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Rapid separation of uranium and plutonium by extraction chromatography for determination by thermal ionisation mass spectrometry

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A rapid method based upon extraction chromatography was developed for the separation of U and Pu from solutions of spent nuclear fuel for thermal ionization mass spectrometry. The method involves retention of Pu(IV) and U(VI) on a UTEVA column, thereby accomplishing a separation of these actinides from fission products. A separation of Pu from U was then achieved by selective elution of Pu. Two approaches for accomplishing this selective elution were investigated: (a) competitive complexation using oxalic acid and (b) reduction of Pu(IV) to Pu(III) using ascorbic acid. The latter method yielded a purer isolate as the former method yielded a Pu isolate that was contaminated with an unacceptable amount of U. The UTEVA separation was 3–5 times more rapid than the existing separation and was considered to be more suitable for automation.

Introduction

Materials control and accountancy (MC&A) is a vital task within the nuclear industry and is demanded by both international treaty and the requirements of plant safety. As part of this task, the precise and accurate determination of uranium and plutonium is essential and thermal ionization mass spectrometry (TIMS) is accepted widely as the benchmark.

The determination of U and Pu by TIMS requires pure U and Pu isolates. The current method of chemical separation used in these laboratories is based upon two separation columns. An initial separation of Pu from uranium/fission products is accomplished on a Dowex AG-1X4 column. A second separation of U from fission products utilizes a di(2-ethylhexyl)phosphoric acid extractant supported on an inert polymeric substrate. The effluent from the first separation, containing U and accompanying fission products, is the feed for the second stage of the separation. The separation procedure is slow, costly and, owing to the use of concentrated mineral acids, not suited to automation.

Extraction chromatography, using a number of highly selective extractants, has been developed to permit the rapid separation of the actinides on an analytical scale. The characteristics and behaviour of these materials were discussed fully by Horwitz *et al.* [1] Analytical separations of the actinides have generally utilized a multi-column approach[1–6] and often utilize a mixture of classical ion exchange and extraction chromatography. The use or adaptation of one of the known multi-column extraction chromatographic procedures would require little development but would offer little advantage over the separation schemes employed currently within these laboratories. However, careful examination of the properties of the commercially available materials suggested that a single solid phase extraction (SPE) cartridge could form the basis for a rapid separation of U and Pu from solutions of spent fuel. The advantages of a single column method were perceived to be (1) fewer manipulations and increased throughput; (2) reduction in solid waste generated per analytical cycle; (3) reduction in liquid waste generated per analytical cycle; and (4) ease of automation as the most aggressive reagent, 3 M nitric acid, was compatible with stainless steel.

The chemical separation has the following requirements: (1) removal of fission products from the analytes of interest; (2) effect a mutual separation of U from Pu; (3) separation of Pu from Am due to the m/z = 241 isobar; and (4) analytes of interest in the nitrate form.

It was considered that a UTEVA column (EiChroM Industries, Darien, IL, USA), consisting of an alkyl phosphonate extractant supported on an inert polymer, was the basis for a single column separation of U from Pu and of U/Pu from fission products. The initial approach relied upon competitive complexation using an oxalate ligand to elute Pu selectively with respect to U. An alternative route was based upon manipulation of the redox states of Pu to allow the selective elution of Pu with respect to U. Other commercial extraction chromatographic materials such as TEVA or TRU.Spec were considered not to have the required properties. TEVA does not retain U from nitric acid and would therefore not be capable of providing a single column solution. TRU.Spec, although retaining U and Pu strongly, had four failings: (i) the extractant had some affinity for selected fission products; (ii) the Pu complex with the extractant was very strong and would probably not allow selective elution *via* a competitive complexation; (iii) the extractant retains +3 actinides, thus preventing selective elution of Pu *via* manipulation of redox states; and (iv) retention of +3 actinides would not allow the separation of Pu from Am(III).

Experimental

Sample pre-treatment

Two procedures for sample pre-treatment were followed. The procedure depended upon the individual analytical requirements of the fuel dissolver being analysed. The first procedure involved a simple 250-fold dilution of the original sample from the fuel dissolution plant in a shielded hot cell facility. This allowed the determination of the Pu:U ratio in the original sample but did not allow the accurate and precise determination of the individual actinides. The second procedure involved the use of a large-scale dried spike, added to the original sample, to calibrate the subsequent 500-fold dilution. To satisfy standard isotope dilution methodology, a parallel dilution of the original sample, without the addition of the large scale dried spike, was required. The large scale dried spike consisted of milligram amounts of high enrichment ^{235}U and ^{239}Pu. This large scale dried spike procedure allowed the precise and accurate determination of the individual actinide concentrations in the original sample. In both cases, the diluted samples were transferred to the analytical laboratory where all subsequent manipulations of the sample could be performed within a radiological standard fume-hood. Mixed plutonium and uranium working standard solutions were prepared by gravimetric dilution from stock standard solutions of the individual analytes.

