DETERMINATION OF ACTINIDE ELEMENTS IN ENVIRONMENTAL SAMPLES BY ICP-MS

by

Jason Bedford Truscott, B.Sc. (Hons), GRSC.

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LGC (Formerly known as the Laboratory

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Road, Teddington, Middlesex,

TW11 0LY, UK

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I dedicate this thesis to my late father,

Roger Doney Truscott

ABSTRACT

DETERMINATION OF ACTINIDE ELEMENTS

IN ENVIRONMENTAL SAMPLES BY ICP-MS

Jason Bedford Truscott

Methods for the determination of the actinide elements in water, biological, soil and sediment samples have been developed using on-line solid phase extraction and high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) Initial applications utilised a commercially available resin, namely TRU-Spec resin, for efficient removal of the matrix prior to elution of uranium and thorium analytes Comparative analyses of reference materials and natural water samples from Plymouth and Dartmoor demonstrated significant improvement in precision and speed of analysis by using TRU-Spec coupled to ICP-MS compared with alpha spectrometry.

Further applications of the TRU-Spec resin for the determination of the transuranic actinide elements neptunium, plutonium and americium, resulted in the successful determination of ^{239}Pu and ^{237}Np in biological reference materials Detection limits were 700, 850, and 600 attograms (ag) for ^{237}Np, ^{233}Pu, and ^{241}Am, respectively, for a 0 5 ml sample injection, and better than 200 ag g^{-1} with 50 ml pre-concentration when sector field (SF) ICP-MS was used A method for the selective sequential elution of uranium and plutonium was also developed to facilitate the determination of ^{239}Pu without interference due to the $^{238}U^{1}H^{+}$ polyatomic ion, caused by high concentrations of ^{238}U in sediment samples

Investigations were performed into the use of a polymeric substrate, which was dynamically coated with chelating dyes such as xylenol orange and 4-(2-pyridylazo) resorcinol, and a silica substrate coated with permanently bonded iminodiacetic acid The latter was used for the successful determination of uranium and thorium in certified reference material waters However, the column was found to have a high affinity for iron, making it unsuitable for the determination of the actinides in soil and sediment samples

Subsequently, a polystyrene substrate which was dynamically coated with dipicolinic acid was used for HPLC coupled with SF-ICP-MS Using this column it was possible to separate the various actinides from each other and from the matrix In particular, it was possible to separate plutonium and uranium to facilitate interference-free determination of the former. The column also exhibited some selectivity for different oxidation states of Np, Pu and U Two oxidation states each for plutonium and neptunium were found, tentatively identified as Np(V) and Pu(III) eluting at the solvent front, and Np(IV) and Pu(IV) eluting much later Detection limits were 12, 8, and 4 fg for ^{237}Np, ^{239}Pu, and ^{241}Am, respectively, for a 0 5 ml injection, and the system was successfully used for the determination of ^{239}Pu in water, biological and soil reference materials

ACKNOWLEDGEMENTS

I would like to acknowledge the help and support of all those people (past and present) that have contributed to the completion of this work In particular, I must sincerely thank Dr E Hywel Evans for his guidance and for making this research more enjoyable with his ability to simplify even the most complicated of subjects A big thank you also goes to my second supervisor, Dr Phil Jones whose exhaustive knowledge of the fundamentals of chromatography has been of immense help in this study

I am very grateful to Dr Ben E Fairman, my supervisor at LGC, for his guidance with the high resolution ICP-MS and ability to keep me focused during my time in Teddington Also, to my colleagues at the LGC who always made me very welcome, in particular to Mrs Justine Turner who, from day one, could not have been more helpful

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To my family, in particular, Mum, Tiffany and Nan, who were always a great source of strength and support to me, not forgetting Poppy and Lilly the dogs and Gemini the cat To Uncle Ivor, for his continuous support and helpful advice Finally to Elena, *muchas gracias por tu amabilidad, por revisar esta tésis y por ser tú.*

AUTHOR'S DECLARATION

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award

This study was financed with the aid of a studentship from LGC (Formerly known as the Laboratory of the Government Chemist) Queens Road, Teddington, Middlesex, United Kingdom. The work described in this thesis was also supported in part by the Department of Trade and Industry, UK, as part of the Government Chemist Programme

A programme of advanced study was undertaken, which included instruction in ICP-MS theory, design and operation and attendance to a MSc accredited short course on analytical atomic spectrometry There has also been an active involvement with the inter-laboratory comparison for High Accuracy Analysis by Mass Spectrometry (HAAMS) (Study I, II, III and IV) for conventional analysis and isotope dilution analysis of the cadmium isotopes, instigated by the LGC, the programme has run from August 1998 to current date

Relevant scientific seminars and conferences were regularly attended, external institutions were visited for consultation purposes, and several papers were prepared for publication (detailed below)

Academic Conferences and Meetings Attended

1 Analytical Division of the RSC, meeting on "Research and Development Topics in Analytical Chemistry" 6th to 9th April 1998, University of Durham, Durham U K

2 Analytical Division of the RSC joint with Electroanalytical Group and Zeneca Ltd on "Water, Water Everywhere! Sensing and Making Sense of the Aquatic Environment" 23rd April 1998, Brixham Environmental Laboratory Zeneca Ltd, Brixham, UK

3 Royal Society of Chemistry, Analytical Division and Atomic Spectroscopy group, "Ninth Biennial National Atomic Spectroscopy Symposium" 8th to 10th July, 1998, University of Bath, Bath, U K.

4 Eichrom Users' Group Meeting, 4th December, 1998, University of Manchester, Manchester, UK.

5 European Winter Conference on Plasma Spectrochemistry 10th to 15th January, 1999, Pau, France

6 LGC "Workshop on Intercomparison Studies" RSC Analytical Methods Committee - High Accuracy Analysis by Mass Spectrometry (HAAMS), 27th January ,1999, Teddington, London, UK.

7 Analytical Division of the RSC, meeting on "Research and Development Topics in Analytical Chemistry" University of Woolwich, U K 12th-15th April 1999

8 Analytical Sciences Network - Young Scientists' Meeting A meeting arranged jointly by AD's Western Region and AstraZeneca, 17th November 1999, University of Plymouth, Plymouth, UK

9 LGC meeting associated with the "RSC Analytical Methods Committee - Sub-Committee on High Accuracy Analysis by Mass Spectrometry (HAAMS), 18th January , 2000, Belgrave Square, London, UK

10 LGC meeting associated with the RSC Analytical Methods Committee - Sub-Committee on High Accuracy Analysis by Mass Spectrometry (HAAMS), 6th July, 2000, Belgrave Square, London, UK.

11 Royal Society of Chemistry invited lectures presented at the University of Plymouth, 1997-2000

Presentations

1 Truscott, J B , Jones, P , Fairman, B E , Evans, E H , "Determination of Actinide Elements in Environmental Samples by ICP-MS" Poster presented at the Analytical Division of the RSC, meeting on "Research and Development Topics in Analytical Chemistry," 6th to 9th April 1998, University of Durham, Durham U K

2 Truscott, J B , Jones, P , Fairman, B E , Evans, E H., "The Determination of Uranium & Thorium using ICP-MS" Paper presented at the University of Plymouth Environmental Sciences inter-departmental meeting, 3rd March, 1998, Plymouth, UK

3 Truscott, J B , Jones, P , Fairman, B E , Evans, E H , "The Determination of Uranium and Thorium in Environmental Samples by ETV-ICP-MS" Poster presented at the Royal Society of Chemistry, Analytical Division and Atomic Spectroscopy Group, "Ninth Biennial National Atomic Spectroscopy Symposium," 8th to 10th July, 1998, University of Bath, Bath, U K

4 Truscott, J B , Jones, P , Fairman, B E , Evans, E H , "Determination of actinide elements in environmental samples using ICP-MS" Paper presented to the Department of Trade and Industry at the LGC, 16th November, 1998, Teddington, London, UK

5 Truscott, J B , Jones, P , Turner, J , Fairman, B E , Evans, E H , "Column Pre-concentration and Detection of Actinide Elements in Environmental Samples by ETV-ICP-MS" Poster presented at the European Winter Conference on Plasma Spectrochemistry , 10th to15th January, 1999, Pau, France

6 Truscott, J B , Jones, P , Fairman, B E , Evans, E H , "Pre-concentration and detection of actinide elements in environmental samples by ETV-ICP-MS" Paper presented at the University of Plymouth Environmental Sciences inter-departmental meeting, 3rd February, 1999, Plymouth, UK

7 Truscott, J B , Jones, P , Fairman, B E , Evans, E H , "Determination of Actinide Elements in Environmental Samples by ICP-MS" Poster presented at the Analytical Division of the RSC, meeting on "Research and Development Topics in Analytical Chemistry" 12th to 15th April, 1999, University of Greenwich, Woolwich, U K.

8 Truscott, J B , Jones, P , Fariman, B E , Evans, E H., "Trace Metal Analysis How Low Can You Get?" Paper presented at Analytical Sciences Network - Young Scientists' Meeting A meeting arranged jointly by the Analytical Division's Western Region and AstraZeneca at the Robins Conference Centre, 17th November 1999, University of Plymouth, Plymouth, UK

9 Truscott, J B , Jones, P , Fairman, B E , Evans, E H., "Separation of the Actinide Elements using HPLC-ICP-MS" Paper presented at the University of Plymouth Environmental Sciences inter-departmental meeting, 7th April, 2000, Plymouth, UK

10 Truscott, J B , Jones, P , Fairman, B E , Evans, E H , "Detection of Actinide Elements in Environmental Samples by Column Pre-concentration Inductively Coupled Plasma Mass Spectrometry" Paper presented at Analytical Division of the RSC, meeting for the "Young Researchers' Meeting and Specialist Symposia, combined with 'The Age of the Molecule' Annual Conference 2000," 16th to 20th April, 2000, University of Manchester (UMIST), Manchester, U K

11 Truscott, J B , Jones, P , Fairman, B E , Evans, E H , "The Determination of Actinides in Environmental Samples by Inductively Coupled Plasma Mass Spectrometry" Paper presented at the Royal Society of Chemistry Analytical Division Atomic Spectroscopy Group "Tenth Biennial National Atomic Spectroscopy Symposium," Sheffield Hallam University, 17th to 20th July, 2000, Sheffield, UK

Other Activities (undertaken throughout the PhD study)

1 Demonstrating to undergraduates and MSc students within the classroom and laboratory environment

2 Assignment of 3rd year degree students for their main project work, initiating the project experimental direction and offering guidance until completion

3 Attending various weekly seminars at the University of Plymouth, specifically for post graduates, 1997-2000

Publications

1 Evans, E H , Truscott, J B , Bromley, L , Jones, P , Turner, J , and Fairman, B E , "Evaluation of Chelation Pre-concentration for the Determination of Actinide Elements by Flow Injection ICP-MS" *Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations* Second Volume, ASTM STP 1344, R.W Morrow and J S Crain, Eds , American Society for Testing and Materials, 1998 (A copy is provide and in the Publications section of this thesis, page 184)

2 Truscott, J B , Bromley, L , Jones, P , Evans, E H , Turner, J , Fairman, B , " Determination of natural uranium and thorium in environmental samples by ETV-ICP-MS after matrix removal by on-line solid phase extraction" *J. Anal At Spectrom* , 1999, **14**, 627-631 (A copy is provide and in the Publications section of this thesis, page 184)

3 Truscott, J B , Jones, P , Fairman, B E., Evans, E H., "Determination of actinide elements at femtogram per gram levels in environmental samples by on-line solid phase extraction and sector-field-ICP-MS" *Anal Chim. Acta,* 2001, **433**, 245-253 (A copy is provide and in the Publications section of this thesis, page 184)

4 Truscott, J B , Jones, P , Fairman, B E , Evans, E H , Determination of actinides in environmental and biological samples using high performance chelation ion chromatography coupled to Sector-Field ICP-MS, *J. Chromatogr. A* , 2001 Submitted for publication

Signed .

Jason Bedford Truscott

November 2000

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A plausible impossibility
is always preferable to an
unconvincing possibility.

Aristotle (384-322 B C)

Chapter 1

INTRODUCTION

Chapter 1

INTRODUCTION

1.1 THORIUM, URANIUM, NEPTUNIUM, PLUTONIUM AND AMERICIUM IN THE ENVIRONMENT

1.1.1 A brief historical overview of the discovery of radioactivity and radioactive elements

M H Klaproth discovered uranium in pitchblend from Saxony in 1789 It had been previously thought that the mineral was in fact a complex iron tungstate, but Klaproth demonstrated that it was in fact a new element and named it after the planet Uranus, discovered by Herschel in 1781 Later, in 1841, a French investigator B Péligot was able to show that it was not purely uranium, but the oxide of uranium, UO_2, and was subsequently able to produce uranium by reduction chemistry Jons Jakob Berzelius discovered thorium in 1828 in a Norwegian mineral and named it after the Scandinavian god of war, Thor[1]

In 1894, Rontgen discovered x-rays observing that a fluorescent screen would glow some metres away from an electrical discharge, but was unable to explain their origins Two years later, Henri Becquerel experimented with fluorescent crystals (containing a mixture of potassium and uranium sulphates) and non-fluorescent crystals on photographic plates After a series of experimental deductions he concluded that the only requirement for the fluorescence was that the crystal should contain uranium Marie Curie, a co-worker of Becquerel, called this phenomenon,

radioactivity[2]. Continuing with investigations into the properties of the uranium ores, in 1898 Marie and husband Pierre Curie isolated two new radioactive elements which were named radium and polonium[3] Marie Curie and G C Schmidt independently added thorium to the list of naturally occurring radioactive elements[1] In 1903 the Curies received the Nobel Prize in physics (with Bequerel) for the discovery of radioactivity Later, Marie Curie also received the Nobel Prize for discovering radium and polonium thus becoming the first person to receive two Nobel Prizes[3]

In 1940, E M. McMillian and P H Abelson discovered the element neptunium (^{239}Np), and weighable quantities of the long lived isotope ^{237}Np was later synthesised by the neutron capture of uranium[1] (Equation 1.1), where $t_{1/2}$ is the half-life and is the time taken for the concentration of a substance to fall to half its initial value For radioactive elements the half-life is 0.69 x $1/\lambda$ where λ is the decay constant[4] In 1940, G T Seaborg, E M McMillan, J W. Kennedy, and A.C Wahl produced plutonium by, first, bombarding uranium with deuterons, and then by the decay of $^{238}_{93}$Np[1] (Equation 1 2)

$$^{238}\mathrm{U}\,(\mathrm{n},2\mathrm{n})\,^{237}\mathrm{U} \xrightarrow{\beta^-} {}^{237}\mathrm{Np} \qquad t_{1/2} = 6.75\ \text{days}$$

(Equation 1.1)

$$^{238}_{92}U + ^{2}_{1}H \rightarrow ^{238}_{93}Np + 2n$$

$$^{238}_{93}Np \xrightarrow{\beta-} ^{238}_{94}Pu \qquad (\alpha\text{ - emitter, } t_{1/2} = 87\ 74 \text{ years}) \qquad \textbf{(Equation 1.2)}$$

$t_{1/2} = 2\ 1$ days

With the discovery of neptunium and plutonium, and with the understanding of the physical interactions of various nuclear particles, it became evident to the scientists of the time that there were a number of other transuranic elements to be discovered Americium, being the fourth of the transuranic elements, was first synthesised and identified at the wartime Metallurgical Laboratory (now the Argonne National Laboratory) of the University of Chicago (USA) by G T Seaborg, R.A. James, L O Morgan, and A. Ghiorso in late 1944 and early 1945[1] Its formation was the result of intense neutron bombardment of ^{239}Pu to give the first characterised isotope of americium[5], ^{241}Am (Equation 1 3)

$$^{239}Pu\,(n,\gamma)\ ^{240}Pu\,(n,\gamma)\ ^{241}Pu \xrightarrow{\beta-} ^{241}Am \qquad \textbf{(Equation 1.3)}$$

$t_{1/2} = 14\ 4$ years

1.1.2 Actinides in Nature

Radioactive isotopes can occur naturally, and can also be the result of anthropogenic input Their main pathways into the environment are detailed below

1.1.2.1 Thorium

Thorium is a very common element, being widely distributed within the earth's crust, with the average concentration in the uppermost crust being approximately 12 parts per million[4,6] (the concentration of lead in the crust is about 16 parts per million, so thorium is almost as abundant as lead[1]) With the exception of ^{229}Th (a product of synthetic ^{233}U) all the other isotopes are present in nature by the decay of actinium or uranium The isotopes ^{230}Th (ionium) and ^{232}Th are considered to be the main naturally occuring isotopes[1], the former of which is formed as part of the natural decay of ^{238}U, and is present in only very small amounts Table 1 1 gives details of some of the known short and long lived isotopes of thorium

1.1.2.2 Uranium

The natural abundance of uranium is approximately one third that of thorium, however, it is found in significant concentrations in many varieties of rocks as well as in the ocean (Table 1.2). The average concentration of uranium in the earth's crust is approximately 4 parts per million[1,4] Natural Uranium consists of 99 2745 % ^{238}U, 0 720 % ^{235}U, and 0 0055 % ^{234}U which is a decay product of ^{238}U (Equation 1 4) The majority of known uranium isotopes is shown in Table 1 3

$$\underset{t_{1/2} = 4\,46 \times 10^{9}\ \text{years}}{^{238}_{92}U} \xrightarrow{\alpha} \underset{24\,10\ \text{days}}{^{234}_{90}Th} \xrightarrow{\beta} \underset{6\,69\ \text{hours}}{^{234}_{91}Pa} \xrightarrow{\beta} {^{234}_{92}U} \qquad \textbf{(Equation 1.4)}$$

Table 1.1 Table of thorium isotopes[a]

Isotope	Atomic Mass (g)	Natural Abundance (%)	Half Life[b] ($T_{1/2}$)	Decay Mode	Source
^{212}Th	212 012890	-	≈30 ms	α	-
^{213}Th	213 012940	-	0 14 s	α	-
^{214}Th	214 011430	-	0 09 s	α	-
^{215}Th	215 011690	-	1 2 s	α	-
^{216}Th	216 011030	-	28 ms	α	-
^{217}Th	217 013050	-	0 25 ms	α	-
^{218}Th	218 013252	-	0 11 μs	α	-
^{219}Th	219 015510	-	1 05 μs	α	-
^{220}Th	220 015724	-	10 μs	α	-
^{221}Th	221 018160	-	1 7 ms	α	-
^{222}Th	222 018447	-	2 8 ms	α	-
^{223}Th	223 020659	-	0 65 s	α	^{227}U decay
^{224}Th	224 021449	-	1 05 s	α	^{228}U decay
^{225}Th	225 023922	-	8 72 m	α	^{229}U decay
^{226}Th	226 024885	-	30 6 m	α	^{230}U decay
^{227}Th	217 027703	-	18 72 d	α	Natural
^{228}Th	228 028715	-	1 913 y	α	Natural
^{229}Th	229 031755	-	7 9 x 10^3 y	α	^{233}U decay
^{230}Th	230 033127	-	7 5 x 10^4 y	α	Natural
^{231}Th	231 036298	-	1 063 d	β^-	Natural
^{232}Th	232 038054	100	1 4 x 10^{10}y	α	Natural
^{233}Th	233 041577	-	22 3 m	β^-	^{232}Th (n,γ)
^{234}Th	234 043593	-	24 10 d	β^-	Natural
^{235}Th	235 047510	-	7 2 m	β^-	^{234}Th (n, γ)
^{236}Th	not available	-	37 5 m	β^-	-

[a] Table adapted from information given in Katz[1] and Lide[7]

[b] ms = (milli)seconds, μs = (micro)seconds, m = minutes, d= days, y = years

Table 1.2 **Concentration of uranium in the environment[1]**

Occurrence	Concentration $\mu g\ g^{-1}$
Igneous Rocks	4
Basalts	0 2
Granites	25
Sedimentary rocks[a]	2
Phosphate rock[b]	100
Bituminous shale[c]	65
Lignite[d]	50
Ocean water[e]	0 001
Living matter	0 001 – 100
Meteorites[f]	<0 001

[a] The sedimentary rock of the Colorado Plateau and similar formations in Soviet Kazakstan.

[b] For phosphate rock formations of marine origin.

[c] For the Chattanooga formation

[d] For South Dakota lignite

[e] Varies somewhat with the salt content of the water; the value is 3 5% salinity

[f] *This is an upper limit, there are reasons to suspect that the* true value may actually be much smaller

Table 1.3 Table of uranium isotopes[a]

Isotope	Atomic Mass (g)	Natural Abundance (%)	Half Life[b] ($T_{1/2}$)	Decay Mode[c]	Source
^{222}U	not available	-	≈1 μs	α	-
^{225}U	not available	-	0 08 s	α	-
^{226}U	226 029170	-	0 5 s	α	-
^{227}U	227 030990	-	1 1 m	α	^{232}Th (α, 9n)
^{228}U	228 031356	-	9 1 m	α	^{232}Th (α, 8n)
^{229}U	229 033474	-	58 m	80% E C., 20% α	^{232}Th (α, 7n)
^{230}U	230 033921	-	20 8 d	α	^{231}Pa (d, 3n)
^{231}U	231 036270	-	4 2 d	E C	^{231}Pa (d, 3n)
^{232}U	232 037130	-	68 9 y	α	^{232}Th (α, 4n)
^{233}U	233 039628	-	1 59 x 10^5 y	α	^{233}Pa decay
^{234}U	234 040946	0 0055(5)	2 45 x 10^5 y	α	Natural
^{235}U	235 043924	0 720(1)	7 04 x 10^8 y	α	Natural
^{236}U	236 045562	-	2 34 x 10^7 y	α	^{235}U (n, γ)
^{237}U	237 048724	-	6 75 d	β^-	^{238}U (d, p2n)
^{238}U	238 050784	99 2745(15)	4 46 x 10^9 y	α	Natural
^{239}U	239 054289	-	23 5 m	β^-	-
^{240}U	240 056587	-	14 1 h	β^-	-
^{242}U	not available	-	16 8 m	β^-	-

[a] Table adapted from information given in Katz[1] and Lide[7]
[b] ms = (milli)seconds, μs = (micro)seconds, m = minutes, h = hours, d= days, y = years
[c] E C = orbital electron capture

There is some uncertainty over the actual abundance of the ^{235}U isotope A recent reference manual[7] has stated that the percentage by weight of ^{235}U can vary by as much as 0 1 % depending on the source This variation is accountable, because the ^{235}U isotope is considered to be of independent origin[1] to that of ^{238}U

1.1.2.3 Neptunium and Plutonium

The isotopes ^{237}Np, ^{239}Np and ^{239}Pu do, in fact, occur in nature in minute quantities[1,7], as a result of neutron capture in uranium containing ores (Equation 1 1) Hence, a plausible route for the formation of ^{239}Np and ^{239}Pu is given in Equation 1 5

$$^{238}U(n,\gamma)\ ^{239}U \xrightarrow{\beta^-} {}^{239}Np \xrightarrow{\beta} {}^{239}Pu$$
$$t_{1/2} = 23\ 5 \text{ minutes} \qquad 2\ 355 \text{ days}$$

(Equation 1.5)

Peppard *et al.*[8] isolated ^{237}Np in Belgian Congo uranium ore concentrate, at a maximum $^{237}Np/^{238}U$ mass ratio of 1.8×10^{-12}. The majority of known neptunium isotopes are given in Table 1 4

The existence of ^{239}Pu in ore has been established[9,10], approximately 1 microgram of ^{239}Pu has been recovered from 100 tonnes of processed ore[9] The actual concentration of plutonium has been estimated as approximately 10^{-15} g g^{-1} (1 fg g^{-1}) in certain uranium ores[11] such as pitchblende, and can, due to peculiar physical and geochemical reasons, reach 10^{-11} to 10^{-12} g g^{-1} (0 1-1 pg g^{-1}) The solar-system has been calculated to have formed around 4 7 billion years ago, so, even the most stable isotope (i e ^{244}Pu, half life of 8 3 $x10^7$ years), formed during genesis is now only present in estimated quantities[11] of $<10^{-29}$ g g^{-1}

Table 1 5 gives details of the majority of known plutonium isotopes

Table 1.4 Table of neptunium isotopes[a]

Isotope	Atomic Mass (g)	Natural Abundance (%)	Half Life[b] ($T_{1/2}$)	Decay Mode[c]	Source
^{226}Np	not available	-	0 03 s	α	-
^{228}Np	not available	-	0 51 s	α	-
^{229}Np	229 036230	-	4 0 m	α	-
^{230}Np	230 937810	-	4.6 m	97% E C 3% α	-
^{231}Np	231 038240	-	48 8 m	98% E C 2% α	^{238}U (d, 9n) ^{235}U (d, 6n)
^{232}Np	232 040020	-	14 7 m	99% E C 1% ?	^{235}U (d, 3n)
^{233}Np	233 040800	-	36 2 m	E C	^{235}U (d, 4n)
^{234}Np	234 042888	-	4 4 d	β^+, E C.	^{235}U (d, 3n)
^{235}Np	235.044056	-	1 085 y	99 9% E C 0 1% α	^{235}U (d, 2n)
^{236}Np	236 046550	-	1 55 x 10^5 y	91% E C 9% β^-	^{238}U (d, 4n) ^{237}Np (n, 2n)
^{237}Np	237 048167	-	2 14 x 10^6 y	α	^{237}U β^- decay
^{238}Np	238 050941	-	2.117 d	β^-	^{238}U (d, 2n) ^{237}Np(n, γ)
^{239}Np	239 052933	-	2 355 d	β^-	^{239}U β^- decay
^{240}Np	240 056050	-	1 032 h	β^-	^{238}U(α, pn)
^{241}Np	241 058250	-	13 9 m	β^-	^{238}U(α, p)
^{242}Np	242 061640	-	5.5 m	β^-	-

[a] Table adapted from information given in Katz[1] and Lide[7].
[b] ms = (milli)seconds, μs = (micro)seconds, m = minutes, d= days, y = years
[c] E C = orbital electron capture, β^+ = positron emission

Table 1.5 Table of plutonium isotopes[a]

Isotope	Atomic Mass (g)	Natural Abundance (%)	Half Life[b] ($T_{1/2}$)	Decay Mode[c]	Source
^{230}Pu	not available	-	-	α	
^{232}Pu	232 041169	-	34 ms	E C >80% α >20%	^{235}U (α, 7n)
^{233}Pu	233 042970	-	20 9 m	99 9% E C 0 1% α	^{233}U (α, 4n)
^{234}Pu	234 043299	-	8 8 d	94% E C 6% α	^{235}U (α, 5n) ^{238}Cm α decay
^{235}Pu	235 045260	-	25 3 m	99+% E C 0 003% α	^{235}U (α, 4n)
^{236}Pu	236 046032	-	2 87 y	α	^{240}Cm α decay ^{235}U (d, n,)
^{237}Pu	237 048401	-	45 2 d	99 9% E C 0 003% α	^{238}U (α,5n)
^{238}Pu	238 049554	-	87 74 y	α	^{238}U (d, 2n) ^{242}Cm α decay
^{239}Pu	239 052157	-	2 41 x 10^4 y	α	^{239}Np β^- decay
^{240}Pu	240 053808	-	6537 y	α	^{239}Pu(n, γ)
^{241}Pu	241 056845	-	14 4 y	99+% β^- 0 002% α	^{240}Pu(n, γ)
^{242}Pu	242 058737	-	3 76 x 10^5 y	α	^{241}Pu(n, γ)
^{243}Pu	243 061998	-	4 956 h	β^-	^{242}Pu(n, γ)
^{244}Pu	244 064199	-	8 2 x 10^7 y	99 9% α 0 1% S F	^{243}Pu(n, γ)
^{245}Pu	245 067820	-	10 5 h	β^-	^{244}Pu(n, γ)
^{246}Pu	246 070171	-	10 85 d	β^-	^{245}Pu(n, γ)

[a] Table adapted from information given in Katz[1] and Lide[7]

[b] ms = (milli)seconds, μs = (micro)seconds, m = minutes, d= days, y = years

[c] E C = orbital electron capture, S F = spontaneous fission.

1.1.2.4 Americium

Americium is not known to exist naturally in nature because the half life of even the longest lived americium isotope (i e ^{243}Am) is only 7 37 x 10^3 years (Table 1 6) and therefore no quantity would have survived since genesis Intense neutron activity is required to produce the various isotopes of americium, which is not likely to happen under normal environmental conditions Thus, the element can be considered to be of anthropogenic source

1.1.3 Anthropogenic sources of actinides

There are two main anthropogenic sources of the actinides, mainly consisting of plutonium and the long-lived isotopes (having a longer half-life) of Np, and Am

1.1.3.1 Industrial sources of the actinides

Uranium is the main source material for the production of the other actinide elements, 44,000 tonnes of uranium being mined in the 1980's for the western world alone[4] Radioactive substances have been historically used for colouring glass or ceramics (e g uranium gives colours ranging from orange-red to lemon yellow), and thorium and uranium have also been found in ophthalmic lenses, by natural association with rare earth elements used to tint the glass More recent uses include, gas mantles (between 250 and 400 mg of thorium per mantle), smoke detectors (approximately 2 5g of ^{241}Am in total, for the 12 million units per year, sold in the mid-80's), power generation (nuclear reactors use 2 0-2 5% ^{235}U enriched natural uranium)

Table 1.6 Table of americium isotopes[a]

Isotope[b]	Atomic Mass (g)	Natural Abundance (%)	Half Life[c] ($T_{1/2}$)	Decay Mode[d]	Source
^{232}Am	not available	-	0 9 m	E C	
^{234}Am	not available	-	2 6 m	E C	
^{237}Am	237 050050	-	1 22 h	99 98% E C 0 02% α	^{239}Pu (d, 4n)
^{238}Am	238 051980	-	1 63 h	E C 0 0001% α	^{239}Pu (d, 3n)
^{239}Am	239 053016	-	11 9 h	99 99% E C. 0 01% α	^{239}Pu (d, 2n)
^{240}Am	240 055278	-	2 12 d	E C α	^{239}Pu (d, n)
^{241}Am	241 056823	-	432 2 y	α	^{241}Pu β^- decay
^{242m}Am	-	-	141 y	99 5% I T 0 5% α	^{241}Am (n, γ)
^{242}Am	242 059541	-	16 02 h	83% β^- 17% E C	^{241}Am (n, γ)
^{243}Am	243 061375	-	7 37 x10^3 y	α	^{242}Am (n, γ)
^{244}Am	244 064279	-	10 1 h	β^-	^{243}Pu β^- decay
^{245}Am	245 066444	-	2 05 h	β^-	^{243}Am (n, γ)
^{246}Am	246 069770	-	39 m	β^-	^{245}Pu β^- decay
^{247}Am	247 072170	-	22 m	β^-	^{246}Pu β^- decay

[a] Table adapted from information given in Katz[1] and Lide[7]
[b] m = denotes a nuclear isomer of the isotope
[c] ms = (milli)seconds, μs = (micro)seconds, m = minutes, d= days, y = years
[d] E C = orbital electron capture, I T = isomeric transition from upper to lower isomeric state

Scientific and communication equipment aboard space satellites use ^{238}Pu as a source of heat and power (e g the Galileo exploration satellite mission used 16 3 kg of ^{238}Pu for the voyage to Jupiter in the mid-1980s[12])

1 1 3 1 1 Nuclear Power Stations

Nuclear power stations are the main industrial source of anthropogenic plutonium and other heavier actinides ^{235}U enriched natural uranium is used in nuclear reactors and, other actinide elements are synthesised within the reactors due to the reactions described earlier in section 1 1 2 The isotopic abundances of plutonium isotopes, typically are in the range 50-60% ^{239}Pu, 11-12% ^{240}Pu and 1 4-3% of ^{238}Pu, ^{242}Pu, and ^{241}Pu These patterns of abundance can subsequently be used to identify the source of plutonium. It has recently[13] been estimated that approximately 650 tons of plutonium has been produced as a result of the operation of atomic power stations and scientific reactors throughout the world It is interesting to note that even a catastrophic event such as the melt down of the nuclear reactor of the Chernobyl power station in Russia, on 26th April 1986, only contributed 1-2% of the total plutonium content in the environment Nevertheless, a survey[14] undertaken in the UK a week later on the 2nd May 1986 reported detectable radioactivity in the UK, 2000 km away from the site Atmospheric transfer had deposited ^{239}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Am throughout the country

The concentration typically found in soils from radioactive fallout areas[15] containing between 10-50 fg of ^{239}Pu and ^{240}Pu, which is contributing to the total

global mean concentration of man-made ^{239}Pu in surface soils, now approaching[11,13] 10^{-13} g g^{-1}

1.1.3.2 Military sources

Nuclear weapons testing is considered the main anthropogenic source of plutonium in the biosphere Approximately 260 ±40 tons of weapons-grade Pu were manufactured during the arms race between 1945-1994, with 140 ±20 tons coming from Russia[13] The isotopic abundances of weapons-grade plutonium are approximately[13] 93-94% ^{239}Pu, 6% ^{240}Pu, 0 5% ^{241}Pu, and trace amounts of ^{242}Pu and ^{238}Pu In contrast to the civil sources mentioned in section 1 1 3 1 1 Hence, a high relative level of ^{239}Pu ratios compared to the other plutonium isotopes is indicative of pollution by weapons-grade plutonium. Other military sources include atomic engine ships and atomic bomb carriers It is now estimated[13] that about 7-10 tons of plutonium has been introduced into the environment over the last 40 years with only 0 1-1% of this amount being a consequence of incomplete chemical separations of plutonium performed on reactor fuel elements from nuclear power stations

1.1.4 Radiation effects on humans

A great deal of research[12] has been undertaken into the effects of radiation on humans Since 1942, studies have been directed towards understanding the mechanisms of radiation injury and the ecological relationships that exist in an environment contaminated with radioactive substances This has also included animal

studies, but results are not always comparable to data obtained from studies in humans From close inspection of the literature, there would seem to be some contradiction regarding the quantities of radioactivity that would be harmful or even fatal Perelygin *et al* [11,13] stated that, due to the current concentrations of plutonium in the environment, it is important to attract the attention of the international community to its hazards. At this moment in time, man-made plutonium is widely distributed over the globe and the endpoint of the food cycle is the human body, where plutonium can be accumulated to the dangerous level[11,13] of $\geq 10^{-12}$ g g^{-1}. These authors then go on to say that studies into the chemical behaviour of plutonium in the biological cycle, including the human body, has been poorly investigated Current studies variably conclude that plutonium is not a significant hazard, based on the assumption that plutonium cannot be deposited in human body tissues, at one end of the scale, to stating that a lethal dose is in the region of 10^{-6} to 10^{-7} g in the human body[11] at the other. Taylor[16], has calculated that a base load of $10^{3} - 10^{5}$ atoms (<0 2 amol) of ^{244}Pu from primeval times, remains in the human body, plus approximately 300 fmol of ^{239}Pu from anthrorogenic source Based on current knowledge of radiotoxicity these levels would not cause any recognisable health problem Voelz *et al.*[17] compared twenty-six white male workers, who were involved in plutonium research and development at Los Almos National Laboratory (in the USA) over the last 50 years to 876 unexposed workers, and to mortality rates of white males (U S A) in the general population They found that there was no significant statistical difference between the number of deaths of those who had been exposed to plutonium to those who were not. Subjects exposed to plutonium had levels of between 2 2 x 10^{-8} to 2 2 x 10^{-6} g in their bodies (assuming the isotope to be solely ^{239}Pu) Priest *et*

al [18] highlighted the fact that the distribution of the so-called "bone seekers" such as ^{241}Am and ^{239}Pu throughout the skeleton of baboons was higher in younger primates due to growth, but much less in the more developed adults Photographs showed damage to the edosteum (a fibrous membrane covering the bone) and adjacent to the bone marrow, by alpha particles, their tracks being visible under a microscope The effects of exposure to short term bursts of high concentrations of radioactivity or the accumulation effects of minute concentrations and/or repeated doses over large periods of time (e g the lifetime of an individual) will not be immediately apparent, making it difficult to calculate a safe dose level Symptoms include somatic effects (non-hereditary genetic disorders) and hereditary-genetic disorders, as well as carcinogenic illnesses (such as Bone, Lung, Liver cancers to name a few)[12], so the effect will not necessarily be confined to one generation

To summarise the current literature, it would appear that the potential for ill health effects due to radioactive sources arise from a combination of the activity of the radionuclide, type of decay (e g alpha decay), mobility of the element in a particular system, and whether the radioactivity is received internally or externally The vast majority of literature concerns plutonium release into the environment, and some dealing with neptunium and americium. However, as a general rule, whenever there is an anthropogenic input of plutonium, there may also be neptunium and possibly americium, this being dependent on the source

1.1.5 Environmental legislation regarding storage and release

There are essentially only two main types of disposal schemes[2], containment and dispersal, usually implemented through the United Kingdom Atomic Energy Authority (UKAEA) disposal facilities

Containment is used mainly for medium to high level waste (radioactive elements having long half-lives of 1000s of years) The waste is securely held in a shielded container, away from highly populated human areas, and left until the activity has fallen to a level that does not constitute a hazard The containers must be made of inert materials and be able to resist transmutation of the radioactive material due to decay

Dispersal is used for low-level wastes (less than a few microcuries) The radioactive material is usually diluted with other waste, solid or liquid, until the average activity does not present a hazard If the low-level waste contains no alpha emitters and no strontium-90 it can be disposed of at local authority tips No single article should have an activity of greater that 1 microcurie or a combined load of 10 microcuries in a total volume of 0 1 cubic metres Incineration and dilution in the sewage system are also allowed but there are limits to the amount and frequency of disposal All discharges must be monitored

1.2 RADIOCHEMICAL METHODS OF ANALYSIS

Radiochemical methods are the main, long-standing, accepted methods of analysis within the radiochemical community Radiation detection methods generally rely on measuring the radionuclide decay (the decay rate being a constant for each element) which result in alpha-, beta-, or gamma-radiation Hence the analysis is dependent on the decay route and the quality of the detectors[19]

Alpha-spectrometry and neutron activation have commonly been employed for the determination of actinides such as thorium and uranium[20] Often these methods are limited by high sample volume requirements (alpha spectrometry), expensive and rare equipment (neutron activation), and long counting times (alpha spectrometry)[19,20] Usually, the sample preparation required involves separation of the actinide elements, a pre-concentration step[21], two extraction procedures, electrodeposition, and then counting by alpha-spectrometry The resolution of currently available alpha spectrometers is not sufficient to separate all the alpha energies (from emissions) for most of the actinides For example, in a recent paper[22] a single-step ion-exchange method was used to separate the actinides in a sample, into the following fractions -

i ^{237}Np

ii ^{243}Am, ^{241}Am, $^{243\text{-}244}Cm$

iii ^{242}Pu, $^{239\text{-}240}Pu$, ^{238}Pu

Each fraction was then analysed separately by alpha-spectrometry It should be noted that results for Cm and Pu were for the isotopes 243-244 and 239-240 mass units, respectively This is due to the inability of alpha-spectrometry to resolve these isotopes (e g ^{239}Pu and ^{240}Pu have alpha-energies of 5 155 and 5 168 MeV, respectively) Consequently, radiochemists quote total activity of the combined isotopes when reporting findings Research into ways of resolving the plutonium isotopes by high-resolution alpha-spectrometry[23] is in progress to try and solve this problem

Although these methodologies have their place in the scientific community, the long sample preparation and analysis times required, large quantities of samples normally needed, and subsequent costs to laboratories, justify research into other methods which would also satisfy the needs for low-level detection required of transuranic actinides for environmental mobility studies

1.3 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Inductively coupled plasma mass spectrometry (ICP-MS) would seem to be ideally suited for the determination of the actinide elements[19,20,24,25,26,27,28,29] It has excellent sensitivity, elemental and isotopic selectivity, nearly simultaneous detection, and rapid analysis capability

For example, extractions of ^{237}Np from certain samples can take up to 2 days with counting times of up to 15 hours by alpha spectrometry[30], whereas analysis by ICP-MS can be up to 10 times more rapid.

The development of ICP-MS stemmed from the work of Gray[31,32,33,34,35], and Fassel[36] who coupled an atmospheric ICP and a mass spectrometer to form the basis for all ICP-MS instruments.

1.3.1 Quadrupole ICP-MS

The basic instrumental layout is shown in Figure 1.1.

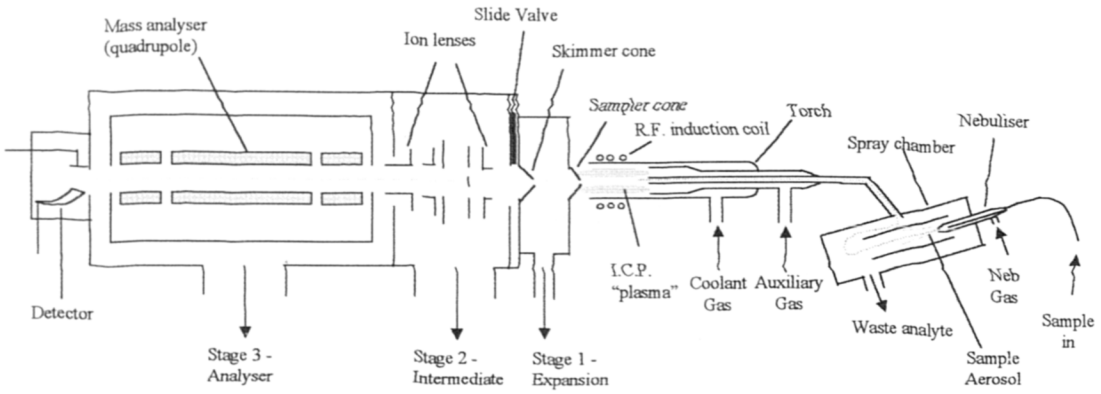

Figure 1.1 Basic quadrupole ICP-MS

Starting from the right on Figure 1.1 the liquid sample is introduced into a nebuliser which produces an aerosol. The aerosol passes through a spray chamber,

which removes ca 98% of the sample before it passes through the torch and into the plasma The plasma can be defined as a partially ionised gas, commonly argon, containing electrons and free positive ions, formed at high temperatures between 5000 - 10,000 K During the passage into and through the plasma the aerosol particles are desolvated, decomposed, atomised and ionised The ions then pass through a sampler cone with an orifice of approximately 1 mm in diameter, into an expansion stage evacuated to 2 x 10^{-3} bar A proportion of these ions pass through the skimmer cone and are subsequently focused by the ion lenses in the intermediate stage 2 (<1 x10^{-7} bar) These cones and vacuum stages are necessary in order to allow the interface of an atmospheric pressure plasma with the vacuum conditions of the final stage 3, or the analyser stage (<5 x 10^{-9} bar) This stage contains the mass analyser or quadrupole, so named because it consists of four parallel electrically conducting rods A variable radio frequency voltage is applied to two pairs of rods, one pair being held at negative polarity and the other with positive polarity out of phase[37] Ions passing between the rods will experience oscillations, which can either cause them to collide with the rods, or allow them to pass through. Adjustment of the bias on the rods allows ions of a particular mass-to-charge ratio (*m/z*) to pass through and others to collide with the rods before reaching the detector. Hence, a quadrupole acts as a mass filter The detector in its simplest description is an ion counter

1 3 1 1 1 Electro-thermal vaporisation (ETV) –ICP-MS

The ETV unit is effectively a replacement for the nebuliser and spray chamber arrangement shown previously in Figure 1 1. Figure 1 2 shows the ETV system attached to the ICP front-end, normally associated with ICP-MS instrumentation

The ETV is very similar to the set-up normally seen on graphite furnace atomic absorption spectrometers.

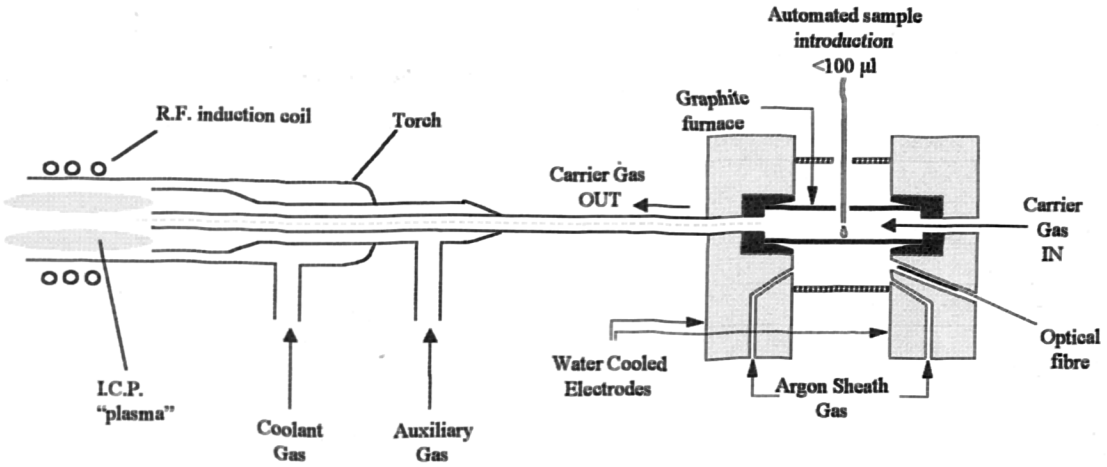

Figure 1.2 Typical ETV device, coupled to an ICP unit

The sample is injected into a graphite tube and a series of pre-programmed ramped heating cycles are applied. On one of the heating cycles, a carrier gas, usually of argon, is introduced directing the vapour to the plasma and subsequently into the mass spectrometer. Peaks of the various analytes of interest are then quantified to give the various concentrations in the original sample. The tube is then conditioned, normally a short burst at high temperature to clear any remaining matrix before the next injection. Careful manipulation of the heating cycles can allow several injections to be introduced in any one run, to give a pre-concentration of analyte. Using different temperature ranges can also allow for separation of more volatile species (importantly, H_2O) leaving others to be measured without interference.

The main advantages are that small sample volumes can be introduced into the plasma (typically <100 µl), matrix separation and an improved sample transport, which will improve detection limits[38]

Stability and sensitivity enhancement of ETV-ICP-MS have been investigated[39,40] showing highest sensitivity for single ion monitoring, when compared with pneumatic (PN) -ICP-MS as well as an ability to analyse more complex matrices Unfortunately, it is not always possible to obtain multi-element information due to the transient nature of the signal often resulting in poor reproducibility (>10% RSD) Memory effects can occur from refractory elements[41]

1.3.2 Sector Field (SF)-ICP-MS

Most sector field instruments are fundamentally similar in design to each other and usually only differ in arrangement There are two types of sector instrument, single-focusing and double focusing Figure 1 3 shows a generalised layout for a double-focusing instrument Generally the sample introduction system and plasma is identical to most quadrupole instruments The most important difference being that the analyser comprises of electric and magnetic sectors rather than a quadrupole to separate masses

In both single and double-focusing instruments, the ions are accelerated via a series of electrostatic slits, their velocity being controlled by the potential applied to

the slits. When the ions enter the magnetic sector, they are subject to a magnetic field, parallel to the slits but perpendicular to the ion beam.

