	^{241}Am	^{243,244}Cm	^{242}Cm	^{239,240}Pu	^{238}Pu
Vitrified	1270 ± 57	250 ± 13	11.2 ± 1.7	68.5 ± 2.6	159 ± 5.6
waste 1	1190 ± 27	258 ± 7.5	8.51 ± 0.72	68.8 ± 2.6	147 ± 4.4
Vitrified	1270 ± 55	245 ± 13	12.9 ± 1.8	70.7 ± 3.3	165 ± 6.3
waste 2	1190 ± 27	258 ± 7.5	8.51 ± 0.72	68.8 ± 2.6	147 ± 4.4
Tank	25.8 ± 1.3	1.08 ± 0.09	0.107 ± 0.02	2.00 ± 0.08	0.560 ± 0.03
waste 1	22.2 ± 1.1	0.921 ± 0.07	nm	1.99 ± 0.5	0.570 ± 0.03
Tank	23.8 ± 1.2	0.781 ± 0.07	0.112 ± 0.02	2.07 ± 0.07	0.574 ± 0.03
waste 2	22.2 ± 1.1	0.921 ± 0.07	nm	1.99 ± 0.59	0.570 ± 0.03
Tank	(5.59 ± 0.34) × 10^{-2}	(3.57 ± 0.23) × 10^{-2}	(3.46 ± 1.5) × 10^{-4}	(3.70 ± 0.16) × 10^{-2}	(4.96 ± 0.20) × 10^{-2}
waste 3	(5.59 ± 0.34) × 10^{-2}	(3.50 ± 0.13) × 10^{-2}	nm	(3.63 ± 0.10) × 10^{-2}	(5.18 ± 0.14) × 10^{-2}
K-basin 1	0.770 ± 0.040	nm	nm	4.14 ± 0.17	0.770 ± 0.05
	0.807 ± 0.052			4.23 ± 0.18	0.855 ± 0.07
K-basin 2	37.0 ± 2.1	nm	nm	130 ± 4.9	16.7 ± 0.97
	39.6 ± 1.6			139 ± 4	18.4 ± 0.97
K-basin 3	85.5 ± 5.6	nm	nm	1200 ± 47	139 ± 8.8
	80.3 ± 5.1			1240 ± 35	158 ± 7.3
K-basin 4	122 ± 6.5	nm	nm	1390 ± 55	188 ± 11.9
	114 ± 9.0			1550 ± 44	193 ± 9.4

[a] kBq g^{-1} for vitrified glass and K-basin samples; kBq ml^{-1} for tank waste samples. [b] Error is ± 1σ. [c] nm not measured.

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