The first procedure required the addition of a mixed tracer to the diluted sample. An aliquot (*ca.* 0.200 cm^3) of the diluted sample was transferred into a small beaker and an aliquot of a mixed isotope dilution spike was added (^{233}U, ^{242}Pu). The sample was taken to dryness under a lamp. The second procedure, *i.e.*, the large scale dried spike method, did not require the addition of a tracer. Simple aliquots (0.200 cm^3) of the diluted samples were transferred into small beakers and taken to dryness under a lamp.

The dried residues were then treated to ensure isotopic equilibrium and to fix the analytes in the required oxidation states. An aliquot of hydroxylamine hydrochloride in dilute HCl was added to the dried residues to ensure reduction of all Pu to the +3 state. The resultant solution was then taken to dryness, the residue was treated carefully with concentrated nitric acid, the solution was re-evaporated to dryness, the residue was treated again with concentrated nitric acid and the final solution was taken to dryness. This process ensured that the spike was equilibrated isotopically with the sample and that all Pu was fixed in the +4 redox state.

Separation Procedures

Two methods based upon EiChroM columns were investigated: (a) single column (UTEVA) with Pu removed selectively by complexation with oxalic acid and (b) single column (UTEVA) with Pu removed selectively by reduction with ascorbic acid. The column consisted of an extractant, dipentylpentyl phosphonate (DPPP), supported on a poly(methyl acrylate) resin.

A variety of separation schemes were used during method development and validation and are summarized in Table 1 (oxalic acid case) and Table 2 (ascorbic acid case). Validation was achieved by comparison with the current analytical method.

Dual column methodology—the current method

The existing method for the separation of Pu and U from spent fuel solutions is a combination of anion chromatography and extraction chromatography. The sample solution was pretreated, the residue was dissolved in nitric acid (8 mol dm^{-3}) and the solution was loaded on an anion exchange column. Plutonium(IV) was retained strongly on this column and, after washing to remove U(VI) and fission products, the Pu was stripped from the column using hydroxylamine hydrochloride in dilute hydrochloric acid. This isolate was taken to dryness and the residue was treated with concentrated nitric acid to destroy the reductant and convert the analyte of interest into the nitrate form.

The anion column effluent, containing U(VI) and fission product species, was then loaded on an extraction column consisting of D$_2$EHPA supported on an inert polymeric substrate. This column retains U(VI) strongly but has little affinity for fission products. After washing to remove the latter, a pure U(VI) isolate was eluted with concentrated hydrochloric acid. This isolate was taken to dryness and the residue was dissolved in concentrated nitric acid and re-evaporated to dryness to convert the analyte of interest into the nitrate form.

Table 1 Elution programmes for the separation of uranium and plutonium on UTEVA using oxalic acid reagent

	Condition	Load	Wash 1	Pu elution 1	Wash 2	Wash 3	U elution	U elution
[HNO$_3$]/ mol dm^{-3}	3	3	3	3	3	3	0.02	×
[Oxalic acid]/ mmol dm^{-3}	×	×	×	100	100	×	100	×
A	3 × 2 cm^3	2 cm^3	4 × 2 cm^3	10 × 2 cm^3	—	—	10 × 2 cm^3	—
Destination[a]	Waste	Analysis	Analysis	Analysis	—	—	Analysis	—
B	3 × 2 cm^3	2 cm^3	4 × 2 cm^{-3}	3 × 2 cm^3	2 × 2 cm^3	—	4 × 2 cm^3	—
Destination[a]	Waste	Waste	Waste	Analysis	Waste	—	Analysis	—

[a] Destination refers to the fate of the column effluent collected during the specified operation. Waste = column effluent diverted to a waste stream. Analysis = column effluent collected and submitted for analysis by TIMS, ICP-MS radiometric counting, *etc.*

Table 2 Elution programmes for the separation of uranium and plutonium on UTEVA using ascorbic acid