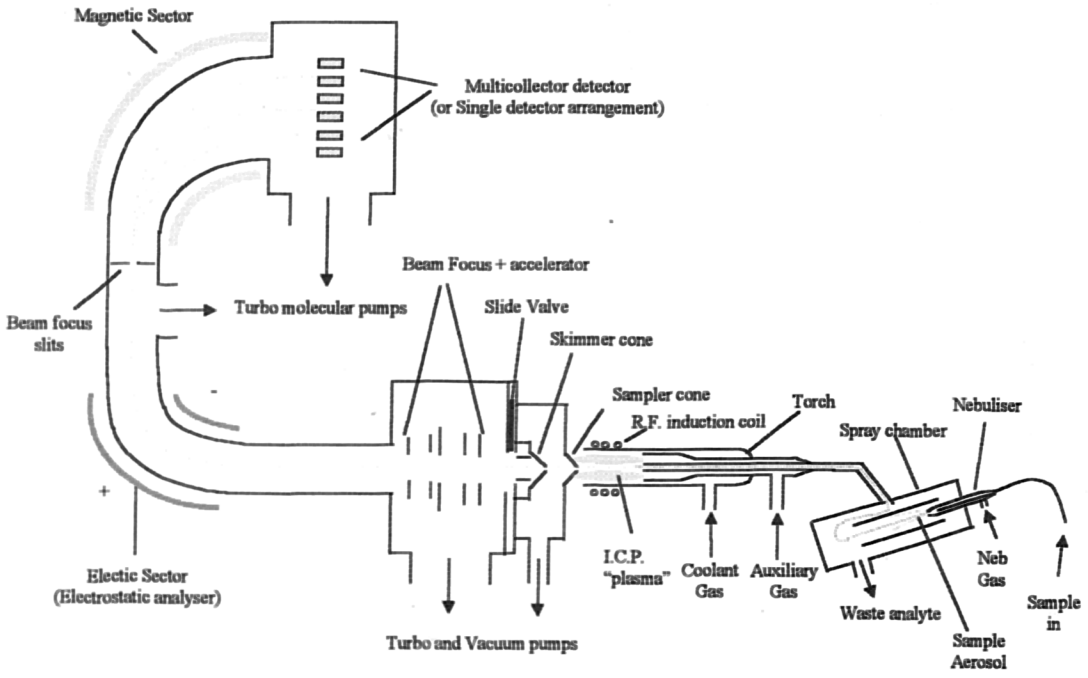

Figure 1.3 Generalised layout for a double-focusing Sector Field ICP-MS instrument, with a multi-collector detector arrangement

The magnetic field causes ions to deviate from their initial path in a curved trajectory. Subsequently, each ion has its own unique trajectory according to its mass to charge ratio (*m/z*), and by changing the magnetic field individual ions can be directed through the detector slit. A double-focusing instrument contains an additional electrostatic sector which disperses ions with respect to their energy. A narrow slit is used to transmit a narrow band of ion energies causing an improvement in resolution but with a loss of sensitivity, due to fewer ions reaching the detector[37].

1.3.3 Instrumental Performance

Typically, ICP-MS is capable of precision and accuracy in the range 2-5% depending on the sample type, however, in situations where the sample matrix is complex or concentrated, interference can arise which degrades the accuracy and precision significantly[42] In the simplest case, a high concentration of total dissolved solids (TDS) can lead to salt deposits on the torch and sample cone, which results in a reduction in sensitivity, instrument drift and degrades precision Other problems encountered in ICP-MS determinations are matrix effects and spectroscopic interferences which are discussed below

1.3.3.1 Matrix Suppression or Enhancement

Matrix suppression and enhancement is thought to be caused primarily by space charge effects in the ion beam, whereby lighter analyte ions are scattered off-axis by coulombic repulsions of heavier matrix ions It is also possible that a degree of ionisation suppression or antipolar diffusion occurs in the plasma itself[43] There is no single solution to this problem, however, its effects can be minimised by dilution of the sample, matrix matching of standards, use of internal standards, flow injection and, ideally, separation of the matrix from the analyte by chromatographic techniques

1.3.3.2 Spectrometric Interferences

Quadrupole ICP-MS instruments are only capable of a resolving power of approximately 0 5 m/z, so these instruments suffer from numerous spectroscopic

interferences caused by isobaric and polyatomic ions of the same nominal mass as the analyte of interest

Polyatomic ions are formed from water, plasma, matrix constituents and reagents used for dissolution, so that the first requisite should be to avoid the use of reagents which can lead to their formation (e g the use of HCl precludes the determination of ^{75}As because of the interference due to ArCl at *m/z* 75) The most common method of eliminating spectroscopic interference caused by the matrix is to separate the matrix from the analyte using a chromatographic sample pre-treatment step There are numerous other methods that have been described for the removal of polyatomic ion interferences, including sample introduction using ETV, desolvation, addition of molecular gas, use of alternative gas (e g helium[44]), shield torches for cold plasma operation, and the use of collision cells Alternatively, SF-ICP-MS can be used to resolve many spectroscopic interferences, when operated in high resolution mode

Investigations[45] into polyatomic interferences on actinide determinations have shown that, if ^{233}U and ^{239}Pu are to be analysed in the presence of a large amount of ^{232}Th and ^{238}U, then interference due to $^{232}Th^{1}H^{+}$ and $^{238}U^{1}H^{+}$ is likely Unfortunately, SF-ICP-MS in is not capable of resolving these interferences, for which resolutions of >50,000 are required, hence, the use of chromatographic techniques for pre-concentration and matrix removal is an attractive option

1.4 APPLICATION OF ICP-MS FOR THE DETERMINATION OF ACTINIDE ELEMENTS

The application of ICP-MS for the determination of actinides in high level spent nuclear fuels has been well reported in the literature, with good results[46,47,48] Normally for applications using highly radioactive isotopes, analysis is performed using a glove-box[47] attached to one end of the ICP-MS The use of glove box HPLC-ICP-MS with a Dionex CS 10 column[48,49] demonstrated the potential of the column to separate U from Pu in spent nuclear fuels, thus, eliminating the $^{238}U^{1}H^{+}$ interference and allowing quantification of ^{239}Pu

Many workers have also been attempting to achieve the fg ml^{-1} detection limits required for environmental analysis[27,29] Examples include Crain *et al.*[29], who have quoted 20 fg ml^{-1} detection limits, by using an off-line TRU-Spec™ Resin as a pre-concentration step, whereby 0 1M tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) was used to separate Th, Np and Pu, then 0 1M ammonium bioxalate to elute the remaining uranium fraction. On-line flow injection ICP-MS (FI-ICP-MS) with TRU-Spec™ Resin (EichroM Industries) has been used[50], limits of detection for ^{230}Th and ^{234}U were 50 and 30 pg g^{-1} respectively, in a soil reference material TRM-4 Aldstadt *et al*[51] also report good results for a FI-ICP-MS using TRU-Spec™ Resin (EichroM Industries) for the determination of ^{238}U in ground water with a potential 0 3 pg ml^{-1} detection limit using pre-concentration Pre-concentration and isotope dilution techniques[52,53,54,55] with ICP-MS have been compared to radioanalytical methods, demonstrating that ICP-MS is capable of producing comparable results for the actinides determinations, with far greater speed The use of 8-

hydroxyquinoline[56,57] for pre-concentration has been reported with detection limits as low as 30 pg ml^{-1} for ^{238}U

Pneumatic nebulization and ultrasonic nebulization (USN) have been compared[58], with sub pg ml^{-1} detection limits for most actinides in industrial wastewater, with ^{238}U Kim *et al* [59] achieved detection limits of 0 02 pg ml^{-1} for both ^{238}U and ^{232}Th, when using ultrasonic nebulization with high resolution ICP-MS (SF-ICP-MS), improving on previous investigative applications by the group[60,61,62] Sample pre-treatment was off-line using an anion exchange (Dowex 1- X8) combined with other radiochemical extraction processes Chiappini *et al.*[63] demonstrated the potential of SF-ICP-MS for actinide determination, quoting close to 1.2 fg detection limits[64] for ^{237}Np, but only in weak nitric acid solutions

1.4.1 Applications of ETV-ICP-MS

Losses can result from poor transfer of analyte through the transfer line or by inefficient vaporisation, leading to a loss of sensitivity and signal stability Chemical modifiers are a useful method for improving poor analyte transfer[65], palladium nitrate having potential for uranium determination. Gray *et al.*[66] discussed the possibilities of chemical modification for ETV-ICP-MS using freon gas added to the nebuliser gas to improve uranium determination, because uranium forms stable carbides A Chelex-100 ion-exchange column for pre-concentration of uranium in seawater was also used to remove the salt matrix, resulting in an improvement of sensitivity and stability of the ETV system for real samples[66]

The role and effect of chemical modifiers for ETV-ICP-MS and analyte transport losses have been reported[67,68,69] with improvements in signal for uranium and thorium when using freon-23 (CHF_3) Goltz *et al*[68] demonstrated that at temperatures below 2000°C, signal suppression resulted due to the accelerated rate of carbide formation The use of 0 3% CHF_3 mixed with the argon carrier gas was found to be effective at preventing intercalation of uranium in the graphite tube, and subsequently uranium carbide formation

1.5 CHROMATOGRAPHIC SEPARATION OF ACTINIDES

Chromatography is a very well established technique, early developments being attributed to Tswett who, in 1903, separated leaf pigments on a polar solid phase[70]. The possibilities for separation are vast but, unfortunately, there is rarely a single column method which is totally suited to any one particular application. The modern approaches of flow injection analysis (FIA) and chromatographic column pre-concentration techniques have been described as being well suited to ICP based applications[71]

1.5.1 Extraction Chromatography

EichroM Industries[72] *produce a number of resins specific for the actinides,* namely TRU-Spec™, TEVA-Spec™ and U/TEVA-Spec™, and provide details of chemical structure (Figure 1 4) and acid-dependency. Some extraction procedures and application of these resins have been addressed at recent EichroM group

meetings[73,74] and by Horwitz[75,76,77,78,79], who has carried out much useful experimentation of the resins' properties By careful selection of oxidation and reduction reagents it is possible to fix the various actinides in oxidation states that are retained on the column On-column reduction and elution can then be used to sequentially separate the elements An additional benefit is that the matrix is not retained on the column so separation of analyte and matrix is possible

For the Tru-Spec resin (Figure 1 4) the extractant is octylphenyl-N,N-di-isobutylcarbamoylphosphine oxide (CMPO), dissolved in tri-n-butyl phosphate (TBP) supported on an inert polymeric substrate (polymethacrylate resins, typically, Amberchrom CG71) The U/TEVA-Spec resin uses dipentylpentylphosphonate (DP[PP]), which is simply coated neat onto the resin TEVA-Spec resin uses a aliphatic quaternary amine, whose function is similar to the functional groups that are found on anion exchange resins However, experimentation has shown that the TEVA-Spec resins have a greater affinity to the actinides than other ion-exchange resins[72] The range of oxidation states of the actinides and their various aqueous solution forms are given later in section 5 3 2, Table 5 2 and Table 5 3 respectively Figure 1 5 shows the typical mechanisms for the Spec resins

The metal (M) forms a complex with the anion (X) and the complex is extracted into the organic phase Under different conditions, the complex can be back extracted into the aqueous phase, indicated by the arrows

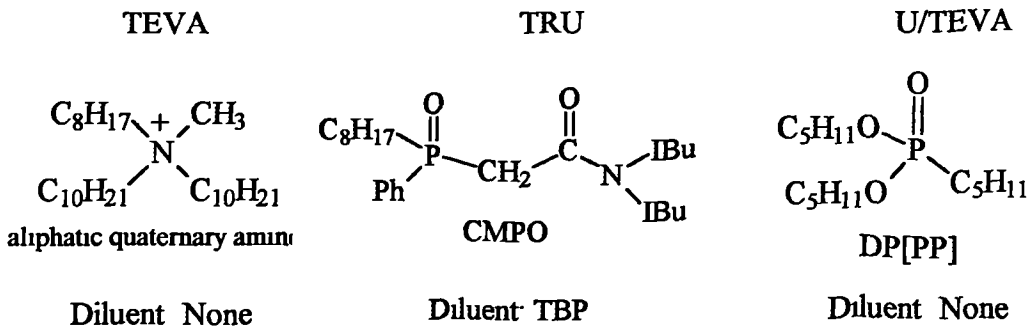

Figure 1.4 Chemical structure of the TEVA-Spec, TRU-Spec and U/TEVA-Spec extractants.

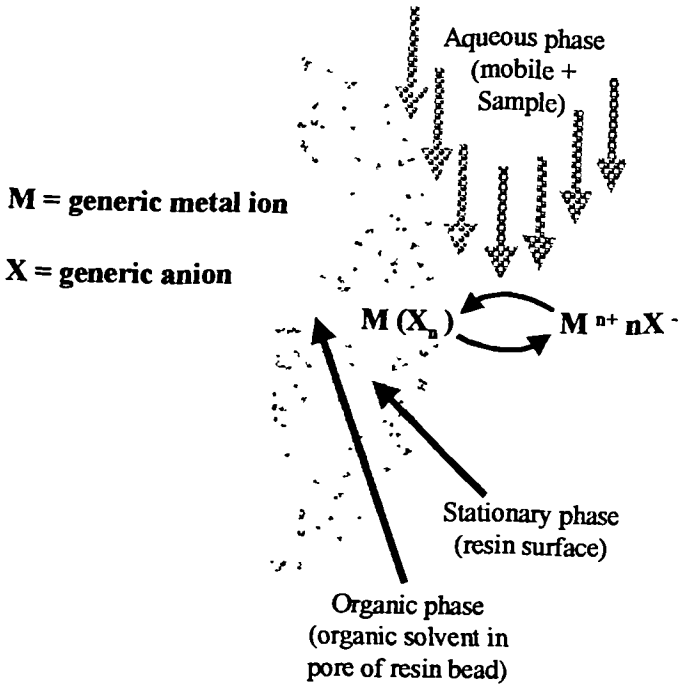

Figure 1.5 Diagram showing typical extraction resin bead for the Eichrom Spec resins.

The stronger the extracted complex, the greater time it will remain in the organic (stationary) phase to that of the aqueous (mobile) phase Therefore, stronger extracted complexes will elute much later than other metals Equation 1 6, Equation 1 7 and Equation 1 8 describe this extraction equilibrium, for Tru-Spec resin, where

(E) represents the extractant Americium is coordinated by three CMPO molecules (Equation 1 6), while the other actinides are coordinated by only two (Equation 1 7 and Equation 1 8).

$$Am^{3+} + 3NO_3^- + \overline{3E} \Longleftrightarrow \overline{Am(NO_3)_3 \cdot E_3} \qquad \textbf{(Equation 1.6)}$$

(Ln^{3+})

$$Pu^{4+} + 4NO_3^- + \overline{2E} \Longleftrightarrow \overline{Pu(NO_3)_4 \cdot E_2} \qquad \textbf{(Equation 1.7)}$$

(Np^{4+})

$$UO_2^{2+} + 2NO_3^- + \overline{2E} \Longleftrightarrow \overline{UO_2(NO_3)_2 \cdot E_2} \qquad \textbf{(Equation 1.8)}$$

As a consequence of this complex dependency, the concentration of acid in the mobile phase has significant effects on the retention of analytes (Figure 1 6(a) and (b) taken from Horwitz *et al.*[79]) It is observed from Figure 1 6(a) that the retention behaviour of U(VI) and Np(IV) on the U/TEVA-Spec resin is nearly indistinguishable over the entire range of acidities, with U(VI) being more strongly retained than Th(IV) but for the lowest acidities For the TRU-Spec resin, the k' values for the ions are typically 100 to 1000 times greater than on the U/TEVA-Spec resin, indicating a greater potential for pre-concentration over the later (A typical definition for k' is given later in section 5 3 3) More importantly, the TRU-Spec retains all but the pentavalent actinides over a wide range of acidities Figure 1 6(b) shows the effects

of hydrochloric acid on the retention of the actinides *k'* values for TRU-Spec resin are typically much higher than the U/TEVA-Spec and TEVA-Spec resins Considering that U(VI) is very strongly retained even in high HCl concentrations, indicates potential for separation of the analyte from interfering matrix ions and or other actinides, if the need arises This strong retention characteristic is also particularly advantageous if a pre-concentration step is required Previous studies by Siddall[80,81] would give indication as to the possible mechanism of the the TRU-Spec functional group, presumably, it is a chelating extractant by means of its bidentate organophosphorous group The TBP diluent may also play some part as a trivalent actinide extractant from nitric acid solutions Although, monodentate compounds such as TBP are poor extractors of trivalent actinides from nitric acid solutions[80], subsequently, this would also give some evidence to explain the weaker extraction capabilities of the U/TEVA which is also of a monodentate variety Altering the molecular structure in which these organophoshorous groups are contained has been described as a means of improving the extracting strength of the compounds[80], hence, this would give some indication of the size and complexity of the CMPO molecule used in the TRU-Spec resin In contrast, the TEVA resin somewhat differing from the others resins, having an apparent anionic association with the metal ions (positive charge on the nitrogen) It is presumed that its mechanism is controlled by means of a ligand-actinide species interaction in nitric and hydrochloric acid solutions (particularly with tetravalent ions[72]), which forms a complex with the extractant (e g E_2^+ $Pu(NO_3)_6^{2-}$) this being characteristic to a more "ion-ion" interaction mechanism, thus pertaining to its selectivity to certain actinide species

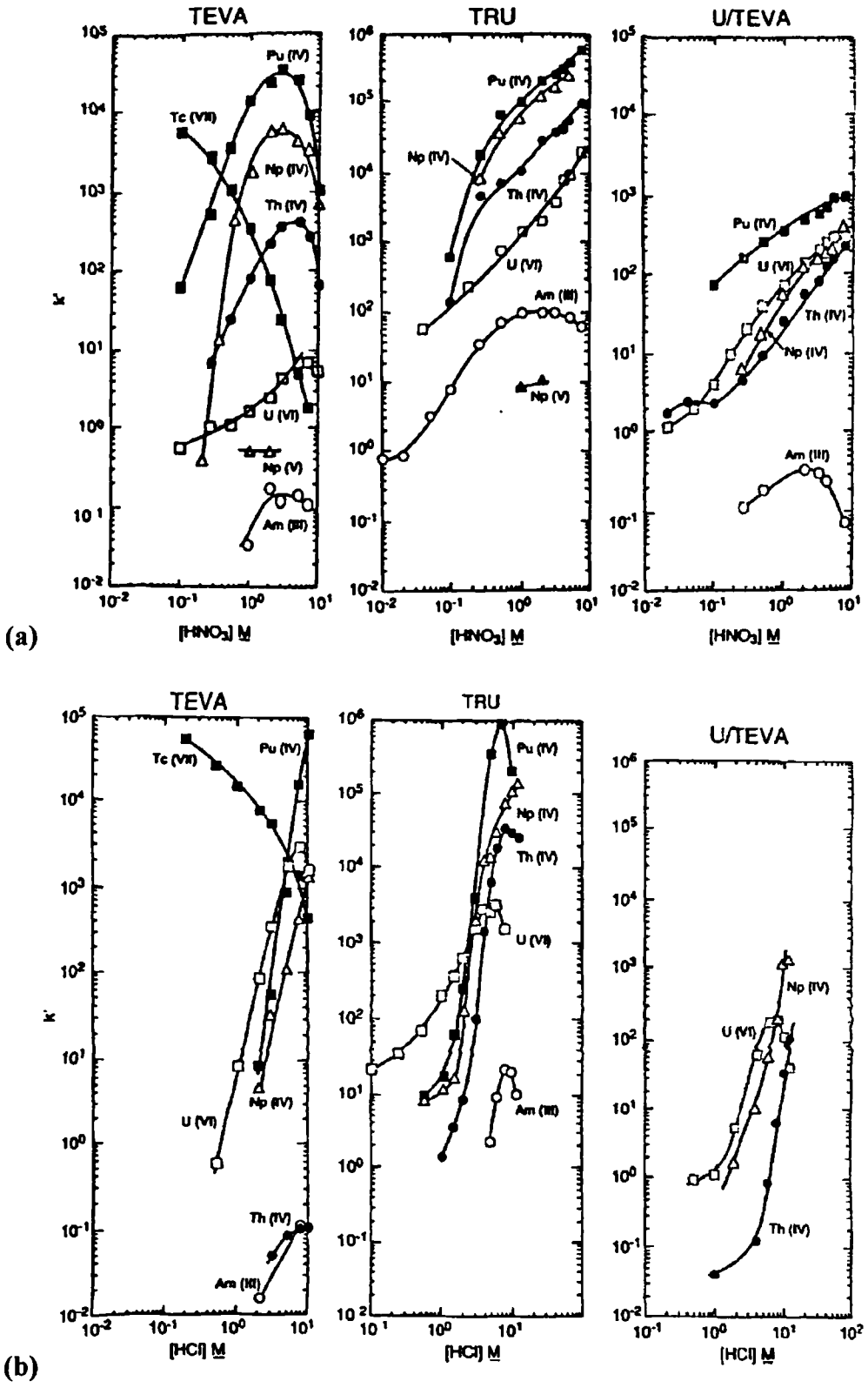

Figure 1.6 **(a) Nitric acid and (b) hydrochloric acid dependency of *k'* for actinides at 23-25°C[79]**

1.5.2 Applications of extraction chromatography

Sr-Spec, TRU-Spec and U/TEVA-Spec resins have been tested with good results on high level nuclear waste solutions[79,82] Sr-Spec resin is primarily for use in strontium extraction and analysis, however, it does have some affinity for Pu(IV) and Np(IV), the others actinides being poorly retained TRU-Spec™ resins have also been used for Am, Cm and Pu determination[83] Chernobyl-derived ^{239}Pu, ^{240}Pu and ^{241}Am have been determined in organic matter and soil solutions[84], using combinations of TRU-Spec and TEVA-Spec resins

TEVA-Spec™ resins have also been used for plutonium separations from biological and soil samples[85], but only obtaining at best 70% recoveries for $^{239}Pu+^{240}Pu$ U/TEVA-Spec resin has been used for the pre-concentration of uranium isotopes[86], allowing the determination of $^{234}U/^{238}U$ activity ratio calculations from samples of Bauxite and aluminium compounds. U/TEVA-Spec and TRU-Spec resins have been arranged in a simplified layout to partition individual actinides from water, soil and sediment samples before analysis by liquid scintillation spectrometry[87] It was found that recoveries were accurate to ±5 to ±20% for low $\mu g\ g^{-1}$ levels of U, Pu, and Np isotopes in up to 27g of reference materials TRU-Spec™ resins have also been used[88], for the determination of ^{241}Am in air filters and urine

A relatively new Diphonix™ ion-exchange resin (also from Eichrom) being extremely specific to the actinides has been used to extract all actinides from large soil samples[89] (typically sample sizes being up to 20 g) with the aim of improving actinide recoveries Typical procedures involve a microwave digest, acid digest or a fused

sample being passed through the Diphonex column, the actinides are then separated from the matrix, and the fraction containing the actinides is boiled to dryness and made up in column feed solution The final fraction is then passed through a TRU-Spec and then a TEVA-Spec column to allow selective separation of the actinides prior to analysis Results have given better agreement with certified values, but these procedures are still considerably lengthy[89]. Diphonix has been also used for the extraction of naturally occurring radionuclides in marine sediments[90]

Dowex resins are historically the more widely used substrates, and the basis for other manufacturers' work on new resins[72], matrix structure is primarily microporous styrene / divinyl benzene (DVB) for both anion and cation exchange The anion exchanger Dowex 1X8 has been used for uranium and thorium separations[91,92,93] Other Dowex based resins[94] with varying cross-linking have also been tested, with the objective of altering the selectivity of lanthanide retention Low recoveries for uranium and thorium have been observed[95], with subsequent experiments revealing that these elements had adsorbed non-reversibly onto glassware as well as the resin. Uranium and thorium separations using Dowex 1X2 and Dowex 1X8 consecutively and Dowex 1X4 for Pu separations from Am and Cs have been reported[96,97] Dowex 1X8 resins have also been used for separation of uranium and thorium with good agreement with reference values for river sediment, sea sediment, stream sediment, sea plant[98], and uranium separations from fish samples[99]

1.5.2.1 Sample digestion techniques

Various digestion techniques have been described[100,101] for air, soil and sediment. Examples include aqua regia for soils and sediments, finding rock materials containing radionuclides within their lattice structure may require a more vigorous HF digest, microwave digests or fusions to obtain full recoveries. Co-precipitation is a method adopted by the radiochemists, whereby, the actinides are co-precipitated on $Fe(OH)_2$ with the water phase. This approach being of particular use for seawater samples[96,102]. For freshwaters, the actinides are also co-precipitated with $Fe(OH)_3$, then the pH is raised to 9 with NH_4OH and the precipitate dissolved in acid. Typical recoveries[103] for ^{242}Pu and ^{243}Am were 113 ± 10 % and 83 ± 3 % respectively for seawater samples and 92% for ^{238}U in freshwater[104]. Biological samples are typically ashed in a muffle furnace and are then leached or dissolved in 8M to 16M nitric acid[105] respectively, before analysis. Leaching of sediments with 6M hydrochloric acid is the most widely adopted procedure for extracting adsorbed actinides[106].

1.6 AIMS OF THE STUDY

The aims of this study are to determine the actinide elements (mainly long lived alpha emitters having half lives of several years) in environmental samples, such as waters, biologicals, soils and sediments to very low limits of detection, without interference. This will ultimately be achieved by using on-line solid phase extraction and high performance liquid chromatography for pre-concentration and separation of actinide elements from the matrix coupled to ICP-MS.

It was also proposed to investigate novel methods of chelation chromatography for more efficient separation of the actinide elements from each other and from interfering elements

Chapter 2

DETERMINATION OF NATURAL URANIUM AND THORIUM IN ENVIRONMENTAL SAMPLES USING SOLID PHASE EXTRACTION AND QUADRUPOLE ICP-MS

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2.1 INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) is ideally suited to the determination of the concentration and isotopic composition of the actinide elements The principal advantages of quadropole ICP-MS are speed and sensitivity, with the capability of determining all the actinide elements within a minute, at concentrations as low as 1 pg ml^{-1} in liquid samples In addition, there is no need to separate the elements one from another, as there is in α-spectrometry, because this is achieved by the mass spectrometer, hence, the number of sample pre-treatment stages can be greatly reduced However, it is still necessary to separate the radionuclides from the matrix, a procedure for which column pre-concentration methods are ideal Recently, a number of very specific chelating resins, which are particularly suited to this task, have become available Some extraction procedures and applications for these resins, as discussed in chapter 1, have been addressed by Horwitz[75,76,77,78,79] and Crain *et al* [29], who have quoted 20 fg ml^{-1} detection limits for ^{239}Pu and ^{235}U using TRU-Spec™ resin as a pre-concentration step prior to analysis by ICP-MS Alvardo and Erickson[67] obtained 5 fg and 2 fg detection limits for ^{238}U and ^{232}Th respectively when using electrothermal vaporisation (ETV) coupled with ICP-MS and trifluoromethane (CHF_3) as a modifier gas, compared to 180 fg and 1600 fg for an

unmodified ETV Wyse and Fisher[28] have reported a potential 3 fg absolute detection limit for plutonium using ICP-MS and TRU-Spec™ resin, and concluded that results for the determination of ^{239}Pu in urine were comparable to those obtained using alpha-spectrometry Similarly, ^{230}Th and ^{234}U have been determined in the soil reference material TRM-4[50] using hydrofluoric acid for sample digestion Chiappini et al[63] has quoted a 1 2 fg detection limit for uranium, using a new high sensitivity ICP-MS[64] and a high-efficiency desolvating nebulizer Aldstadt *et al.*[51] have also reported good results for the determination of ^{238}U by FI-ICP-MS using TRU-Spec™ Resin The use of ^{209}Bi or ^{205}Tl as internal standards has been quoted to be applicable for use in thorium and uranium determination in biological samples[24] In this work the application of an actinide-specific resin for pre-concentration and matrix removal prior to analysis by ICP-MS, with and without ETV sample introduction, has been addressed[107,108]

In order to establish the benefits of using ICP-MS over α-spectrometry, it was desirable to carry out a brief comparative study of the two techniques This was performed on a number of real water samples collected from areas of Plymouth and Dartmoor (Devon, UK) The ICP-MS methodology used for this comparison has been described in this chapter and subsequent papers[107,108]

2.2 EXPERIMENTAL

2.2.1 Instrumentation

2.2.1.1 Pneumatic Nebulization (PN)-ICP-MS Detection

An inductively coupled plasma mass spectrometer (PlasmaQuad 2+, VG Elemental, Cheshire, UK) was used Data was acquired using the time resolved analysis software, which allows time resolved monitoring of multiple isotopes, and manipulated off-line using MassLynx software Operating conditions are shown in Table 2 1

2.2.1.2 Electrothermal Vaporisation (ETV)-ICP-MS Detection

An inductively coupled plasma mass spectrometer (Elan 5000A, Perkin Elmer) interfaced with and electrothermal vaporisation (ETV) sample introduction system (HGA 600MS, Perkin Elmer) was used Data was acquired in transient peak hopping mode, which allows time resolved monitoring of multiple isotopes Operating conditions for the ICP are shown in Table 1, with the associated temperature program for the ETV shown in Table 2 2

Samples (detailed later in section 2 2 5) were eluted with 5 ml of 0 1 M ammonium bioxalate from the injection manifold (described later in 2 2 3) into ETV auto-sampler vials Portions (30 µl) were pipetted into the ETV furnace tube and the temperature program initiated (Table 2 2)

Table 2.1 Operating conditions for ICP-MS.

	VG PQ2+	PE ELAN 5000A
ICP		
Forward power (W)	1350	1080
Plasma gas (l min^{-1})	16 5	15
Auxiliary gas (l min^{-1})	0 7	1 0
Nebulizer gas (l min^{-1})	0 8	0 8
Sampling depth (mm)	10	15
Sample flow (ml min^{-1})	0 5	1 0
Torch	Fassel (quartz)	Fassel (quartz)
Nebulizer	Concentric (quartz)	Cross-flow (Gem-tip)
Spray Chamber	Scott type (quartz)	-
Interface		
Sampler	Ni	Pt
Skimmer	Ni	Pt
Mass Spectrometer		
Ion masses (m/z)	^{232}Th, ^{238}U, ^{209}Bi	^{232}Th, ^{238}U, ^{235}U
Data acquisition	Time resolved mode	Transient, peak hopping
Points per peak	3	1
DAC step	3	N/a
Dwell time (ms)	20	40
Time-slice duration (s)	1	-

Table 2.2 Operating conditions and gas flows for the ETV system.

Program step	Temp (°C)	Ramp time (s)	Hold time (s)	Internal furnace gas flow (ml min^{-1})
1	100	10	15	300 (Ar)
2	120	10	60	300 (Ar)
3	800	5	30	10 (CHF_3)
4	2500	0 2	2	0 (to ICP)
5	2700	0	1	0 (to ICP)
6	20	15	1	0 (to ICP)

2.2.2 Alpha Spectrometry (AS)

The water samples were also analysed independently by alpha spectrometry, the data being supplied by the LGC (formally known as the Laboratory of the Government Chemist, Teddington, UK) No pre-treatment of the sample was performed prior to submission. 500 ml of each sample was used for the α-spectrometry determination (normally, 1-2 litres of sample is required to improve detection limits and precision) Detection limits for water samples were typically 10 and 30 ng l^{-1} for ^{238}U and ^{232}Th respectively

2.2.3 Injection Manifold

The flow injection manifold comprised a 500 µl injection loop on a 6 port valve (Model 5020, Rheodyne, Cotati, California) and was interfaced with the PN-

ICP-MS instrument as shown in Figure 2.1. This manifold constitutes the final optimised version, which was used for analysis of the samples and reference materials given later in this chapter (The stages for optimisation of this manifold are discussed later in 2.3.1). For ETV-ICP-MS analysis, samples were pre-concentrated off-line.

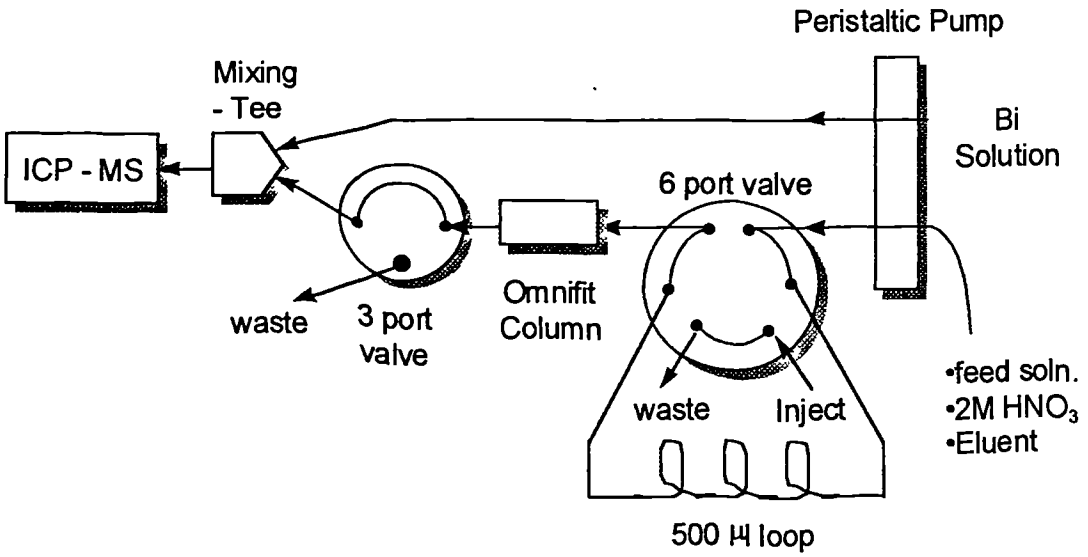


Figure 2.1 Schematic of the flow injection manifold interfaced with ICP-MS.

2.2.3.1 Analytical Columns

Columns were prepared with a dry powder of resin (50-100 µm, TRU-Spec™, EiChrom Europe, 75010 Paris, France) in commercially available glass chromatography columns of 3 mm i.d. and 50 mm length (Omnifit microbore columns, Omnifit, Cambridge, UK). When not in use the columns were filled with 2M HNO_3, and prior to use they were washed with successive portions of 0.1M ammonium bioxalate and 2M HNO_3 at a flow rate of 0.5 ml min^{-1} for 6 minutes, and

finally 1 ml of column feed solution (detailed in 2 2 4) The aluminium ($Al(NO_3)_3$) in the feed solution improves breakthrough capacity, particularly in samples having a high phosphate content, which can reduce column performance

2.2.4 Reagents

All solutions were prepared using analytical grade reagents and distilled deionised water (DDW) (Ultra Pure Water, Elgastat Maxima, Elga Ltd, Bucks, UK) Analytical reagents were nitric acid [2M] (Aristar, Merck, BDH, Poole, UK), eluting solution 0 1M ammonium bioxalate ($NH_4HC_2O_4$) (Fisons Scientific Equipment, Loughborough, UK) filtered through a 47 mm diameter 0 45 µm sterile membrane filter paper (Whatman Laboratory Division, Maidstone, UK), internal standard solution [15 ng ml^{-1} Bi] prepared in 2% HNO_3 from 10,000 µg ml^{-1} stock solution (BDH Laboratories, Poole, UK) to allow correction for instrumental drift, column feed solution [1M $Al(NO_3)_3$] (Analytical Grade, Fisher Scientific U K , Leicestershire, UK) purified by passing through a 1.2 cm^3 bed of Dowex 1-X8 anion exchange resin then a 0 6 cm^3 bed of Tru-Spec resin then diluted to concentration of 0 5M in 2M HNO_3 A mixed standard solution of 10 µg ml^{-1} ^{232}Th and 10 µg ml^{-1} ^{238}U, was prepared in 5% HNO_3 from 1000 µg ml^{-1} stock solutions of the individual elements (Johnson Matthey Ltd , Reading, UK) Lithium metaborate (Spectroflux, Johnson Matthey, UK) was used for fusion digests Iron (III) nitrate (BDH Laboratories, Poole , UK) was used to prepare solutions with high iron concentrations. Sodium formaldehyde sulfoxylate solution (Fisons Scientific Equipment, Loughborough, UK) was prepared by dissolving approximately 0 3g of the solid compound in 10 ml of 2M

HNO_3 solution then 0 5 ml of this was added to every 10 ml of standard to be analysed

2.2.5 Standard and Sample Preparations

2.2.5.1 Standard Solution Preparation

In order to ensure that the analytes were in the correct oxidation states to be retained on the column (i e U (VI) and Th (IV)), 10 ml of the 10 μg ml^{-1} standard solution was boiled to dryness in two successive 10 ml portions of concentrated HNO_3 Finally, standards were made up in column feed solution for on-column calibrations or 0 1M ammonium bioxalate if off-column calibration was required

2.2.5.2 Sample Preparation - Water Reference Materials

Two certified reference materials were studied, namely NASS-4 Open Ocean Sea Water and SLRS-3 River Water (National Research Council, Ottawa, Canada) Samples, 10 ml of NASS-4 and 25 ml of SLRS-3, were treated in the same way as the mixed standard solution, except that they were made up to final volumes of 25 ml and 50 ml respectively with column feed solution

2.2.5.3 Sample Preparation – Natural Waters

Water samples were collected in 1 litre pre-acid washed Nalgene narrow neck HDPE sample bottles and then acidified with 1 ml of concentrated Aristar nitric acid, for every 1 litre of sample Sampling points (Figure 2 2) are listed as follows.

i Burrator Reservoir (Dartmoor, Devon, UK) - Fresh Water

ii Clearbrook (along the River Meavy at the bridge in Clearbrook, Dartmoor, Devon, UK) - Fresh River Water

iii Oreston (along the River Plym, just South of Laira Bridge, Plymouth, Devon, UK) - Estuarine Water

iv Devonport (Hamoaze, Along the Tamar Estuary on the Devonport side, Plymouth, Devon, UK) - Estuarine Water

With respect to Oreston and Devonport, both samples were collected during mid to high tide

2 2 5 3 1 Sample pre-treatment

5 ml aliquots of the samples were made up to 10 ml with 4 M HNO_3 The reference materials were treated as follows a 1 5 ml aliquot of NASS-4 open ocean water was diluted with 1 5 ml of 4M HNO_3,and made up to 10 ml with DDW A 5 ml measure of SLRS-3 Freshwater was made up to 10 ml of 4M HNO_3

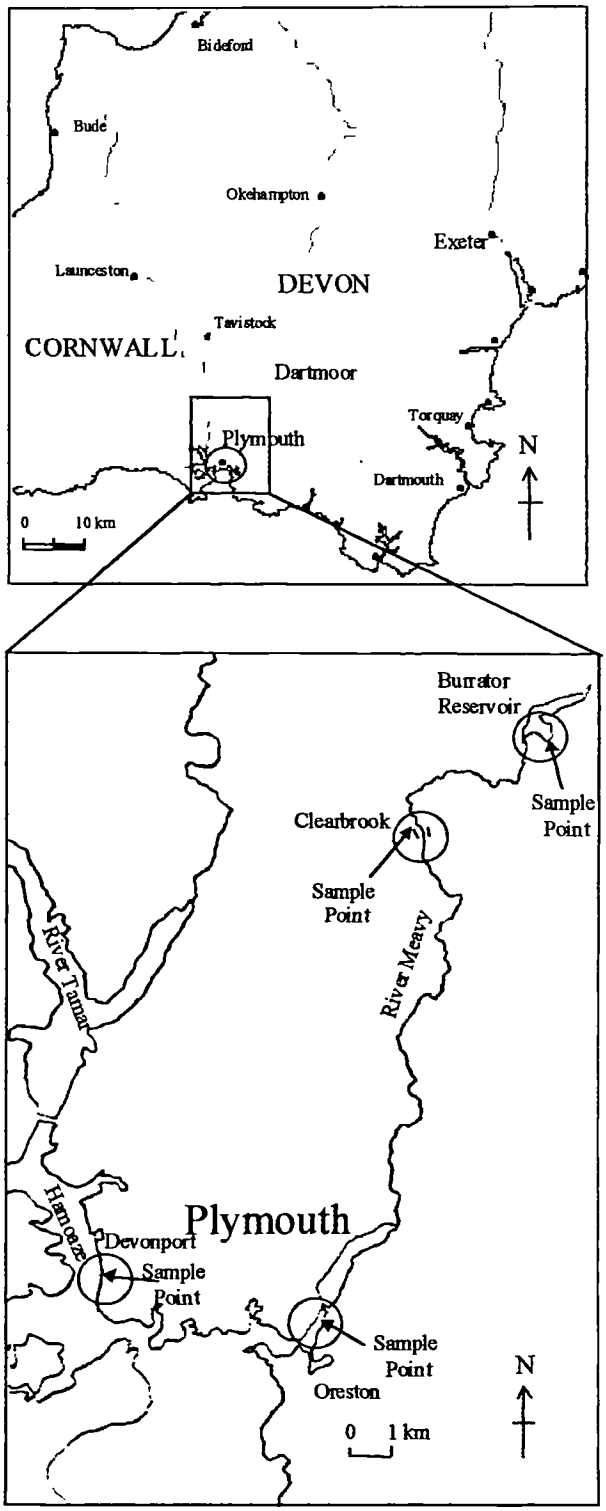


Figure 2.2 Map showing sampling points for natural waters

Prior to ETV-ICP-MS analysis, samples were pre-concentrated on column by means of the peristaltic pump and then eluted in approximately 2 5 ml measures This in effect gave a partial dilution of the pre-concentrated sample Hence, it was desirable to use 8 73 ml of sample or reference material made up to 10ml with concentrated nitric acid to give a 2M HNO_3 solution

The reference materials were analysed at the same time as the samples in order to assess the accuracy and precision of the method It was not necessary to treat the samples with reducing solution in this case, because they did not contain high concentrations of Fe(III) Appropriate blanks were prepared throughout

2.2.5.4 Sample Preparation - Biological Samples

Initially the sample preparation procedure was based on a method by Nelson and Fairman[109] Two certified reference materials (CRMs) were studied, namely NIST 1566a Oyster Tissue and NIST 1575 Pine Needles (National institute of Science and Technology, Gaithersburg, USA) Samples (0 5g) were weighed into porcelain crucibles, placed in a muffle furnace and dry-ashed at 200 °C for 2 hours, 400 °C for 2 hours, 600 °C for 2 hours, and 800 °C for 2 hours The dry-ash step was omitted for the oyster tissue Nitric acid (10 ml) was added to each sample and then they were warmed gently on a hot-plate to digest them and boiled to dryness This was repeated until a white ash was left On the last iteration, the samples were boiled down until almost dry, then 10 ml of the column feed solution was added to each beaker to dissolve the ash Samples were made up to final volumes of 50 ml and

25 ml, with column feed solution for oyster tissue and pine needles, respectively Three digestion blanks were also prepared.

2.2.5.5 Sample Preparation - Fusion of Samples with lithium metaborate

Sample preparations were also performed by lithium metaborate fusion A similar procedure applied to soil samples has recently been used for the determination of uranium and plutonium[110] Several certified reference material were studied, namely NIST 1575 Pine Needles, GBW 08304 River Sediment, GBW 07310 Stream Sediment, IAEA-312 Soil and IAEA-375 Soil Samples (0 3-0 5 g) were weighed into platinum crucibles and 0 8 g of lithium metaborate was added to each, then heated over a Meeker burner A platinum lid was placed on the top of the crucible to improve heat retention and thus encourage fusion Some flaming was initially observed from the pine needles while the organic matter was burnt off The fused sample while in its molten state was poured quickly into a beaker containing approximately 30 ml of column feed solution. Any undissolved fused matter was allowed to dissolve in the solution and mixing was aided by use of a magnetic stirrer Samples were made up to final volumes of 50 ml in column feed solution (additional dilutions were made for samples analysed using PN-ICP-MS, due to high $\mu g\ g^{-1}$ levels) . Three fusion blanks were also prepared

2.2.6 Calibration

A series of calibration standards containing both ^{232}Th and ^{238}U (0 25 to 1 ng ml^{-1}) were prepared and deposited onto the column by flow injection into a carrier stream of column feed solution at a flow rate of approximately 0 5 ml min^{-1} for 1 minute During deposition the outlet from the column was diverted to waste to prevent the column feed solution entering the ICP-MS instrument After a deposition, the column was rinsed with 1 ml of 2M HNO_3 to remove any residual column feed solution before the column was diverted back to the ICP-MS, the analytes were eluted with 0 1 M ammonium bioxalate and the analyte masses monitored After elution the column was again diverted away from the ICP-MS and flushed with 1 ml of column feed solution to remove residual ammonium bioxalate solution *prior to further* deposition. Each injection was repeated three times

2.2.7 Analysis of Samples

An accurate volume of the prepared sample was either measured into a clean polypropylene centrifuge tube or injected into the 500 µl sample loop, depending on whether a pre-concentration step was required. The solution was deposited onto the column by pumping through the manifold using the tubing normally immersed in the carrier stream During deposition the column was diverted to waste The centrifuge tube was rinsed with 1 5 ml of 2M HNO_3, to remove any residual sample from the tube, and subsequently with 1 ml of 2 M HNO_3 to flush through any residual column feed solution prior to diverting the column to the ICP-MS The column was diverted to the ICP-MS instrument, the analytes eluted with 0 1 M ammonium bioxalate, and

the analyte masses monitored (For the ETV-ICP-MS, the flow was diverted (off line) and collected into 30 ml polystyrene vials, approximately 2 5 g (i e 2 5 mins, 1 ml min^{-1} flow rate) weighed portions were taken These were later diluted further and transferred to the auto-sampler system on the ETV-ICP-MS for analysis) After elution the column was again diverted away from the ICP-MS and flushed with 1 ml of column feed solution to remove residual ammonium bioxalate solution prior to further deposition Each injection was repeated at least three times

2.3 RESULTS AND DISCUSSION

2.3.1 Optimisation of the injection manifold

Several factors were important for correct optimisation of the manifold, namely, flow rate, manifold tubing diameter, column packing (frit porosity, substrate particle size and column length)

2.3.1.1 Manifold Tubing

The columns used for the work are normally provided with 0 8 mm internal diameter PTFE tubing suitable for low pressure liquid chromatography work This was considered too large for this work and likely to cause band broadening effects Subsequently trials were made using a 0 3 mm i d PTFE tubing which resulted in higher back pressures but reduced band broadening and sample throughput time. This suppressed some of the pulsing effects that are characteristic to peristaltic pump

systems To prevent leaks the tubing was connected using barbed end fittings that could be joined with existing connections, which proved satisfactory up to pressures of c a 10 psi (tested using a HPLC pump) This was sufficient for most applications using the short Omnifit columns and the flow rate through the column could then be increased up to 2 ml min^{-1}

2.3.1.2 Column Packing

Initially, Tru-spec of 100-150 μm particle size was used, however, it was considered desirable to increase the capacity for pre-concentration purposes, subsequently a 50-100 μm particle size was employed Eichrom quote[72] a capacity of 9 1 mg of americium (least retained ion) per ml of slurry resin bed for the 50-100 μm particle size Considering the column was of 3 mm i d by 50 mm, this would equate to a column volume of 0.35 ml, giving the column a potential capacity of 3 2 mg ml^{-1} for americium The largest pore sized frits of 25 μm were used, as smaller sizes (5 and 10 μm) suffered from high back-pressure problems, making the packed columns unusable for peristaltic pump operation The method of column packing had a considerable effect on the efficiency of the column Initially, the column was packed with a slurry of Tru-Spec in DDW and tested using a fusion of pine needles diluted in the column feed A typical elution profile is shown in Figure 2 3

An internal standard of bismuth solution (15 ng ml^{-1}) was introduced through a PEEK mixing tee (Alltech, UK) and subsequently used as a means of correcting for any instrumental drift Thorium eluted with a peak width of approximately 30 s and

uranium approximately 2 5 min (with considerable tailing), suggesting that the column packing was ineffective under these conditions A back-flushing manifold (Figure 2 4) where the load and elution of the analytes occurred in opposite directions was also tested, and resulted in reduced tailing (Figure 2 5) As can be seen, both thorium and uranium eluted with a peak width of approximately 30 s, indicating that the uranium was being retained more strongly on the head of the column

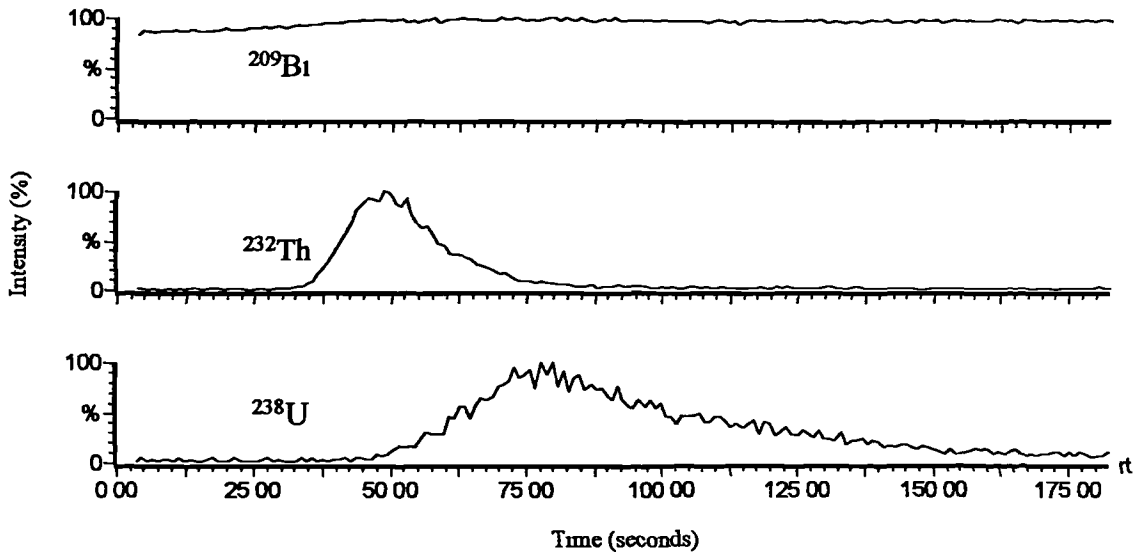


Figure 2.3 Elution profiles for 0.5 ng (0.5 ml loop) of ^{238}U and ^{232}Th obtained using slurry – packed columns.