	Condition	Load	Wash 1	Pu elution 1	Pu elution 2	Pu elution 3	Wash 2	Wash 3	U elution 1	U elution 2
[HNO$_3$]/mol dm^{-3}	3	3	3	3	3	3	3	3	0.02	×
[Ascorbic acid]/ mmol dm^{-3}	×	×	×	100	10–100	10	10	×	×	×
[HCl]/mmol dm^{-3}	×	×	×	×	×	×	×	×	×	20
C	3 × 2 cm^3	2 cm^3	4 × 2 cm^3	3 × 2 cm^3						
Destination[a]	Waste	Waste	Waste	Analysis						
D	3 × 2 cm^3	2 cm^3	4 × 2 cm^3	4 × 2 cm^3	—	—	—	—	—	—
Destination[a]	Waste	Waste	Waste	Analysis	—	—	—	—	—	—
E	3 × 2 cm^3	2 cm^3	4 × 2 cm^3	—	3 × 2 cm^3	—	—	—	—	—
Destination[a]	Waste	Waste	Waste	—	Analysis	—	—	—	—	—
F	3 × 2 cm^3	2 cm^3	4 × 2 cm^3	—	—	5 × 2 cm^3	—	—	—	—
Destination[a]	Waste	Waste	Waste	—	—	Analysis	—	—	—	—
G	3 × 2 cm^3	2 cm^3	4 × 2 cm^3	—	—	3 × 2 cm^3	2 × 2 cm^3	3 × 2 cm^3	4 × 2 cm^3	4 × 2 cm^3
Destination	Waste	Waste	Waste	—	—	Analysis	Waste	Waste	Analysis	Analysis

[a] See Table 1.

Single column methodology using oxalic acid complexant

SPE was based upon the extraction of the nitrate complexes of U(VI) and Pu(IV) from dilute nitric acid (3 mol dm^{-3}) into DPPP supported upon an inert polymeric substrate. After washing to remove fission products, the Pu(IV) was stripped selectively from the column using oxalate as a complexant. Uranium(VI) was eluted by lowering the nitrate concentration on column by washing with very dilute nitric acid. Recovery of U(VI) was aided by the use of oxalate. Evaporation of the fractions to dryness, followed by dissolution in concentrated nitric acid and hydrogen peroxide and re-evaporation to dryness resulted in samples suitable for measurement using TIMS. The oxalic acid solutions were prepared freshly for each batch of samples.

An elution programme was designed to optimize the separation and clean-up (Table 1, separation A). The results of this optimization were then applied to the final analytical separation design (Table 1, separation B). The use of a vacuum manifold was investigated to augment the eluent flow and provide a rapid separation (Visiprep Manifold, Supelco, Poole, Dorset, UK). In general, flow augmentation was used for all but the preliminary investigation.

Destruction of oxalic acid residue

The oxalic acid residue was destroyed by the careful addition of concentrated nitric acid (3 cm^3) and 30% v/v hydrogen peroxide (0.5 cm^3). The solution was warmed gently to initiate the reaction, whereupon hydrogen peroxide was either consumed or decomposed thermally. When this reaction was complete, the solutions were taken to dryness under a lamp. The hydrogen peroxide-containing solution was not evaporated directly because, without the preliminary digestion, a vigorous reaction occurred with resultant ‘foaming over’ of the sample.

Single column extraction using ascorbic acid for selective stripping of Pu

SPE was based upon the extraction of the nitrate complexes of U(VI) and Pu(IV) into DPPP supported upon a poly(methyl acrylate) resin. After washing to remove fission products, the Pu(IV) was stripped selectively from the column. This was accomplished by reduction of the Pu(IV) using ascorbic acid. The ascorbic acid was destroyed by wet ashing with fuming nitric acid.

Uranium(VI) was eluted by washing with very dilute nitric acid–oxalic acid (0.02 mol dm^{-3} nitric acid, 0.1 mol dm^{-3} oxalic acid). The U fraction was taken to dryness and the residue was treated with concentrated nitric acid–hydrogen peroxide to destroy the oxalic acid as described previously.

Alternatively, U(VI) could be eluted with very dilute hydrochloric acid (0.02 mol dm^{-3}). The U(VI) fraction was taken to dryness under a lamp and this residue was converted to the nitrate form by dissolution in concentrated nitric acid and evaporation to dryness.

The various separation schemes involving ascorbic acid are detailed in Table 2 (separations C–G).