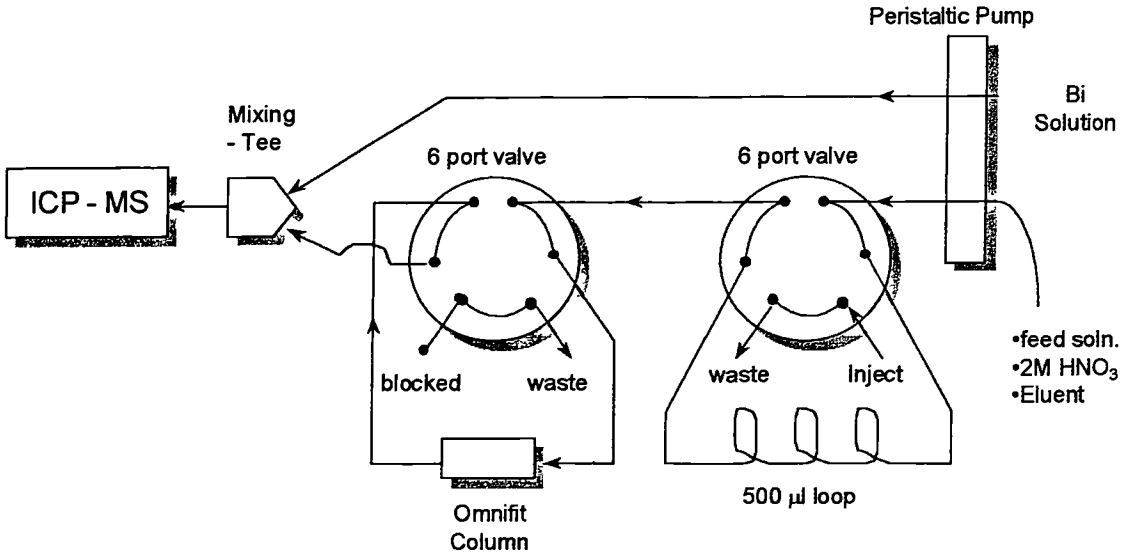


Figure 2.4 **Schematic of an alternative flow injection manifold interface with ICP-MS. (Back-flushing elution system)**

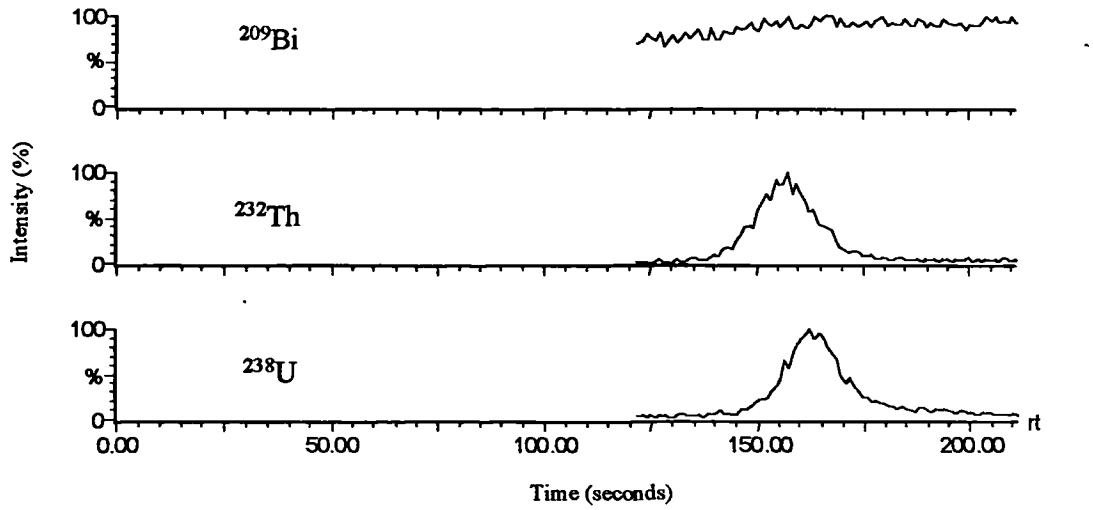


Figure 2.5 **Elution profiles for pine needles certified reference material using Back-flushing manifold (DDW Slurry packing of column).**

However, when the manifold was used for the analysis of real samples, poor accuracy and precision was attained for the determination of Th, and poor precision for U (Table 2 3, from fusion method validated later in 2 3 5 2), this method was consequently abandoned

Table 2.3 Results of the determination of uranium and thorium in the pine needles certified reference material by ICP-MS and using the back flushing flow injection manifold.

CRM	U		Th	
	Certified value (ng ml^{-1})	Found (ng ml^{-1})	Certified value (ng ml^{-1})	Found (ng ml^{-1})
1575 pine needles	20 ± 4	20 93 ± 5 3[a]	37 ± 3	19 64 ± 28 2[a]

[a] n = 3

The original manifold shown in Figure 2 1 was also tested using dry-packed columns The elution peaks for volumes of 0 4 ml ^{238}U and 0 25 ml ^{232}Th using this system are shown in Figure 2 6 The standards were deposited from a 500 µl loop so under these circumstances both ^{238}U and ^{232}Th were eluted in a smaller volume than the sample loop Peak widths were 50 s and 30 s for U and Th, respectively, which were comparable with the back-flushing manifold, with improved precision and accuracy in the analysis of real samples This improvement in elution volume was considered an effect of the packing method itself, as it produced an improved and homogeneous distribution of the resin particles within the column Hence, it was

decided to use the simple manifold (Figure 2 1) in combination with a dry-packed column for all future work

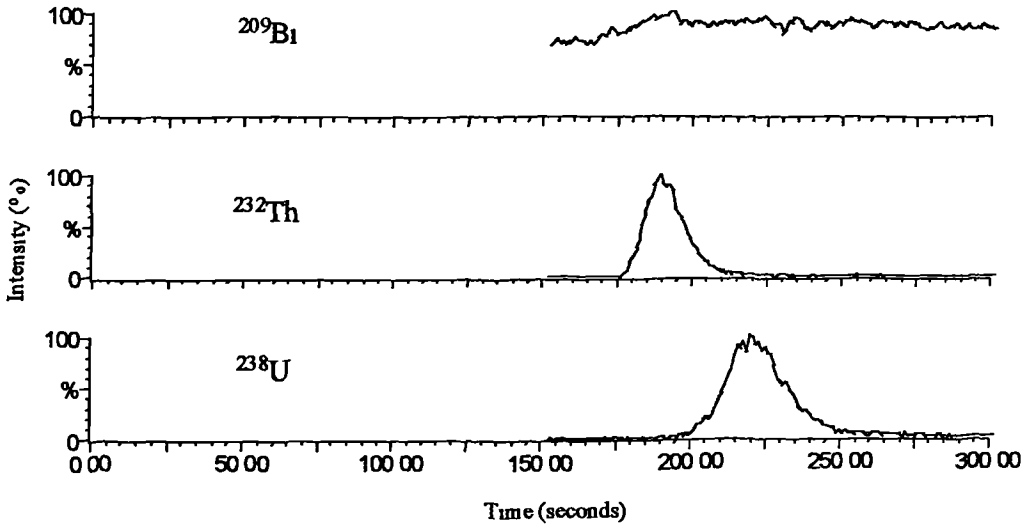


Figure 2.6 Elution profiles for a 0.5 ng (0.5 ml loop) of ^{238}U and ^{232}Th using optimised manifold system.

2.3.2 Optimisation of ETV using freon gas

Vaporisation profiles for ^{238}U and ^{232}Th with and without freon added during the ashing stage are shown in Figure 2.7 and Figure 2 8 In the absence of freon (Figure 2 7) the peaks were approximately 2.5 seconds wide, and ^{232}Th vaporised slightly later than ^{238}U However, when freon was added (Figure 2 8), peak height and peak area signals increased by approximately 10 times and 50 times for ^{238}U and ^{232}Th respectively, resulting in much improved detection limits Other workers have also noted the beneficial effect of freon gas in ETV[67,68,69], which prevents the formation of refractory carbides on the surface of the graphite tube, however, it is

advisable to only introduce the gas during the ashing stage If freon is introduced during the vaporisation stage, tube lifetimes are reduced substantially

2.3.3 Detection Limits

Instrumental and method detection limits for ^{238}U and ^{232}Th are shown in Table 2 4 Instrumental detection limits were determined using solutions prepared in the column-eluting solution (0 1M ammonium bioxalate) which had not been eluted from the column, thus reflecting the level of the blank in the column-eluting solution Method detection limits were determined by pre-concentrating a 0 5 ml aliquot of column feed solution (blank) onto the column and eluting with 0 1M ammonium bioxalate solution

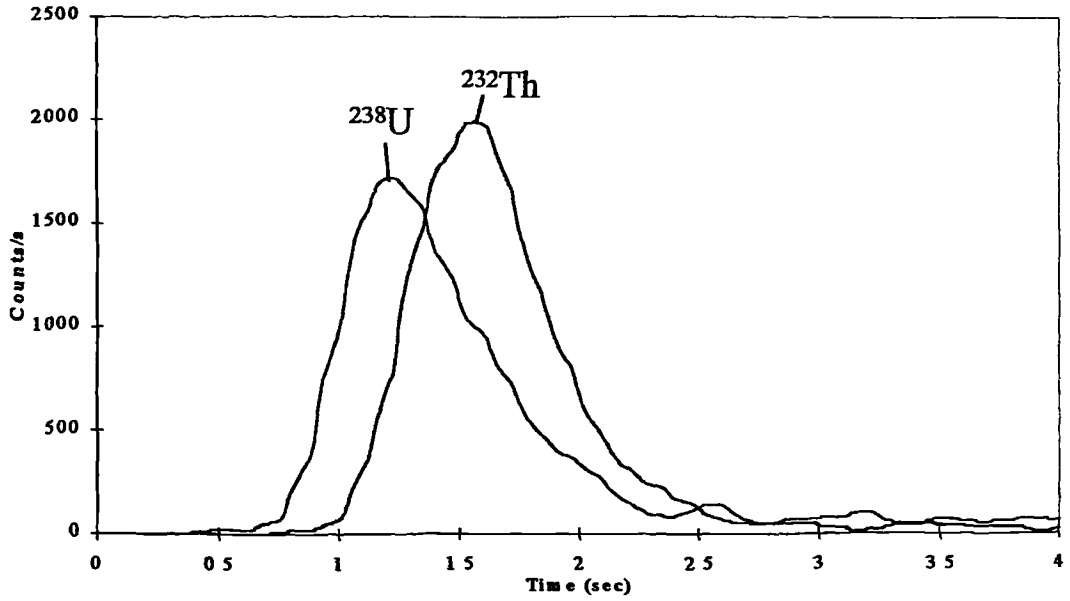


Figure 2.7 Vaporisation profiles for ^{238}U and ^{232}Th: 3 pg ^{238}U and 30 pg ^{232}Th for ETV-ICP-MS using only argon gas.

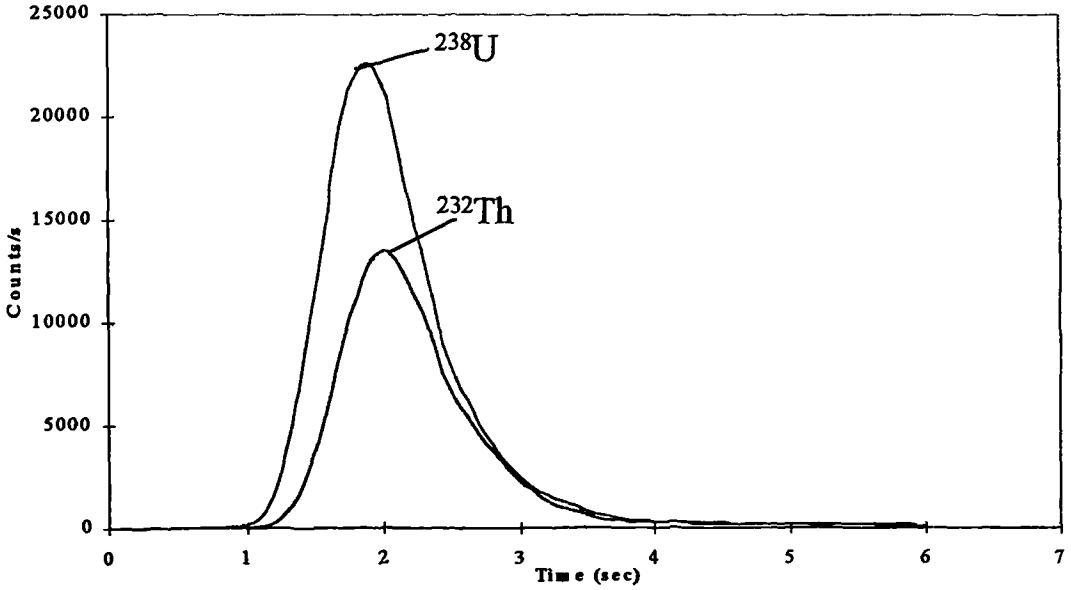


Figure 2.8 **Vaporisation profiles for ^{238}U and ^{232}Th: 3 pg ^{238}U and ^{232}Th for ETV-ICP-MS using CHF_3 modifier gas.**

Table 2.4 **Instrumental and method detection limits for uranium and thorium using pneumatic nebulization (PN) ICP-MS and ETV-ICP-MS.**

	U		Th	
	Absolute (pg)	**Relative (pg ml^{-1})**	**Absolute (pg)**	**Relative (pg ml^{-1})**
Instrumental (PN)	2 7	5 4	3 1	6 2
Method (PN)	24	48	60	120
Instrumental (ETV)	0 03	0 9	0 009	0 3
Method (ETV)	0 6	21	0 3	9

The method detection limits were blank limited and can be improved by a factor of at least 100 if the reagents are purified more effectively This will also allow greater pre-concentration factors to be realised, thereby improving detection limits further.

2.3.4 Effects of iron(III) on uranium and thorium retention

As discussed in Chapter 1, Tru-Spec resin has a high affinity for iron (III), hence saturation with iron (III) in competition with other actinides may result in low recoveries Iron is at approximately 5% abundance by weight in the Earth's crust[111] and is present in high concentrations in clay based soils

Tru-Spec has a very low affinity for iron(II), so, it is desirable to reduce any iron(III) to (II) Sodium formaldehyde sulphoxalate (Rongalite), an appropriate reducing agent for the reduction of Fe(III) to Fe(II), has been used by workers for this purpose[109]. However, the levels of Fe(III) encountered in this work were much higher than previously encountered, so it was decided to evaluate the performance of the column in the presence of high concentrations of Fe(III), and the effectiveness of Rongalite as a reducing agent

Two separate series of solutions each containing 1 ng ml^{-1} of uranium and thorium with an increasing concentration of Fe(III) in 2M HNO_3 without the Rongalite reductant, were loaded onto the column and eluted in 0 1M ammonium bioxalate Results are shown in Figure 2 9 and Figure 2.10

The results show that the Fe(III) had a marginal effect on the recovery of uranium and thorium from the column Recovery dropped from 100% to approximately 85-90%, with Fe(III), having very little effect until its concentration was increased to 10,000 μg ml^{-1} The drop in recovery in this instance was small but significant, if the determination of uranium and thorium in real soil or sediment samples was required

When the same experiment was repeated with the addition of the Rongalite reducing solution (Figure 2 11 and Figure 2 12) recoveries between 98-105% for thorium and 96-111% for uranium were obtained, demonstrating the efficiency of Rongalite as a reductant and its practical use in this work

All plots for this experiment show similar trends for the uranium and thorium recoveries, particularly at the 5000 μg ml^{-1} iron concentration. It should be noted that it is not fully understood the reasons for this phenomena, however, the effects are very reproducible in both cases, indicating that it is not likely to be instrumental and more likely a chemical effect

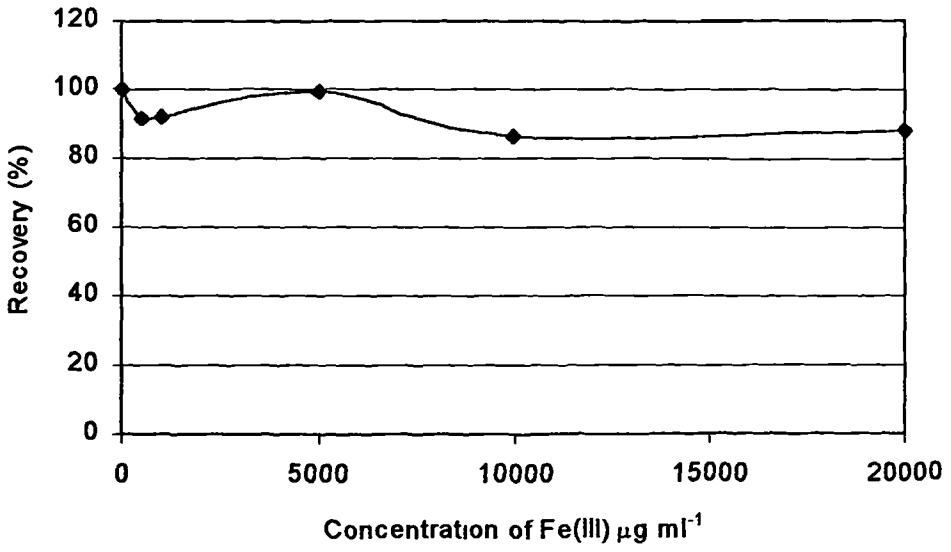


Figure 2.9 **The effect of iron(III) on the recovery of 0.5 ng of thorium from Tru-Spec resin**

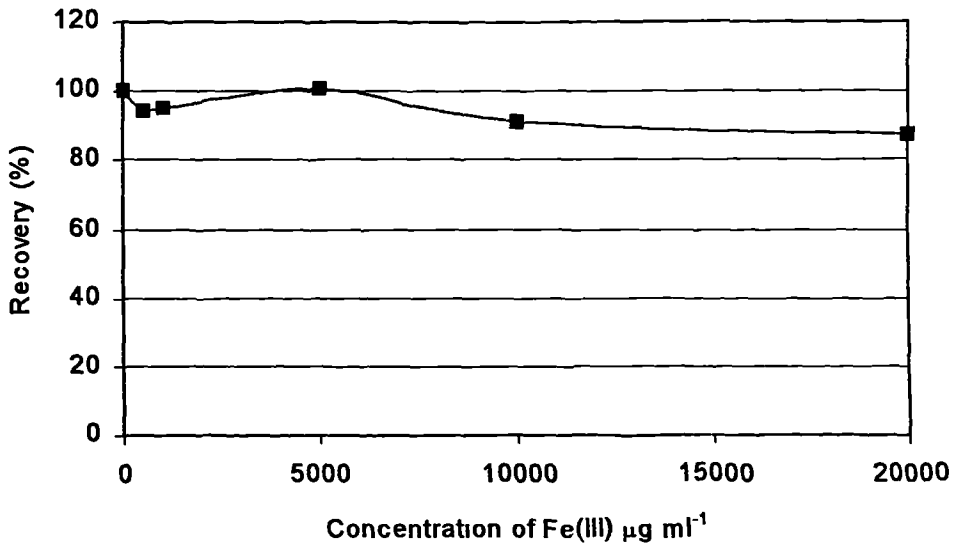


Figure 2.10 **The effect of iron(III) on the recovery of 0.5 ng of uranium from Tru-Spec resin**

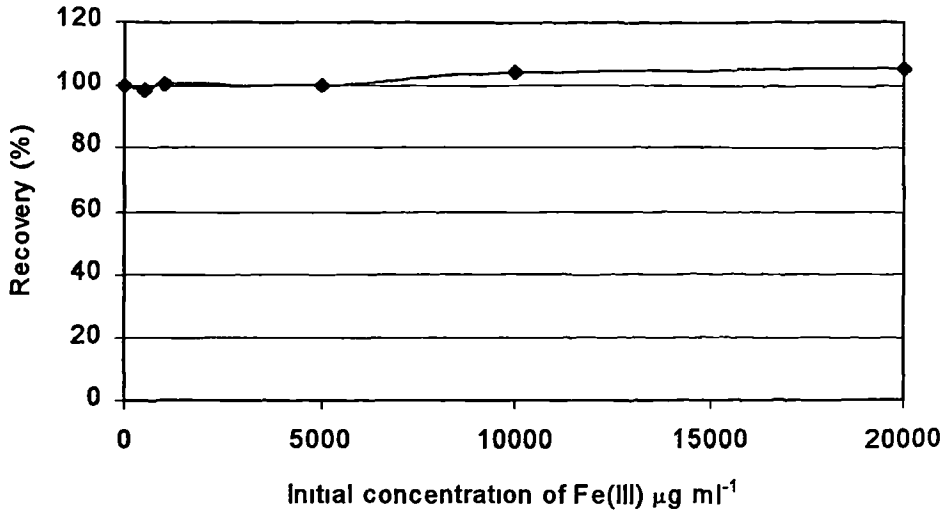


Figure 2.11 **The recovery of 0.5 ng of thorium from Tru-Spec column after reducing iron(III) to iron(II) using Rongalite as the reductant.**

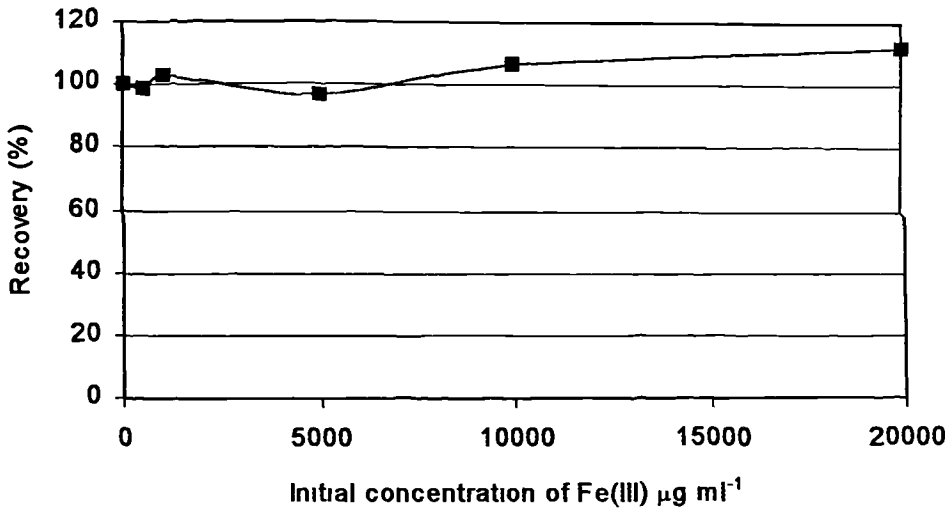


Figure 2.12 **The recovery of 0.5 ng of uranium from Tru-Spec column after reducing iron(III) to iron(II) using Rongalite as the reductant.**

2.3.5 Analysis of Reference Materials

2.3.5.1 Waters

The certified reference materials NASS-4 (seawater) and SLRS-3 (river water) were analysed for the determination of uranium (thorium is not certified in these reference materials) by pre-concentrating known volumes of the prepared material, eluting and comparing the peaks to the calibration curve after normalising using the bismuth internal standard The results obtained are shown and compared to the certified values in Table 2 5

Table 2.5 Results for the determination of uranium in certified reference materials NASS-4, SLRS-3 by PN -ICP-MS and ETV-ICP-MS.

Detection	Certified Reference Material	Certified value (ng ml^{-1})	^{238}U found (ng ml^{-1})	
			Analysed without column 10 x dilution[a]	Analysed with column[a]
PN	NASS-4	2 68 ± 0 12		2 13 ± 0 28
ETV	NASS-4	2 68 ± 0.12	1 98 ± 0 11	2 81 ± 0 54[b]
PN	SLRS-3	(0.045)[c]		0 043 ± 0 002
ETV	SLRS-3	(0 045)[c]	0 042 ±0 002	0 045 ±0 004[d]

[a] mean ± s , [b] 0 5 ml sample, [c] Uncertified indicative value, [d] 2 5 ml sample

Low recoveries were obtained for uranium in NASS-4 seawater samples using PN-ICP-MS However full recoveries were found for uranium in NASS-4 when using ETV-ICP-MS, with no significant difference between the found value and the

mean of the certified value at the P = 0 05 level The analysis was repeated on two separate days and with analogous results Good agreement was obtained between the analytical result and the indicative value for SLRS-3, though no firm conclusions can be drawn because this material was not certified for uranium This clearly shows the value of pre-concentration since the indicative value of 0 045 ng ml^{-1} was close to the detection limit for the ICP-MS instrument used, and was twice the absolute detection limit for the method detailed here However, a pre-concentration factor of 5 effectively raised the level of uranium to 10 times the detection limit, making analysis feasible

2.3.5.2 Biological Samples

Results for the analysis of oyster tissue and pine needles after sample preparation by dry/wet ashing are shown in Table 2 6 (PN-ICP-MS only) For oyster tissue no significant difference was found between the found value and the certified mean for uranium at the P = 0 05 level For the pine needles, low recoveries for both thorium and uranium were observed in comparison with the certified mean However, there was no significant difference between the found value and the bottom of the certified range for both uranium and thorium (i.e. 16 ng g^{-1} and 34 ng g^{-1} respectively) at the P=0 05 level

Table 2.6 Results of the determination of uranium and thorium in certified reference materials by PN-ICP-MS after dry/wet ashing.

Certified Reference Material	U		Th	
	Certified value ($ng\ g^{-1}$)	Found ($ng\ g^{-1}$)	Certified value ($ng\ g^{-1}$)	Found ($ng\ g^{-1}$)
1566a oyster tissue	132 ± 12	121 ± 21^{b}	$(40)^{a}$	29 ± 8^{c}
1575 pine needles	20 ± 4	14.6 ± 3.4^{c}	37 ± 3	28.3 ± 4.5^{c}

[a] Indicative value, [b] n = 11, [c] n = 5

Other workers have reported losses of uranium through the use of porcelain crucibles[112,113], by adsorption of ^{238}U onto the surface However, low recoveries could also be the result of analyte losses by volatilisation in the muffle furnace, or by incomplete sample digestion of silicate material. When the lithium metaborate fusion method was used (Table 2 7) recoveries were within the certified range, probably due to complete digestion of silicates within the pine needle matrix, with no significant difference between the found value and the certified mean for both uranium and thorium at the P = 0 05 level In order to try and speed up the analysis, the effect of calibrating the analysis by simply flow injecting the standards, rather than depositing them on the column, was investigated Results are shown in Table 2 7 for both PN and ETV-ICP-MS and indicate that full recoveries were obtained for both ^{238}U and ^{232}Th When the pre-concentration factor was increased by a factor of 10 (i e 5ml were deposited instead of 0 5ml) recoveries were still within the certified range, with no significant difference between the found value and the certified mean for both uranium and thorium at the P = 0 05 level

Table 2.7 **Results of the determination of uranium and thorium in pine needles by PN-ICP-MS and ETV-ICP-MS after lithium metaborate fusion, by calibration with and without the column.**

Detection	Calibration method	U		Th	
		Certified value ($ng\ g^{-1}$)	Found ($ng\ g^{-1}$)	Certified value ($ng\ g^{-1}$)	Found ($ng\ g^{-1}$)
PN	Calibration with column[a]	20 ± 4	23 3 ± 2 0	37 ± 3	36 2 ± 5 6
PN	Calibration without column[a]	20 ± 4	18 1 ± 1 4	37 ± 3	33 6 ± 6 8
PN	Calibration without column, 5 ml preconc [b]	20 ± 4	16 6 ± 1 5	37 ± 3	38 1 ± 0 8
ETV	Calibration without column[c]	20 ± 4	19 5 ± 1 7	37 ± 3	38 8 ± 2 2

[a] n=3 , [b] n=1, 3 injections, [c] n=6

2.3.5.3 Soils and Sediments Analysis

Results for the analysis of GBW 07311 (Sediment) and IAEA -312 (Soil) by PN-ICP-MS were found to be in good agreement with certified values for uranium in both samples, shown in Table 2 8 Thorium values were found to be higher than in the certified value for GBW 07311 sediment

Results for the analysis of GBW 07311, GBW 08304 (Sediment) and IAEA 312, IAEA 375 (Soil) by ETV-ICP-MS were found to be in good agreement with certified values shown in Table 2 8

Table 2.8 **Results of the determination of uranium and thorium in soil and sediment certified reference materials by ETV-ICP-MS and PN-ICP-MS (Lithium metaborate fusion method) using Tru-spec resin.**

		^{238}U		^{232}Th	
Detection	**CRM**	**Certified value** ($\mu g\ g^{-1}$)	**Found**[a] ($\mu g\ g^{-1}$)	**Certified value** ($\mu g\ g^{-1}$)	**Found**[a] ($\mu g\ g^{-1}$)
ETV	GBW 08304 (Sediment)[b]	31 7 ± 1 3	40 3 ± 1 3	14 8 ± 1 8	14 8 ± 0 8
ETV	GBW 07311 (Sediment)[b]	9 1 ± 1.3	11 ± 2 3	23 3 ± 1 8	19 ± 4 0
PN	GBW 07311 (Sediment)[b]	9 1 ± 1 3	5.8 ± 1 4	23 3 ± 1 8	36 7 ± 3 2
ETV	IAEA –312 (Soil)[b]	16 5 ± 0 1[c]	22 ± 1 6	91 4 ± 10 1[c]	98 ± 8 8
PN	IAEA –312 (Soil)[b]	16 5 ± 0 1[c]	12 5 ± 3 0	91 4 ± 10 1[c]	102 9 ± 8 3
ETV	IAEA –375 (Soil)[b]	5 10 ± 0 16[c]	5.43 ± 0.2	1 82 ± 0 15[c]	3 1 ± 0 3

[a]mean ± *s*, [b]n = 2, 3 injections, [c]uncertified indicative value

High recoveries for uranium in GBW 08304 may be attributed to the presence of other 238 *m/z* actinides in the sample (such as ^{238}Pu), as this sediment was particularly contaminated Poor recoveries for GBW 07311 sediment using PN-ICP-MS may have been due to manifold failure and clearly not the sample type, as recoveries are acceptable when repeated for ETV-ICP-MS. Results were generally comparable but improved upon those of the PN-ICP-MS methodology, suggesting that the method was functioning well in terms of reproducibility and accuracy

2.3.6 Survey Analysis of Natural Waters

2.3.6.1 Elution profiles for natural waters

The typical elution peaks widths for ^{238}U and ^{232}Th using Tru-Spec resin and PN-ICP-MS are shown in Figure 2 13 Uranium was eluted completely in approximately 50 s and thorium approximately 30 s The peak widths corresponded to volumes of approximately 1 ml and 0 6 ml for ^{238}U and ^{232}Th respectively due to higher concentration of analyte (typically around 2 ng)

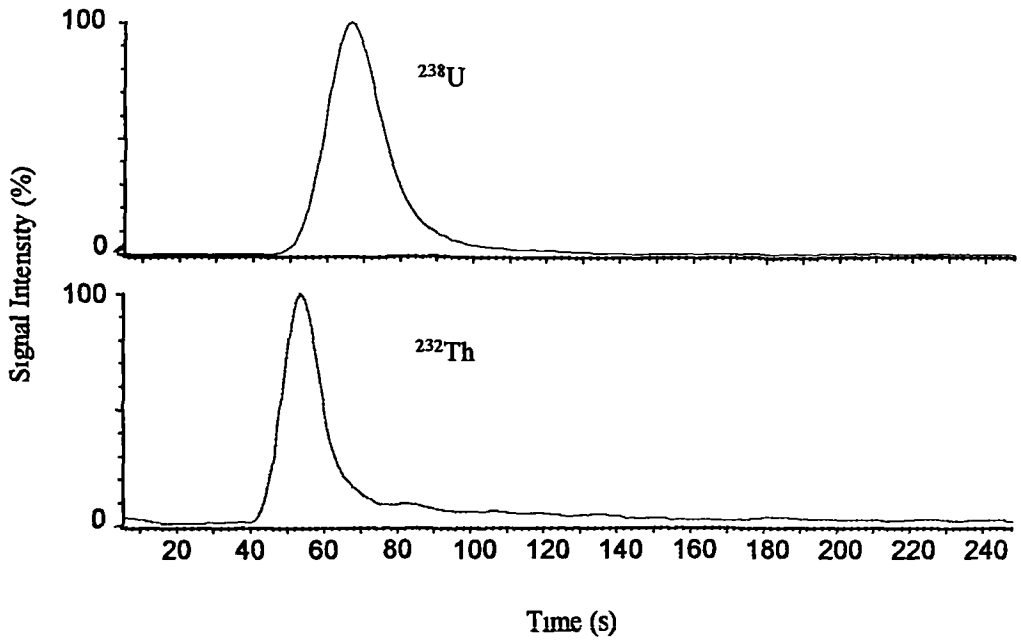


Figure 2.13 Typical elution profiles for a Devonport water sample using PN-ICP-MS.

2.3.6.2 PN and ETV-ICP-MS - Analysis of Survey- Waters

Results are shown in Table 2 9 NASS-4 open ocean reference material and SLRS-3 River water was used to ascertain if the column was functioning correctly

Full recoveries were found for uranium in NASS-4 when using PN-ICP-MS, within the upper certified value and comparable values were found for SLRS-3 River water (Indicative value only), indicating that the column had been functioning correctly (Table 2 9) Thorium was not detected in all samples, as concentrations were below the limits of detection

Table 2.9 Comparison of ^{238}U and ^{232}Th results obtained by PN-ICP-MS, ETV-ICP-MS and Alpha-Spectrometry.

Sample	Uranium		
	PN-ICP-MS[a,b] (ng ml^{-1})	ETV-ICP-MS[a,c] (ng ml^{-1})	Alpha Spectrometry[a] (ng ml^{-1})
NASS-4[d]	3 11 ± 0 06	2.94 ± 0 39	-
SLRS-3[e]	0 047 ± 0 003	0 034 ± 0 01	-
Clearbrook	0 099 ± 0 007	0 072 ± 0 02	0 18 ± 0 64
Burrator	0 216 ± 0.02	0 227 ± 0 01	0 72 ± 0 73
Oreston	3 20 ± 0 90	3 08 ± 0 23	2 27 ± 0 97
Devonport	3 12 ± 0.70	3 12 ± 0 01	3.44 ± 0 73
	Thorium		
NASS-4[d]	0 018 ± 0 06	0 007 ±0 001	-
SLRS-3[e]	0 024 ± 0 002	0 033 ± 0 006	-
Clearbrook	<0 006	0 0005 ± 0 0003	<0 03
Burrator	0 010 ± 0 002	0 003 ± 0 001	<0 03
Oreston	<0 006	0 004 ± 0 001	<0 03
Devonport	0 016 ± 0 002	0 012 ± 0 001	<0 03

[a] mean ± *s*; [b] n=3, 3 injections, [c] n=3, 2 ETV injections,
[d] NASS-4 certified U level = 2 68 ± 0 12 ng ml^{-1},
[e] SLRS-3 indicative U level = 0 045ng ml^{-1}

Full recoveries were found for uranium in NASS-4 when using ETV-ICP-MS, within the upper certified value and comparable values were found for SLRS-3 River water (Indicative value only) The values for uranium and thorium in the certified reference materials are good indicators for environmental values (typical ocean concentrations of uranium and thorium are summarised in Table 2 10[114]) The survey samples were found to have very similar levels Thorium was found in all samples, as signals from sample pre-concentrations were above the limits of detection

Table 2.10 Typical concentrations of uranium and thorium in ocean waters[114]

Nuclide	Concentration ng ml^{-1}
^{232}Th	0 00036-0 0045
^{238}U	2 7-3 4

Considering the uranium values given by alpha-spectrometry, the results for Oreston and Devonport are directly comparable to both ETV and PN-ICP-MS Only the freshwater samples show discrepancies However, the high standard deviations quoted for the freshwater alpha spectrometry results, show poor precision for the technique, and go some way into explaining the differences between the ICP-MS and alpha-spectrometry results Most certainly, the PN and ETV-ICP-MS systems showed superiority in regard to their limits of detection and small sample volume

requirement This subsequently allowing for the analysis of thorium in all waters using ETV-ICP-MS, and even some analysis using PN-ICP-MS

2.4 CONCLUSIONS

The studies on the injection manifold for either on-line pre-concentration coupled to PN-ICP-MS or off-line with ETV-ICP-MS showed that the use of a smaller bore (0 3 mm i d) PTFE tubing reduced pulsing from the peristaltic pump and reduced sample throughput times Slurry packing of the column with Tru-Spec resulted in considerable tailing of peaks and attempts at back flushing the analyte improved these elution times but at a cost to accuracy and precision in the determination of thorium Shorter elution times were achieved by dry packing the columns with resin, with the advantage of improved accuracy and precision over the back flush methodology The addition of freon gas to the ETV improved sensitivity for ^{238}U and ^{232}Th by 10x and 50x respectively

An interference study for uranium and thorium on the Tru-Spec column was performed in 0-20,000 μg ml^{-1} solutions of iron (III) Full recoveries were found for uranium and thorium up to 5,000 μg ml^{-1} Fe (III) Uranium and thorium recoveries fell to approximately 85% for 20,000 μg ml^{-1} Fe (III) A solution of reducing agent namely sodium formaldehyde sulphoxalate (Rongalite), was tested in the reduction of Fe (III) to Fe(II) Full recoveries were obtained for uranium and thorium in concentrations up to 20,000 μg ml^{-1} Fe (III), demonstrating the effectiveness of the method

The determination of ^{238}U and ^{232}Th in certified reference materials generally showed good agreement with certified and indicative values Low recoveries were observed for the determination of ^{238}U in NASS-4 sea water without matrix removal using the column pre-treatment for ETV-ICP-MS When column pre-treatment was used, full recoveries were obtained Results for the freshwater (SLRS-3) were in good agreement with the indicative value Agreement with certified values was observed for the determination of ^{238}U and ^{232}Th in NIST 1575 pine needles after pre-concentration and matrix elimination on column, after lithium metaborate fusion, and detection by ICP-MS and ETV-ICP-MS These results were an improvement of the dry/wet ashing method

GBW 08304 (Sediment) and GBW 07311 (Sediment) were analysed for ^{238}U and ^{232}Th after pre-concentration and matrix elimination on the Tru-Spec column, and detection by ETV-ICP-MS (GBW 07311 was only analysed by PN-ICP-MS) Good agreement was found for the certified values and column pre-treatment for ETV-ICP-MS detection of analytes, with the exception of a higher uranium value for GBW 08304 PN-ICP-MS gave slightly lower values than the certified value for uranium and higher for thorium in GBW 07311. IAEA-312 (Soil), IAEA-375 (Soil) were also analysed for ^{238}U and ^{232}Th after pre-concentration and matrix elimination on the Tru-Spec column, and detection by PN-ICP-MS and ETV-ICP-MS Excellent agreement was also found with the indicative values and column pre-treatment for both PN-ICP-MS and ETV-ICP-MS detection of analytes Again with the exception of uranium recovery for IAEA-312 being low for PN-ICP-MS and high for ETV-ICP-MS A

higher value for thorium was also found for IAEA-375 (N B values for uranium and thorium are indicative only for both soil reference materials)

NASS-4 certified reference material and SLRS-3 river water was analysed for ^{238}U after pre-concentration and matrix elimination on a chelating column, and detection by PN-ICP-MS and ETV-ICP-MS Excellent agreement was found for the certified values using the column pre-treatment for both PN-ICP-MS and ETV-ICP-MS detection of analytes, indicating that the manifold was functioning correctly (Table 2 9) The results for uranium and thorium show good comparisons with ETV and PN for all water samples

A comparison study between alpha-spectrometry and the ICP-MS, analysing real water samples for uranium and thorium, showed the ICP-MS method to be significantly better than alpha-spectrometry, successfully determining uranium in all samples and thorium in all but two samples Comparatively, alpha-spectrometry suffered from very poor precision for uranium and was unable to detect thorium in any samples

Chapter 3

DEVELOPMENT OF A SEQUENTIAL ELUTION METHOD FOR THE DETERMINATION OF NEPTUNIUM, PLUTONIUM AND AMERICIUM IN ENVIRONMENTAL SAMPLES WITH DETECTION BY SECTOR FIELD ICP-MS

Chapter 3

DEVELOPMENT OF A SEQUENTIAL ELUTION METHOD FOR THE DETERMINATION OF NEPTUNIUM, PLUTONIUM AND AMERICIUM IN ENVIRONMENTAL SAMPLES WITH DETECTION BY SECTOR FIELD ICP-MS

3.1 INTRODUCTION

The importance of being able to determine the actinide elements in the environment is highlighted in a recent paper[13] which quotes the mean concentration of man-made ^{239}Pu in the environment to be approaching 10^{-13} g/g (100 fg g^{-1}) in the surface level of soil The dangerous level[11] for accumulated Pu in the human body is $\geq 10^{-12}$ g/g (1000 fg/g), which highlights the requirement to monitor much lower levels in the surrounding environment in order to evaluate accumulation effects

As covered earlier, in Chapters 1 and 2, inductively coupled plasma mass spectrometry (ICP-MS) is ideally suited for the determination of the concentration and isotopic composition of the actinide elements To detect environmental levels of plutonium or other transuranic elements below 100 fg ml^{-1} requires either a pre-concentration step (being blank limited) and/or having a much more sensitive instrument SF-ICP-MS operated in low resolution mode (typically having a resolution of 400), is capable of attaining sub fg ml^{-1} levels without pre-concentration This additional sensitivity is particularly advantageous, as it reduces the amount of sample required and subsequently shortens sample preparation times However, as

before, it is still necessary to separate the radionuclides from the matrix which may contain elements that will produce polyatomic and or isobaric interferences, this being achieved using column sequential elution techniques

Other workers[115] in the field of actinide analysis have recently applied a two column extraction method with isotope dilution (ID) high resolution inductively coupled plasma spectrometry (HR-ICP-MS) for plutonium isotope determination, achieving detection limits for ^{239}Pu, ^{240}Pu and ^{242}Pu of about 4 fg ml^{-1}, 3 fg ml^{-1} and 6 fg ml^{-1} respectively when employing a microconcentric nebulizer, MCN-6000® (Cetac technologies, Omaha, NE, USA) The method gives full recoveries for reference materials, but is somewhat marred by a complex series of extraction steps

In order to reduce the sample throughput times, it would be preferable to use a single column extraction method, which would require less extraction steps and allow for easy coupling to ICP-MS techniques As shown in Chapter 2, the Tru-Spec single column extraction method has potential to achieve successful separations of the analytes from the matrix with speed and simplicity

Previous work undertaken in this laboratory[107,108] (also Chapter 2) has resulted in the successful determination of uranium and thorium in waters and biological matrices using the TRU-Spec™ resin for pre-concentration and matrix removal prior to analysis by PN-ICP-MS and ETV-ICP-MS respectively In the following sections the application of Tru-Spec to the analysis of actinides in environmental samples will be extended by extraction and sequential elution of ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Am

and ^{243}Am in sediments from the column and coupled to PN-ICP-MS. The potential for eliminating interferences such as $^{238}U^{1}H^{+}$ interference on $^{239}Pu^{+}$ [107] will be explored.

3.2 EXPERIMENTAL

3.2.1 Instrumentation

All analyses were performed using a sector-field inductively coupled plasma mass spectrometer (SF-ICP-MS, ELEMENT 1, Finnigan-MAT, Germany) interfaced with the flow injection sample injection system shown in Figure 3.1.

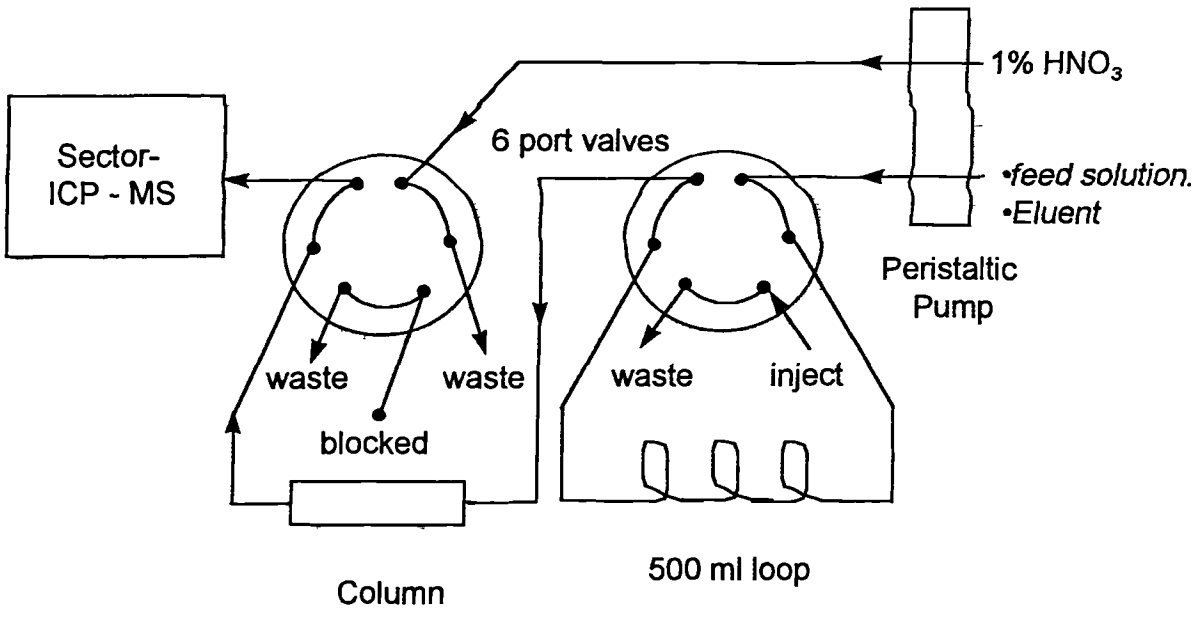


Figure 3.1 Schematic of the flow injection manifold interface with SF-ICP-MS.

A PlasmaQuad 3, (PN-ICP-MS, VG Elemental, Cheshire, UK) was used to perform a $^{238}U^{1}H+$ interference study Data was acquired in transient peak hopping mode, which allows time resolved monitoring of multiple isotopes Operating conditions are shown in Table 3 1

3.2.2 Analytical Columns

Columns were prepared using Tru-Spec resin (50-100 μm Eichrom, Paris, France), dry packed into PEEK columns of 4 mm i d and 50 mm length (Dionex UK Ltd, Camberley, Surrey, UK) When not in use the columns were filled with 2M HNO_3, and prior to use they were washed with successive portions of 0 1M ammonium bioxalate and 2M HNO_3 at a flow rate of 0.5 ml min^{-1} for 6 minutes , and finally 1 ml of column feed solution

3.2.3 Reagents

All solutions were prepared using analytical grade reagents and distilled deionised water (DDW, Ultra Pure Water, Elgastat Maxima, Elga Ltd, Bucks, UK) The following analytical reagents were prepared as described in Chapter 2[107,108] 2 M nitric acid (Aristar, BDH, Poole , UK), 0 1 M ammonium bioxalate eluting solution (Fisons Scientific Equipment, Loughborough, UK),

Table 3.1 Operating conditions for ICP-MS instuments.

	Finnigan MAT ELEMENT 1	VG PQ3
Forward power (W)	1100	1350
Plasma gas (l min^{-1})	14 0	16 5
Auxillary gas (l min^{-1})	0 9	0 7
Nebulizer gas (l min^{-1})	1 1	0 8
Sample flow (ml min^{-1})	0 5 - 2	0 5 – 1
Torch	Fassel (quartz)	Fassel (quartz) with guard electrode
Nebulizer	Concentric MicroMist (quartz)	Concentric (quartz)
Spray Chamber	Scott type (quartz)	Scott type (quartz)
Interface		
Sampler	Ni or Pt	Ni
Skimmer	Ni or Pt	Ni
Mass Spectrometer		
Ion masses (m/z)	^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{237}Np, ^{238}U, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{243}Am	^{232}Th, ^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{209}Bi
Data acquisition		Scan mode
Dead time (ns)	25	-
Dwell time (ms)	30	20
Time-slice duration (s)	1	1

0 5 M aluminium nitrate dissolved in 2 M nitric acid (Analytical Grade, Fisher Scientific U K) column feed solution, off-column reducing solution prepared from 0 3 g iron ammonium sulphate and 0 3 g sodium formaldehyde sulfoxylate dissolved in 10 ml of 2M HNO_3 In addition, an on-column reducing solution was prepared from titanium (III) chloride greater than 10% w/v solution in 20-30% HCl (Aldridge, Dorset, UK) to produce a final solution of 0 006M $TiCl_3$ in 4M HCl.

A mixed stock solution of 1 pg ml^{-1} of ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am, was prepared by boiling to dryness in nitric acid and made up in either column feed or eluting solution An off-column reducing solution was then used in order to ensure that the analytes were in the correct oxidation states (details given later in 3 3 4) to be retained on the column

3.2.4 Sample Preparation

The certified reference materials (CRMs) NIST 4352 Human Liver and NIST 4351 Human Lung (National institute of Science and Technology, Gaithersburg, USA) were subjected to a dry and wet ashing procedure as described in Chapter 2[107,108] Approximately 10 g portions of the human liver were used, however, it was necessary to digest the whole sample of human lung (approx 45 g), as required by the certificate, due to inhomogeneity caused by the presence of hot particles

Samples (0 5 g) of dried and homogenised cabbage (Ministry of Agriculture, Fisheries and Food, UK) which had been spiked with ^{239}Pu were treated using a

microwave digestion procedure The samples were measured into microwave bombs, 4 ml of concentrated HNO_3 acid and 1 ml of concentrated HCl were added, and the bombs were irradiated in the microwave digester (Perkin Elmer PAAR Physica Multiwave Sample Preparation System), for 5 min at 500 W and 15 min at 800 W Samples were then quantitatively transferred into clean vials and made up to a known weight with approximately 6 g of 2M HNO_3 and 0 3 ml of off-column reducing solution

Samples of the CRMs NIST 4350B River Sediment (10 g) and NIST 4253 Rocky Flats Soil Number 1 (6 g) were ashed in a muffle furnace then leached with concentrated nitric acid as described in Chapter 2[107]

3.2.5 Investigation of $^{238}U^{1}H^{+}$ interference

In order to establish the effect of the uranium hydride ($^{238}U^{1}H^{+}$) interference on the determination of ^{239}Pu, a series of uranium standards were eluted from the column (TRU-Spec resin) into the PN-ICP-MS. ^{238}U was only monitored from the lower concentration range to avoid detector saturation It was not possible to directly monitor the ^{238}U isotope because the signal was too large for the detector, so the isotopes ^{234}U and ^{235}U were monitored and the signal for ^{238}U calculated from the known abundance

3.2.6 Procedure for the separation of actinides from CRMs

Two analytical procedures were adopted depending on whether it was necessary to elute the analytes simultaneously or sequentially using the Tru-Spec resin

3.2.6.1 Simultaneous analyte elution

Standard solutions were introduced in duplicate by flow injection through a 500 µl injection loop, into a carrier stream of 0.1M ammonium bioxalate solution at a flow rate of approximately 0 5 ml min^{-1}, so that the analytes passed through the column without retention

Prior to deposition, approximately 0.5 ml of off-column reducing solution was added to each 10 ml of sample (0 3 g iron ammonium sulphate and 0 3 g sodium formaldehyde sulfoxylate dissolved in 10 ml of 2M HNO_3). Sample solutions were deposited in a carrier stream of either column feed solution or 2 M HNO_3 at a flow rate of approximately 0 5 ml min^{-1} for 1 minute. During deposition, the outlet from the column was diverted to waste The column was then rinsed with 1 75 ml of 2M HNO_3 to remove any residual column feed solution, diverted back to the ICP-MS instrument and the analytes eluted with 0 1 M ammonium bioxalate After elution the column was diverted away from the ICP-MS and flushed with 1 ml of column feed solution or 2M HNO_3 to remove residual ammonium bioxalate solution prior to further deposition

3.2.6.2 Sequential analyte elution

The procedure was the same as above except that both standard and sample solution were deposited onto the column in a carrier stream of the column feed solution Americium and plutonium were eluted with a solution of 0 006 M titanium (III) chloride in 4 M HCl The other analytes were eluted with 0 1 M ammonium bioxalate

3.3 RESULTS AND DISCUSSION

3.3.1 Figures of Merit

Elution peaks for depositions of 35 fg of ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am in 0 1M ammounium bioxalate are shown in Figure 3 2 Instrumental detection limits for ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am are shown in Table 3 2, with absolute detection as low as 0 6 fg for ^{241}Am

In order to reduce detection limits further a pre-concentration step was included, such that 50 ml of an approximately 200 attogram (ag) ml^{-1} solution of ^{239}Pu, ^{237}Np, ^{241}Am, and ^{243}Am in 2M HNO_3 was deposited at 2 ml min^{-1} onto the column, eluted, and recoveries calculated relative to a 500 µl injection volume

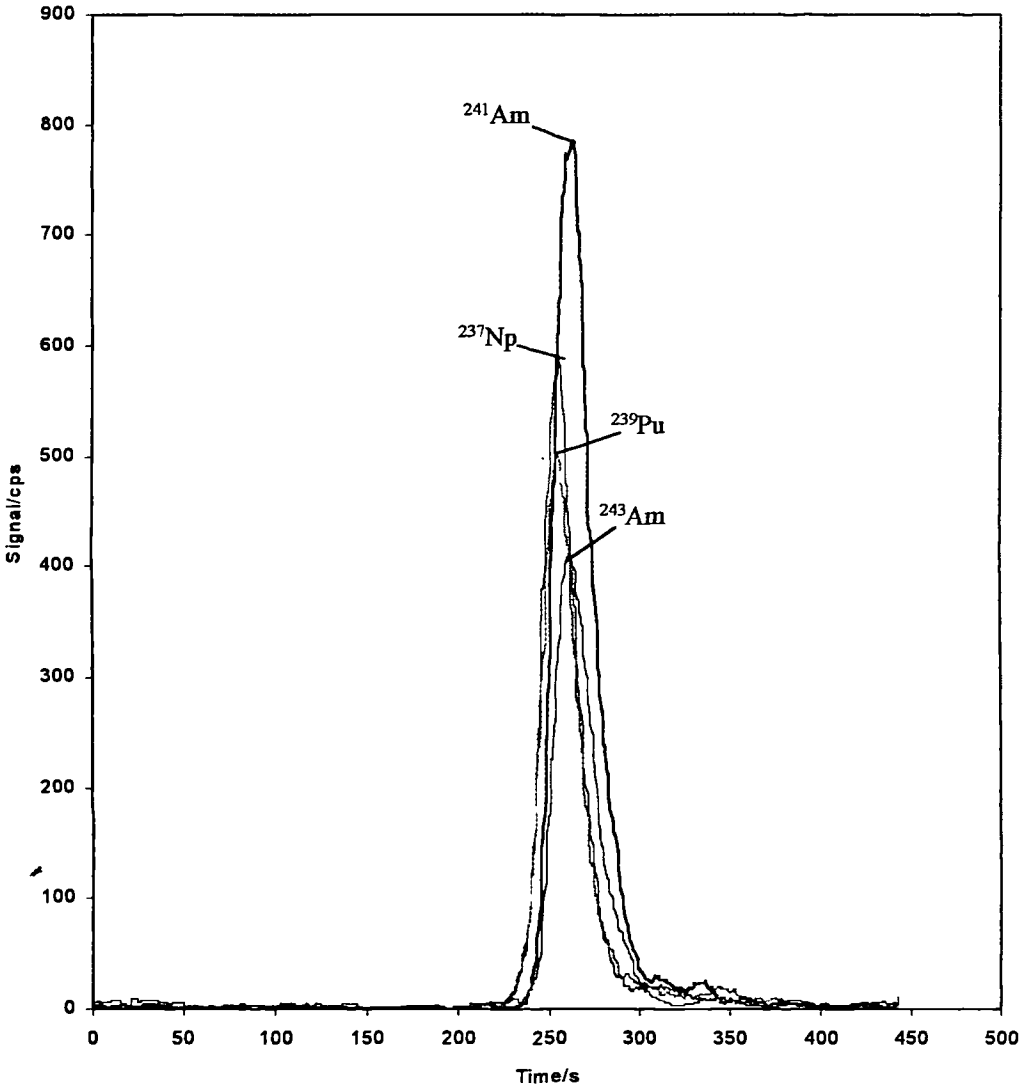


Figure 3.2 **Elution profiles obtained for a 70 fg g^{-1} solution of americium, neptunium and plutonium after deposition on Tru-Spec resin and SF-ICP-MS detection (0.5 ml loop).**

Table 3.2 Instrumental detection limits for the actinide elements in 0.1M ammonium bioxalate (500 µl injections for Sector-ICP-MS).

Element	Sensitivity (cps/fg)	R^2	Detection Limit	
			Relative (fg/g)	Absolute (fg)
^{237}Np	336	0 9995	1 4	0 70
^{239}Pu	287	1 0000	1 7	0 85
^{241}Am	487	0 9992	1 2	0.60
^{243}Am	280	0 9996	1 3	0 65

The elution profiles for this experiment are shown in Figure 3 3 Mean recoveries for duplicate pre-concentrations were 93%, 62%, and 54% for ^{237}Np, ^{241}Am, and ^{243}Am respectively (Table 3 3) It is clear from the elution profiles shown in Figure 3 3 that detection limits of well below 200 ag ml^{-1} should be possible using pre-concentration

Excellent recoveries were obtained for the relatively well retained Np species, but low recoveries were observed for Am ions, which are less well retained on the column in these acidities In the work shown here the analytes were deposited in 2M HNO_3 It should be possible to improve recovery using $Al(NO_3)_3$ + 2M HNO_3 as the feed solution, which is known to increase the breakthrough capacity[76]

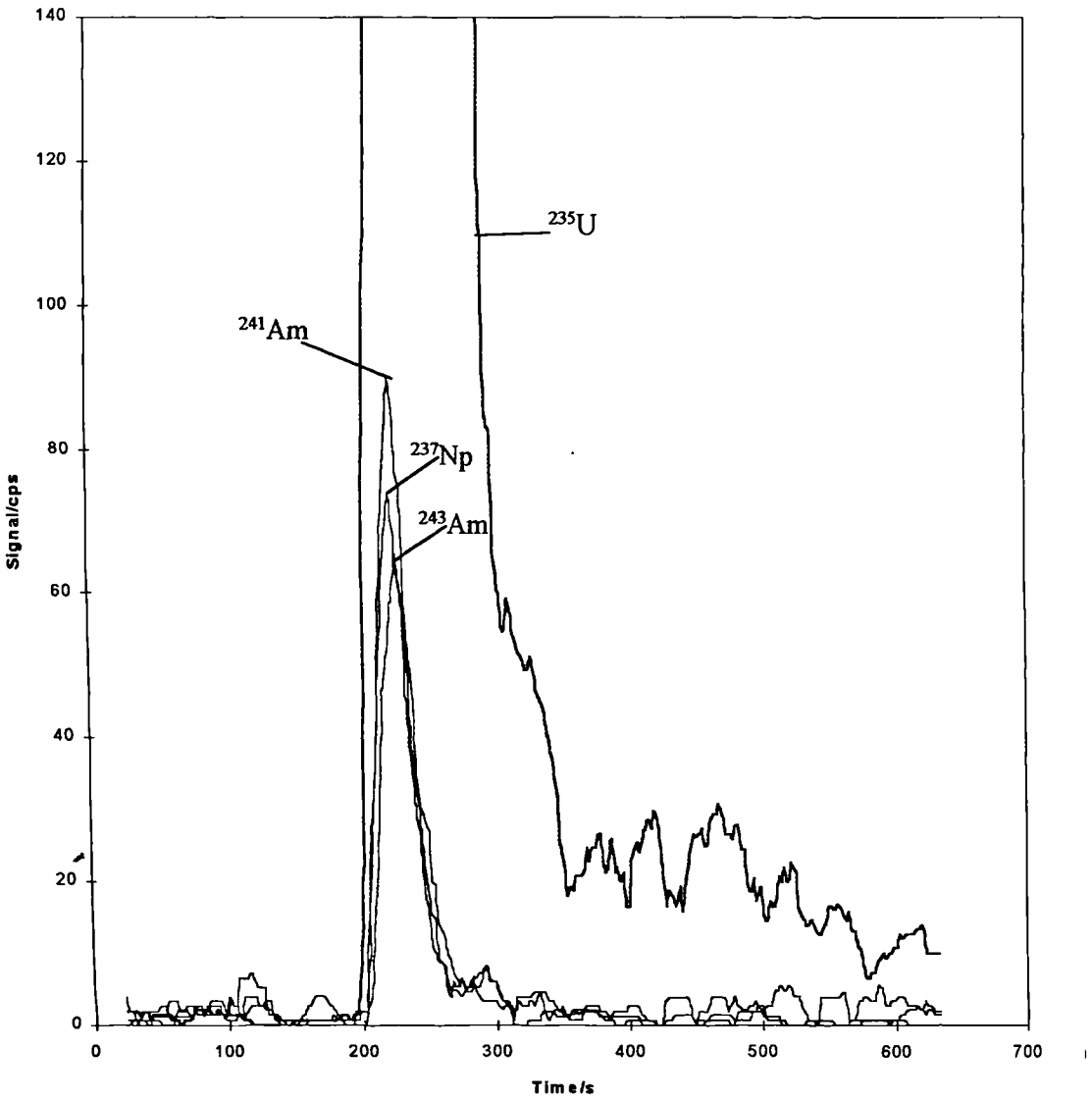


Figure 3.3 **Elution profiles obtained after deposition on Tru-Spec resin and using SF-ICP-MS detection, 50 ml of a 200 ag g^{-1} solution.**

Table 3.3 50 ml pre-concentration of actinides in 2M HNO_3

Run 1	Isotope	Concentration ag ml^{-1}	Recovery (%)
	^{237}Np	152	95
	^{241}Am	283	70
	^{243}Am	227	50
Run 2			
	^{237}Np	254	90
	^{241}Am	474	54
	^{243}Am	380	57

It was not possible to determine the recovery for ^{239}Pu due to an interference caused by $^{238}U^{1}H^{+}$ at m/z 239 due to ^{238}U being present as either a contaminant in the standards and/or the acid solution Therefore, should be noted that large quantities of acids may contribute to a significant source of uranium The worker should be aware of this when developing hybrid chromatographic techniques for the determination of the actinides and preferably use ultra pure acids or acids purified by sub-boiling techniques to avoid excess uranium pre-concentration.

3.3.2 Analysis of Reference Materials

Results for the determination of ^{239}Pu and ^{237}Np in both NIST 4352 Human Liver and MAFF Spiked Cabbage are given in Table 3 4

Table 3.4 Results for the determination of ^{239}Pu and ^{237}Np in certified reference materials with simultaneous analyte elution

Material	Certified value (fg g^{-1}) ^{239}Pu	Conc.found (fg g^{-1}) ^{239}Pu	Conc.found (fg g^{-1}) ^{237}Np
NIST 4352 human liver	848[a] ± 161[b]	963 ± 596[c]	35 ± 24[c]
MAFF spiked cabbage	467[d]	394 ± 108[e]	

[a]assuming 6 % of activity due to ^{240}Pu
[b]95% confidence
[c]95% confidence, n=4, 1 injection
[d]indicative value
[e]95% confidence, n=2, 3 injections

In both cases, the concentrations of ^{239}Pu were within the certified range (human liver) or encompassed the indicative value (cabbage) In the case of the human liver sample the certified value was quoted as activity due to ^{239}Pu+^{240}Pu, so it was necessary to calculate the concentration of ^{239}Pu by assuming that 6 % of the activity was due to ^{240}Pu Measurable quantities of ^{237}Np were found in the human liver sample, however, the sample is not certified for this element A typical elution curve for the ^{239}Pu in the NIST Human Liver sample is shown in Figure 3 4 As can be seen, ^{239}Pu eluted completely over a period of 60 s within 150 s of injection.

An attempt was also made to determine ^{239}Pu in NIST River Sediment (Figure 3 5) using simultaneous analyte elution, however, this resulted in a gross overestimation of ^{239}Pu concentration, possibly as a result of a $^{238}U^{1}H^{+}$ interference due to the relatively high concentration of ^{238}U in the sample Hence it was decided to develop a sequential elution procedure to separate uranium from plutonium and facilitate the interference-free determination of ^{239}Pu

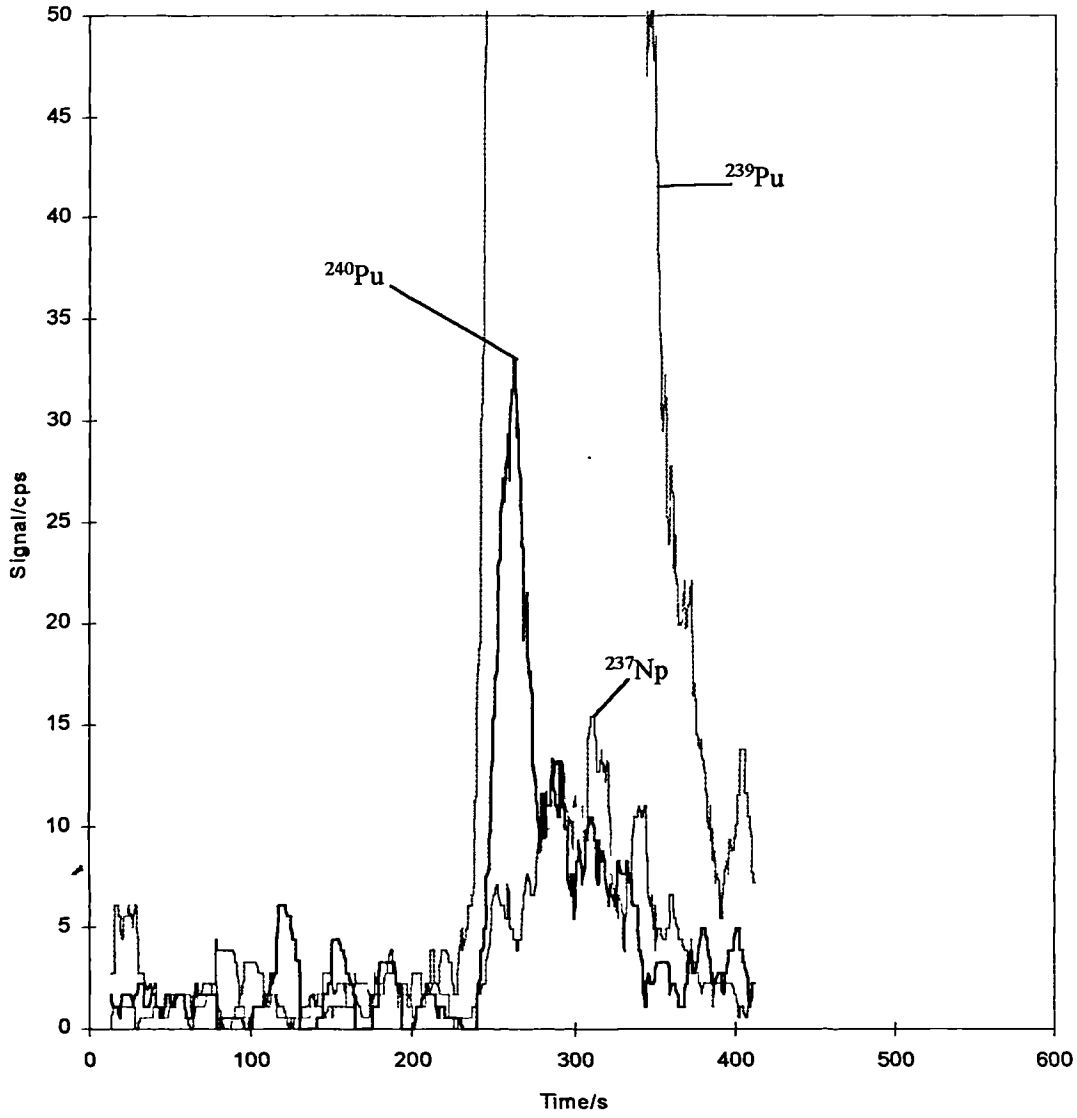


Figure 3.4 **Elution profiles *obtained after deposition on Tru-Spec resin and* using SF-ICP-MS detection, 0.5 ml of a digest of NIST 4352 Human Liver.**

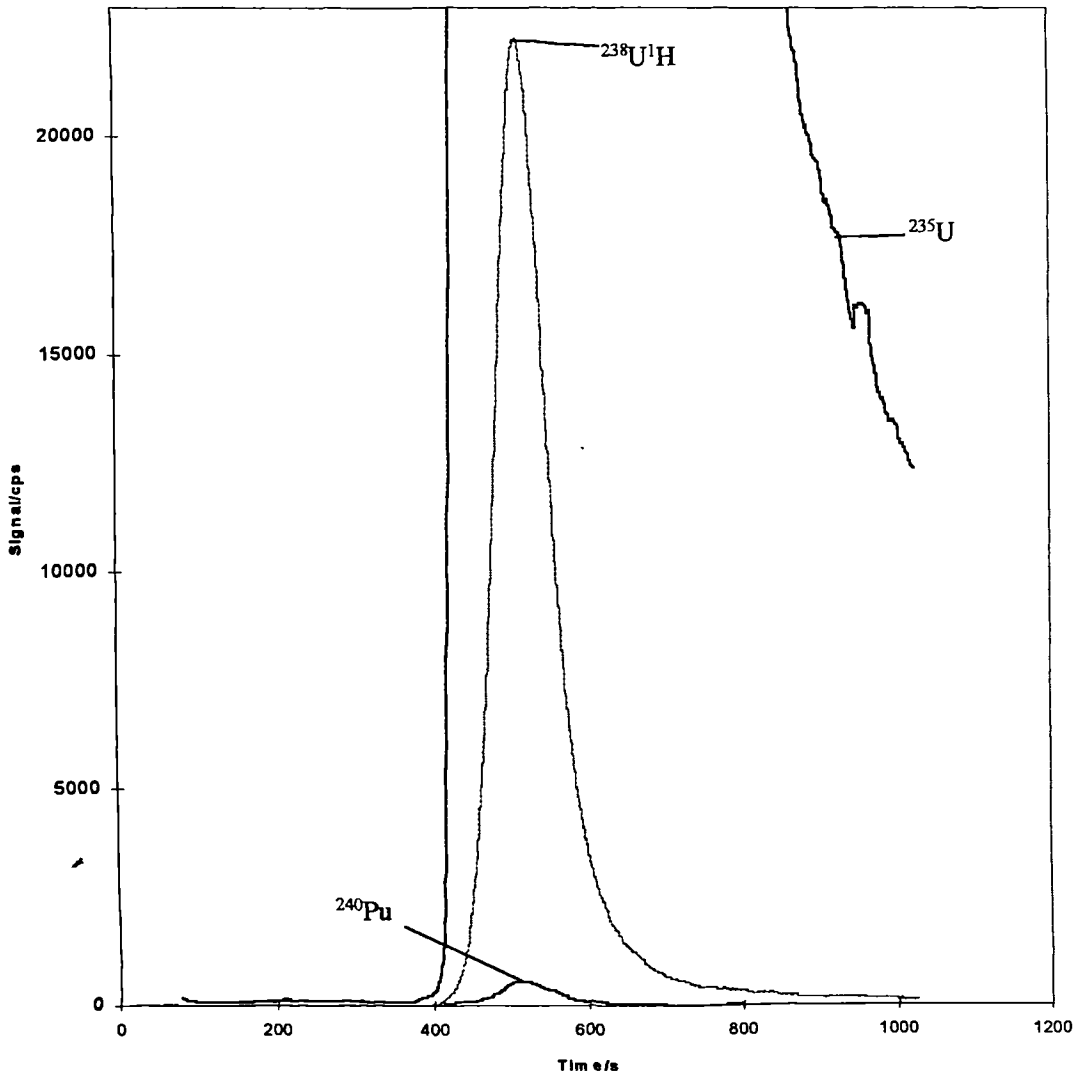


Figure 3.5 **Elution profiles obtained after deposition on Tru-Spec resin a using SF-ICP-MS detection, 0.5 ml of a digest of NIST 435(River Sediment containing approximately 1 µg ^{238}U and 100 ^{239}Pu from digest.**

3.3.3 Investigation of $^{238}U^{1}H^{+}$ interference

Results (Figure 3 6) show that there are no problems associated with the uranium hydride species at levels approaching 1000 ng ml^{-1} of ^{238}U, using the VG PlasmaQuad 3 This concentration value may vary dependant on the sensitivity of the instrumentation being used I should also be noted that the calibration is also unaffected by any possible ^{239}Pu content in the standard, as only 10^{-13} % (1 fg g^{-1} in certain uranium ores[11]) of the uranium standard may contain ^{239}Pu That would equate to a probable 1 ag ml^{-1} of ^{239}Pu in 10 µg ml^{-1} of ^{238}U standard This value being significantly below the detection limits of the instrument

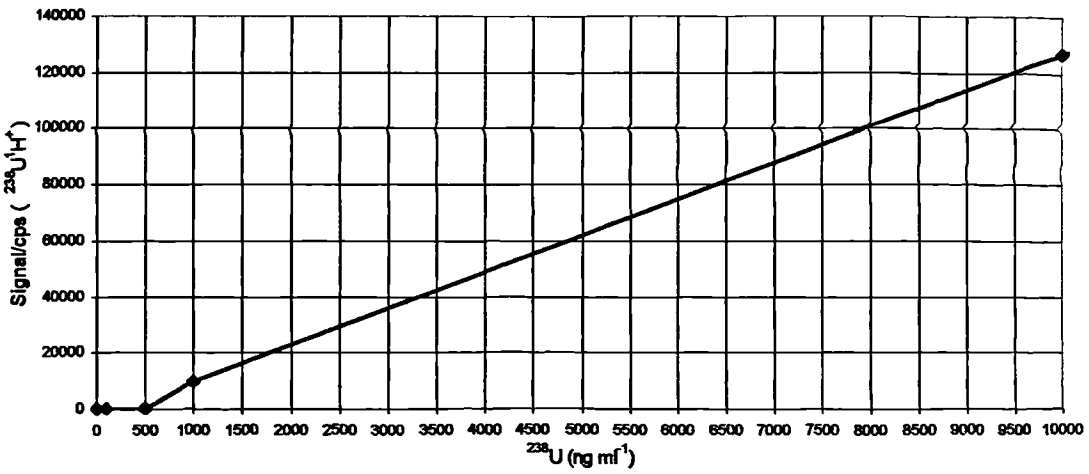


Figure 3.6 Graph showing $^{238}U^{1}H^{+}$ signal against ^{238}U concentration. 1 ml min^{-1} using elution from Tru-Spec resin in 0.1M ammonium bioxalate, detection by PN-ICP-MS.

Ironically, the problem of polyatomic ion interferences is even more pronounced when using SF-ICP-MS for sub-fg determinations in unit mass resolution mode because polyatomic ions which would not normally be observed using a quadrupole ICP-MS can cause significant interferences with highly sensitive SF-ICP-MS For example, it was found that platinum skimmer and sampler cones resulted in the formation of platinum-argon species (e g $^{190}Pt^{40}Ar$ or $^{194}Pt^{36}Ar$) at m/z 230, which interfere with ^{230}Th determination The platinum-argon polyatomic ions caused count rates of approximately 100 cps at ^{232}Th, ^{234}U, ^{235}U and ^{238}U, particularly when using high concentrations of HCl or HNO_3, and the interferences were reduced to < 3 cps when Ni cones were used The number of other possible polyatomic interferences are extensive, a few of these are given in Table 3.5 The most important of these polyatomic interferences for this work are the hydrides, which are not resolvable by instrumentation alone (e g SF-ICP-MS) Examples of these hydrides include $^{238}U^{1}H^{+}$ which interfere with ^{239}Pu determination (as mentioned in this section) or $^{232}Th^{2}H^{+}$ interfering with ^{234}U determinations Others may include $^{208}Pb^{35}Cl^{+}$ which can interfere with ^{243}Am determinations if solutions of HCl containing high levels of lead are used The actual effect of a particular polyatomic is only significant if the isotopic compositions of the two ions forming the molecule are of high isotopic abundance For example, isotopes of different elements which have abundance's of <0 01% of each in a polyatomic molecule would only produce small changes in signal, and may not even constitute a sufficient interfering molecule

3.3.4 Sequential Analyte Elution

This method was developed in order to allow the separation of uranium from plutonium and the determination of ^{239}Pu free of the interference caused by $^{238}U^{1}H^{+}$ Four plutonium elution schemes were investigated, in order to establish their viability for low concentration plutonium separations Initially, 0 1M quinol in a solution was used to reduce plutonium on-column. Quinol is known to reduce plutonium[107,116,117] from its higher oxidation states to Pu(III) Due to the poor retention of Pu(III) in HCl on the TRU-Spec column, plutonium should be selectively removed from the column Figure 3 7 shows an elution using 0 1M quinol in 4M HCl, 0 1M ammonium bioxalate was used in the final fraction to elute uranium and any remaining plutonium The reduction of plutonium was found to be too slow, giving broad peak profiles, with typically only 25% of the ^{239}Pu being recovered in the 0 1M quinol in 4M HCl fraction This was evident when observing the plutonium peak from the ammonium bioxalate fraction, as not all the plutonium had been eluted by the HCl

Table 3.5 Possible polyatomic interferences formed in the plasma

^{230}Th Polyatomic Interferences		
		m/z
^{190}Os	^{40}Ar	229 92084
^{190}Pt	^{40}Ar	229 92232
^{190}Os	^{38}Ar	229 92422
^{193}Ir	^{37}Cl	229 92884
^{194}Pt	^{36}Ar	229 93023
^{194}Au	^{33}S	229 93802
^{195}Pt	^{35}Cl	229 93364
^{196}Pt	^{34}S	229 93282
^{198}Hg	^{32}S	229 93883
^{198}Pt	^{32}S	229 93995
^{199}Hg	^{31}P	229 94203

^{232}Th Polyatomic Interferences		
		m/z
^{201}Hg	^{31}P	231 94405
^{200}Hg	^{32}S	231 94039
^{199}Hg	^{33}S	231 93973
^{198}Hg	^{34}S	231 93575
^{198}Pt	^{34}S	231 93463
^{197}Au	^{35}Cl	231 93069
^{196}Pt	^{36}Ar	231 93250
^{195}Pt	^{37}Cl	231 93541
^{194}Pt	^{38}Ar	231 92541
^{192}Pt	^{40}Ar	231 92343
^{192}Os	^{40}Ar	231 92387

^{234}U Polyatomic Interferences		
		m/z
^{232}Th	^{2}H	234 05215
^{203}Tl	^{31}P	233 94610
^{202}Hg	^{32}S	233 94270
^{201}Hg	^{33}S	233 94175
^{200}Hg	^{34}S	233 93619
^{199}Hg	^{35}Cl	233 93712
^{198}Hg	^{36}Ar	233 93431
^{198}Pt	^{36}Ar	233 93543
^{197}Au	^{37}Cl	233 93246
^{196}Pt	^{38}Ar	233 92768
^{194}Pt	^{40}Ar	233 92506

^{235}U Polyatomic Interferences		
		m/z
^{204}Pb	^{31}P	234 94680
^{204}Hg	^{31}P	234 94724
^{203}Tl	^{32}S	234 94441
^{202}Hg	^{33}S	234 94209
^{201}Hg	^{34}S	234 93816
^{200}Hg	^{35}Cl	234 93717
^{199}Hg	^{36}Ar	234 93582
^{198}Hg	^{37}Cl	234 93266
^{198}Pt	^{37}Cl	234 93378
^{197}Au	^{38}Ar	234 92929
^{195}Pt	^{40}Ar	234 92717

^{237}Np Polyatomic Interferences		
		m/z
^{206}Pb	^{31}P	236 94822
^{205}Tl	^{32}S	236 94648
^{204}Pb	^{33}S	236 94450
^{204}Hg	^{33}S	236 94494
^{203}Tl	^{34}S	236 94021
^{202}Hg	^{35}Cl	236 93948
^{201}Hg	^{36}Ar	236 93784
^{200}Hg	^{37}Cl	236 93422
^{199}Hg	^{38}Ar	236 93100
^{197}Au	^{40}Ar	236 92894

^{238}U Polyatomic Interferences		
		m/z
^{207}Pb	^{31}P	237 94965
^{206}Pb	^{32}S	237 94653
^{205}Tl	^{33}S	237 94587
^{204}Pb	^{34}S	237 94091
^{204}Hg	^{34}S	237 94135
^{203}Tl	^{35}Cl	237 94119
^{202}Hg	^{36}Ar	237 93818
^{201}Hg	^{37}Cl	237 93619
^{200}Hg	^{38}Ar	237 93105
^{198}Hg	^{40}Ar	237 92914
^{198}Pt	^{40}Ar	237 93026

^{239}Pu Polyatomic Interferences		
		m/z
^{238}U	^{1}H	239 05862
^{208}Pb	^{31}P	238 95040
^{207}Pb	^{32}S	238 94796
^{206}Pb	^{33}S	238 94592
^{204}Hg	^{35}Cl	238 94233
^{205}Tl	^{34}S	238 94228
^{204}Pb	^{35}Cl	238 94189
^{203}Tl	^{36}Ar	238 93989
^{202}Hg	^{37}Cl	238 93653
^{201}Hg	^{38}Ar	238 93302
^{199}Hg	^{40}Ar	238 93065

^{240}Pu Polyatomic Interferences		
		m/z
^{238}U	^{2}H	240 06489
^{209}Bi	^{31}P	239 95415
^{208}Pb	^{32}S	239 94871
^{207}Pb	^{33}S	239 94735
^{206}Pb	^{34}S	239 94233
^{205}Tl	^{35}Cl	239 94326
^{204}Pb	^{36}Ar	239 93406
^{204}Hg	^{36}Ar	239 94103
^{203}Tl	^{37}Cl	239 93824
^{202}Hg	^{38}Ar	239 93336
^{200}Hg	^{40}Ar	239 93070

^{241}Am Polyatomic Interferences		
		m/z
^{209}Bi	^{32}S	240 95246
^{208}Pb	^{33}S	240 94810
^{207}Pb	^{34}S	240 94376
^{206}Pb	^{35}Cl	240 94331
^{205}Tl	^{36}Ar	240 94196
^{205}Tl	^{36}S	240 94149
^{204}Pb	^{37}Cl	240 93894
^{204}Hg	^{37}Cl	240 93938
^{203}Tl	^{38}Ar	240 93507
^{201}Hg	^{40}Ar	240 93267

^{243}Am Polyatomic Interferences		
		m/z
^{209}Bi	^{34}S	242 94826
^{208}Pb	^{35}Cl	242 94549
^{207}Pb	^{36}Ar	242 94344
^{206}Pb	^{37}Cl	242 94036
^{205}Tl	^{38}Ar	242 93714
^{203}Tl	^{40}Ar	242 93472

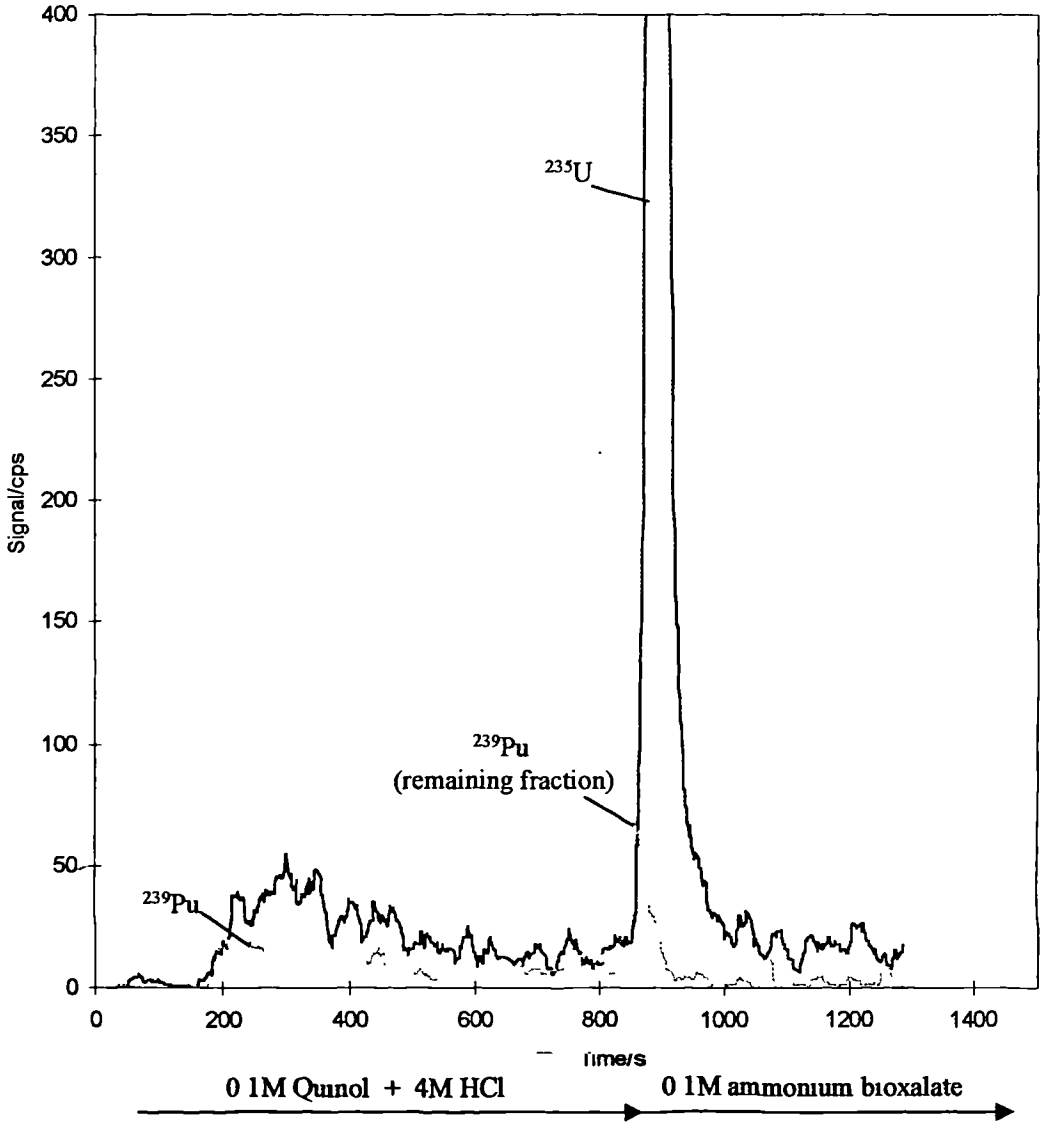


Figure 3.7 **Sequential elution of approximately 100 fg of plutonium using 0.1M quinol in 4M HCl and SF-ICP-MS detection (with typically 25% recovery of ^{239}Pu in the 0.1M quinol + 4M HCl fraction)**

Subsequently, another known reducing agent for plutonium was employed[116,117], 0 1M semicarbazide again in 4M HCl (plot not shown) The elution profile was very similar to the quinol separation, again giving similar recoveries in the initial fraction

Ferrous sulphamate is a very fast plutonium reducing agent[116,117], therefore, a 0 05M solution was prepared in 4M HCl, the peak was much sharper (Figure 3 8) demonstrating a potential for plutonium sequential separations for real samples Typically greater that 80% recovery of 239Pu was obtainable in the ferrous sulphamate fraction However, the 0 1M ammonium bioxalate fraction also contained some plutonium, demonstrating that elution was not complete It was also observed, that repeated use of ferrous sulphamate through the ICP-MS resulted in deposits of the salt forming in the torch and sampler cones, causing a reduction in sensitivity

Improved elution profiles were also obtained (Figure 3 9) when employing a titanium (III) chloride solution, which again is used to reduce Pu to the +3 oxidation state[116,117]. This procedure normally requires fixing Pu in the +4 oxidation state using sodium nitrite, but this was found to be unnecessary in this case In this instant recoveries were typically in the order of 98% or greater from the $TiCl_3$ in 4M HCl fraction Americium, which is usually found only in the +3 state, was also eluted in the $TiCl_3$/4M HCl fraction but Th, U and Np were retained on the column in the +4, +6 and +4 states respectively, and subsequently eluted using 0 1M ammonium bioxalate If an additional separation of Th and Np from U is required (not shown),

this can be achieved using a solution of 1M HCl + 0 03M oxalic acid[107], leaving U to be eluted with 0 1M ammonium bioxalate

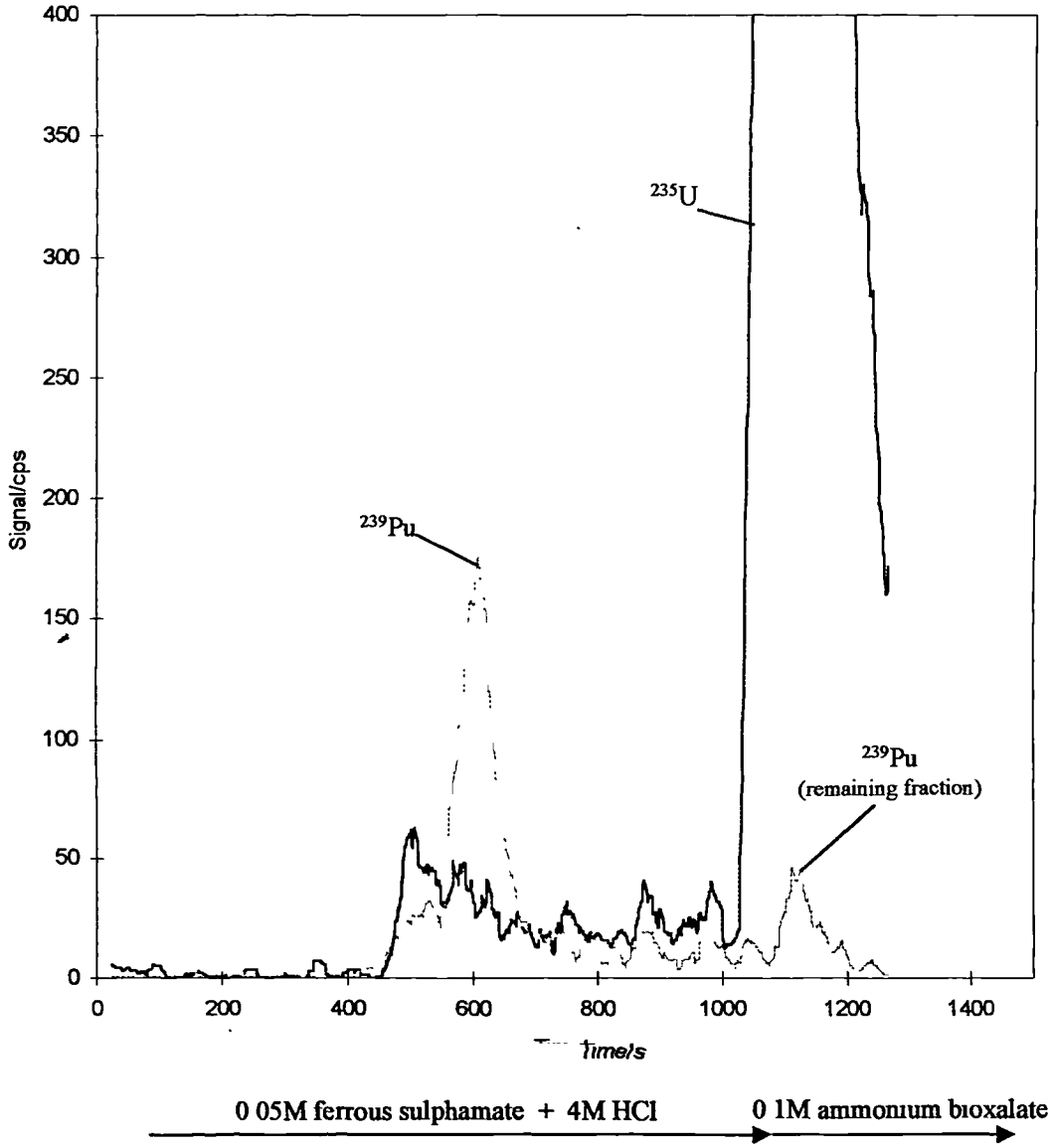


Figure 3.8 **Sequential elution of approximately 100 fg of plutonium using 0.05M ferrous sulphamate in 4M HCl and SF-ICP-MS detection (with typically 80% recovery of ^{239}Pu in the 0.05M ferrous sulphamate + 4M HCl fraction)**