Destruction of ascorbic acid residue

The Pu isolate (3 mol dm^{-3} nitric acid, 0.01 mol dm^{-3} ascorbic acid) was taken to incipient dryness, two drops of concentrated nitric acid were added and the residue was taken to dryness under a high-power lamp to induce charring of the residue. This residue was treated with fuming nitric (1 cm^3) and warmed to oxidize and dissolve the partially charred residue. This solution was transferred into a coned beaker in three small portions. Each portion was taken to incipient dryness before the next portion was added. When taken to dryness, a small amount of charred residue could remain, this was destroyed by addition of a few drops of fuming nitric to the warm beaker. If necessary, this process was repeated.

This procedure resulted in a sample that, when mounted on a TIMS filament, left no visible residue.

Thermal ionization mass spectrometry

The pure isolates were dissolved in dilute nitric acid (3 mol dm^{-3}) and mounted, by evaporation, on the side filament of a triple mass spectrometry bead (Cathodeon, Cambridge, UK). The bead consists of an Re centre and W outer filaments.

The samples were transferred to the TIMS instrument, a double focusing system fitted with nine Faraday collectors (VG Sector-54; MicroMass UK, Altrincham, UK). The centre filament was heated to produce a ^{187}Re ion current of 2 pA and the side filament to produce ion currents of 30 and 10 pA for ^{238}U and ^{239}Pu, respectively. Quantification was obtained by standard isotope dilution methodology.

Results

Single column using oxalic acid complexant.

Uranium and plutonium standards. Elution profiles for the separation of U(VI)/Pu(IV) from fission products and the separation of Pu(IV) from U(VI) were determined using elution programme A (Table 1). The fission product elution profile was obtained using a highly diluted sample of a spent fuel digest. The U and Pu elution curves were produced using aqueous standards of the relevant analyte. The results are given in Table 3 for the removal of (a) fission products, (b) Pu and (c) U. The majority of the β,γ activity was washed off the column within the first 5 cm^3 of dilute nitric acid. Similarly, most of the Pu(IV) and U(VI) was removed within 8 and 5 cm^3 of their respective stripping solutions. These results were used to design elution programme B (Table 1). To ensure that all β,γ activity was removed, the column was washed with a total volume of 8 cm^3 of nitric acid (3 mol dm^{-3}).

Two batches of six U/Pu mixed standards were separated according to elution programme B (Table 1). One batch was separated using gravity fed columns. The second batch was separated with augmentation of the eluent flow using a vacuum manifold. The complete separation was accomplished in less than 1 h including changing of the solvent guides on the manifold, preparation of the stripping solutions and conditioning of the columns. The oxalic acid stripping solutions were prepared freshly for each batch by dissolution of solid oxalic acid in the appropriate matrix.

The results of the determination are shown in Table 4 for (a) the gravity column and (b) the vacuum column. The values for the U and Pu content, derived using the gravity and augmented flow columns, were indistinguishable statistically at the 99% confidence level from the true value (*t*-test). Similarly, the precision of the determinations, using either the gravity or augmented flow columns, was indistinguishable at the 99% confidence level (*F*-test). It was therefore concluded that the use of a vacuum manifold did not introduce any bias or degrade the precision of the determination.

Determination of uranium to plutonium ratio in dissolved spent fuel. The results from the analysis of the U/Pu standards were so encouraging that it was decided that there was sufficient

Table 3 Elution profiles

(a) Elution profile for fission product activity from UTEVA using oxalic acid (0.1 mol dm^{-3}) in nitric acid (3 mol dm^{-3})—

Wash volume/ cm^3	β-Activity/Bq cm^{-3}	γ-Activity/Bq cm^{-3}
0	(5.14 ± 0.095) × 10^4	(2.10 ± 0.015) × 10^4
2	(24.3 ± 0.47) × 10^4	(9.63 ± 0.032) × 10^4
4	(0.288 ± 0.006) × 10^4	(0.117 ± 0.005) × 10^4
6	40 ± 9	0 ± 30
8	14 ± 7	0 ± 30

(b) Elution profile for Pu(IV) from UTEVA using oxalic acid (0.1 mol dm^{-3}) in nitric acid (3 mol dm^{-3})—

Wash volume/ cm^3	Total α-activity/ Bq cm^{-3}	Uncertainty/ Bq cm^{-3}	Activity (%)
2	181	13	7.6
4	1090	242	45.8
6	1040	232	43.7
8	54	2	2.3
10	5	0.7	0.2
12	3.5	0.8	0.15
14	0.9	0.4	< 0.1
16	1.07	0.4	< 0.1
18	0.8	0.3	< 0.1
20	1	0.4	< 0.1