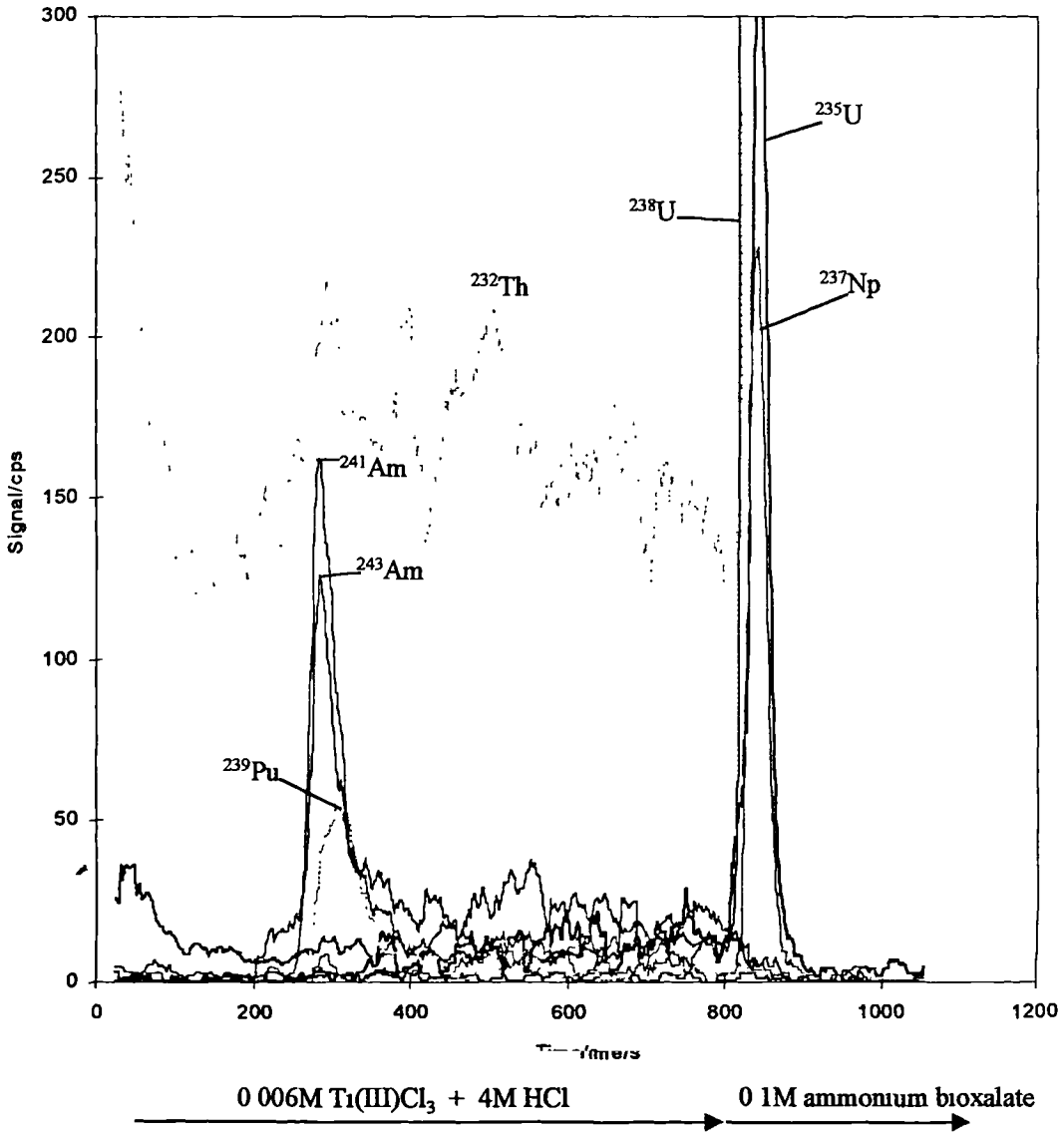


Figure 3.9 **Sequential elution of approximately 100 fg of each of the actinides using 0.006M $TiCl_3$ in 4M HCl and SF-ICP-MS detection (with typically >98% recovery of ^{239}Pu in the 0.006M $TiCl_3$ + 4M HCl fraction)**

Sensitivity was not effected when using the titanium(III) chloride solution, therefore, subsequent analysis was performed on samples using the later sequential separation procedure

3.3.5 Analysis of reference materials using sequential elution method

Results for the determination of ^{239}Pu in NIST 4351 Human Lung and NIST 4353 Rocky Flats Soil (No 1) are shown in Table 3 6 In the case of the human lung the found concentration for ^{239}Pu fell within the certified range, but low recoveries were observed for the rocky flats soil. In the latter case the low recoveries could have been due to incomplete leaching because the certificate states that approximately 8% of the Pu resists HNO_3 leaching Another possible explanation is that column breakthrough occurred because 6 g aliquots of the digested soil were pre-concentrated onto the column rather than deposited from a 0 5 ml loop

Table 3.6 Results for the determination of ^{239}Pu in certified reference materials with sequential analyte elution

Material	Certified value[a] ($fg\ g^{-1}$)	Found[a] ($fg\ g^{-1}$)
NIST 4351 Human Lung	453 (227-951)[b]	814 ± 110[c]
NIST 4353 Rocky Flats Soil	3307± 248[d]	2423 ± 272[e]

[a]assuming 6% of activity due to ^{240}Pu
[b]certificate states 453 with an uncertainty of +110% to –50%
[c]95% confidence, n=1, 3 injections
[d]certificate states 7 5% uncertainty
[e]95% confidence, n=3, 1 injection

One problem that was encountered was a change in elution time for ^{239}Pu in the sediment leach compared to the standard This is illustrated in Figure 3 10 which shows that ^{239}Pu started to elute at about 450s, but at 225s in the standard (Figure 3 9) This was thought to be caused by the much higher acidity of the sample due to the leaching procedure, which improved retention on the column

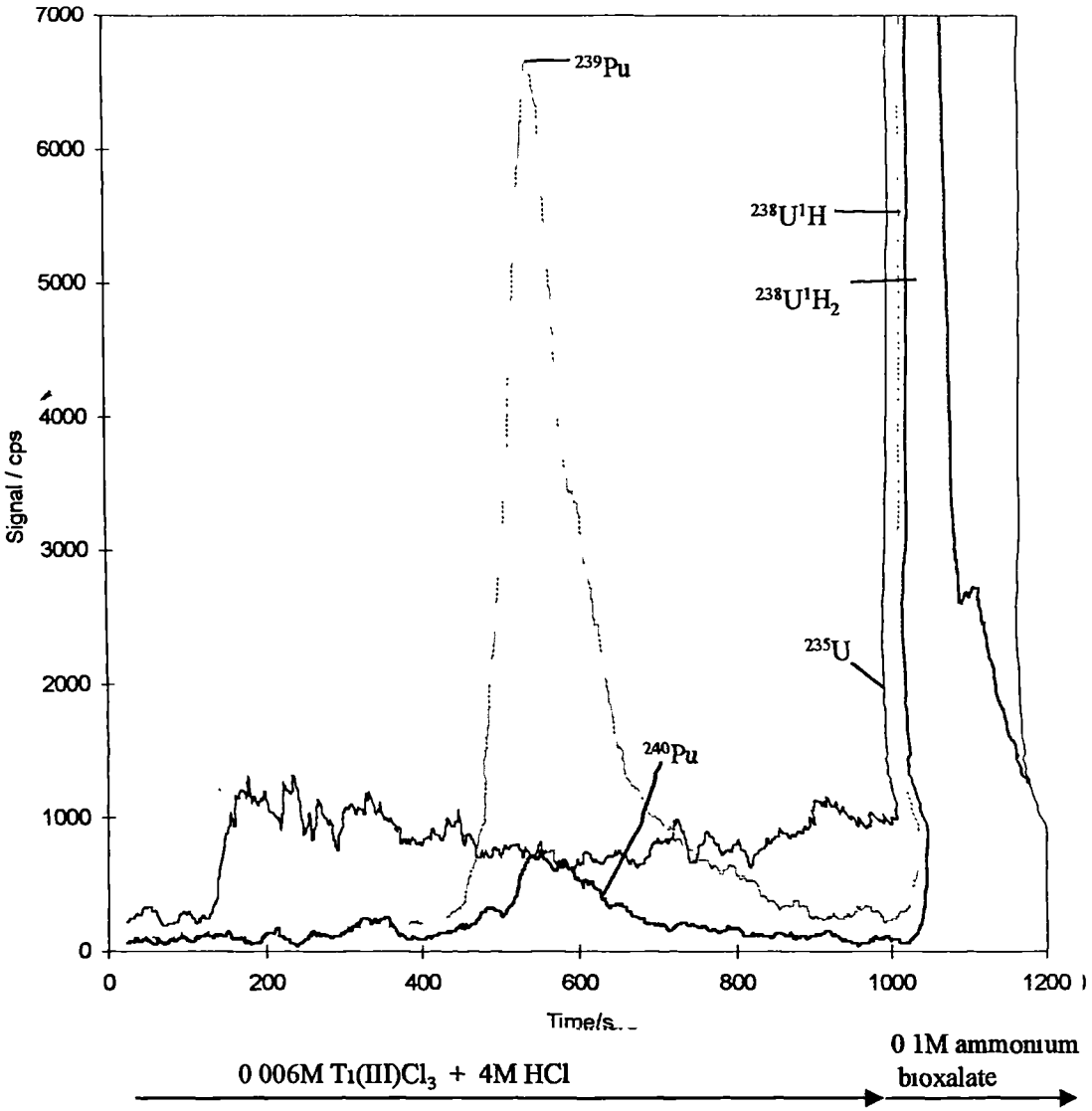


Figure 3.10 Separation of Pu from U in NIST Rocky Flats soil CRM using $TiCl_3$ reduction.

3.4 CONCLUSIONS

The problems associated with polyatomic interferences have been somewhat highlighted Using a PN-ICP-MS (VG PlasmaQuad III) and the Tru-Spec resin to elute increasing concentrations of ^{238}U eventually leads to an apparent ^{239}Pu signal, this demonstrated the problems associated with the formation of $^{238}U^{1}H^{+}$ The $^{238}U^{1}H^{+}$ interference becomes manifest when concentrations of ^{238}U exceeds 1 $\mu g\ ml^{-1}$ (approximately)

Solid phase extraction, using Tru-Spec resin, coupled with SF-ICP-MS has been successfully applied to the determination of actinides in environmental samples, with limits of detection of the order of 2 $fg\ g^{-1}$ The potential for obtaining detection limits less than 152 $ag\ ml^{-1}$ for ^{237}Np has also been achieved using pre-concentration The technique has been successfully applied to the determination of ^{239}Pu in biological CRMs and reference materials, however, it was not possible to determine ^{239}Pu in sediments due to the co-elution of ^{238}U and associated interference due to $^{238}U^{1}H^{+}$ at m/z 239 In order to overcome this interference a sequential elution procedure based on pre-reduction with $TiCl_3$, was applied to separate Pu and U, so that the interference-free determination of ^{239}Pu in human lung and soil was possible

Chapter 4

INVESTIGATION OF CHELATION EXCHANGE FOR THE PRE-CONCENTRATION OF ACTINIDE ELEMENTS

Chapter 4

INVESTIGATION OF CHELATION EXCHANGE FOR THE PRE-CONCENTRATION OF ACTINIDE ELEMENTS

4.1 INTRODUCTION

After the successful application of the Tru-Spec resins in Chapters 2 and 3, an investigation into more novel methods of actinide pre-concentration was undertaken. From reviewing the literature two appropriate chelation exchange dyes were considered for study

The chelating dye xylenol orange (XO) (Figure 4.1) and 4-(2-pyridylazo)resorcinol (PAR) (Figure 4.2), these compounds have been previously used in chelation ion chromatography for the separation and determination of Zn(II), Pb(II), Ni(II) and Cu(II) in seawaters[118], including concentrated KCl and NaCl brines[119], oil-well brines[120] and samples containing high levels of alkali and alkaline earth metals[121]. The dyes are coated onto a suitable substrate, typically a hydrophobic poly-styrene divinylbenzene (PS-DVB) resin, which is packed into a liquid chromatography column, thereby facilitating continuous flow analysis

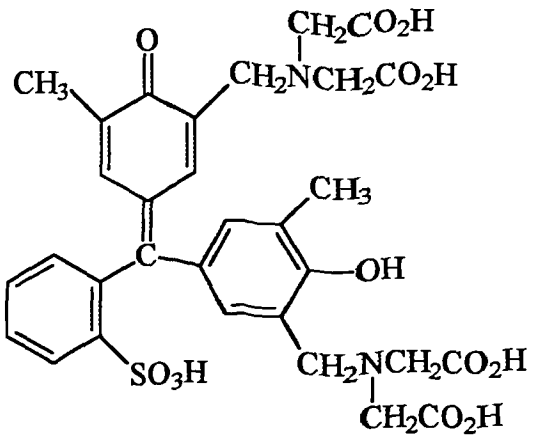


Figure 4.1 Chemical structure for xylenol orange (XO) chelating dye.

The selectivity of these dyes is highly pH dependent[122]. By changing the pH of the eluent, it has been possible to selectively remove a wide range of metal ions from seawater samples[118,121] Typically, +3 metal ions are strongly retained, and +2 metal ions, have a lower affinity for the dye Previous studies[123] into the loading characteristics of the dyes, showed that XO was the strongest chelate and that PAR had a very high loading on the substrate, typically only 4.8% of the dye was actively chelating

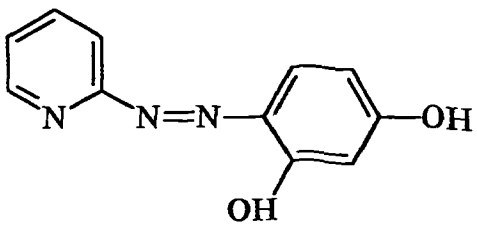


Figure 4.2 Chemical structure for 4-(2-pyridylazo) resorcinol (PAR) chelating dye.

Steric effects on column loading have been discussed and were considered an important factor with regard to the overall capacity because these effects can curtail the chelating ability of the dyes[123] Other workers have reported[124] the use of ultrasonic agitation in order to increase the adsorption rate of PAR on Amberlite XAD-2 resin

Finally, a silica-based chelating exchanger with bonded iminodiacetic acid (IDA) groups (namely, Silasorb 600) was also considered for evaluation. The substrate has already been applied to 2+ and 3+ metals and found to have some affinity for uranium and thorium[122]

4.2 EXPERIMENTAL

4.2.1 Instrumentation

4.2.1.1 Pneumatic Nebulization (PN)-ICP-MS Detection

An inductively coupled plasma mass spectrometer (PlasmaQuad 2+, VG Elemental, Cheshire, UK) was used Data was acquired using the time resolved analysis software, which allows monitoring of multiple isotopes, and manipulated off-line using MassLynx software Operating conditions are given in Chapters 2 and 3

4.2.1.2 Electrothermal Vaporisation (ETV)-ICP-MS Detection

An inductively coupled plasma mass spectrometer (Elan 5000A, Perkin Elmer) interfaced with an electrothermal vaporisation (ETV) sample introduction system (HGA 600MS, Perkin Elmer) was used Data was acquired in transient peak hopping mode, which allows time resolved monitoring of multiple isotopes Operating conditions for the ICP with the associated temperature program for the ETV are given in Chapters 2 and 3

Samples were eluted with 5 g of 2M nitric acid into ETV autosampler vials Aliquots of the samples (30 µl) were pipetted into the ETV furnace tube and the temperature program initiated

4.2.1.3 UV/VIS detection

Initial investigations of the above columns were performed using UV/VIS (Dionex AD20 UV/VIS detector, Dionex UK Ltd, Camberley, Surrey, UK) at 654 nm after a post-column reaction with arsenazo (III) adjusted to pH 2 with concentrated nitric acid Arsenazo (III) chelating dye has been used previously as an effective post-column reagent for UV/VIS detection system, for the determination of uranium and thorium[125,126,127,128,129,130,131]

The flow injection manifold used in Chapter 2 was interfaced with the UV/VIS detector as shown in Figure 4 3. The manifold used with the PN-ICP-MS instrument and for sample preparation for ETV-ICP-MS has been described in Chapters 2 and 3

4.2.1.4 Columns

A Hamilton PRP-1 polystyrene based substrate (Phenomenex, UK) of 35 μm particle size was packed into 3mm i d x 50mm Omnifit columns Again using a 3 mm i d and 50 mm column for the Silasorb 600 substrate, as used in Chapter 4, for assessment of actinide separations using the SF-ICP-MS

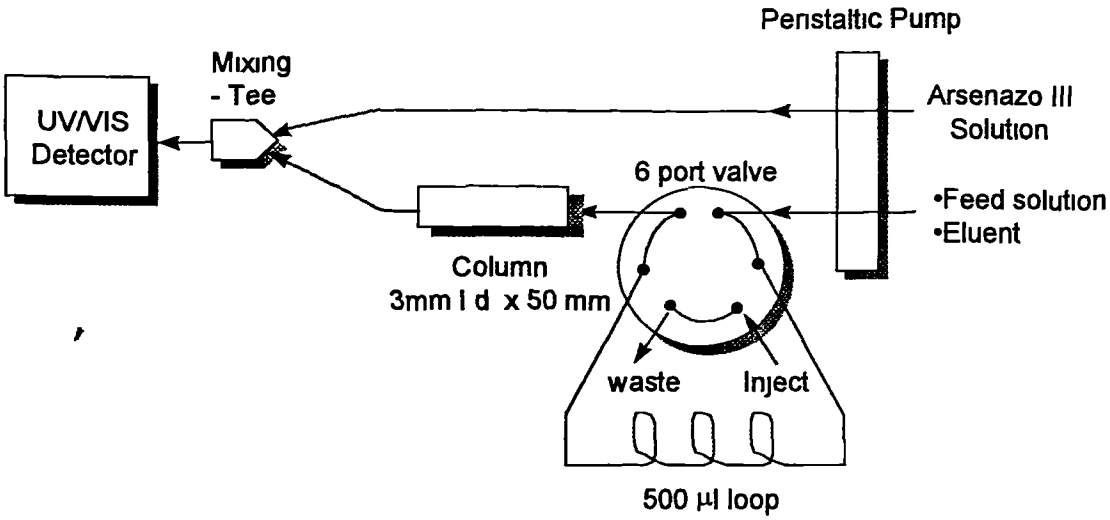


Figure 4.3 Schematic of the flow injection manifold interfaced with UV/Visible detector.

The substrate was made into a slurry using a solution of the chelating dye According to the literature, the best coatings have been achieved[118,119,120,121] using solutions of 0 2 g of xylenol orange in 100 ml of 10% methanol (pH 3) and 0 2 g of PAR in 100ml of 10% methanol (pH7) However, in practice, coating the substrates by passing these solutions through the columns packed with the substrate was found

to be unsuccessful with no apparent visible coating This was probably due to the hydrophobic nature of the substrate, although even using higher methanol concentrations (i e 20%) no substantial coating was achieved Therefore, in order to aid the adsorption of the dye onto the substrate, the dyes and the substrates were mixed in batch in a sonic bath for 4 hours until the dye had visibly coated onto the substrate Then the columns were loaded with the dyed substrate The dyes have a propensity to de-sorb from the substrate in high molar concentrations of nitric acid (typically >2 molar). However, in this case after initial bleeding, both columns appeared to retain a reasonable coating In addition to XO and PAR a silica based substrate (Silasorb 600, 20 μm , Czechoslovakia), which has bonded iminodiacetic acid groups, was also investigated The Silasorb substrate was pumped into the column as a slurry made with distilled de-ionised water (DDW).

4.2.2 Reagents

All solutions were prepared using analytical grade reagents and distilled deionised water (Ultra Pure Water, Elgastat Maxima, Elga Ltd, Bucks, UK) Analytical reagents were as follows 2M HNO_3 (Aristar, BDH, Poole , UK), 15 ng ml^{-1} bismuth solution as an internal standard for ICP-MS detection to allow correction for instrumental drift during the analysis KNO_3 solutions made from the salt (Analar, BDH, Poole, UK)

The reagents used for the UV/VIS detection of analytes were 2 x 10^{-4}M of Arsenazo(III) (Avocado, U K), potassium nitrate (BDH, Poole, UK), Xylenol

Orange (Fluka, U K) and 4-(2-pyridylazo)resorcinol (PAR) (Fluka, U K), 10% methanol was made up using ultra pure water and methanol (HPLC grade, BDH, Poole , UK) and ammonia solution (Aristar, BDH, Poole , UK), used for pH adjustment

4.2.3 Procedure

Initially, standards (1 μg ml^{-1} uranium and thorium) were adjusted to pH 2 in line with (using concentrated nitric acid and/or ammonia solution, as required) and deposited into the solid phase in a mobile phase of KNO_3, also at pH 2 The concentration of the KNO_3, in the mobile phase varied between 0 and 1 M to study the possible effect of competition between ion exchange sites on the resin substrate and the chelation exchange sites of the dye Subsequently, the analytes were eluted with 2 M HNO_3

4.2.3.1 Analysis of Samples by (PN and ETV)-ICP-MS

The following sample load procedure was used for the XO, PAR (PN-ICP-MS only) and Silasorb 600 columns -

i The sample was injected into the 500 μl sample loop at a flow rate of 0 5 ml min^{-1}.

ii The solution was deposited onto the column by pumping the feed solution (0 125M KNO_3, pH 2 2, unless otherwise stated) during deposition, the column was diverted to waste

iii The column was rinsed with 1 ml of ultra pure water (pH ~5 5), to remove the matrix prior to diverting the column to the ICP-MS

iv The column was diverted to the ICP-MS instrument, the analytes eluted with 2 M HNO_3, and the analyte masses monitored

v After elution the column was again diverted away from the ICP-MS and flushed with 2 ml of column feed solution to remove residual 2M HNO_3 solution prior to further deposition.

vi Each injection was repeated at least three times

4.3 RESULTS AND DISCUSSION

4.3.1 Investigation of chelating dyes

4.3.1.1 Effects of KNO_3 concentration on the retention of the analyte

In order to ensure that no ion exchange was occurring rather than chelating exchange, the mobile phase contained KNO_3 The effect of varying the concentration of KNO_3 on the retention and recovery of thorium and uranium on substrates coated with XO and PAR using UV/VIS and arsenazo (III) post-column reagent, is shown in Figure 4 4 to Figure 4 6

4.3.1.1.1 Substrate coated with Xylenol Orange

At pH 2, XO proved to be efficient for the retention of thorium, demonstrating little or no changes when increasing the KNO_3 concentration from 0 to 1 mol l^{-1} (Figure 4.4). However, uranium was only partially held up on the column, giving the broad peak shown in Figure 4.5.

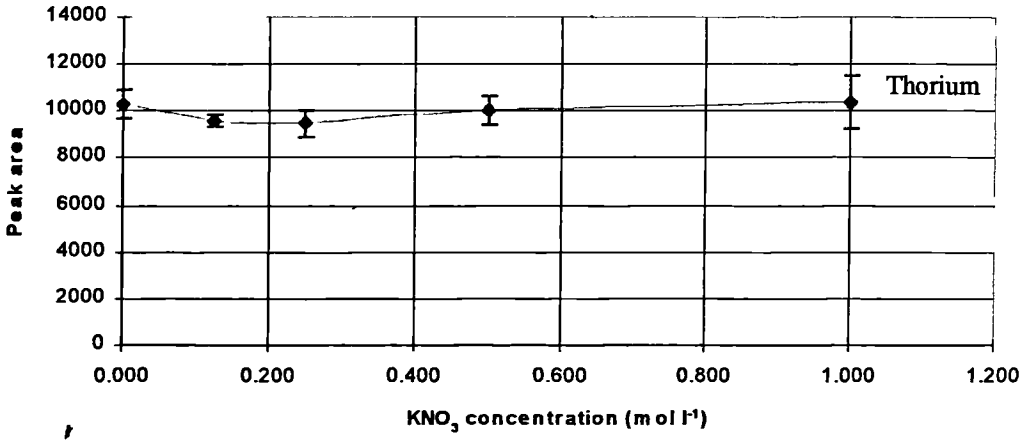


Figure 4.4 Graph showing the effects of KNO_3 concentration on thorium peak area signal for the XO column at a flow rate of 0.5 ml min^{-1}

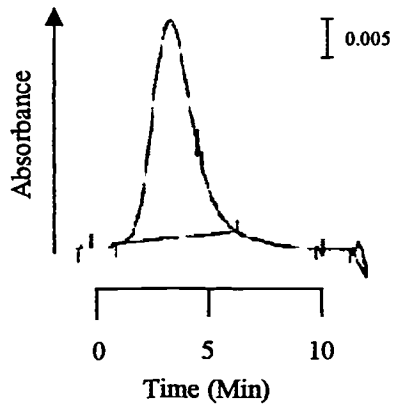


Figure 4.5 XO column with 0.5 µg uranium deposition in 1M HNO_3, pH 2. (Flow rate 0.5 ml min^{-1}).

4 3 1 1 2 Substrate coated with PAR

The behaviour of thorium on the substrate coated with PAR was similar to that for XO, however, in this instance uranium was retained much more effectively with only very slight breakthrough on the solvent front (Figure 4 6) Thorium retention was improved in weak KNO_3 concentrations typically <0 125 M (Figure 4 7), showing an unusual unexplainable change in apparent sensitivity for thorium with a concentration of 0 125 M KNO_3, this not being the case with the uranium signal

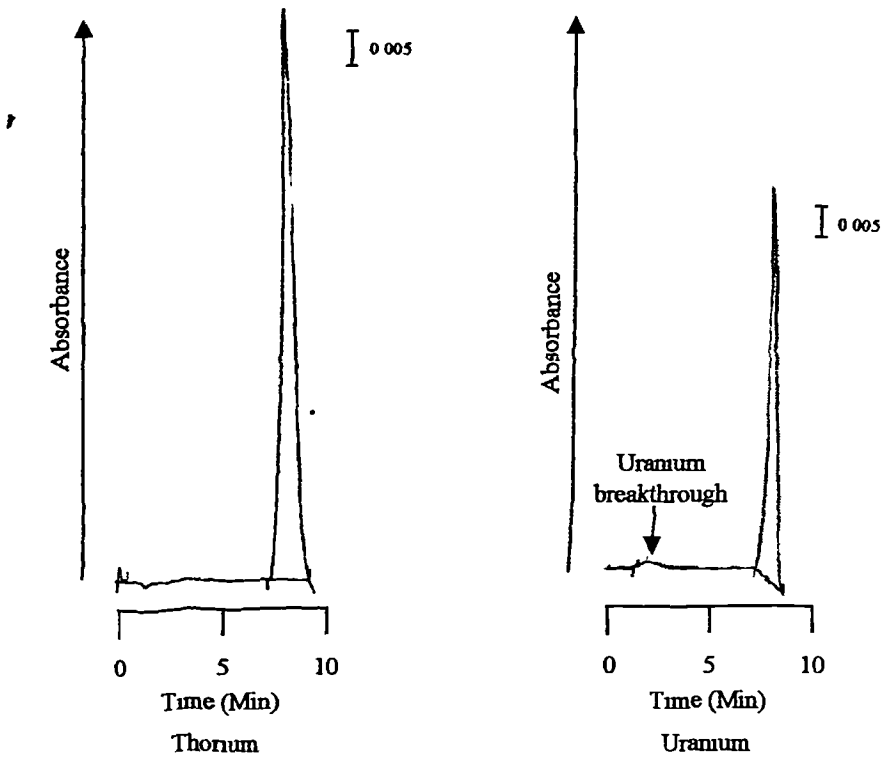


Figure 4.6 PAR column with 5 mg thorium and uranium deposition in 1M KNO_3, pH 2 (2M HNO_3 added at 4 minutes), at a flow rate of 0.5 ml min^{-1}.

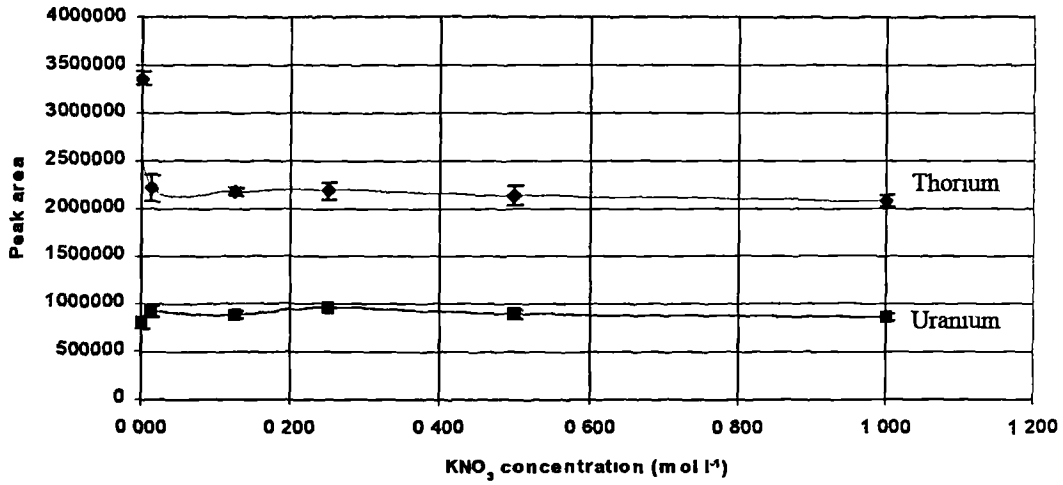


Figure 4.7 Graph showing the effects of KNO_3 concentration at pH 2 on thorium and uranium retention on the PAR column at a flow rate of 0.5 ml min^{-1}

4.3.1.2 Figures of merit for UV/VIS detection

Levels of ^{238}U and ^{232}Th were tested in the 0 03 - 2 mg l^{-1} range, using UV/VIS detection at 654 nm in a solution of Arsenazo (III) adjusted to *p*H 2 2 Detection limits were found to be 0.03 mg l^{-1} for ^{232}Th and 0 1 mg l^{-1} for ^{238}U (compromised by the wavelength setting for the UV/VIS system)

4.3.1.3 Analysis of Reference Materials using ICP-MS detection

Uranium and thorium eluted completely with a peak width of approximately 100 seconds using 2M HNO_3 (Figure 4.8) This elution profile being representative for both XO and PAR columns

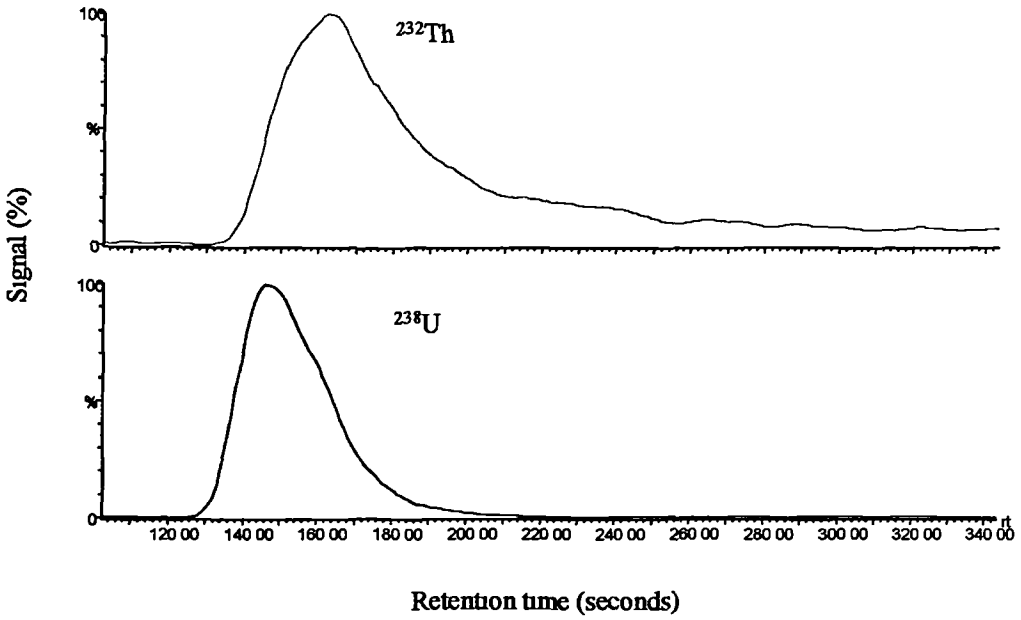


Figure 4.8 Typical elution profile for CRM waters using XO or PAR. 0.125M KNO_3 at pH 2.2 and flow rate 1 ml min^{-1} with PN-ICP-MS detection.

The certified reference material SLEW-2 (Estuarine water) was analysed by pre-concentrating known volumes of the prepared material, eluting and comparing the peaks to the calibration curve after normalising with the bismuth internal standard Results for XO and PAR for SLEW-2 reference material are given in Table 4 1

The poor precision seen in these results was later found to be a consequence of the dyes bleeding off the columns Visible removal of the normally distinct orange colour XO and purple colour of the PAR was observed Due to the repeated application of 2M HNO_3 used as the eluent This resulted in a reduction in capacity and ability to retain the analytes This discovery demonstrated the unsuitability of

these columns for pre-concentration applications Subsequently, no further work was carried out on these columns.

Table 4.1 Results for the determination of uranium and thorium in certified reference material waters by conventional ICP-MS using XO and PAR dye coated substrate (load solution, pH 2.2 in 0.125M KNO_3).

		U		Th	
Column + Detection	**CRM**	**Certified value (ng ml^{-1})**	**Found[a] (ng ml^{-1})**	**Certified value (ng ml^{-1})**	**Found[a] (ng ml^{-1})**
XO with PN	SLEW-2 (Estuarine water)[c]	1 2[b]	1 04 ± 0 94	None given	12 5 ± 17
PAR, with PN	SLEW-2 (Estuarine water)[c]	1 2[b]	0 89 ± 1 49	None given	33 5 ± 52

[a]mean ± *s*; [b]uncertified indicative value, [c]n = 1, 3 injections

4.3.2 Investigation of Silica bonded IDA substrates

After the unsuccessful application of dye coating substrates, it was decided to experiment with a silica based chelating exchanger, which already has IDA groups bonded to the substrate With the premise that it would not suffer from the active groups leaching off the substrate, when applied to real samples and also under fairly acidic conditions (i e. 2M HNO_3)

4.3.2.1 Investigation of ion exchange effects

The effect of KNO_3 on the retention of uranium and thorium on the Silasorb 600 substrate was pronounced (Figure 4 9) Increasing concentration of KNO_3 reduced the retention efficiency of the column In addition, breakthrough of uranium was also observed at pH 2 and in the presence of KNO_3 (Figure 4 10)

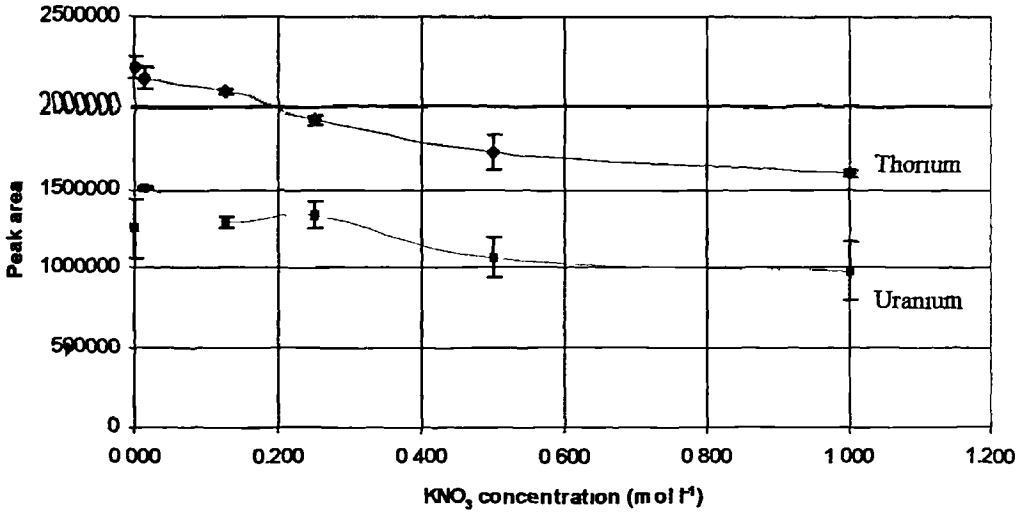


Figure 4.9 The effects of KNO_3 at pH 2 on thorium and uranium retention for the Silasorb 600 column at a flow rate of 0.5 ml min^{-1}

Analyte loading was affected if the time between passing the column feed solution and elution with 2M HNO_3 was reduced

In all cases, a re-equilibration time of at least 4-5 minutes with column feed solution was required between load and elution cycles, otherwise, the breakthrough was more pronounced because of the high concentrations of nitric acid used as eluent

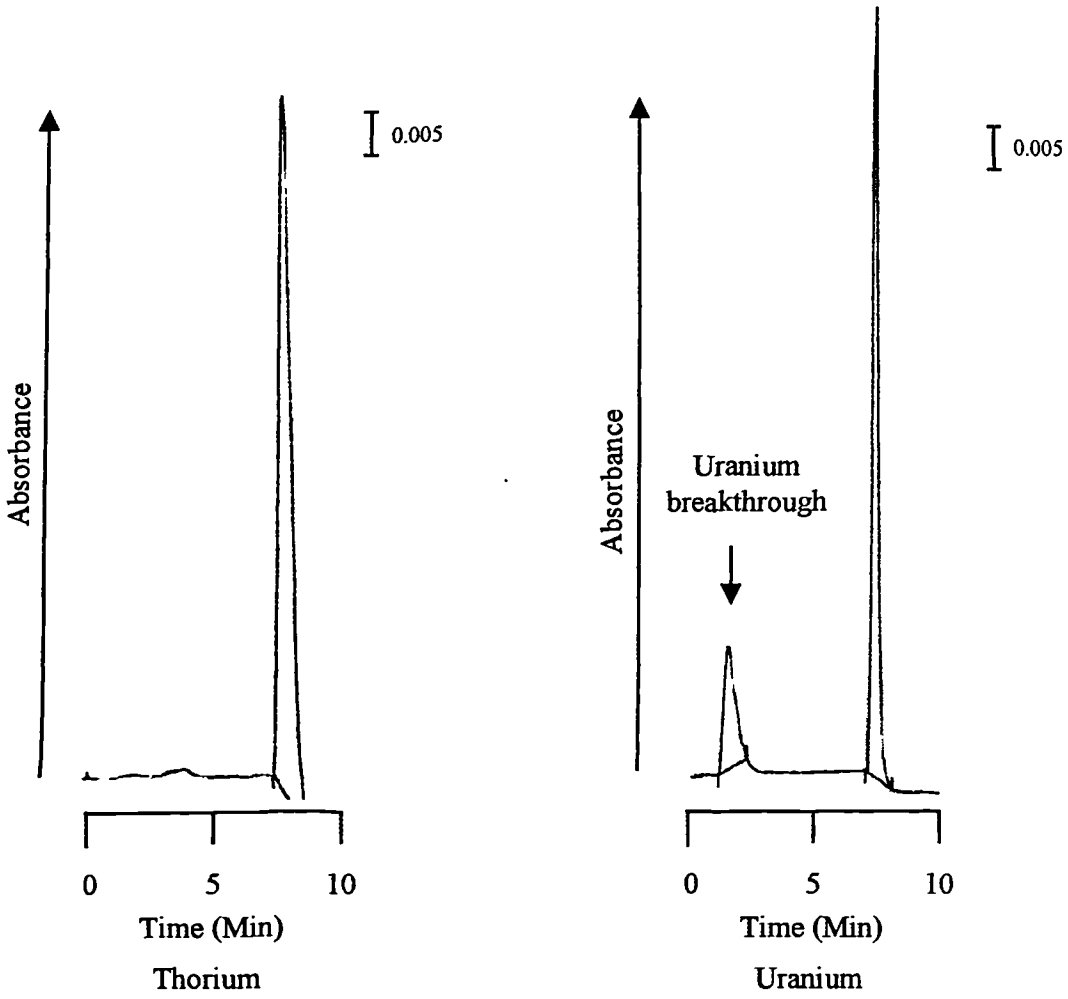


Figure 4.10 Silasorb 600 column with 5 mg thorium and uranium deposition in 1M KNO_3, pH 2 (2M HNO_3 added at 4 minutes), flow rate 0.5 ml min^{-1}.

4.3.2.2 Investigation of pH dependency

Having studied the effects of KNO_3 on retention, it was observed, that the Silasorb 600 suffered most from uranium breakthrough. In order to establish the retention characteristics of the Silasorb 600 column, the effect of pH on deposition of uranium and thorium were studied using ICP-MS as the detection method. This would also allow any breakthrough to be observed at much lower concentrations than

UV/VIS detection The concentration of KNO_3 was fixed at 0 0125M which was significantly high to mask ion exchange effects, but sufficiently low to prevent salt build-up on the cones and nebuliser tip

The effect of pH on the detection of uranium and thorium is shown in Figure 4 11 As can be seen, there was very little effect on the retention of thorium between pH 1 to 3 5 However, there is a slight increase in tailing during the elution step above pH 2 In comparison, considerable breakthrough was observed for uranium at pH 1 and 1 5, slight breakthrough at pH 2, and literally no breakthrough above pH 2

Therefore, a pH between 2 and 2 5 would be sufficient for the purpose of uranium determination, this would also be sufficient for thorium, having a greater retention than uranium

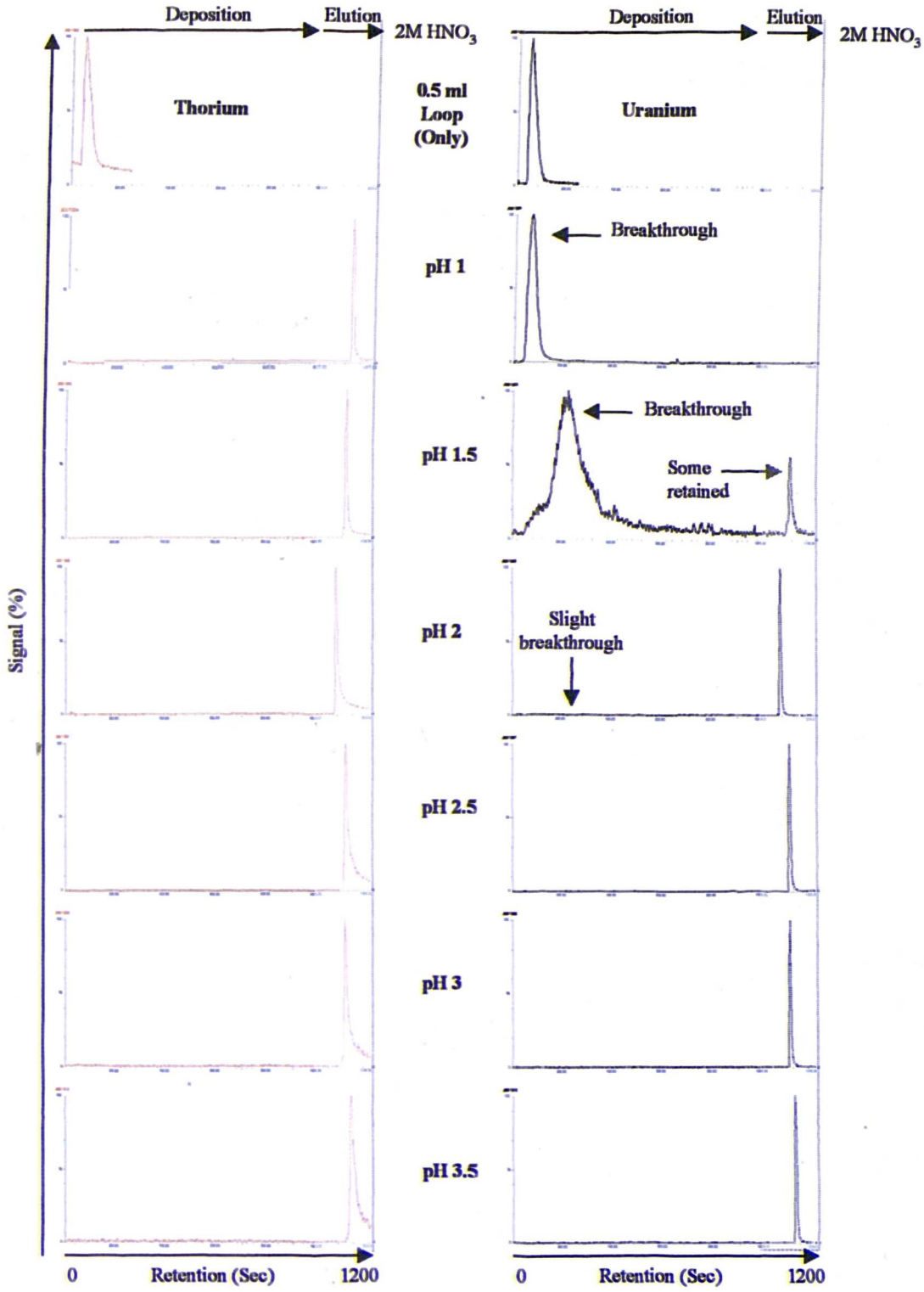


Figure 4.11 **The effects of pH on injections of 62.5 pg thorium and uranium for the Silasorb 600 column. 0.0125M KNO_3 mobile phase and a flow rate of 0.5 ml min^{-1}. (PN-ICP-MS)**

4.3.2.3 Silasorb 600 and pH dependency for the transuranic actinides

The effect of pH was also tested upon the other actinides using SF-ICP-MS (with the same operating conditions as in Table 3.1 from Chapter 3). The intention was to selectively remove uranium, while retaining plutonium (^{235}U was only present as a contaminant but was monitored to assess its behaviour on the column). The pH range was varied from pH 2.2 to pH 1. Figure 4.12 shows a standard run at pH 2.2 and eluted with 2M HNO_3. Initial studies show that plutonium and neptunium are less efficiently retained than the two americium isotopes.

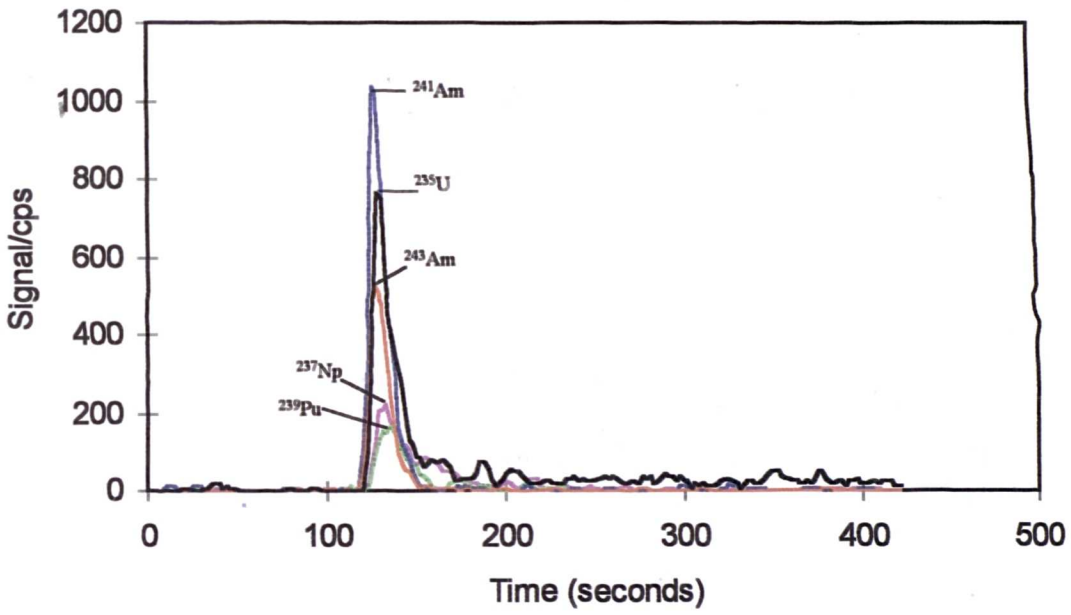


Figure 4.12 Actinide retention on Silasorb 600 column at pH 2.2 in 0.0125M KNO_3 with elution by 2M HNO_3, SF-ICP-MS.

Lowering the pH to 1.5 gave full recovery for americium but also some losses for neptunium and plutonium (Figure 4.13). At this pH, the retention of uranium had started to diminish, with a significant drop in americium retention, the all other elements also being effected to some degree (Figure 4.14). The over-sensitivity of the column to pH conditions, would require significant pH adjustment with an appropriate buffer applied.

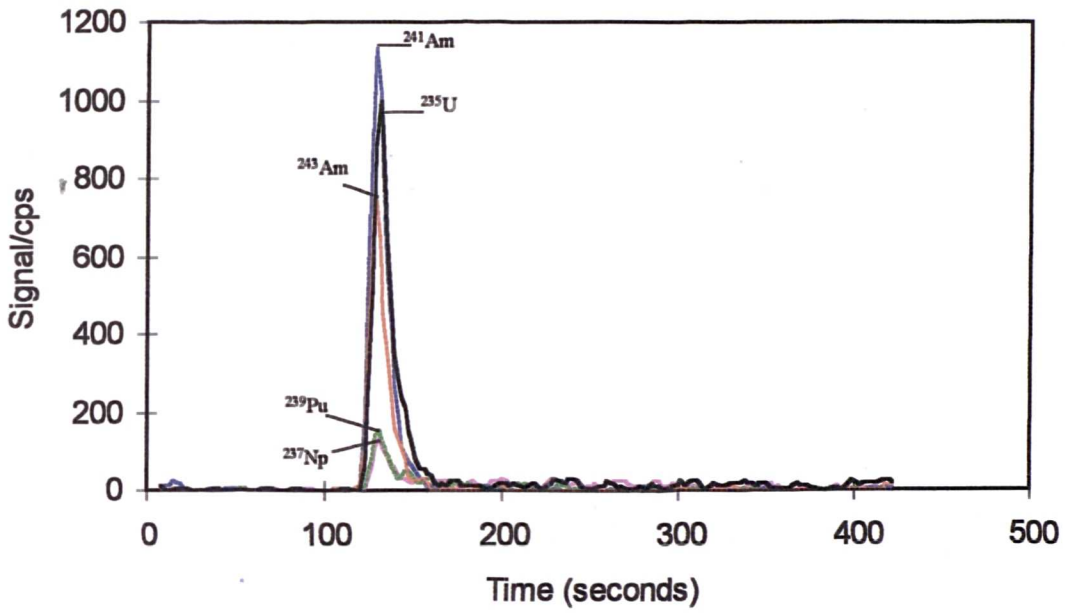


Figure 4.13 Actinide retention on Silasorb 600 column at pH 1.5 in 0.0125M KNO_3 with elution by 2M HNO_3, SF-ICP-MS.

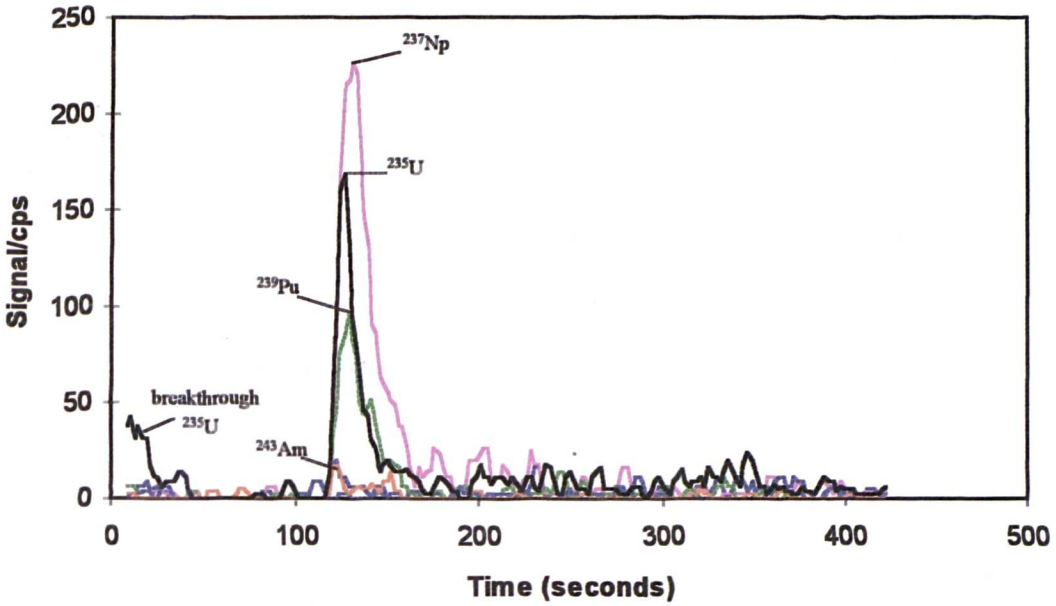


Figure 4.14 Actinide retention on Silasorb 600 column at pH 1 in 0.0125M KNO_3 with elution by 2M HNO_3, SF-ICP-MS.

Studies have shown that it was not possible to selectively remove uranium from the column without simultaneously eluting some of the neptunium, plutonium and americium.

4.3.2.4 Investigation of Iron Interference

As mentioned in Chapter 2, environmental samples can contain high levels of iron, particularly in soils and sediments. Therefore a series of iron(III) and iron(II) solutions were prepared, with fixed concentrations of KNO_3, uranium and thorium. The iron(II) was prepared by reducing with ascorbic acid (0.1 mol l^{-1}).

Two separate series of solutions each containing 0 5 ng ml^{-1} of uranium and thorium with an increasing concentration of Fe(III) in 0 0125M KNO_3, were loaded onto the column and eluted in 2M HNO_3 Results are shown in Figure 4 15 and Figure 4 16

The results show that the Fe(III) had a dramatic effect on the recovery of uranium and thorium from the column Recovery dropped from 100% to 0%, for Fe (III) concentrations of 5000 µg ml^{-1}. This drop in recovery in this instance is significant, if the determination of uranium and thorium in real soil or sediment samples is required

When the same experiment was repeated with the addition of the ascorbic acid as the reducing solution (Figure 4 17 and Figure 4.18), some improvement in recoveries was observed for thorium (Figure 4 17) For iron concentrations of 1000 µg ml^{-1}, recoveries increased from approximately 17% without ascorbic acid to 88% with ascorbic acid This was also the trend for uranium (Figure 4 18), with recoveries improving from approximately 14% without reduction to 62% with redution for 1000 µg ml^{-1} iron

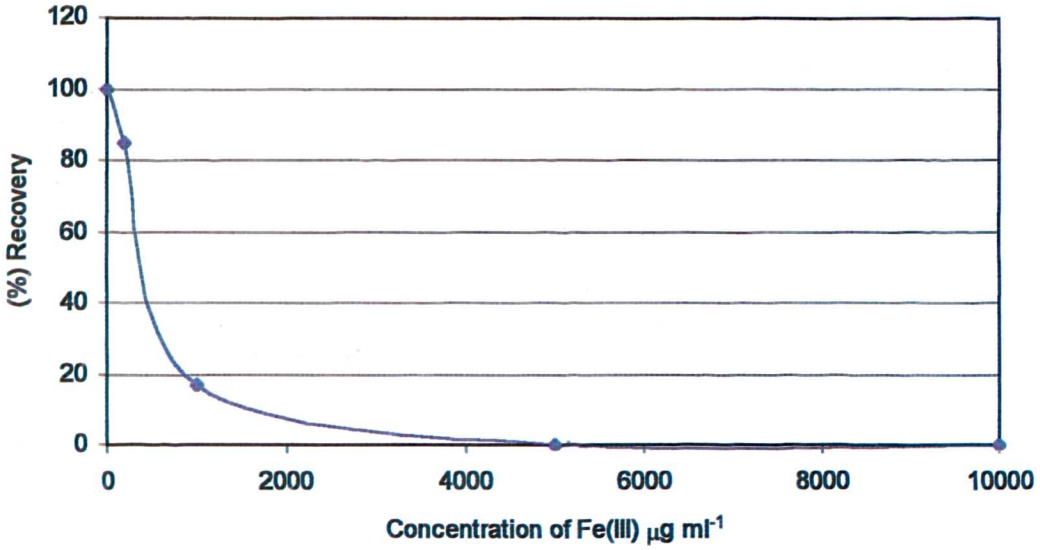


Figure 4.15 The effect of iron(III) on the recovery of 0.5 ng of thorium from Silasorb 600.

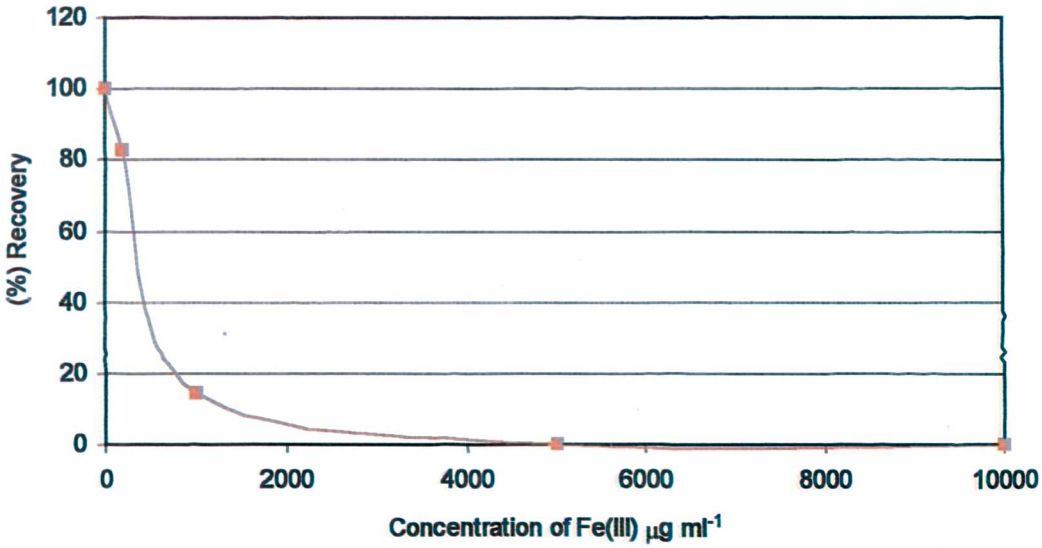


Figure 4.16 The effect of iron(III) on the recovery of of 0.5 ng uranium from Silasorb 600.

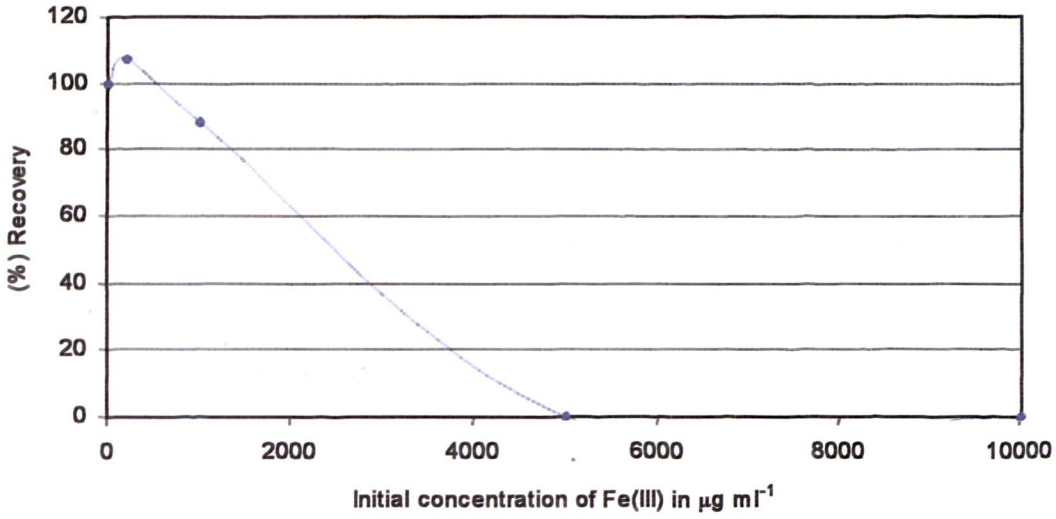


Figure 4.17 The effect of iron(III) reduced to iron(II) using ascorbic acid on recovery of 0.5 ng of thorium from the Silasorb 600 column.

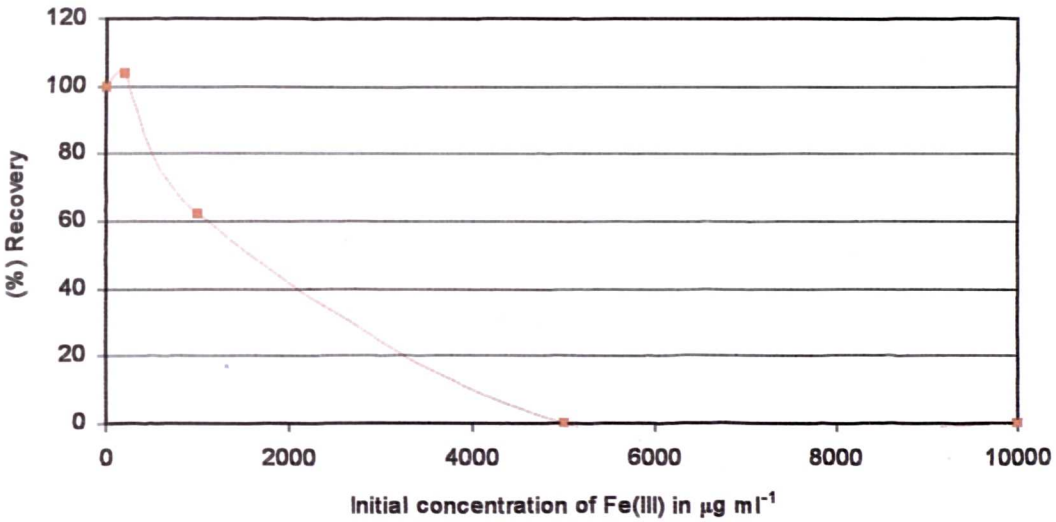


Figure 4.18 The effect of iron(III) reduced to iron(II) using ascorbic acid on recovery of 0.5 ng of uranium from the Silasorb 600 column.

The results indicate that the resin would not be appropriate in studies requiring determination of the actinides in samples containing levels of iron greater that 500 μg ml^{-1} However, it still may be used in the determination of actinides in environmental waters

4.3.2.5 Analysis of Certified Reference Materials

The certified reference materials NASS-4 (seawater) and SLEW-2 (estuarine water) were analysed as detailed in section 4 3 1 3 earlier Elution profiles had characteristics similar to XO and PAR (Figure 4 8) The results for the determination of uranium and thorium using Silasorb 600 column are given in Table 4 2

The reference materials were only certified for uranium One particular problem encountered was that the reproducibility for thorium was poor, and this element was prone to carry-over effects and high blank values Full recoveries were found for uranium in NASS-4 using the Silasorb 600 column and PN-ICP-MS detection Comparable recoveries were obtained for uranium in SLEW-2 However, the values given in the CRMs certificate are only indicative

Around 82% recovery was obtained for uranium in NASS-4 seawater samples using Silasorb 600 and ETV-ICP-MS (Table 4 2)

Table 4.2 **Results for the determination of uranium and thorium in certified reference material waters by conventional ICP-MS and ETV-ICP-MS using retention on Silasorb 600 chelating substrate (load solution, pH 2.2 in 0.125M KNO_3).**

		U		Th	
Detection	**CRM**	**Certified value (ng ml^{-1})**	**Found[a] (ng ml^{-1})**	**Certified value (ng ml^{-1})**	**Found[a] (ng ml^{-1})**
PN	SLEW-2 (Estuarine water)[c]	1 2[b]	1 06 ± 0 03	none given	0 16 ± 0 02
PN	NASS-4 (Seawater)[c]	2 68 ± 0 12	2 82 ± 0 37	none given	Method LOD
ETV	NASS-4 (Seawater)[d]	2 68 ± 0 12	2 20 ± 0.09	none given	Method LOD

[a]mean ± *s*, [b]uncertified indicative value, [c]n = 1, 3 injections, [d]n=1, 6 injections

4.4 CONCLUSIONS

The chelating dyes (XO and PAR) loaded onto PS-DVB have been investigated as alternative retention media for the separation of actinides. Results for the determination of uranium in SLEW-2 (estuary water) after retention on XO and PAR were very poor This was mainly due to, the dye coatings not being sufficiently stable on the substrate The dyes may more readily penetrate the pores if used under higher pressures (i e HPLC applications)

A Silasorb 600 column was tested for retention of uranium and thorium, finding that the pH and concentration of iron had a significant effect on the retention of both uranium and thorium However, some improvement in recovery was observed when ascorbic acid was used to reduce the iron, which was present at levels

of 1000 μg ml^{-1}, indicating that the column would only be suitable for analysing samples with low iron concentrations

The effects of pH (1-2 2) on the retention of uranium, neptunium, plutonium and americium isotopes on Silasorb 600 was also tested It was not possible to separate uranium from plutonium by pH adjustment alone. The pH of the mobile phase has shown to be a critical factor in the retention of the actinides and adequate buffering must be applied, particularly, when dealing with real samples This would be particularly so, if samples were digested using high acid concentrations then losses of analyte due to this pH sensitivity would most certainly occur

The Silasorb 600 resin was later applied to CRM waters, finding that is was possible to obtain full recoveries for uranium in SLEW-2 and NASS-4 for PN-ICP-MS (NASS-4 only) and ETV-ICP-MS Generally, the results indicate that the Silasorb column may have some potential for the determination of uranium in water samples However, from this study, the column would be unsuitable for more difficult samples, such as soils and sediments

Chapter 5

HIGH PERFORMANCE CHELATION ION CHROMATOGRAPHY COUPLED TO SECTOR-FIELD ICP-MS

Chapter 5

HIGH PERFORMANCE CHELATION ION CHROMATOGRAPHY *COUPLED TO SECTOR-FIELD ICP-MS*

5.1 INTRODUCTION

Successful application of a low pressure chelation exchange system for uranium determinations (Chapter 4) in water reference materials, has lead the way to the investigation of an alternative methodology, high performance chelation ion chromatography (HPCIC) systems Such a system may offer considerable improvement in the separation of the actinides, particularly in the separation of ^{238}U from ^{239}Pu, subsequently removing the $^{238}U^{1}H$ interfering polyatomic (discussed earlier in Chapter 3) This could be achieved by constant flow of a simple mobile phase through a chosen column and injecting small quantities of sample, thus, reducing the number of reagent changes, and thus simplifying the separation procedure for on-line ICP-MS applications Careful selection and adjustment of the methodology should allow for the separation of actinides in high acid and complex matrix conditions

Investigation of relevant literature, has shown that studies[132,133,134] into the application of chelation chromatography utilising a dynamically modified substrate with 2,6 pyridinedicarboxylic acid (dipicolinic acid, Figure 5 1) has special potential for the determination of uranium and thorium in real samples These dynamic systems have successfully separated U(VI) from Fe(III), La(III) and Th(IV), illustrating the

potential for real sample separations to be performed for the determinations of uranium and thorium A recent paper[135] described the quantification of uranium in certified waters and stream sediments at ng ml^{-1} levels using UV/Vis spectroscopy with post-column reaction (PCR) detection systems utilising arsenazo (III) These separations were undertaken using 0 1mM dipicolinic acid in 0 5M HNO_3 and 1M KNO_3 to prevent ion exchange with the column substrate The retention time and column efficiency could be adjusted by changing the acid concentration Under these conditions the column substrate polystyrene divinyl benzene (PS-DVB) was dynamically coated with the chelating reagent (i e dipicolinic acid) Dynamic coating of the substrate is thought[135] to occur through a combination of hydrophobic and π-π interactions between the aromatic group on the dipicolinic acid and the benzene groups on the resin Eventually, a state of equilibrium is set up between the sorbed layer of dipicolinic acid on the substrate, and in the mobile phase, called dynamic modification[135]

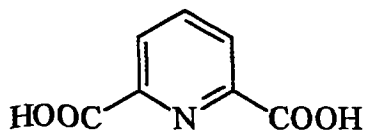


Figure 5.1 Dipicolinic acid (2,6-pyridinedicarboxylic acid)

The aim of this study, was to use the dipicolinic dynamic system with an appropriate substrate to separate thorium, uranium, neptunium, plutonium and americium from matrix ions, in order to facilitate their determinations in

environmental samples Virtually all +2 and +3 metal ions, such as the lanthanides and iron, exhibit minimum retention on the HPCIC system[135]. Hence, it is possible to separate these elements from the actinide elements such that they elute in, or close to, the solvent front This is an advantage for the analysis of soils and sediments, which can contain high concentrations of transition metals Finally, the potential of this system to separate analytes under high acid conditions is also a useful characteristic for this work

5.2 EXPERIMENTAL

5.2.1 Instrumentation

All analyses were performed using either a PN quadrupole (PlasmaQuad 2+, VG Elemental, Cheshire, UK) or sector-field inductively coupled plasma mass spectrometer (SF-ICP-MS, ELEMENT 1, Finnigan-MAT, Germany) interfaced with a high pressure liquid chromatography (HPLC) pump (Varian 9010 HPLC pump, Surrey , UK), the sample injection system is shown in Figure 5 2, using a Rheodyne Model 9010 injection valve (Rheodyne Inc, California, USA) Data was acquired in transient peak hopping mode, which allows time resolved monitoring of multiple isotopes Operating conditions are shown in Table 5 1.

5.2.2 Analytical Column

Columns were prepared using PRP-1 polystyrene divinyl benzene (PS-DVB) substrate (7 μm Hamilton, Reno, USA) and PLRP-S (PS-DVB) substrate (5 μm

Polymer Laboratories, UK), packed into PEEK columns of 4.6 mm i.d. and 100 mm length.

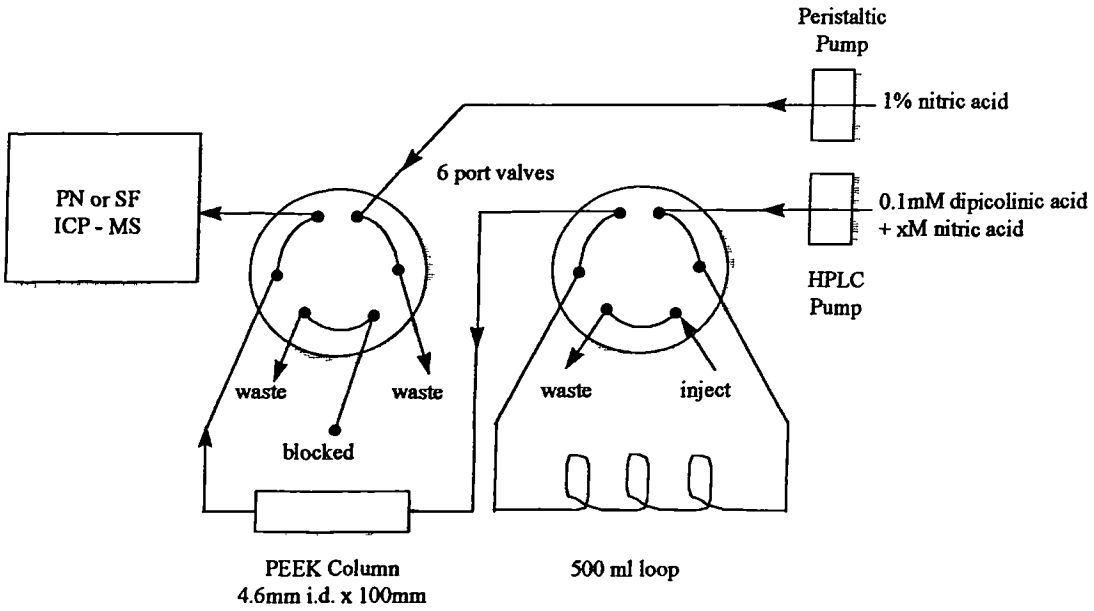


Figure 5.2 Schematic of the flow injection manifold interface with PN or SF-ICP-MS.

5.2.3 Reagents

All solutions were prepared using analytical grade reagents and distilled deionised water (DDW, Ultra Pure Water, Elgastat Maxima, Elga Ltd, Bucks, UK). nitric acid (Aristar, BDH, Poole., UK); dipicolinic acid (Aldridge, Dorset, UK); off-column reducing solution prepared from 0.3 g sodium formaldehyde sulfoxylate (Rongalite) or 0.3 g of ammonium iron(II) sulphate dissolved in 10 ml of mobile phase.

Table 5.1 Operating conditions for PN and SF-ICP-MS

	VG PQ2+	Finnigan MAT ELEMENT
ICP		
Forward power (W)	1350	1100
Plasma gas (l min^{-1})	16 5	14 0
Auxiliary gas (l min^{-1})	0 7	0 9
Nebulizer gas (l min^{-1})	0 8	1 1
Sampling depth (mm)	10	-
Sample flow (ml min^{-1})	0 5	0 5 – 2
Torch	Fassel (quartz)	Fassel (quartz)
Nebulizer	Concentric (quartz)	Concentric MicroMist (quartz)
Spray Chamber	Scott type (quartz)	Scott type (quartz) or Jacketed Cyclonic
Interface		
Sampler	Ni	Ni
Skimmer	Ni	Ni
Mass Spectrometer		
Ion masses (m/z)	^{139}La, ^{232}Th, ^{238}U	^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{237}Np, ^{238}U, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{243}Am
Data acquisition	Time resolved mode	
Points per peak	3	25
Dwell time (ms)	20	30
Time-slice duration (s)	1	1

0 35 g of sodium nitrite was used as an oxidation state fixing solution in 10 ml of mobile phase A mixed standard solution of individual stock solutions (approximately 1 fg ml^{-1}) ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am (Amersham International plc, Bucks, UK), was prepared by boiling to dryness in nitric acid and made up in the mobile phase

5.2.4 Sample Preparation

The certified reference material NIST 4351 Human Lung (National Institute of Science and Technology, Gaithersburg, USA) was subjected to a dry and wet ashing procedure as described in 2 2 5 4 and in recent papers[107,108] It was necessary to digest the whole sample of human lung (approx. 45 g), as required by the certificate, due to inhomogeneity caused by the presence of "hot particles". A blank was also prepared

A microwave leach was performed on 1 g of NIST 4353 Rocky Flats Soil No 1 (National Institute of Science and Technology, Gaithersburg, USA) The samples were weighed into microwave bombs, 5 ml of concentrated HNO_3 acid were added, and the bombs were irradiated in the microwave digester (Perkin Elmer PAAR Physica Multiwave Sample Preparation System), for 6 min at 700 W and 15 min at 1000 W power Samples were then quantitatively transferred into clean vials and made up to a known weight with approximately 7 g of 2M HNO_3 A blank was also prepared

5.2.5 Calibration

Standard solutions (mixed actinides of 0 to 1 pg g^{-1}) were introduced by flow injection through a 500 µl injection loop on a 6 port valve (Model 9010, Rheodyne, Cotati, California), into a carrier stream of 0.1mM dipicolinic acid solution in a chosen molarity of HNO_3 at a flow rate of approximately 1 ml min^{-1} and the analyte masses monitored

5.2.6 Analysis of samples

The samples were diluted further by mixing approximately 3 g of sample plus 2 g of 0 1mM dipicolinic acid solution giving a total of 5 g Samples were then injected onto the column via the 500 µl loop and the analysis was performed

5.3 RESULTS AND DISCUSSION

5.3.1 Choice of Substrate

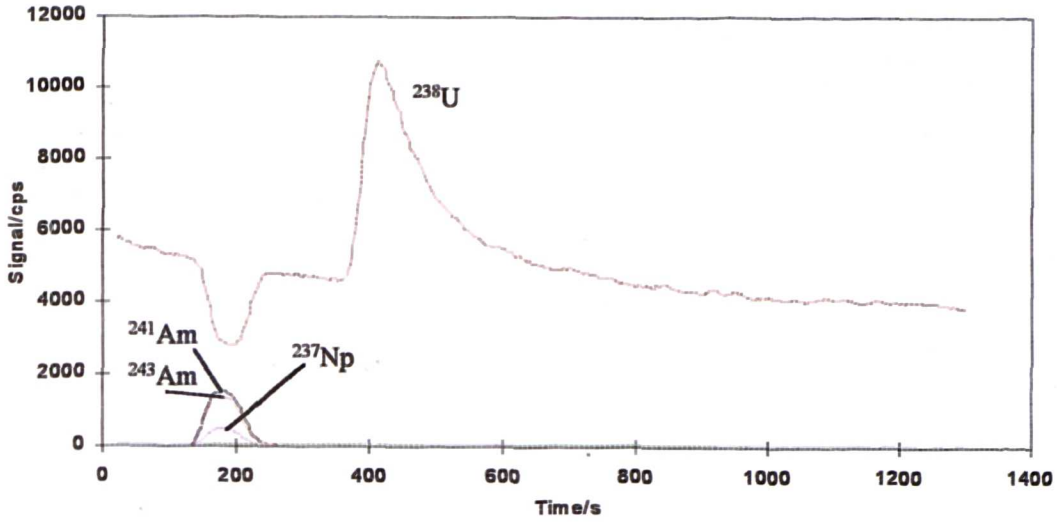
Initially, two different substrates were tested to ascertain which yielded the best separations, namely Hamilton PRP-1 (7 μm) and Polymer Labs PLRP-S (5 μm) Two separate columns were packed with the substrates and a 100 fg solution of each actinide, ^{237}Np ^{239}Pu, ^{241}Am and ^{243}Am were injected into a mobile phase of 0 1mM dipicolinic acid + 1 75M HNO_3 at a flow rate of 0 5 ml min^{-1} Chromatographs for the Hamilton and Polymer Labs columns are shown in Figure 5 3 and Figure 5 4, respectively. It is evident from Figure 5 3 that uranium and plutonium exhibit

considerable broadening effects using the Hamilton column, whereas the Polymer Labs column yielded much improved peak shapes (Figure 5 4) The peak shapes for neptunium and americium were much the same for the two columns because these species elute close to the solvent front The improvement in peak shape attained with the Polymer Labs column was thought to be due to the smaller particle size of this substrate Two separate peaks were observed for neptunium using the Polymer Labs column, probably due to different oxidation states of neptunium (see section 5 3 2) All further studies were performed using the Polymer Labs column

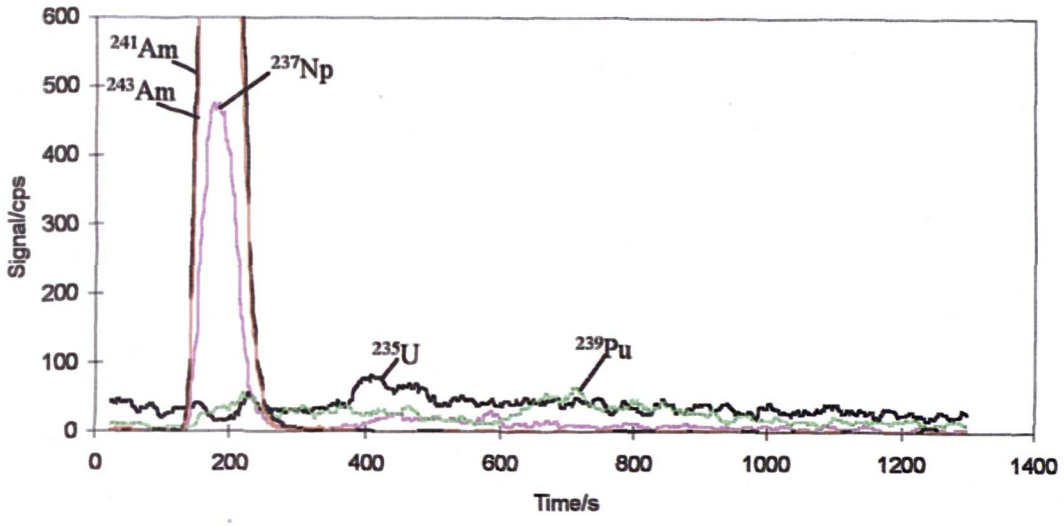
5.3.2 Oxidation state of retained ions

It is apparent from the chromatograms shown in Figure 5 3 and Figure 5 4 that two different oxidation states of neptunium and plutonium were separated by the column.

Fortunately, there has been much research into the behaviour of the actinides under different conditions The range of possible oxidation states have been summarised in Table 5 2, bold text shows the most stable oxidation state and plain text figures show oxidation states that are possible under certain conditions

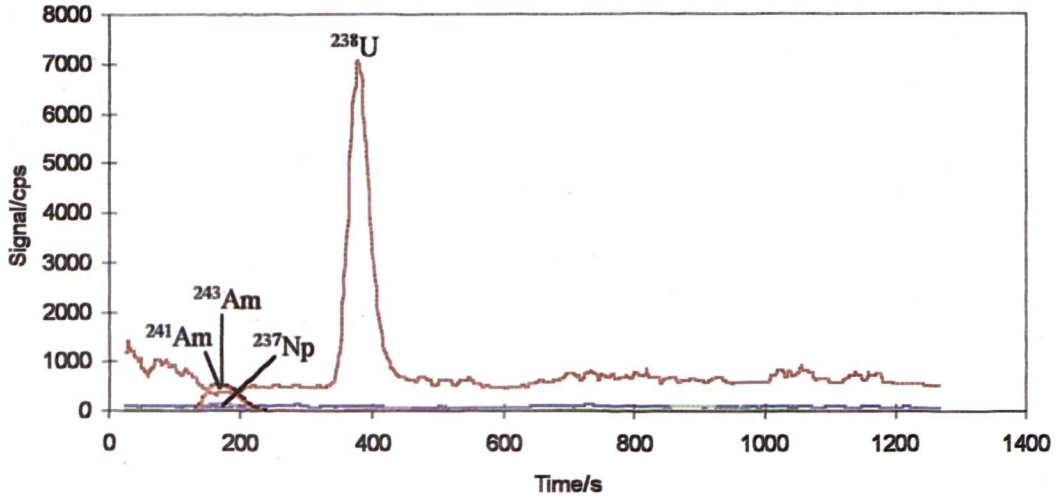


(a)

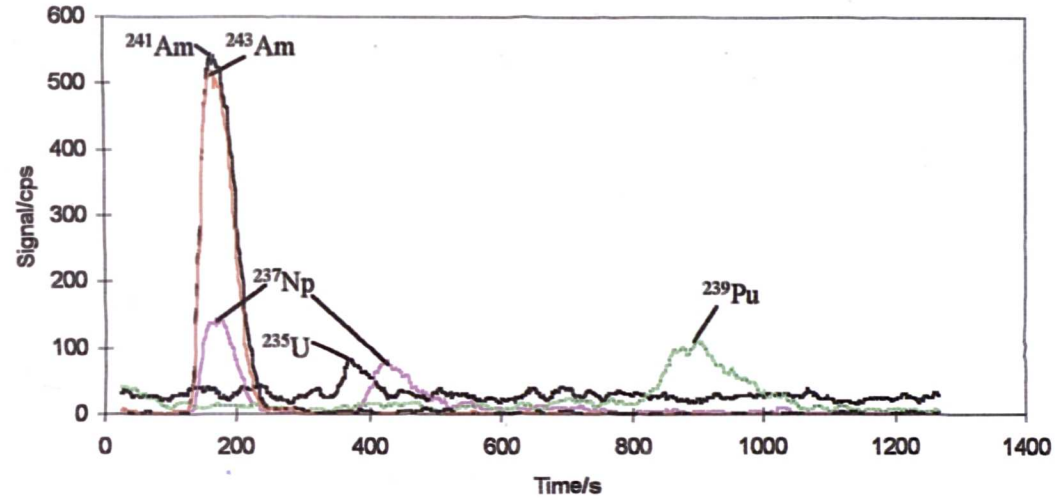


(b)

Figure 5.3 **Chromatogram attained using the Hamilton column for an approximate injection of 100 fg each actinide with 0.1mM dipicolinic acid plus 1.75M HNO_3 mobile phase at a flow rate of 0.5 ml min^{-1}: (a) full scale; (b) expanded scale.**



(a)



(b)

Figure 5.4 **Chromatogram attained using the Polymer Laboratories column for an approximate 100 fg injection of each actinide with 0.1mM dipicolinic acid plus 1.75M HNO_3 mobile phase at a flow rate of 0.5 ml min^{-1}: (a) full scale; (b) expanded scale.**

Table 5.2 Oxidation states of Th, U, Np, Pu and Am[136]

Element	Th	U	Np	Pu	Am
					2[c]
Oxidation	3[a]	3	3	3	**3**
States	**4**[b]	4	4	**4**	4
		5	**5**	5	5
		6	6	6	6
			7[d]	7[d]	

[a] Solid state only
[b] Bold numbers represent most stable state.
[c] In CaF_2 lattice
[d] only in alkaline conditions

The stability of the actinides species in aqueous solution are summarised[1,136] in Table 5 3 which gives only the main species that would exist under normal conditions For thorium, only the 4+ oxidation state is known in aqueous solutions, with the uranium, neptunium and plutonium redox chemistry being varied

The chemistry of neptunium and plutonium is somewhat complicated, particularly that of plutonium, as it can coexist in the +3, +4, +5 and +6 oxidation states[136], although, in strong acid the +5 oxidation state is very unstable[I] and tends to disproportionate to the +3, +4 and +6 (Equation 5 1)[137] In general, lower oxidation states are more stable in acidic solutions while basic solutions favour the higher oxidation states[138]

$$3Pu^{4+} + 2H_2O \leftrightarrow PuO_2^{2+} + 2Pu^{3+} + 4H^+$$

$$2Pu^{4+} + 2H_2O \leftrightarrow PuO_2^{+} + Pu^{3+} + 4H^+ \qquad \textbf{(Equation 5.1)}$$

$$PuO_2^{+} + Pu^{4+} \leftrightarrow PuO_2^{2+} + Pu^{3+}$$

Table 5.3 Stability of Th, U, Np, Pu and Am in aqueous solutions[1,136]

Ion	Stability
(III) state	
U^{3+}	Aqueous solutions evolve hydrogen on standing (easily oxidised by H_2O)
Np^{3+}	Stable to water, but readily oxidised by air to Np^{4+}
Pu^{3+}	Stable to water and air, but easily oxidised to Pu^{4+}, oxidises slightly under the action of its own alpha-radiation
Am^{3+}	Stable, difficult to oxidise
(IV) state	
Th^{4+}	Stable, but hydrolysed at *p*H higher than 3
U^{4+}	Stable to water, but slowly oxidised by air to UO_2^{2+}
Np^{4+}	Stable to water, but slowly oxidised by air to NpO_2^+
Pu^{4+}	Stable in concentrated acid, e g , 6M HNO_3, but disproportionates to Pu^{3+} and PuO_2^{2+} at lower acidities
Am^{4+}	Not known in solution
(V) state	
UO_2^+	Disproportionates to U^{4+} and UO_2^{2+}, most stable at *p*H 2-4
NpO_2^+	Stable, disproportionates only at high acidities
PuO_2^+	Always tends to disproportionate, most stable at very low acidities
AmO_2^+	Disproportionates in strong acid, reduces fairly rapidly under the action of its own alpha radiation at low acidities (in form of ^{241}Am)
(VI) state	
UO_2^{2+}	Stable, difficult to reduce
NpO_2^{2+}	Stable, easy to reduce
PuO_2^{2+}	Stable, fairly easy to reduce, reduces slowly under the action of its own alpha radiation (in form of ^{239}Pu)
AmO_2^{2+}	Reduces fairly rapidly under the action of its own alpha radiation (in form of ^{241}Am)

Similarly, neptunium can coexist in the +4, +5 and +6 oxidation states in 2-6 M nitric acid at approximately 100°C. However, the +5 state should be most predominant[139]

5.3.2.1 Experiments performed for oxidation state assignment

Initially, assumptions are made as to the oxidation state of the particular ions from studies made previously on actinide aqueous chemistry in current literature In order to verify these assumptions, a series of experiments were performed using reducing and oxidation agents to aid in the final designation of the oxidation states Initially, a single unoxidised standard (comprising of only standard diluted in the mobile phase) of plutonium (Figure 5 5) and neptunium (Figure 5 6) was passed through the column It should be emphasised that the mixed oxidation states of neptunium and plutonium were found in the standard solution There was no indication of oxidation state on the containers and it was not possible to find out the standard preparation method

By looking at the initial evidence (Figure 5 3 and Figure 5 4), a plausible hypothesis for elution order may be given as follows M^{3+} ions (M^{n+} the simple aquo ions) are unretained or have minimal retention, M^{4+} is greater than M^{3+} having some retention and the MO_2^+ up to MO_2^{2+} ions having the highest retention over all species (to summarise the retention of $M^{n+} < MO_2^{2+}$) This hypothesis would bear some credibility as americium and thorium have only one main basic oxidation state, those of Am^{3+} and Th^{4+} Also, uranium is normally found in the UO_2^{2+} (this being the most

stable and difficult to reduce oxidation state), considering there is only a single peak for each in the elution order described, would suggest this to be the trend

However, this becomes more difficult when looking at the chemistry of neptunium and plutonium, as both can co-exist in several oxidation states simultaneously making assignment more difficult It was found (Figure 5 5) that plutonium eluted on the solvent front with the remainder coming off later Complexing acids such as HNO_3 have been found to favour Pu(IV) (very stable complexes[140] - $[H_2Pu(NO_3)_6]$), with the Pu(V) disproportionating to Pu(III) and Pu(VI) oxidation states[141] At first glance, the Pu(IV) is probably the more likely candidate for the last peak (for reference having the highest proportion in terms of integrated area ratio), this is somewhat substantiated by the trend of +3 ions being un-retained (evidence of which is given by americium, which is extremely difficult to maintain in any higher oxidation states) The high acid condition would also suggest that the +5 state for plutonium would have disproportionated, thus the peak close to the solvent front could be attributed to Pu(III) and Pu(VI) Although, it should be noted that finding Pu(VI) at the solvent front, is not in keeping with the trend suggested for the original hypothesis

For neptunium, it should be bear in mind that Np^{4+} is slowly oxidised to NpO_2^+ in air or more rapidly in HNO_3 Consequently, the elution is more likely to be neptunium in the +5 state, as the original standard was stored in nitric acid for considerable time (Figure 5 6) However, again, this would not be in keeping with the initial hypothesis

Further investigations using, a single oxidised standard of neptunium (prepared as described in 5 2 3) was also passed through the column (Figure 5 7) , this time resulting in two peaks This would agree with earlier studies by Mckay *et al* [142], on the oxidation states of neptunium These authors found neptunium to be mainly in the +4 and +5 oxidation states, the +3 is stable but readily oxidised by air to +4, and the +6 state was found to be stable but easily reduced The oxidation of Np(IV) to Np(V) in HNO_3 at 25°C has been described[1] as being very slow Hence, giving some supporting evidence to the single peak in Figure 5 6 from the neptunium standard, which had been left standing in nitric acid solution for several months This stills leaves the question unanswered as to the actual assignment of oxidation state for the neptunium and plutonium peaks

Sodium nitrite solutions are known to fix plutonium in the +4 oxidation state[140,143,144]. Therefore, a plutonium standard was prepared to give a final solution of 0 01M sodium nitrite and injected onto the column The resultant plot shows only the second peak, suggesting that the oxidation state for this peak was of Pu(IV) (Figure 5 8)

Two reducing agents were used to treat a standard solution containing americium, neptunium plutonium and uranium, and the effects on the resultant chromatograms observed These reducing agents and their intended chemical effects, are shown in Table 5 4

The effect of sodium formaldehyde sulphoxylate (Rongalite) is shown in Figure 5 9 As can be seen, plutonium eluted solely in the solvent front (c f Figure 5 5 and Figure 5 6), suggesting that the Pu(IV) had been completely reduced to a much lower oxidation state, presumably, Pu(III) The presence of the two neptunium peaks, one in the solvent front and the other eluting later, also suggests that a proportion of the neptunium was reduced from Np(V) to a lower oxidation state, possibly Np(IV)

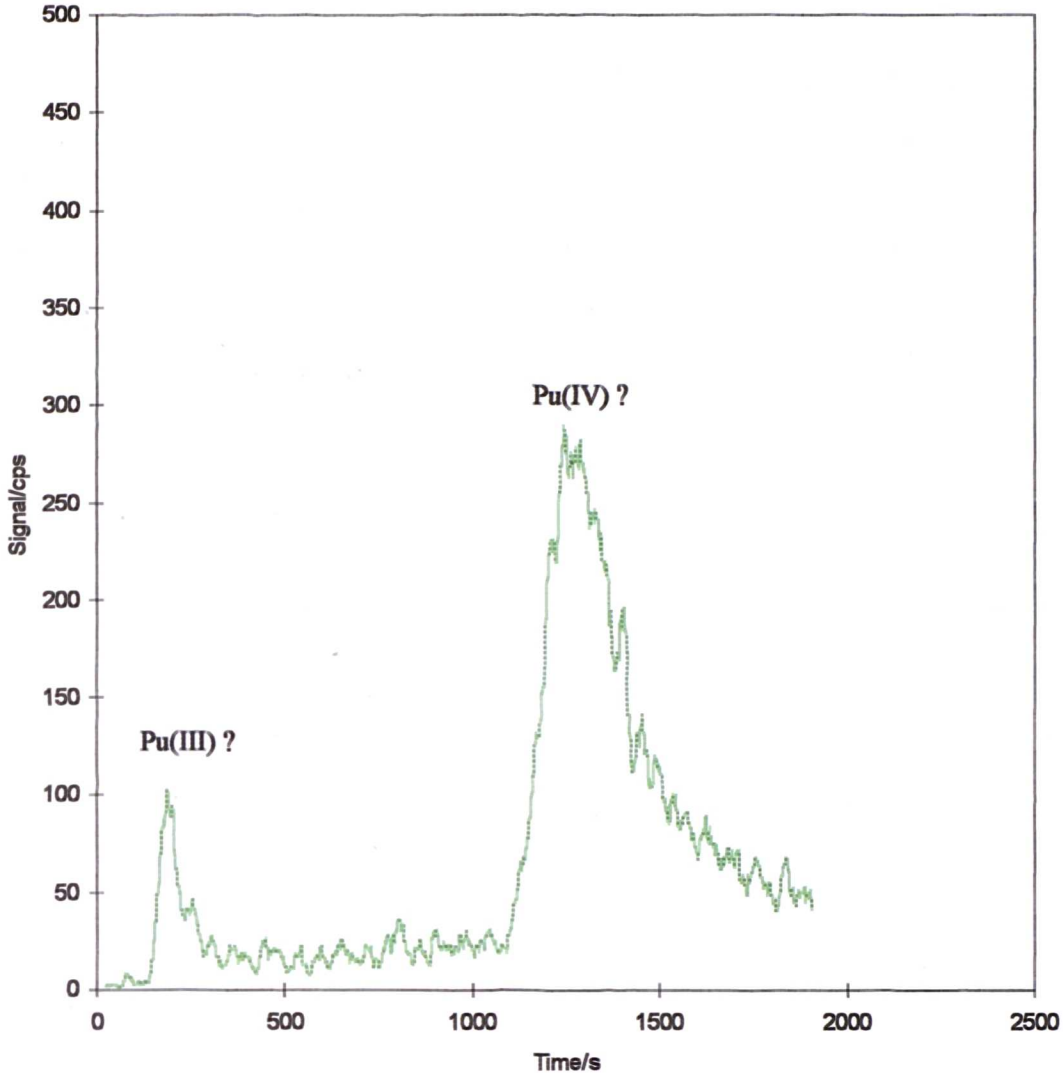


Figure 5.5 **Injection of approximately 500 fg of unoxidised ^{239}Pu on Hamilton column with 0.1mM dipicolinic acid plus 1M HNO_3 mobile phase at a flow rate of 0.5 ml min^{-1}**

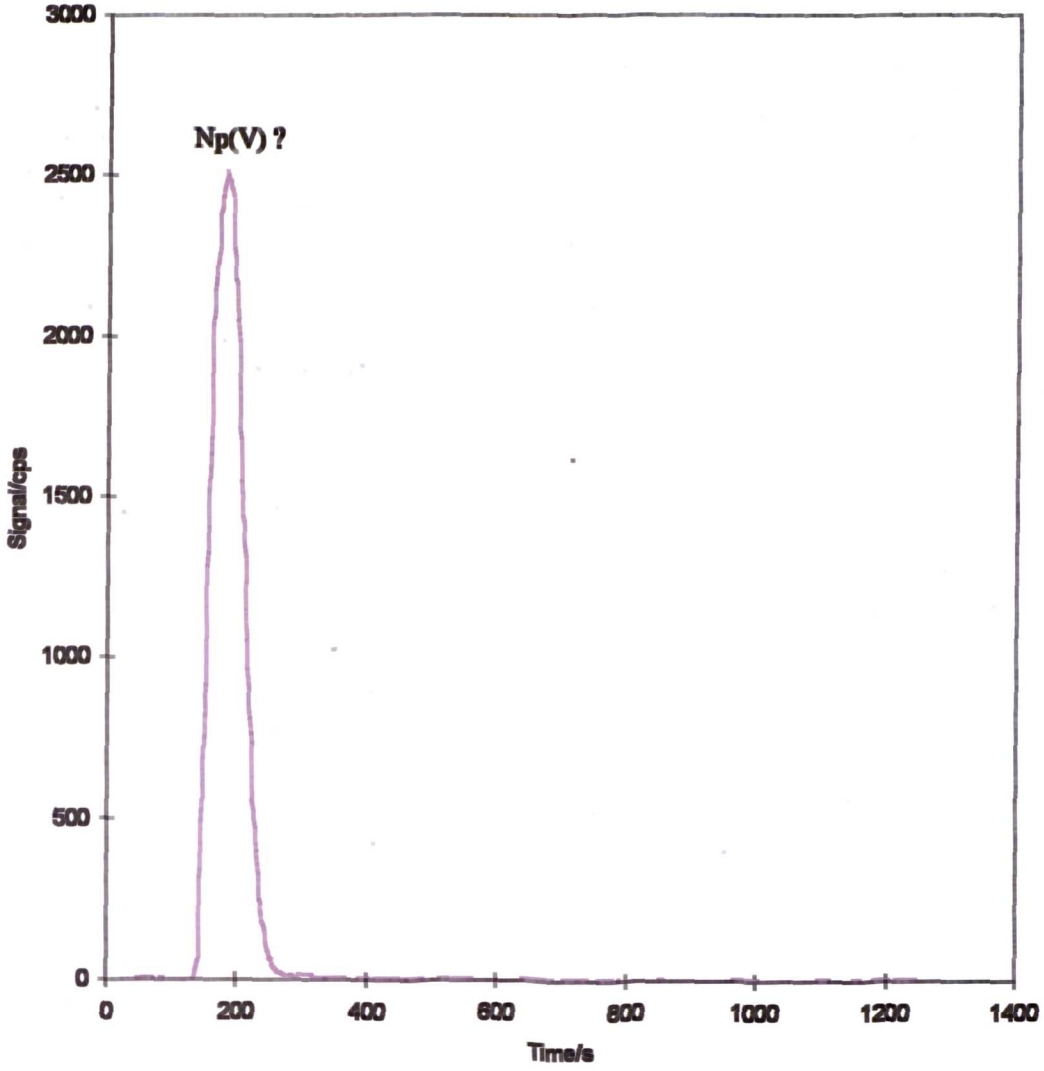


Figure 5.6 **Injection of approximately 350 fg of unoxidised ^{237}Np on Hamilton column with 0.1mM dipicolinic acid plus 1M HNO_3 mobile phase at a flow rate of 0.5 ml min^{-1}**