(c) Elution profile for U(VI) from UTEVA using oxalic acid (0.1 mol dm^{-3}) in nitric acid (3 mol dm^{-3})—

Wash volume/ cm^3	U/μg cm^{-3}	RSD (%)	Recovery (%)
2	0	96	0
5	142	0.86	93
7.5	0.91	17.6	< 1
10	1.1	6.8	< 1
12.5	0.99	8.8	< 1
15	1.35	6.6	< 1
17.5	2.14	5.2	< 1
20	1.44	18.2	< 1
22.5	1.25	14.5	< 1
25	1.7	14.2	< 1

confidence in the method that the analysis of simulates would not be required. It was therefore decided to test the method on a sample derived from one of the on-site re-processing dissolvers. This sample was subjected to a 250-fold dilution in a shielded hot cell facility before transfer to the laboratories. All manipulations of this diluted sample could then be performed at a radiobench. It should be noted that the required measurement was the ratio of the U and Pu contents of the original dissolver solution and therefore an accurate dilution was not required. If absolute concentrations were required, addition of an appropriate mixed tracer prior to dilution would be required, *i.e.*, the large scale dried spike procedure described in the Experimental section. The samples were spiked, equilibrated, redox conditioned and supplied as a dry residue. A pair of U/Pu standards were prepared and run within each batch as a quality control measure. The results are given in Table 5 and the precision of the method, as applied to samples or standards, was indistinguishable at the 99% confidence level.

The accuracy of the single column method was tested by comparison with the existing separation method. Parallel determinations were performed on the same sample solution. The samples were run in duplicate and the results are given in Table 6. The precisions quoted for these determinations are the 95% confidence intervals and are derived from instrumental and method control charts. These results demonstrate clearly that there was no detectable bias between the two separation methods.

The method as developed demonstrated one major problem, which only became apparent as the method was applied to a greater range of "real" samples. The Pu fraction was contaminated with U, and although not present at levels that would adversely affect the analysis, did result in a significant ion current in the mass spectrometer multi-collector head channel positioned to detect ions of m/z 238. This was undesirable with respect to the detector lifetime.

The efficiency of the separation was estimated by loading the column with a known mass of U and processing the column according to the relevant separation procedure (Table 1, procedure B). The U was determined in the Pu isolate fraction (Table 1, procedure B, Pu elution 1) using ICP-MS. The decontamination factor (DF) was defined as the ratio of the mass of U added to the column to the mass of U recovered in the Pu fraction. The results of this determination indicated that

Table 4 Separation of U(VI) and Pu(IV) standards

Sample	10^3 Pu/U	Pu		U	
		[Pu]/μg g^{-1}	Recovery (%)	[U]/mg g^{-1}	Recovery (%)
(a) Using a gravity fed column—					
1	2.5998	2.2640	100.12	0.8705	100.12
2	2.5989	2.2616	100.01	0.8702	100.08
3	2.6038	2.2643	100.13	0.8696	100.01
4	2.5964	2.2654	100.18	0.8725	100.35
5	2.6020	2.2645	100.14	0.8703	100.09
6	2.5952	2.2602	99.85	0.8709	100.16
Mean	2.5994	2.2633	100.07	0.8707	100.14
σ	0.0032	0.00199		0.0009	
RSD (%)	0.125	0.088		0.106	
(b) Using an augmented flow column—					
1	2.6009	2.2659	100.08	0.8712	100.12
2	2.6011	2.2656	100.01	0.8710	100.08
3	2.5965	2.2579	100.13	0.8696	100.01
4	2.5881	2.2599	100.18	0.8732	100.35
5	2.5951	2.2598	100.14	0.8708	100.09
6	2.6037	2.2657	99.85	0.8702	100.16
Mean	2.5976	2.2619	100.024	0.8702	100.17
σ	0.0056	0.0033		0.0011	
RSD (%)	0.217	0.146		0.130	

eluting Pu with an oxalic acid strip resulted in a decontamination factor of only 100 for U in the Pu fraction.

Single column methodology using ascorbic acid reductant for Pu elution

The selective removal of Pu from the UTEVA, using an oxalic acid strip, did not yield an isolate of sufficient purity. The oxalate based separation depended upon: selective complexation of the Pu with respect to U and the competition between the Pu oxalate and Pu DPPP complexes favouring the oxalate species.