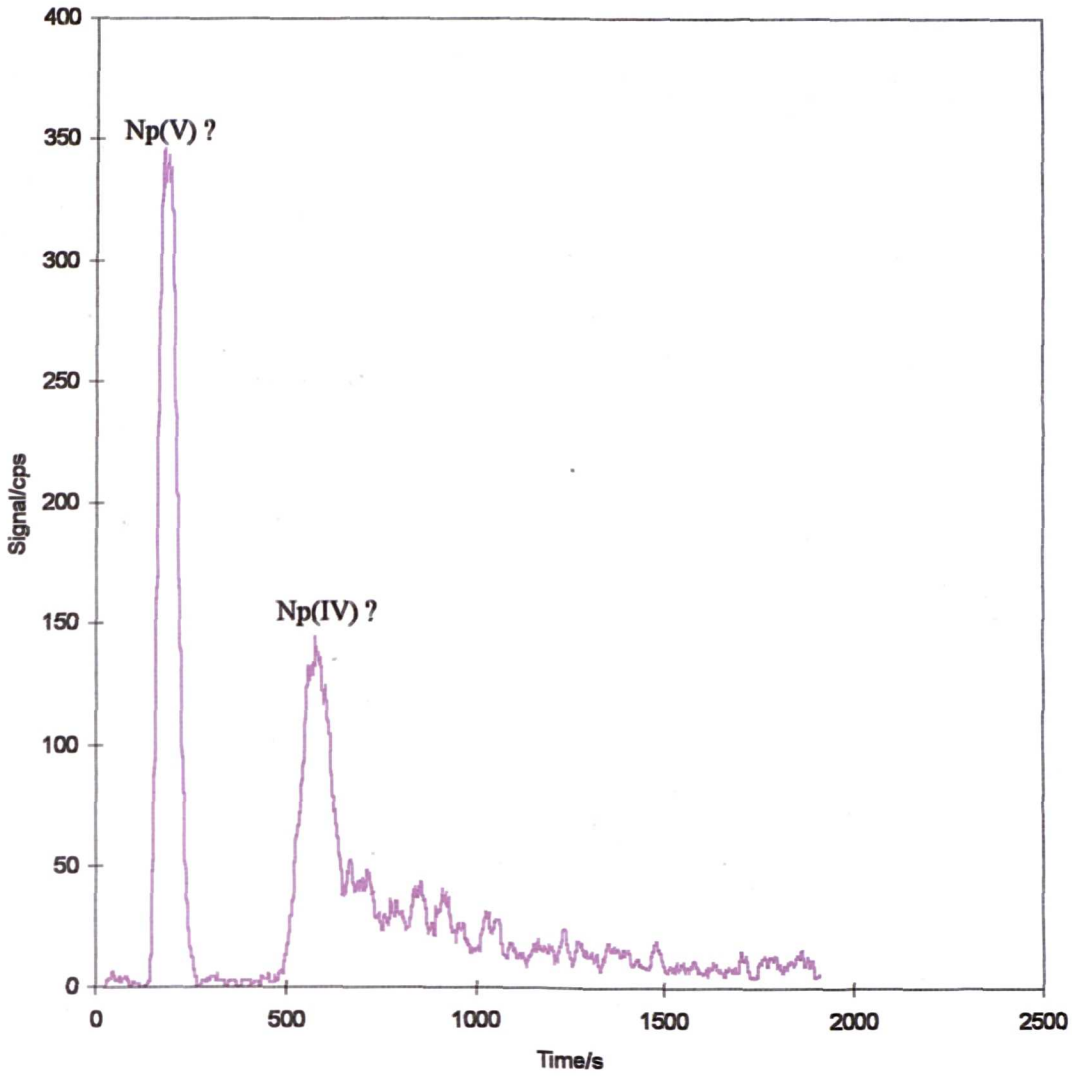


Figure 5.7 **Injection of approximately 100 fg of oxidised ^{237}Np on Hamilton column with 0.1mM dipicolinic acid plus 1M HNO_3 mobile phase at a flow rate of 0.5 ml min^{-1}**

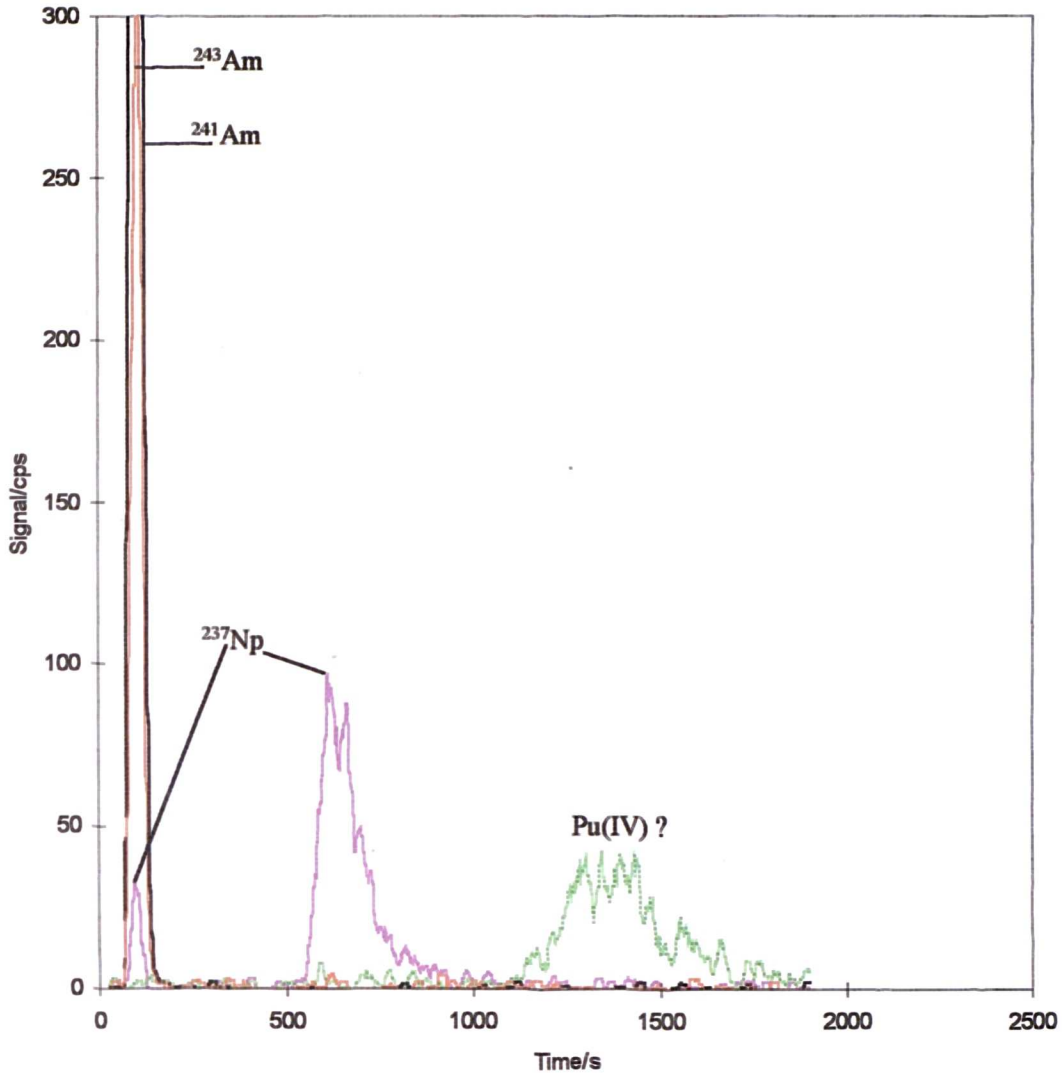


Figure 5.8 **Injection of approximately 200 fg of each actinide oxidised with 0.01M sodium nitrite on Polymer Laboratories column in 0.1mM dipicolinic acid plus 0.75M HNO_3 mobile phase at a flow rate of 1 ml min^{-1}.**

Table 5.4 Reducing agents and chemical effects

Reducing agent	Concentration (Molar)	Intended effect	Reference
Sodium formaldehyde sulphoxylate $HOCH_2SO_2Na\,2H_2O$	0 1	Reduces U(VI) → U(IV) Pu(IV)+(VI)→Pu(III)	140
Ammonium iron (II) sulphate $(NH_4)_2Fe(SO_4)_2\,6H_2O$	0 05	Reduces Np(V) → Np(IV)	72,144,145

Iron(II), is used specifically to reduce Np(V) to Np(IV) and Np(VI) to Np(IV), this would explain the chromatogram shown in Figure 5 10, where almost all the neptunium eluted in the second peak and hardly any in the solvent front The iron(II) experiment has shown that the second peak is more likely the Np^{4+} ion Although, these experiments did not fully established why the solvent front neptunium should be the NpO_2^+ ion (which did not follow the original hypothesis) Considering this discrepancy for neptunium, it would be more appropriate to air on the side of caution regarding the oxidation state assignment for the solvent front peak of plutonium It could easily be presumed that the solvent front peak for plutonium is also possibly PuO_2^{2+}, with the later peak being attributed to Pu^{4+} (Pu^{4+} having been established earlier by use of sodium nitrite reagent)

Finally, it was also noted that there was an apparent effect on the oxidation state of uranium when using rongalite, this was studied and found to be time

dependant As can be seen from Figure 5 11, without any reducing solution present the uranium, permanently present as U(VI) eluted at approximately 550 seconds After treatment for 17 minutes with rongalite a peak appeared at approximately 400 seconds, probably due to U(IV) as in accordance with literature[140]. This peak increases in size and finally disappears over a time period up to 209 minutes, presumably because the U(IV) was re-oxidised back to U(VI) by air when the reducing solution had been consumed The reduction appeared to be incomplete, this presumably was attributed to an insufficient quantity of rongalite to complete the reduction Although literature[140] has designated it to be a reduction from U(VI) to U(IV), which is also in keeping with the two likely and most stable uranium species in solution, U(IV) and U(VI) (Table 5 3), workers should still air on the side of caution when developing this technique further, as there is little evidence to disprove this effect to be a simple reduction to U(V) (effecting uranium's normal characteristic, to disproportionate to the 4+ and 6+ states and then stabalise to the 6+) However, both oxidation states, in terms of elution order, would still follow the original hypothesis for the retention of species, being $M^{n+} < MO_2^{2+}$.

One final important point to note to all of the oxidation state assignment work that has been performed in this chapter There is a distinct possibly that the difficulties encountered with the assignment of peaks to oxidation state could be the result of some unusual oxidative or reductive effect produced on the column itself This as a consequence may have produced the unusual retention characteristic illustrated, making assignment much more difficult

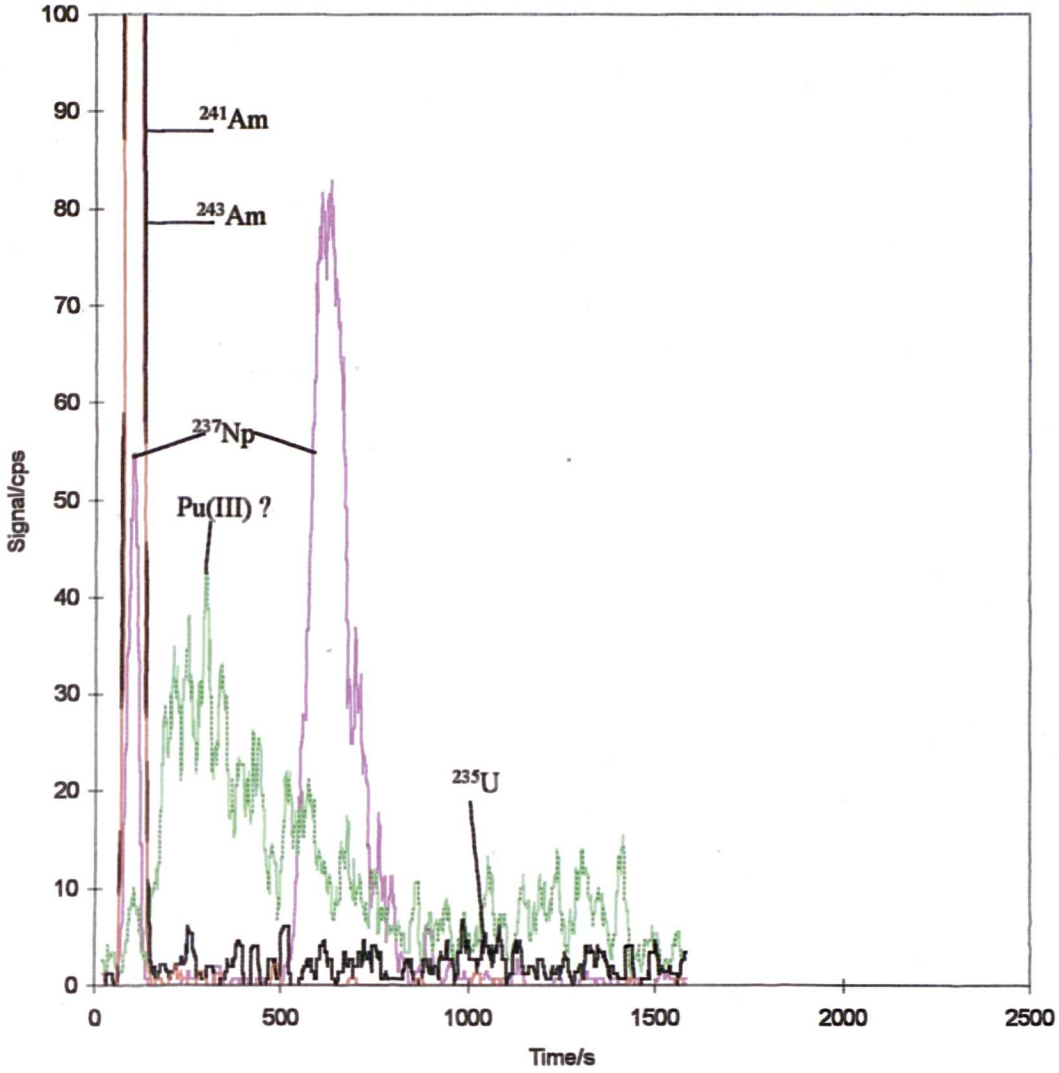


Figure 5.9 **Chromatogram of Np, Pu and Am after treatment with Rongalite solution, with an injection of approximately 200 fg of each actinide onto a Polymer Laboratories column in 0.1mM dipicolinic acid plus 0.75M HNO_3 mobile phase at a flow rate of 1 ml min^{-1}.**

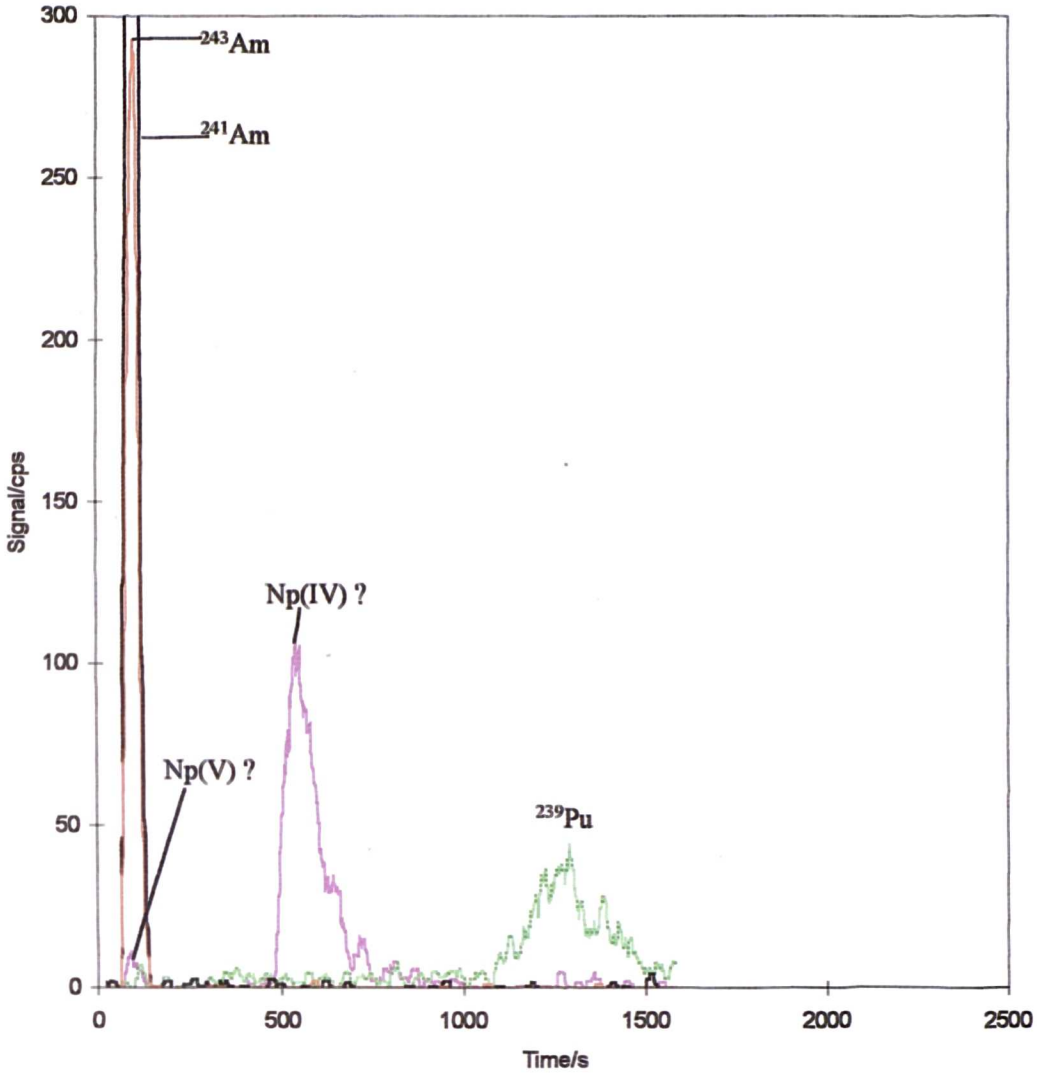


Figure 5.10 **Injection of approximately 200 fg of pre-oxidised actinides with ammonium iron(II) sulphate added to reduce Np(V) to Np(IV), onto a Polymer Laboratories column in 0.1mM dipicolinic acid plus 0.75M HNO_3 mobile phase at a flow rate of 1 ml min^{-1}.**

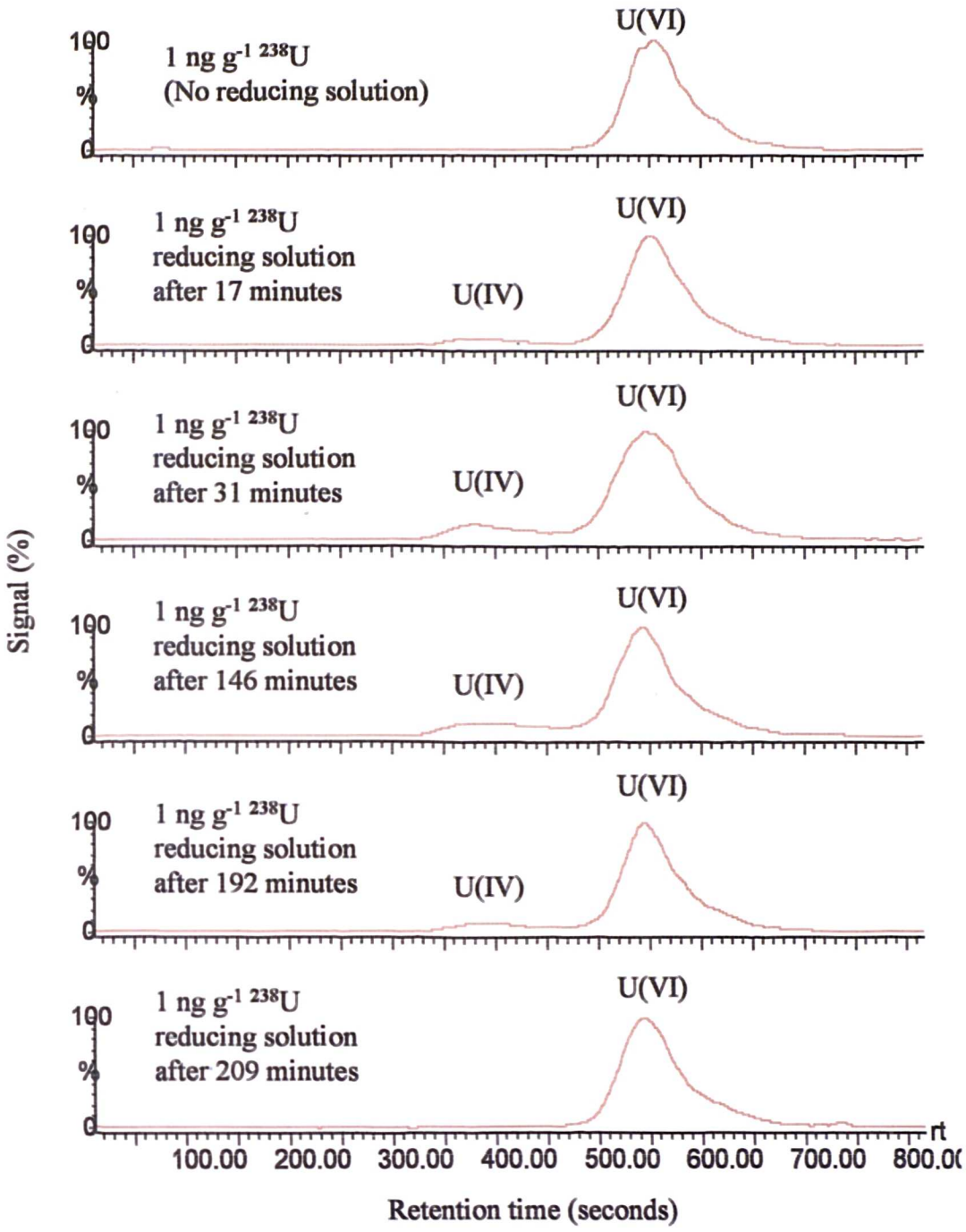


Figure 5.11 The effect of 0.5 ng injections of uranium with Rongalite added into the Polymer Laboratories column using 0.1mM dipicolinic acid plus 0.75M HNO_3 at 1 ml min^{-1}.

5.3.3 Capacity factors (k') of Th, U, Np and Pu.

Capacity factors for Th, U, Np and Pu were calculated[146] using Equation 5 2 Where, t is the retention time of the eluted ion and t_o is the "dead" time or the time taken for an unretained species injected onto the column to be detected The retention time of either La(III) or Am(III) was chosen for the t_o value, as neither of them were retained on the column.

$$k' = \frac{t - t_o}{t_o} \qquad \textbf{(Equation 5.2)}$$

Figure 5 12 shows the k' values for plutonium, uranium, neptunium and thorium as a function of HNO_3 concentration in the mobile phase The dipicolinic acid concentration was constant at 0 1mM throughout the experiment

Thorium eluted just after the solvent front (Figure 5 13), so the k' value was very low U(VI) and the suggested oxidation state for neptunium of (IV) had very similar capacity factors over the range of acid concentrations studied Pu(IV) had the highest capacity factor indicating that the column could potentially be used to separate ^{238}U from ^{239}Pu to overcome the $^{238}U^{1}H^{+}$ interference

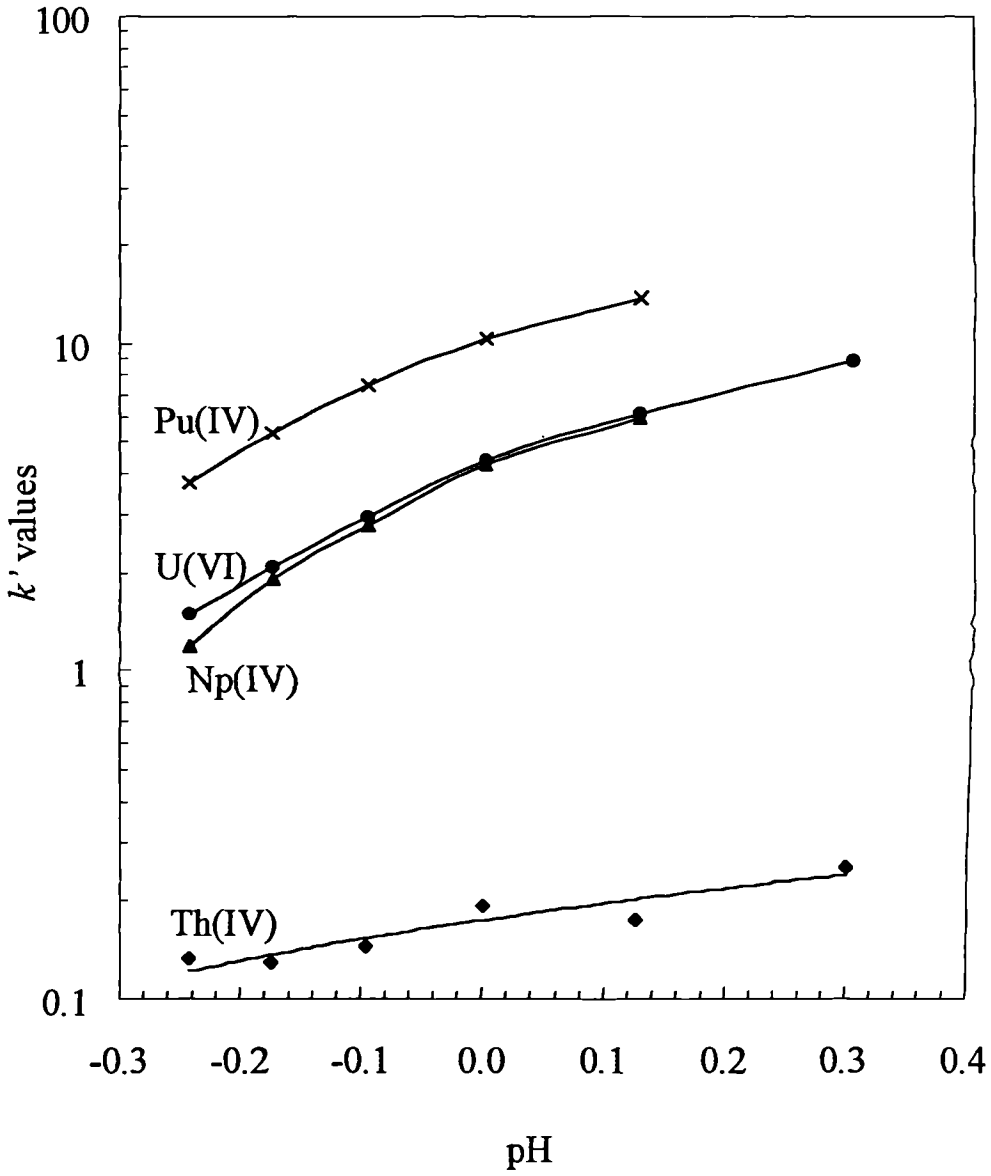


Figure 5.12 **log *k'* values versus pH of nitric acid, for Th, U, Np and Pu using the Polymer Laboratories column with 0.1mM dipicolinic acid mobile phase.**

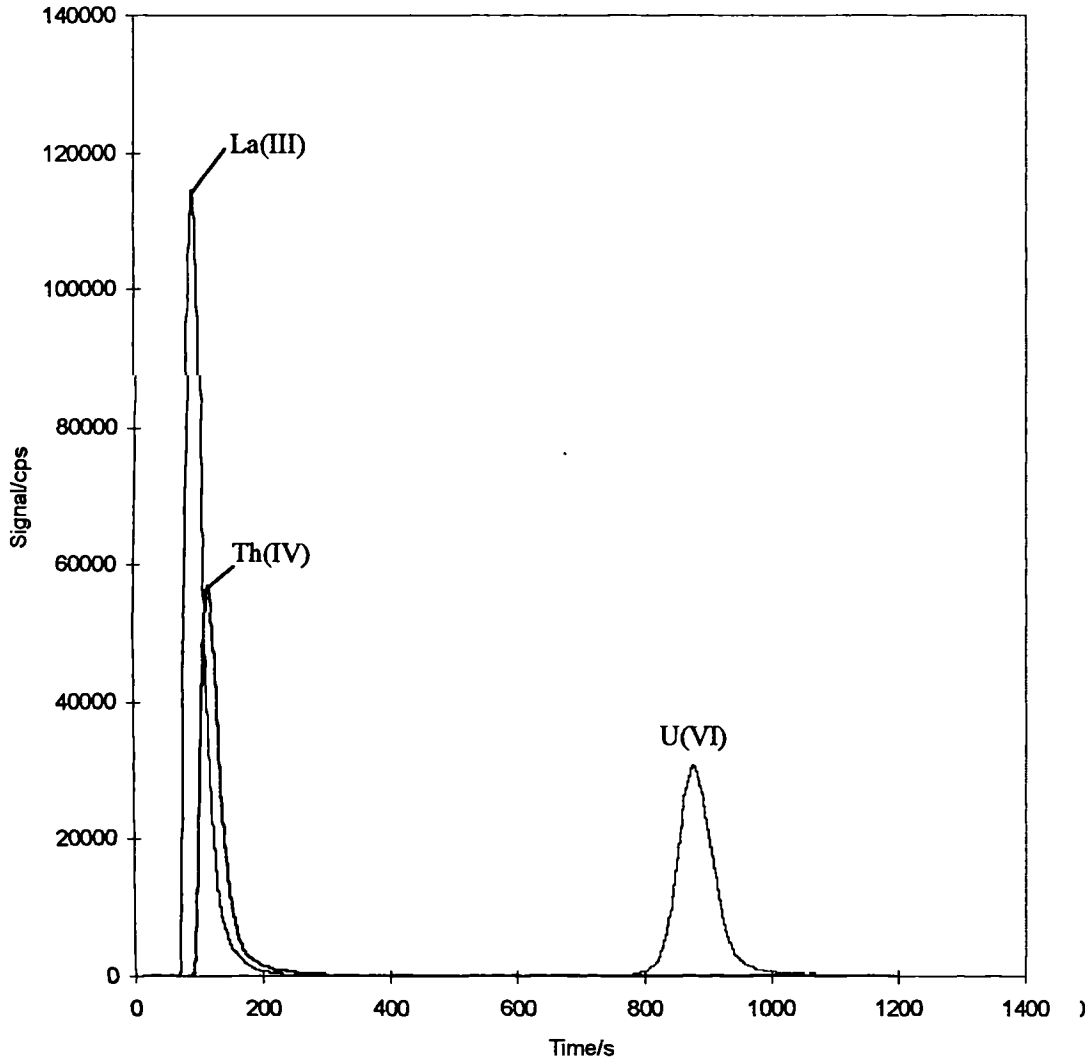


Figure 5.13 **5 ng *injection of La(III), Th(IV) and U(VI) on the Polymer* Laboratories column using 0.1mM dipicolinic acid plus 0.5M HNO_3 as mobile phase. Detection performed by PN-ICP-MS (VG Plasma Quad 2)**

5.3.4 Limits of detection

Instrumental detection limits for ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am are shown in Table 5 5, with an absolute detection limit as low as 3 5 fg for ^{241}Am, using SF-ICP-MS and a jacketed cyclonic spray chamber Solutions containing approximately 30 fg of the actinides were used to determine the instrumental detection limits for the method

Table 5.5 Instrumental detection limits for the actinide elements, on-column in 0.1mM dipicolinic acid + 1.75M HNO_3 (500 µl injections) using SF-ICP-MS jacketed cyclonic spray chamber.

Element	Detection Limit	
	Relative (fg/g)	Absolute (fg)
^{237}Np	24	12
^{239}Pu	15	8
^{241}Am	7	4
^{243}Am	8	4

5.3.5 Analysis of reference materials

Initially, NIST 4351 Human Lung was analysed for Pu with a mobile phase of 0 1mM dipicolinic acid plus 1 75M HNO_3, and a flow rate of 1 ml min^{-1}. Poor peak resolution was observed, with plutonium barely separated from the uranium hydride peak (Figure 5 14) The high acidity due to the digestion procedure was thought to be affecting the separation, so the acid concentration in the mobile phase was changed to 0 75M HNO_3, with a consequent improvement in the separation (Figure 5 15)

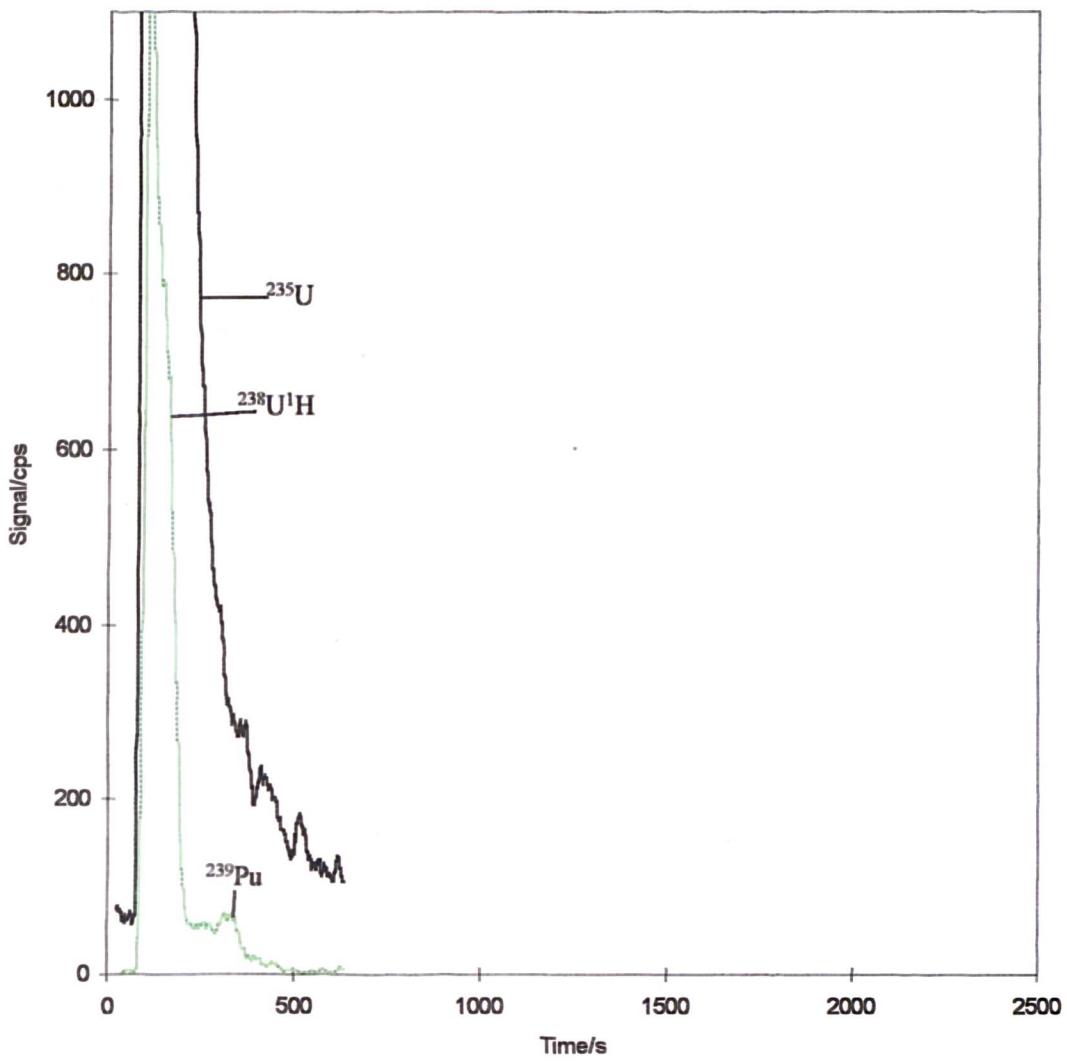
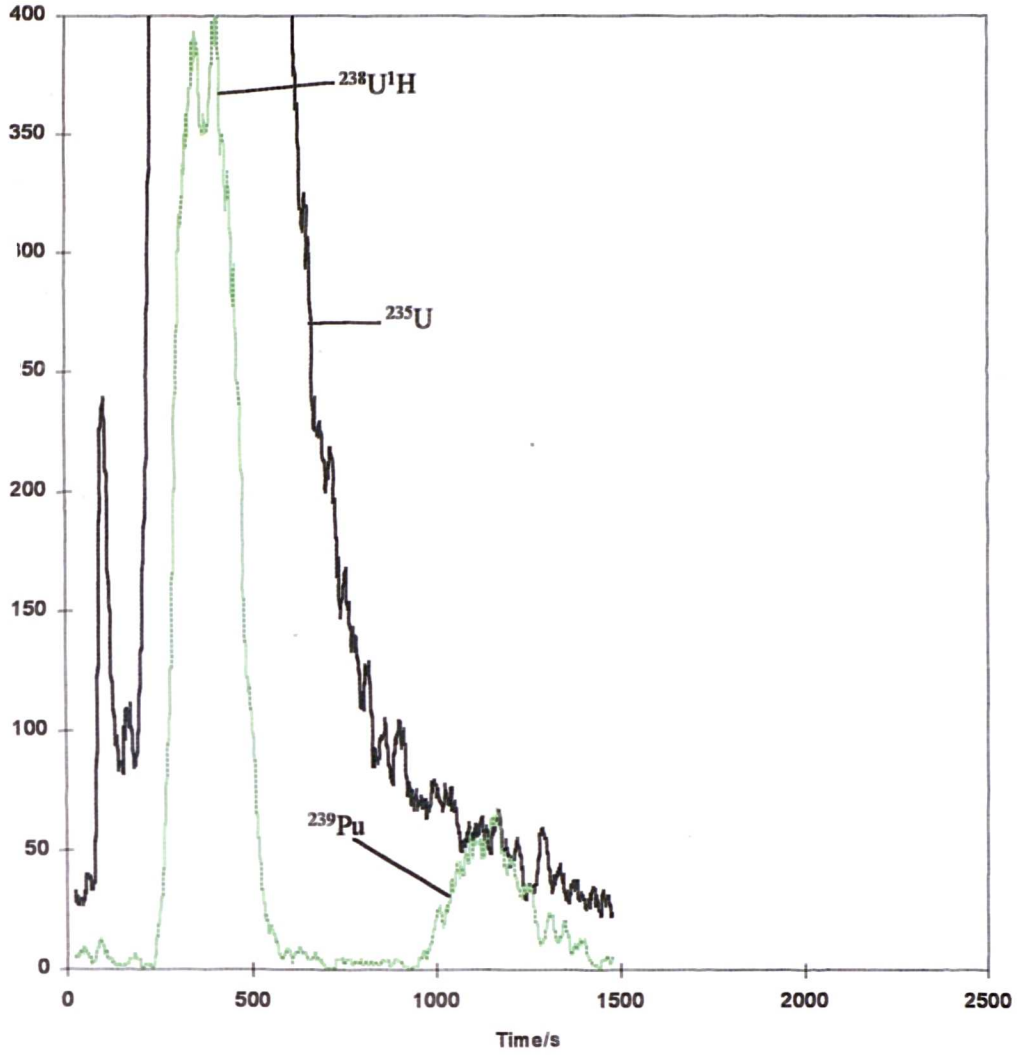


Figure 5.14 **Separation of ^{239}Pu from uranium and subsequently the $^{238}U^{1}H$ for NIST 4351 Human Lung reference material. Polymer Laboratories column with 0.1mM dipicolinic acid plus 1.75M HNO_3 for the mobile phase.**



gure 5.15 **Separation of ^{239}Pu from uranium and subsequently the $^{238}U^{1}H$ for NIST 4351 Human Lung reference material. Polymer Laboratories column with 0.1mM dipicolinic acid plus 0.75M HNO_3 for the mobile phase.**

A NIST 4353 Rocky Flats Soil (No 1) extract was also analysed using these conditions and, as can be seen from Figure 5 16 the separation method was still able to resolve the ^{239}Pu and $^{238}U^{1}H$ peaks, despite the elevated concentration of uranium (2 4 $\mu g\ g^{-1}$ ^{238}U) in the sample The results for the determination of ^{239}Pu in NIST 4351 Human Lung and NIST 4353 Rocky Flats Soil (No 1) are given in Table 5 6 In the case of the human lung the found concentration for ^{239}Pu fell within the certified range, however, the mean recoveries for the Rocky Flats soil were approximately 11% less than the certified value In the latter case, the low recoveries could have been due to incomplete leaching The certificate states that approximately 8% of the Pu resists HNO_3 leaching

Table 5.6 Results for the determination of ^{239}Pu in certified reference materials with HPCIC analyte separation

Material	Certified value[a] ($fg\ g^{-1}$)	Found[a] ($fg\ g^{-1}$)
NIST 4351 Human Lung	453 (227-951)[b]	570 ± 29[c]
NIST 4353 Rocky Flats Soil	3307± 248[d]	2939 ± 226[e]

[a]assuming 6% of activity due to ^{240}Pu
[b]certificate states 453 with an uncertainty of +110% to –50%
[c]95% confidence, n=1, 3 injections
[d]certificate states 7 5% uncertainty
[e]95% confidence, n=3, 1 injection

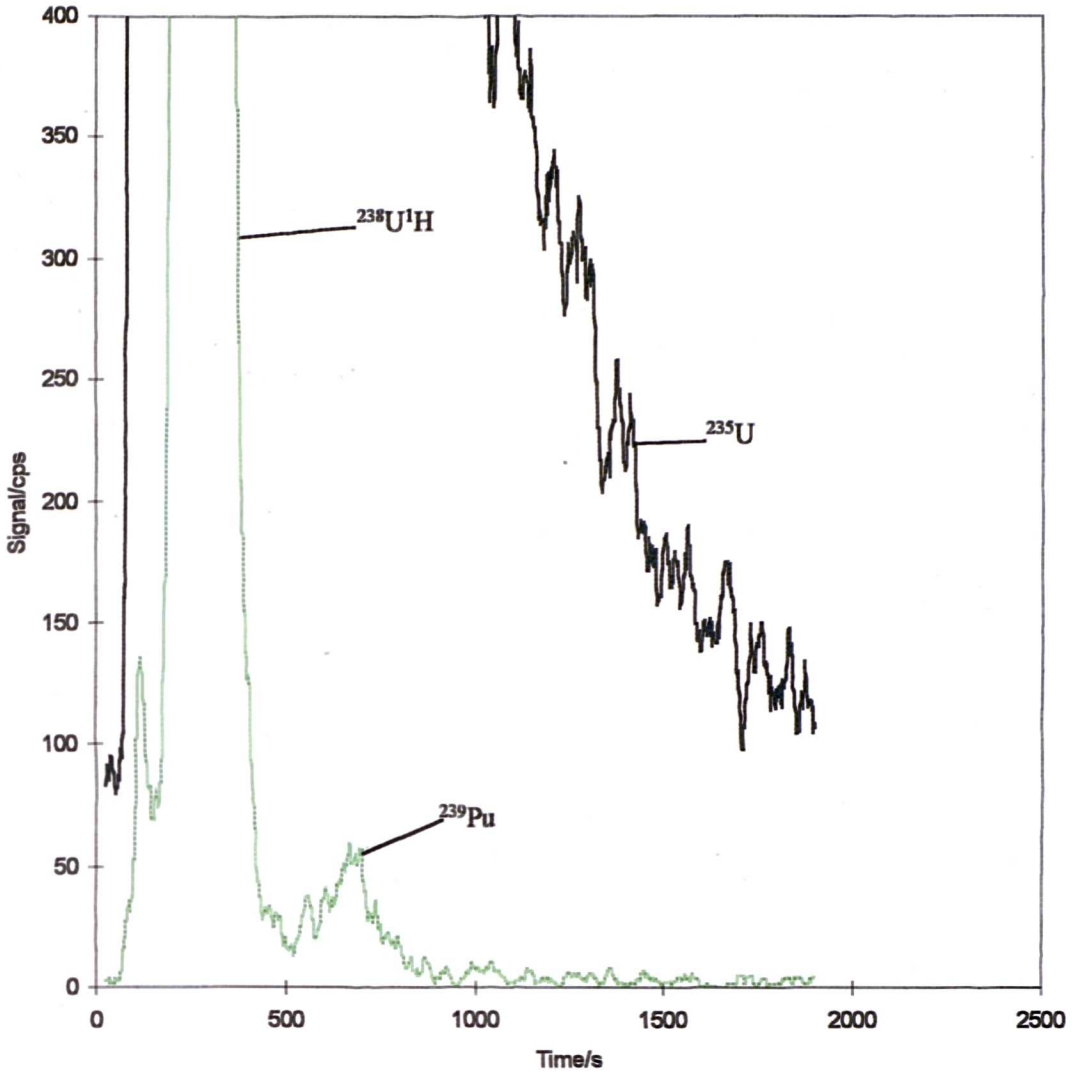


Figure 5.16 **Separation of ^{239}Pu from uranium and subsequently the $^{238}U^{1}H$ for NIST 4353 Rocky Flats Soil (No.1) reference material. Polymer Laboratories column with 0.1mM dipicolinic acid plus 0.75M HNO_3 for the mobile phase.**

5.4 CONCLUSIONS

A novel method for actinide determination has been developed based on the coupling of HPLC and ICP-MS techniques HPCIC, using a Polymer Laboratories PS-DVB substrate dynamically loaded with 0 1mM dipicolinic acid and using variable molar concentrations of HNO_3, coupled with SF-ICP-MS has been successfully used for the separation of the actinides thorium, uranium, americium, neptunium and plutonium

Oxidation effects when using the column were observed for neptunium and plutonium, with reducing solutions giving some indication of the oxidation states of the actinides. The initial hypothesis made for the elution order of the actinides according to the oxidation state was the retention of $M^{n+} < MO_2^{2+}$. When determining the oxidation states of neptunium this hypothesis was found to be contradictory. Neptunium was thought to be Np(IV) eluting at the solvent front and Np(V) near the U(VI) peak Plutonium was also considered to be Pu(III) eluting near the solvent front with Pu(IV) eluting much later and more importantly, after U(VI) Rongalite was also found to reduce U(VI) to U(IV) in accordance with literature[140], although there is no evidence to disprove that the reduction was not from U(VI) to a U(V) species The contradictions to the trends for neptunium could be attributed to unusual oxidative and reductive abilities of the column itself although this idea is not substantiated As a consequence the allocation of oxidation state for these species are given tentatively

NIST 4351 Human Lung and NIST 4353 Rocky Flats Soil (No 1) were analysed for ^{239}Pu using the separating capabilities of the column Results were in agreement with the certified values obtained using the dry and wet ashing and microwave procedures respectively The concentration of plutonium in NIST 4353 Rocky Flats soil was found to be 11% lower than the certified value, however, the low result was attributed to the nitric acid digest, as CRM literature suggests an 8% loss of Pu when using nitric acid extractions

The instrumental method detection limits were found to be as low as 3 5 fg g^{-1} (for ^{241}Am) The method was successful in separating ^{238}U and thus the associated interference due to $^{238}U^{1}H^{+}$ at m/z 239, which is known to interfere with ^{239}Pu determinations

Chapter 6

CONCLUSIONS AND FUTURE WORK

Chapter 6

CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

Initial studies using TRU-Spec resin demonstrated the potential for uranium and thorium determination in waters, biological, soil and sediment samples from the environment The method was robust and performed well in the presence of high iron concentrations and for complex samples such as sediments A simple survey of waters in the Plymouth and Dartmoor area was performed, to compare ^{238}U and ^{232}Th concentrations, using the ICP-MS method and also alpha-spectrometry It was observed that only a few millilitres of sample were required for ICP-MS determinations, whereas, alpha spectrometry required several hundred millilitres and had higher detection limits (typically 30 ng l^{-1} and 10 ng l^{-1} for ^{232}Th and ^{238}U respectively) comparatively, detection limits for ETV-ICP-MS were as low as 9 fg and 30 fg absolute for ^{232}Th and ^{238}U respectively

The TRU-Spec resin was also coupled to SF-ICP-MS and used for the determination of thorium, uranium, neptunium, plutonium and americium. A simple extraction procedure was used for the detection and quantification of neptunium and plutonium in certified reference materials such as human liver The analysis of sediment samples, showed that levels of $^{238}U > 1 \mu g\ ml^{-1}$ produced a significant hydride interference, which could result in an inaccurate determination of ^{239}Pu In order to overcome this problem, it was necessary to physically separate uranium from

plutonium using an on-column reduction and elution Thus americium and plutonium would be eluted first, and then, the remaining actinides This sequential elution enabled the accurate quantification of ^{239}Pu in both biological and soil certified reference materials, containing high levels of uranium (typically >1μg g^{-1}) Detection limits were as low as 600 ag absolute for ^{241}Am A 50 ml pre-concentration step lowered this further to approximately 200 ag ml^{-1}

Investigations were performed into the feasibility of using substrates coated with chelating dyes However, the dye coating proved unstable, resulting in poor reproducibility and making them unsuitable for pre-concentration. An alternative silica based chelating exchanger, with IDA groups bonded to its surface, eliminated the poor reproducibility However, it was observed that Fe(III) and Fe(II) both had an affinity for the column, so that it could not be used for samples containing high levels of iron (i e. soils and sediments) It was also found that the separation of uranium from plutonium was not possible buy pH adjustment alone However, it was possible to quantitatively determine uranium in waters reference materials, using PN-ICP-MS and ETV-ICP-MS

Investigations were also performed into the use of a high performance chelation ion chromatography system using dipicolinic acid in the mobile phase for the separation and quantification of plutonium in samples containing high concentrations of uranium Oxidation effects when using the column were observed for neptunium and plutonium, with reducing solutions giving some indication of the oxidation states of the actinides The initial hypothesis made for the elution order of the actinides

according to the oxidation state was the retention of $M^{n+} < MO_2^{2+}$ When determining the oxidation states of neptunium this hypothesis was found to be contradictory Neptunium was thought to be Np(IV) eluting at the solvent front and Np(V) near the U(VI) peak Plutonium was also considered to be Pu(III) eluting near the solvent front with Pu(IV) eluting much later and more importantly, after U(VI) It was also possible to separate different oxidation states of plutonium, neptunium and uranium using this column The contradictions to the trends for neptunium could be attributed to unusual oxidative and reductive abilities of the column itself although this idea is not substantiated As a consequence the allocation of oxidation state for these species are given tentatively Using the column, it was possible to quantify ^{239}Pu without interference from the $^{238}U^{1}H^{+}$ Absolute detection limits were as low as 4 fg for ^{241}Am.