To improve the purity of the Pu isolate, an alternative selective stripping procedure was considered. This was based upon manipulation of redox states as follows: the UTEVA complexant has little affinity for Pu(III); reduction of Pu(IV) to Pu(III) could be accomplished selectively using ascorbic acid; and repeated wet ashing of the ascorbic acid residue yielded an isolate suitable for filament mounting.

An elution profile for Pu(IV) was determined (Table 2, separation procedures C + D). The results of this experiment suggested that Pu was eluted quantitatively within the first 6 cm^3 of the stripping solution, *i.e.*, recovery = 91 ± 1% for 3 × 2 cm^3 of eluent and recovery = 91 ± 1.3% for 4 × 2 cm^3 of eluent.

The clean-up of the Pu fraction, with respect to U, was determined for a separation based upon an ascorbic acid strip (Table 2, separation procedure C). A procedural blank was run in which the ascorbic acid solution (0.1 mol dm^{-3} ascorbic acid, 3 mol dm^{-3} nitric acid) was replaced with dilute nitric acid (3 mol dm^{-3}). The results of these determinations yielded decontamination factors of 1×10^4 (ascorbic acid) and 1.6×10^4 (procedural blank). These decontamination factors were at least two orders of magnitude better than were observed with an oxalic acid reagent (100) and suggested that the presence of ascorbic acid in solution had little effect upon the retention of U(VI). It was believed that this improvement in the purity of the Pu isolate, with respect to ^{238}U, would be sufficient to attenuate the unwanted mass spectral response.

This procedure was repeated and the isolate was taken to dryness and treated repeatedly with fuming nitric acid until the majority of the ascorbic acid residue was destroyed. This residue was mounted on a filament and treated as a Pu containing sample for TIMS. No ^{238}U was detected, indicating that the clean-up of the Pu isolate was now fit for the purpose.

The product of the initial oxidation of ascorbic acid was surprisingly indifferent to further oxidation using either fuming nitric acid or nitric acid–hydrogen peroxide. The complete destruction of the ascorbic acid was required to prepare clean filaments for TIMS. Therefore, the inability to perform an efficient and timely wet ashing of that compound was a threat to the successful implementation of this separation procedure.

It was found that repeated evaporations with fuming nitric acid, coupled with a preliminary charring of the residue under a lamp, would eventually destroy the majority of the residue. The time required for this procedure dominated the separation procedure and removed the competitive advantage of the rapid EiChroM separation.

To avoid the lengthy treatment of the Pu isolate, two approaches were identified: the use of an alternative reductant, *e.g.*, hydroxylamine, and optimization of the amount of ascorbic acid added to the column.

The use of an alternative reductant was investigated by modification of separation procedure C (Table 2). The ascorbic acid strip solution was replaced with 3 × 2 cm^3 of nitric acid–hydroxylamine (3 mol dm^{-3} nitric acid, 0.1 mol dm^{-3} hydroxylamine) and the Pu content of the column effluent was determined using ICP-MS. The results of this experiment indicated that no Pu was recovered from the column using a hydroxylamine strip. Note that hydroxylamine, when employed as a reductant, would normally be prepared in dilute hydrochloric acid. From the known characteristics of UTEVA,[1] retention of U on the UTEVA column would require HCl concentrations of *ca.* 2–3 mol dm^{-3}. This would be incompatible with one of the stated objectives of the method development, *i.e.*, compatibility with off-the-shelf automation.

The optimization of the ascorbic acid concentration of the strip solution was achieved according to separation procedure E (Table 2). The strip was accomplished using 3 × 2 cm^3 portions of nitric acid–ascorbic acid; the concentration of nitric acid was maintained at 3 mol dm^{-3} but the ascorbic acid content was varied between 0.01 and 0.1 mol dm^{-3} (procedure E, Table 2, Pu strip 2). The results are given in Table 7 and suggest that Pu was recovered efficiently over the entire range of ascorbic acid concentrations. The ascorbic acid concentration was set to 10 mmol dm^{-3} for all future experiments. It was believed that the variation in recovery with respect to ascorbic acid concentration was a kinetic effect and the flow through the columns was reduced by a factor of *ca.* 2 in subsequent experiments.

An elution profile for Pu, using a stripping solution of nitric acid (3 mol dm^{-3}) and ascorbic acid (10 mmol dm^{-3}), was determined (Table 2, separation procedure F). The recovery of Pu within the first 6 cm^3 of the strip was $> 91\%$. This was accomplished only by slowing the eluent flow rate by a factor of *ca.* 2. These lower concentrations of ascorbic acid could be wet ashed with relative ease using fuming nitric acid during transfer into a coned 5 cm^3 beaker prior to mounting on a TIMS filament. This yielded a filament with no visible residue and

Table 5 Determination of plutonium to uranium concentration ratio with the oxalic acid method

Sample	10^3 [Pu]/[U]	Sample	10^3 [Pu]/[U]
Sample 1 (batch 1)	7.128	Sample 1 (batch 2)	7.122
Sample 2 (batch 1)	7.126	Sample 2 (batch 2)	7.121
Sample 3 (batch 1)	7.147	Sample 3 (batch 2)	7.109
Sample 4 (batch 1)	7.164	Sample 4 (batch 2)	7.104
Sample 5 (batch 1)	7.161	Sample 5 (batch 2)	7.123
Sample 6 (batch 1)	7.132	Sample 6 (batch 2)	7.122
Mean	7.143	Mean	7.116
σ	0.017	σ	0.0083
RSD (%)	0.24	RSD (%)	0.121

	[U]/ mg g^{-1}	[Pu]/ μg g^{-1}	Recovery (%)			[U]/ mg g^{-1}	[Pu]/ μg g^{-1}	Recovery (%)	
			U	Pu				U	Pu
Standard 1	0.8690	1.932	99.94	99.84	Standard 3	0.8700	1.935	100.1	100.0
Standard 2	0.8685	1.935	100.1	100.0	Standard 4				

could be completed with minimal additional effort compared with the normal transfer procedure. In practice, an intermediate wash with ascorbic acid (Table 2, separation procedure G, wash 2) was used to ensure the complete removal of any residual Pu(IV) from the column prior to elution of the U(VI) fraction.

These results were used to generate a single column separation of U and Pu (Table 2, separation procedure G) using a UTEVA column and an ascorbic acid strip. An intermediate nitric acid wash (Table 2, separation procedure G, wash 3) was used to remove residual ascorbic acid from the column before elution of the U fraction. This avoided the need for the U(VI) fraction to be treated with fuming nitric acid to destroy any ascorbic acid carried over from the Pu elution. Two distinct procedures were used to elute the U(VI) fraction, *i.e.*, elution with nitric acid–oxalic acid (Table 2, U elution 1) or with very dilute hydrochloric acid (Table 2, U elution 2). The latter elution procedure required less processing of the U(VI) isolate to provide a sample suitable for TIMS, *i.e.*, a simple evaporation to dryness followed by dissolution and evaporation with a small volume of concentrated nitric acid to convert the chloride to the nitrate. In contrast, elution with nitric acid–oxalic acid required wet ashing with concentrated nitric acid–hydrogen peroxide to destroy the oxalic acid reagent. The separation chemistry had been designed with future automation as a key parameter and a nitric acid–oxalic acid reagent may be more compatible with a simple robotic sample processor than the very dilute hydrochloric acid reagent. For manual operations, the hydrochloric acid reagent was preferred for elution of the U(VI) fraction because of the simpler post-separation treatment. This procedure was tested by comparison with samples analysed using the existing anion exchange method. The samples were received as isotopically spiked, equilibrated and redox conditioned residues. The pure Pu isolate was treated to destroy ascorbic acid during transfer into a coned beaker prior to mounting for TIMS.

Table 6 Comparison of separation techniques for the determination of U and Pu (oxalic acid method): procedures performed simultaneously

Method	Pu/mg g^{-1}	U/mg g^{-1}
Existing	1.399 ± 0.008	203.4 ± 1.1
UTEVA	1.400 ± 0.008	203.6 ± 1.1

Large scale dried spike methodology applied. Concentrations apply to original sample.

Table 7 Optimization of ascorbic acid concentration

Ascorbic acid concentration/mmol dm^{-3}	100	75	50	25	10
Pu recovery (%)	74	74	68	67	60

The separation was tested for both analytical requirements, *i.e.*, determination of Pu:U ratios and determination of absolute concentrations of the individual actinides. The analyses were conducted over several days, using a variety of samples with distinct and separate addition of spikes. The results are given in Tables 8 (Pu:U ratios) and 9 (absolute concentrations). The uncertainties on the method are quoted as 95% confidence intervals and were generated from instrumental and method control charts. The differences between values derived using the two column (anion exchange) separation and the single column (UTEVA) separation are not significant statistically, *i.e.*, the results agree within the quoted 95% confidence interval. It was therefore concluded that the accuracy and precision of the single UTEVA column method were validated by comparison with an accepted and quality assured method. This accepted method has been in routine, daily use for *ca.* 30 years.

The single column UTEVA based separation has now been accepted by the routine analytical laboratories at this site. The method is perceived as offering at least a 50% improvement in

Table 8 Determination of plutonium to uranium concentration ratio with the ascorbic acid method

		Isotopic abundance					
Separation	Replicate	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	10^3[Pu]/[U]
Existing	1	0.249	68.033	25.5791	4.885	1.254	2.818
	2	0.248	68.063	25.543	4.895	1.249	2.848
	Mean	0.249	68.050	25.560	4.890	1.251	2.833
EiChroM	1	0.243	68.022	25.584	4.889	1.254	2.800
	2	0.249	68.048	25.568	4.884	1.251	2.828
	Mean	0.246	68.030	25.580	4.887	1.253	2.814
Existing	1	0.260	67.360	26.018	5.039	1.322	2.854
	2	0.260	67.360	26.011	5.047	1.321	2.872
	Mean	0.260	67.360	26.010	5.043	1.322	2.863
EiChroM	1	0.260	67.359	26.018	5.041	1.322	2.857
	2	0.260	67.332	26.027	5.057	1.324	2.870
	Mean	0.260	67.350	26.020	5.049	1.323	2.864

Table 9 Determination of plutonium and uranium concentrations with the ascorbic acid method

	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6		Sample 7		Sample 8	
Method	Pu/ mg g^{-1}	U/ mg g^{-1}	Pu/ mg g^{-1}	U/ mg g^{-1}	Pu/ mg g^{-1}	U/ mg g^{-1}	Pu/ mg g^{-1}	U/ mg g^{-1}	Pu/ mg g^{-1}	U/ mg g^{-1}	Pu/ mg g^{-1}	U/ mg g^{-1}	Pu/ mg g^{-1}	U/ mg g^{-1}	Pu/ mg g^{-1}	U/ mg g^{-1}
EiChroM	1.260	179.0	1.274	180.4	1.162	188.6	1.051	173.3	1.189	180.4	1.159	184.9	1.136	174.2	1.161	182.4
Existing	1.259	178.8	1.280	181.0	1.166	188.5	1.054	173.5	1.900	180.5	1.160	185.2	1.138	174.5	1.162	182.6
Difference[a]	0.001	0.2	−0.006	−0.6	−0.004	0.1	−0.003	−0.2	−0.001	−0.1	−0.001	−0.3	−0.002	−0.3	−0.001	−0.2

Uncertainty on Pu determination = ±0.007 mg g^{-1}. Uncertainty on U determination = ± 1.0 mg g^{-1}. Uncertainties on individual determinations, based on 95% confidence interval. Concentrations refer to original samples. [a] Difference = (result from EiChroM) − (result from Existing).

turn-around of the analysis, similar savings in the cost of the analysis, generates 50% less aqueous wastes and potentially reduces operator dose uptake. These benefits were achieved without sacrificing analytical performance.

Conclusions

Methods have been developed for the determination of U and Pu in solutions of spent nuclear fuel, based on extraction chromatography and utilizing a single column with selective elution of Pu and U as pure isolates. These methods are as accurate and precise as the existing analytical scheme.

The preferred method uses a reductant (10 mmol dm^{-3} ascorbic acid, 3 mol dm^{-3} nitric acid) to strip selectively the strongly retained Pu(IV) from the column as Pu(III).

This method is significantly faster than the existing two column method. At least a 50% reduction in the time required for sample preparation has been demonstrated. This method is fully compatible with off-the-shelf automation and this option is being pursued.

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References

1 E. P. Horwitz, M. L. Dietz, R. Chiariza, H Diamond, S. L. Maxwell, III and M. R. Nelson, *Anal. Chim. Acta*, 1995, **310**, 63.
2 E. P. Horwitz, M. L. Dietz, R. Chiariza and H. Diamond, *Anal. Chim. Acta*, 1992, **266**, 25.
3 S. L. Maxwell, III and M. R. Nelson, *Inst. of Nuc. Mat. Management*, Naples, FL, 1994 (MS194).
4 A. G. Adriaens, J. D. Fasset, W. R. Kelly, D. S. Simons and F. C. Adams, *Anal. Chem*., 1992, **64**, 2945.
5 J. R Cadieux, Jr. and S. H. Reboul, *Radioact. Radiochem*., 1996, **7**, 30.
6 J. H. Kaye, R. S. Strebin and R. S. Orr, *J. Radioanal. Nucl. Chem.*, 1995, **194**, 191.

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