6.2 FUTURE WORK

All of the column separation methods used in this work were on-line methods, with the exception of the ETV-ICP-MS method, and have been specifically developed to use the minimal required number of reagents to perform the analysis For this study, the various reagents and eluents for the on-line columns were switched manually It would therefore be desirable to set-up an automatic system Such a system may consist of an auto-sampler, column switching valve and reagent switching valves to allow unmanned operation and potentially reduce analysis times

Commercial solid phases such as TRU-Spec have been developed primarily for batch separation of high concentrations of actinides It would be interesting to

investigate the performance of such resins for HPLC applications, for which a much smaller particle size is required This should improve the efficiency of the separation and improve the reproducibility for on-line analysis of low concentrations with this resin

It would be advantageous to use the dipicolinic acid coated column for the separation and quantification of different oxidation states of the actinide elements in the environment, such as nuclear waste and process streams This could be extended to determine other species of the actinide elements, which may be important factors in the mobilisation of these elements in the environment However, further studies would have to be carried out into the correct assignment of oxidation states for the actinides, bearing in mind, that the trends in retention behaviour may be contradicted by possible reduction or oxidative effect of the column itself, and not purely a result of any reduction or oxidation reagents

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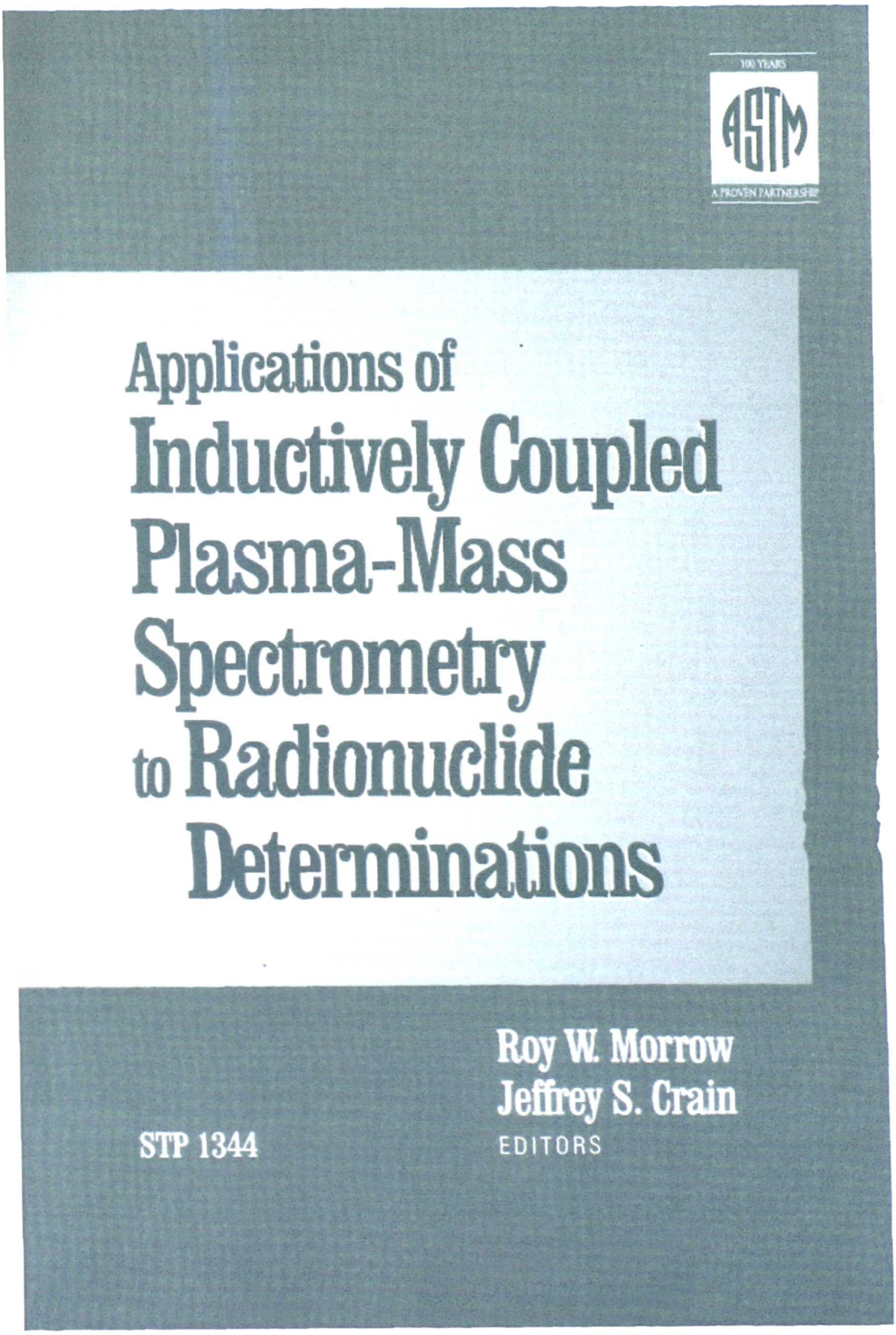
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E Hywel Evans,[1] Jason B Truscott,[1] Lee Bromley,[1] Phil Jones,[1] Justine Turner,[2] and Ben E Fairman[2]

Evaluation of Chelation Preconcentration for the Determination of Actinide Elements by Flow Injection ICP-MS

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ABSTRACT: A chelation column preconcentration method has been developed for the determination of uranium and thorium in waters by ICP-MS Detection limits of 24 pg and 60 pg respectively were obtained, but these were blank limited. Uranium and Thorium were determined in certified reference materials Results for uranium were 121 ± 21 and 15 ± 3 ng g^{-1} in NIST 1566a and NIST 1575 compared with certified values of 132 ± 12 and 20 ± 4 ng g^{-1} respectively Results for thorium were 29 ± 8 and 28 ± 5 ng g^{-1} in NIST 1566a and NIST 1575 compared with indicative and certified values of 40 and 37 ± 3 ng g^{-1} respectively The on-line separation of actinide radionuclides was achieved by selective elution of U, Th, Pu, Np, and Am.

KEYWORDS: ICP-MS, actinides, radioisotopes, chelation, chromatography

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Inductively coupled plasma mass spectrometry (ICP-MS) can be used for the rapid determination of the concentration and isotopic composition of the actinide elements The principal advantages of ICP-MS are speed and sensitivity, with the capability of determining all the radioisotopes within a minute, at concentrations as low as 1 picogram mL^{-1} (10^{-12} g mL^{-1}) in liquid samples In addition, there is no need to separate the elements one from another, as there is in α-spectrometry, because this is achieved by the mass spectrometer, hence, the number of sample pre-treatment stages can be greatly reduced. However, it is still necessary to separate the radionuclides from the matrix, a procedure

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[1] Senior lecturer, research student, research assistant and principal lecturer respectively, University of Plymouth, Dept. of Environmental Sciences, Drake Circus, Plymouth PL4 8AA, UK.

[2] Research technician and research manager respectively, LGC, Queens Road, Teddington, Middlesex TW11 0LY, UK.

for which column preconcentration methods are ideal. A number of resins have been used for the preconcentration and separation of the actinides. Recently a number of very specific chelating resins have become available which are particularly suited to this task. Some extraction procedures and application of these resins have been addressed by Horwitz [*1,2,3*]. Crain et al. [*4*] have quoted 20 fg mL^{-1} detection limits for ^{239}Pu and ^{235}U using TRU-Spec™ resin (Eichrom Industries Inc., Darien, IL) as a preconcentration step. Wyse and Fisher [*5*] reported a potential 3 fg detection sensitivity for plutonium using ICP-MS and TRU-Spec™ resin and concluded that results for ^{239}Pu in urine were comparable to those for alpha-spectrometry. Flow injection ICP-MS (FI-ICP-MS) has been used [*6*] with TRU-Spec™ resin and good results were obtained for ^{230}Th and ^{234}U for soil reference material TRM-4. Aldstadt et al. [*7*] also report good results for FI-ICP-MS using TRU-Spec™ resin for the determination of ^{238}U.

Experimental

Instrumentation

An inductively coupled plasma mass spectrometer (PlasmaQuad 2+, VG Elemental, Cheshire, UK) was used. Data were acquired using the time resolved analysis software, which allows time resolved monitoring of multiple isotopes, and manipulated off-line using MassLynx software (VG Elemental). Operating conditions are shown in Table 1. The flow injection manifold was interfaced with the ICP-MS instrument as shown in Fig. 1.

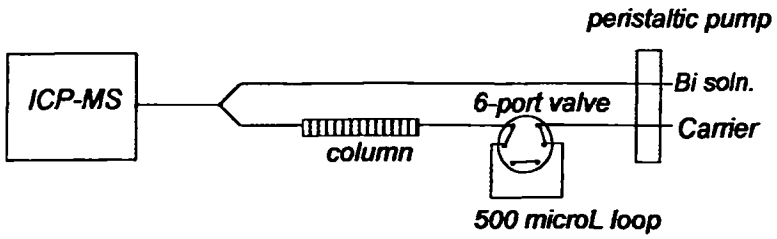

FIG. 1—*Schematic of the flow injection manifold interfaced with the ICP-MS.*

Determination of Natural Uranium and Thorium

Analytical Columns– Columns were prepared, using a slurry of chelating resin (100-150 µm Tru-Spec resin, Eichrom Industries Inc., Darien, IL) in deionized distilled water (DDW), in commercially available glass chromatography columns of 3 mm i.d. and 50 mm length (Ominifit microbore columns, Omnifit, Cambridge, UK.

Reagents and Standards–Reagents were: 2 M HNO_3 (Analar, Fisher Scientific Ltd., UK); 5 ng mL^{-1} Bi internal standard; 1 M $Al(NO_3)_3$ (Analytical Grade, Fisher Scientific) purified by passing through a 10 x 0.5 cm column of Dowex 1-X8 anion

exchange resin, then a 5 x 0 5 cm column of Tru-Spec resin, 0 5 M $Al(NO_3)_3$ + 2 M HNO_3 column feed solution, 0 1 M $NH_4HC_2O_4$ eluting solution.

A 1 μg mL^{-1} mixed standard solution of thorium and uranium was prepared in the column feed solution.

TABLE 1—*Operating conditions for ICP-MS.*

ICP	
Forward power (kW)	1 35 kW
Plasma gas (L min^{-1})	16 5
Auxillary gas (L min^{-1})	0 7
Nebulizer gas (L min^{-1})	0 8
Sampling depth (mm)	10
Sample flow (mL min^{-1})	0 5
Torch	Fassel (quartz)
Nebulizer	Concentric (quartz)
Spray Chamber	Scott type (quartz)
Interface	
Sampler	Ni, 1 0 mm orifice
Skimmer	Ni, 0 7 mm orifice
Pressure (mbar)	2×10^0
Mass Spectrometer	
Ion masses (m/z)	^{209}Bi, ^{230}Th, ^{232}Th, ^{235}U, ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{243}Am, ^{244}Pu
Data acquisition	Time resolved mode
Points per peak	3
DAC step	3
Dwell time (ms)	300
Time-slice duration (s)	1

Sample Preparation—The sample preparation procedure was partly based on a method by Nelson and Fairman [*8*] Two certified reference materials (CRMs) were studied, namely NIST 1566a Oyster Tissue and NIST 1575 Pine Needles (National Institute of Science and Technology, Gaithersburg, USA) Samples (0 5 g) were dry ashed in crucibles at 200 °C for 2 hours, 400 °C for 2 hours, 600 °C for 2 hours, and 800 °C for 2 hours. This step was omitted for the oyster tissue. The samples were digested, with heating, in nitric acid (10 mL), boiled to dryness and heated on a hot hotplate This was repeated until a white ash was left. On the last iteration the samples were boiled down until almost dry, and 10 mL of column feed solution was added to dissolve the ash. Samples were made up to final volumes of 50 mL and 25 mL, for the oyster tissue and pine needles respectively, with column feed solution.

Calibration and Analysis—Calibrant and sample solutions were deposited onto the column, either by flow injection through a 500 μL loop or by uptake of a fixed volume, into a carrier stream of column feed solution at a flow rate of 0 5 mL min^{-1} During deposition the outlet from the column was diverted to waste to prevent the column feed solution entering the ICP-MS instrument After a deposition, the column was rinsed with 1 mL of 2 M HNO_3 to remove any residual column feed solution before the column was diverted back to the ICP-MS The analytes were eluted with 0 1 M ammonium bioxalate, and the analyte masses monitored. Typical elution profiles for uranium and thorium are shown in Fig 2 Peak areas were determined and ratioed to the continuous signal for Bi to compensate for instrumental drift

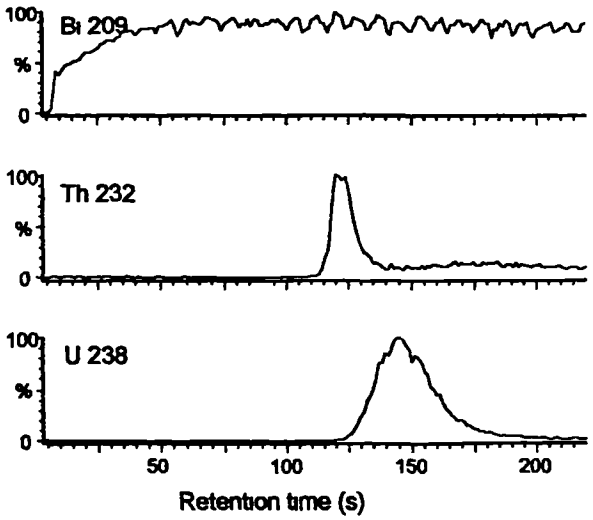

FIG 2—*Elution profiles for 50 pg depositions of U and Th monitored at m/z 238 and 232 respectively.*

It is evident from Fig. 2 that uranium eluted completely over a period of 70 s and thorium over 30 s. In the case of thorium there was a raised backgound after elution of the peak, which may be due to incomplete elution from the column, impurities in the eluting solution, or tailing caused by the spray chamber The elution times corresponded to volumes of approximately 0 6 and 0 25 mL for uranium and thorium respectively Absolute detection limits were 24 pg and 60 pg for uranium and thorium respectively for a 500 μL sample, and were blank limited Relative detection limits can be improved by greater preconcentration factors if the reagents are cleaned more thoroughly

Determination of Actinide Radioisotopes

Analytical Columns—Low pressure preparative chromatography columns, 10 cm long and 0 5 cm i.d (Econo-column, Bio-rad) were used to preconcentrate and/or separate Th, U, Pu, Am, and Np

Reagents and Standards--Reagents were prepared as previously A 10 ng mL^{-1} standard stock solution of each of the isotopes ^{230}Th, ^{232}Th, ^{235}U, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{243}Am, and ^{244}Pu was used for spiking experiments

Sample Preparation—Samples (50g) were weighed into evaporating basins, placed in a muffle furnace and dry-ashed at 200 °C for 2 hours, 400 °C for 2 hours and 600 °C for 2 hours. Concentrated acid (50 mL) was added to each, left to stand for one hour, heated gently on a hot-plate until all nitrous oxide fumes were driven off, then boiled for ten minutes and allowed to cool. The samples were centrifuged for five minutes at 3500 rpm, the supernatant decanted and the sediment was re-extracted as before The combined supernatant was boiled down until precipitation just began to occur, when an equal amount of the column feed solution was added to re-dissolve the precipitate A portion (0 5 mL) of reducing solution, comprising 3 g of iron ammonium sulphate and 3 g of sodium formaldehyde sulfoxylate dissolved in 10 mL of 2 M HNO_3, was added to each sample and allowed to stand for 15 min. This ensured any iron present was reduced to Fe(II) to avoid column interferences

Analysis of Samples— Samples were transferred to the columns, and the beakers were rinsed with 5 mL of column feed solution which was also added to the columns They were then washed with two 5 mL portions of 1 M HNO_3 to ensure that no $Al(NO_3)_3$ remained, eluted with approximately 10 mL of 0 1M ammonium bioxalate and made up to volume External calibration was performed and the samples analysed.

On-line separation—In this case samples were loaded onto the column as before, but eluted sequentially using an elution method developed by Horowitz et al. [*1*] The method is represented schematically in Fig. 3

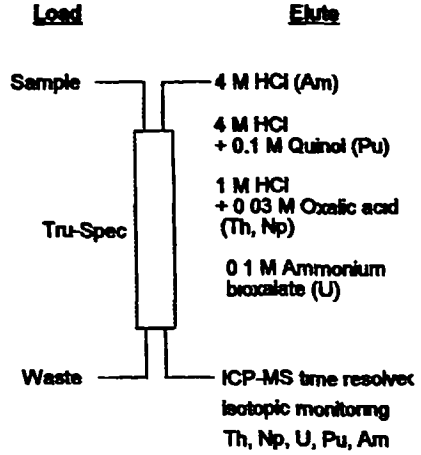

FIG 3--*Schematic of elution method used for on-line separation of actinide radioisotopes.*

Results and Discussion

Determination of Uranium and Thorium

Results for the determination of uranium and thorium in oyster tissue and pine needles are shown in Table 2

TABLE 2--*Results of the determination of uranium and thorium in certified reference materials by ICP-MS.*

CRM	No of samples	U		Th	
		Certified value (ng g^{-1})	Found[a] (ng g^{-1})	Certified value (ng g^{-1})	Found[a] (ng g^{-1})
NIST 1566a oyster tissue	5	132 ± 12	121 ± 21	(40)[b]	29 ± 8
NIST 1575 pine needles	11	20 ± 4	15 ± 3	37 ± 3	28 ± 5

[a] $\bar{x}$ ± s

[b] Uncertified indicative value

For oyster tissue there was no significant difference between the found value and the certified mean for uranium at the P = 0 05 level. For the pine needles, low recoveries for both thorium and uranium were observed compared with the certified mean, though there was no significant difference between the found value and the bottom of the certified range for uranium (i.e 16 ng g^{-1}) at the P = 0.05 level. This may indicate that uranium was associated with siliceous material present in this sample, or that losses occurred during the ashing stage due to adsorption onto the surface of porcelain crucibles at high temperature [9]. Likewise, low recoveries for Th might have been due to association with siliceous material, however, Th has a tendency to adsorb onto glassware, pump tubing, and the column resin, often resulting in low recoveries or high blank values. Ammonium bioxalate should be a sufficiently is a strong chelating agent to prevent such memory effects, however, other chelating agents might improve recoveries

Recovery of Actinide Radioisotopes from Biological Samples

Samples of NIST 1566a oyster tissue were spiked with a solution of mixed actinide elements (10 ng g^{-1}), subjected to the dissolution and column preconcentration method, and recoveries determined by external calibration ICP-MS. Details of the samples are given in Table 3 Recovery data for the spiked samples after blank subtraction are shown in Table 4

Recoveries for the spiked oyster tissue samples were within the range 88-107% (i e sample 2) However, recoveries of between 73-90% were obtained for the control

sample (i e sample 3) The results for sample 3 were probably low because there was no sample matrix present to prevent absorption onto the walls of the beakers

TABLE 3--*Details of spiked samples used for recovery tests.*

Sample No	Sample type	Mass of oyster tissue (g)	Mass of spike (g)
1	Unspiked sample	0 5504	
2	Spiked sample	0 5930	2 0870
3	Control (no matrix)		2 0854
4	Blank		

TABLE 4--*Recovery of actinide radioisotopes from oyster tissue*

	Conc Of isotope in fraction (ng mL^{-1})								
	^{230}Th	^{232}Th	^{235}U	^{237}Np	^{239}Pu	^{240}Pu	^{242}Pu	^{243}Am	^{244}Pu
Sample 2									
Expected conc (ng mL^{-1})	0 84	0 84	0 84	0 84	0 84	0 84	0 84	0 84	0 84
Actual conc (ng mL^{-1})	0 90	0 80	0 74	0 79	0 77	0 77	0 79	0 84	0 77
Recovery (%)	107	95	88	94	92	92	94	100	92
Sample 3									
Expected conc (ng mL^{-1})	0 84	0 84	0 84	0 84	0 84	0 84	0 84	0 84	0 84
Actual conc (ng mL^{-1})	0 76	0 71	0 62	0 61	0 62	0 61	0 63	0 72	0 67
Recovery (%)	90	84	74	73	74	73	75	86	80

Recovery of Actinide Radioisotopes from Sediment Samples

Several different leaching and column methods were attempted for 50 g of spiked sediment. The sediment was chosen to present a worse case scenario That is, it was a sieved and homogenized sediment which had been collected from the river Tamar in the Southwest of England, and contained very high levels of uranium, thorium, lanthanides, and iron, all of which act as interferents during column preconcentration. The results of nitric acid and nitric/hydrochloric acid leaches are given in Tables 5 and 6 respectively

TABLE 5--*Recovery of actinide radioisotopes from sediment using a nitric acid leach.*

	Conc of isotope in fraction (pg mL^{-1})								
	^{230}Th	^{232}Th	^{235}U	^{237}Np	^{239}Pu	^{240}Pu	^{242}Pu	^{243}Am	^{244}Pu
Expected conc (pg mL^{-1})	200	200	200	200	200	200	200	200	200
Actual conc (pg mL^{-1})	105	nd	Nd	104	144	153	143	<1	144
Recovery (%)	52	nd	Nd	52	72	76	72	<1	72

TABLE 6—*Recovery of actinide radioisotopes from sediment using a nitric/hydrochloric acid leach*

	Conc of isotope in fraction (pg mL^{-1})								
	^{230}Th	^{232}Th	^{235}U	^{237}Np	^{239}Pu	^{240}Pu	^{242}Pu	^{243}Am	^{244}Pu
Expected conc (pg mL^{-1})	200	200	200	200	200	200	200	200	200
Actual conc. (pg mL^{-1})	87	nd	nd	84	136	132	130	<1	122
Recovery (%)	44	nd	nd	42	68	66	65	<1	61

Recoveries obtained using the two acid leaches were between 42-76% for most of the radioisotopes, with the exception of Am, which is the least well retained element The low recoveries were probably due to column overloading by Fe, the lanthanides, and naturally occurring uranium and thorium, which were present in this sediment in excess, thereby causing column overloading. To obtain full recoveries it will be necessary to develop chromatographic methods to separate the actinides from other species, with sufficient resolution. We are currently investigating the use of new substrates with immobilized chelating dyes to achieve this aim.

On-line Separation of Actinide Radioisotopes

One of the problems associated with the determination of the actinide elements by ICP-MS is the propensity for polyatomic ion interferences. A particular problem is the determination of ^{239}Pu in samples containing an excess of naturally occurring uranium, due to the positive interference caused by ^{238}UH. One way to overcome this is the separation of the elements prior to ICP-MS detection. This was achieved by sequential elution of the actinides as shown in Fig. 4. In this case Am and Pu were separated from Np, U and Th, thereby eliminating the interference of ^{238}UH on ^{239}Pu. Complete separation of Am and Pu was not obtained, probably due to the propensity for Pu to disproportionate and exist in a number of oxidation states simultaneously.

Chromatographic methods can also be used to reduce problems of column overloading, provided that sufficient resolution is achieved. Such on-line chromatographic methods using novel resins and chelating dyes are currently being investigated in our laboratory.

Acknowledgements

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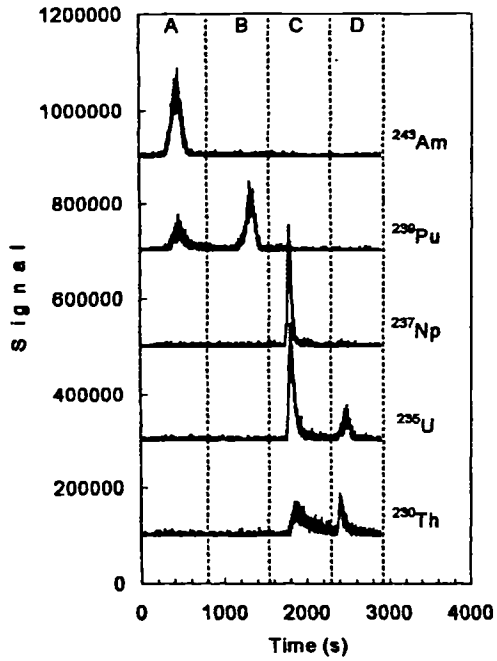

FIG. 4—*Elution profile for sediment spiked with 20 ng each of the actinide elements. A, 4 M HCl; B, 4 M HCl + 0.1 M quinol; C, 4 M HCl + 0.03 M oxalic acid; D, 0.1 M ammonium bioxalate.*

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Determination of natural uranium and thorium in environmental samples by ETV–ICP-MS after matrix removal by on-line solid phase extraction

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Jason B Truscott,[a] Lee Bromley,[a] Phil Jones,[a] E Hywel Evans,*[a] Justine Turner[b] and Ben Fairman[b]

[a]*University of Plymouth, Department of Environmental Sciences, Drake Circus, Plymouth, UK PL4 8AA*
[b]*LGC, Queens Road, Teddington, Middlesex, UK TW11 0LY*

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An on-line solid phase extraction method has been developed for the determination of ^{238}U and ^{232}Th biological certified reference material using inductively coupled plasma mass spectrometry (ICP-MS) Absolute detection limits were 2 7 pg and 3 1 pg for the determination of ^{238}U and ^{232}Th respectively, both being blank limited. The result for the determination of ^{238}U in NASS-4 Open Ocean Sea Water was 2.13 ± 0 28 ng ml^{-1} compared with a certified value of 2 68 ± 0 12 ng ml^{-1} The results for the determination of ^{238}U in SLRS-3 River Water was 0 043 ± 0 002 ng ml^{-1} compared with an indicative value of 0 045 ng ml^{-1} Results for the determination of ^{238}U and ^{232}Th in NIST 1575 Pine Needles were 14 6 ± 3 4 ng g^{-1} and 28 3 ± 4 5 ng g^{-1} respectively compared with certified values of 20 ± 4 ng g^{-1} and 37 ± 3 ng g^{-1}, using a dry and wet ashing sample preparation method Results for the determination of ^{238}U and ^{232}Th in NIST 1566a oyster tissue were 121 ± 21 ng g^{-1} and 29 ± 8 ng g^{-1} for ^{238}U and ^{232}Th compared to certified and indicative values of 132 ± 12 ng g^{-1} and 40 ng g^{-1}, using the same method. When a lithium metaborate fusion method was used, results for ^{238}U and ^{232}Th were 23 3 ± 2.0 ng g^{-1} and 36.2 ± 5 6 ng g^{-1} respectively in NIST 1575 Pine Needles The application of electrothermal vaporisation ICP-MS (ETV ICP-MS) to NASS-4 Open Ocean Sea Water gave 2 81 ± 0 54 ng ml^{-1} and SLRS-3 River Water 0 045 ± 0 004 ng ml^{-1} for ^{238}U When the fused NIST 1575 samples were analysed using ETV–ICP-MS, results for ^{238}U and ^{232}Th were 19.5 ± 1 7 ng g^{-1} and 38 8 ± 2.2 ng g^{-1} respectively Absolute detection limits for ETV–ICP-MS were 30 fg and 9 fg for ^{238}U and ^{232}Th respectively, both being blank limited

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is a technique ideally suited to the determination of the concentration and isotopic composition of the actinide elements. The principal advantages of ICP-MS are speed and sensitivity, with the capability of determining all the actinide elements within a minute, at concentrations as low as 1 pg ml^{-1} in liquid samples. In addition, there is no need to separate the elements one from another, as there is in α-spectrometry, because this is achieved by the mass spectrometer, hence, the number of sample pre-treatment stages can be greatly reduced. However, it is still necessary to separate the radionuclides from the matrix, a procedure for which column pre-concentration methods are ideal. A number of resins have been used for the pre-concentration and separation of the actinides. Recently a number of very specific chelating resins have become available which are particularly suited to this task. Some extraction procedures and application of these resins have been addressed by Horwitz and co-workers,[1–4] and Crain *et al*.[5] have quoted 20 fg mL^{-1} detection limits for ^{239}Pu and ^{235}U using TRU-Spec™ resin as a pre-concentration step prior to analysis by ICP-MS Alvardo and Erickson[6] obtained 5 fg and 2 fg detection limits for ^{238}U and ^{232}Th respectively when using electrothermal vaporisation (ETV) coupled with ICP-MS and trifluoromethane as a modifier gas, compared to 180 fg and 1600 fg for an unmodified ETV Wyse and Fisher[7] have reported a potential 3 fg absolute detection limit for plutonium using ICP-MS and TRU-Spec™ resin, and concluded that results for the determination of ^{239}Pu in urine were comparable to those obtained using α-spectrometry Similarly, ^{230}Th and ^{234}U have been determined in the soil reference material TRM-4 (ref 8) using hydrofluoric acid for sample digestion. Chiappini *et al*.[9] have quoted values close to 1 2 fg detection limits for uranium, using a new high sensitivity ICP-MS[10] and a high-efficiency desolvating nebulizer Aldstadt *et al*.[11] have also reported good results for the determination of ^{238}U by FI-ICP-MS using TRU-Spec™ Resin. The use of ^{209}Bi or ^{205}Tl as internal standards has been quoted to be applicable for use in thorium and uranium determination in biological samples [12] In this work the application of an actinide-specific resin for pre-concentration and matrix removal prior to analysis by ICP-MS, with and without ETV sample introduction, has been addressed.

Experimental

Pneumatic nebulization ICP-MS detection

An inductively coupled plasma mass spectrometer (PlasmaQuad 2+, VG Elemental, Winsford, Cheshire, UK) was used. Data was acquired using the time resolved analysis software, which allows time resolved monitoring of multiple isotopes, and manipulated off-line using MassLynx software (Micromass Ltd., Manchester, UK) Operating conditions are shown in Table 1 The flow injection manifold comprising a 500 μl injection loop on a 6 port valve (Model 5020, Rheodyne,

Table 1 Operating conditions for ICP-MS

	VG PQ2+	PE ELAN 5000A
ICP—		
Forward power/W	1350	1080
Plasma gas/l min^{-1}	16 5	15
Auxiliary gas/l min^{-1}	0 7	1 0
Nebulizer gas/l min^{-1}	0 8	0 8
Sampling depth/mm	10	15
Sample flow/ml min^{-1}	0 5	1 0
Torch	Fassel (quartz)	Fassel (quartz)
Nebulizer	Concentric (quartz)	Cross-flow (Gem-tip)
Spray Chamber	Scott type (quartz)	
Interface—		
Sampler	Ni	Pt
Skimmer	Ni	Pt
Mass spectrometer—		
Ion masses (m/z)	^{232}Th, ^{238}U, ^{209}Bi	^{232}Th, ^{238}U, ^{235}U
Data acquisition	Time resolved mode	Transient, peak hopping
Points per peak	3	1
DAC step	3	n/a
Dwell time/ms	20	40
Time-slice duration/s	1	

Cotati, CA, USA) was interfaced with the ICP-MS instrument as shown in Fig. 1

ETV–ICP-MS detection

An inductively coupled plasma mass spectrometer (Elan 5000A, Perkin Elmer, Beaconsfield, Bucks., UK) interfaced with an electrothermal vaporisation (ETV) sample introduction system (HGA 600MS, Perkin Elmer) was used. Data were acquired in transient peak hopping mode, which allows time resolved monitoring of multiple isotopes. Operating conditions for the ICP are shown in Table 1, with the associated temperature program for the ETV shown in Table 2.

Samples were applied to the column and eluted with 5 ml of 0 1 M ammonium bioxalate into ETV autosampler vials. Portions (30 µl) were pipetted into the ETV furnace tube and the temperature program initiated.

Analytical columns

Columns were prepared with a dry powder of resin (50–100 µm, TRU-Spec™, EiChrom Europe, 75010 Paris, France) in commercially available glass chromatography columns of 3 mm id and 50 mm length (Omnifit microbore columns, Omnifit, Cambridge, Cambs, UK). When not in use the columns were filled with 2 M HNO_3, and prior to use they were washed with successive portions of 0 1 M ammonium bioxalate and 2 M HNO_3 at a flow rate of 0.5 ml min^{-1} for 6 min, and finally 1 ml of column feed solution.

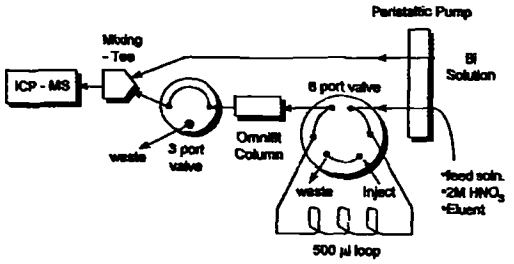

Fig. 1 Schematic of the flow injection manifold interface with ICP-MS.

Reagents

All solutions were prepared using analytical grade reagents and deionised water (Ultra Pure Water, Elgastat Maxima, Elga Ltd, High Wycombe, Bucks, UK) Analytical reagents were: nitric acid, 2 M (Aristar, BDH, Poole, Dorset, UK), eluting solution, (0 1 M $NH_4HC_2O_4$ (Fisons Scientific Equipment, Loughborough, UK) filtered through a 47 mm *diameter 0 45 µm sterile membrane filter paper (Whatman* Laboratory Division, Maidstone, Kent, UK); internal standard solution (15 ng ml^{-1} Bi) to allow correction for instrumental drift; column feed solution, 1 M $Al(NO_3)_3$ (Analytical Grade, Fisher Scientific UK, Loughborough, Leics., UK) purified by passing through a 1.2 cm^3 bed of Dowex 1-X8 anion exchange resin (BDH, Poole, Dorset, UK) then a 0 6 cm^3 bed of Tru-Spec resin, column feed solution, 0 5 M $Al(NO_3)_3$ + 2 M HNO_3

Standard solution preparation

A mixed standard solution of 10 µg ml^{-1} ^{232}Th and ^{238}U, was prepared in 5% HNO_3 from 1000 µg ml^{-1} stock solutions of the individual elements (Johnson Matthey Ltd., Reading, Berks., UK) In order to ensure that the analytes were in the correct oxidation states to be retained on the column [i.e U (VI) and Th (IV)], 10 ml of the 10 µg ml^{-1} standard solution was boiled to dryness in two successive 10 ml portions of conc. HNO_3

Table 2 Operating conditions and gas flows for the ETV system

Program step	Temp/°C	Ramp time/s	Hold time/s	Internal furnace gas flow/ml min^{-1}
1	100	10	15	300 (Ar)
2	120	10	60	300 (Ar)
3	800	5	30	10 (CHF_3)
4	2500	0.2	2	0 (to ICP)
5	2700	0	1	0 (to ICP)
6	20	15	1	0 (to ICP)

Sample preparation

Water samples Two certified reference materials were studied, namely NASS-4 Open Ocean Sea Water and SLRS-3 River Water (National Research Council, Ottawa, Ontario, Canada) Samples, 10 ml of NASS-4 and 25 ml of SLRS-3 were treated in the same way as the mixed standard solution, except that they were made up to final volumes of 25 ml and 50 ml respectively with column feed solution

Biological samples. Initially the sample preparation procedure was based on a method by Nelson and Fairman [13] Two certified reference materials (CRMs) were studied, namely NIST 1566a Oyster Tissue and NIST 1575 Pine Needles (National institute of Science and Technology, Gaithersburg, MD, USA) Samples (0 5 g) were weighed into porcelain crucibles, placed in a muffle furnace and dry-ashed at 200 °C for 2 hours, 400 °C for 2 h, 600 °C for 2 h, and 800 °C for 2 h. This step was omitted for the oyster tissue. Nitric acid (10 ml) was added to each crucible, followed by gentle warming on a hot-plate to digest the samples, boiling to dryness and heating on a hotplate This procedure was repeated until a white ash was left On the last iteration the samples were boiled down until almost dry, then 10 ml of the column feed solution was added to each beaker to dissolve the ash. Samples were made up to final volumes of 50 ml and 25 ml, for oyster tissues and pine needles respectively, with column feed solution. Three sample blanks were also prepared

Fusion of biological samples. Subsequently sample preparations have been performed by lithium metaborate fusion. Similar procedures of lithium metaborate fusions for soil samples have recently been used for uranium and plutonium determinations.[14] One certified reference material was studied, namely NIST 1575 Pine Needles Samples (0 5 g) were weighed into platinum crucibles and 0 8 g of lithium metaborate (Spectroflux, Johnson Matthey) was added to each, then heated over a Meeker burner. A platinum lid for the crucible was used to improve heat retention and thus encourage fusion, some flaming was initially observed from the pine needles, while the organic matter was burnt off The molten fused sample was then quickly poured into a beaker containing approximately 30 ml of column feed solution. Any undissolved fused matter was allowed to dissolve in the solution, mixing was aided by use of a magnetic stirrer Samples were made up to final volumes of 50 ml in column feed solution. Three sample blanks were also prepared.

Calibration

A series of calibration standards containing both ^{232}Th and ^{238}U were prepared and deposited onto the column by flow injection, into a carrier stream of column feed solution at a flow rate of approximately 0 5 ml min^{-1} for 1 min. During deposition the outlet from the column was diverted to waste to prevent the column feed solution entering the ICP-MS instrument. After a deposition, the column was rinsed with 1 ml of 2 M HNO_3 to remove any residual column feed solution before the column was diverted back to the ICP-MS, the analytes were eluted with 0 1 M ammonium bioxalate, and the analyte masses were monitored. After elution the column was again diverted away from the ICP-MS and flushed with 1 ml of column feed solution to remove residual ammonium bioxalate solution prior to further deposition Each injection was repeated three times

Analysis of samples

An accurate volume of the prepared sample was either measured into a clean polypropylene centrifuge tube or injected into the 500 µl sample loop, depending on whether a pre-concentration step was required. The solution was deposited onto the column by pumping through the manifold using the tubing normally immersed in the carrier stream During deposition the column was diverted to waste The centrifuge tube was rinsed with 1 5 ml of 2 M HNO_3, to remove any residual sample from the tube, and subsequently with 1 ml of 2 M HNO_3 to flush through any residual column feed solution prior to diverting the column to the ICP-MS The column was diverted to the ICP-MS instrument, the analytes eluted with 0 1 M ammonium bioxalate, and the analyte masses monitored. After elution the column was again diverted away from the ICP-MS and flushed with 1 ml of column feed solution to remove residual ammonium bioxalate solution prior to further deposition. Each injection was repeated at least three times

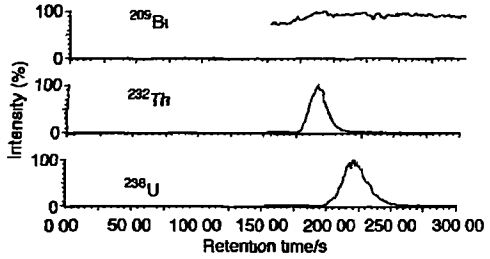

Fig. 2 Elution profiles for ^{238}U and ^{232}Th

Results and discussion

ICP-MS detection

Elution profiles and detection limits. The elution peaks for ^{238}U and ^{232}Th are shown in Fig 2, with uranium being eluted completely in approximately 50 s and thorium in approximately 30 s. The elution times corresponded to volumes of approximately 0 4 and 0 25 ml for ^{238}U and ^{232}Th respectively The standards were deposited from a 500 µl loop so under these circumstances both ^{238}U and ^{232}Th were eluted in a smaller volume than the sample loop

Instrumental and method detection limits for ^{238}U and ^{232}Th are shown in Table 3 *Instrumental detection limits were* determined using solutions prepared in the column-eluting *solution (0 1 M ammonium* bioxalate) but had not been eluted from the column, thus reflecting the level of the blank in the column-eluting solution. Method detection limits were determined by pre-concentrating a 0 5 ml aliquot of column feed solution onto the column and eluting with 0 1 M ammonium bioxalate solution. The method detection limits were blank limited and can be improved by a factor of at least 100 if the reagents are purified more effectively This will also allow greater pre-concentration factors to be realised, thereby improving detection limits further.

Analysis of reference materials. The certified reference materials NASS-4 (Open Ocean Sea Water) and SLRS-3 (River

Table 3 Instrumental and method detection limits for uranium and thorium using pneumatic nebulization PN-ICP-MS and ETV-ICP-MS

	U		Th	
	Absolute/ pg	Relative/ pg ml^{-1}	Absolute/ pg	Relative/ pg ml^{-1}
Instrumental (PN)	2.7	5 4	3 1	6.2
Method (PN)	24	48	60	120
Instrumental (ETV)	0 03	0 9	0 009	0 3
Method (ETV)	0.6	21	0 3	9

Table 4 Results for the determination of uranium in certified reference materials NASS-4, SLRS-3 by PN-ICP-MS and ETV-ICP-MS

Detection	Certified reference material	Certified value/ ng ml^{-1}	^{238}U found/ng ml^{-1} Analysed without column (10 × dilution[a])	Analysed with column[a]
PN	NASS-4	2.68±0 12		2.13±0 28
ETV	NASS-4	2.68±0 12	1 98±0 11	2 81±0 54[b]
PN	SLRS-3	(0 045)[c]		0 043±0 002
ETV	SLRS-3	(0 045)[c]	0 042±0 002	0 045±0 004[d]

[a]mean ± s; [b]0 5 ml sample; [c]uncertified indicative value, [d]2.5 ml sample.

Table 5 Results of the determination of uranium and thorium in certified reference materials by PN-ICP-MS after dry/wet ashing

Certified reference Material	U Certified value/ ng g^{-1}	U Found[a]/ ng g^{-1}	Th Certified value/ ng g^{-1}	Th Found[a]/ ng g^{-1}
1566a Oyster Tissue	132±12	121±21[b]	(40)[c]	29±8[d]
1575 Pine Needles	20±4	14 6±3 4[d]	37±3	28 3±4 5[d]

[a]mean ± s; [b]n = 11, [c]indicative value, [d]n = 5

Table 6 Results of the determination of uranium and thorium in pine needles by PN-ICP-MS and ETV-ICP-MS after lithium metaborate fusion, by calibration with and without the column in place

Detection	Calibration method	U Certified value/ ng g^{-1}	U Found[a]/ ng g^{-1}	Th Certified value/ ng g^{-1}	Th Found[a]/ ng g^{-1}
PN	Calibration with column[b]	20±4	23.3±2.0	37±3	36.2±5 6
PN	Calibration without column[b]	20±4	18 1±1 4	37±3	33 6±6 8
PN	Calibration without column, 5 ml preconc.[c]	20±4	16 6±1 5	37±3	38 1±0 8
ETV	Calibration without column[d]	20±4	19 5±1 7	37±3	38 8±2 2

[a]mean ± s; [b]n = 3, [c]n = 1, 3 injections; [d]n = 6.

Water) were analysed by pre-concentrating known volumes of the prepared material, eluting and comparing the peaks to the calibration curve after normalising using the Bi internal standard. Results are shown in Table 4, though it was only possible to compare uranium as the reference materials were only certified for this element. One particular problem that was encountered was that the reproducibility for thorium was unpredictable, and this element was prone to carry-over and high blank values. Low recoveries were obtained for uranium in NASS-4 samples using pneumatic nebulization (PN)-ICP-MS However full recoveries were found for uranium in NASS-4 when using ETV-ICP-MS, with no significant difference between the found value and the mean of the certified value at the $P = 0$ 05 level. The analyses were repeated on two separate days and the results were very similar Good agreement was obtained between the analytical result and the indicative value for SLRS-3, though no firm conclusions can be drawn because this material was not certified. This clearly shows the value of pre-concentration since the indicative value of 0 045 ng ml^{-1} was close to the detection limit for the ICP-MS instrument used, and was twice the absolute detection limit for the method detailed here However, a pre-concentration factor of 5 effectively raised the level of uranium to 10 times the detection limit, making analysis feasible

Results for the analysis of oyster tissue and pine needles after sample preparation by dry/wet ashing are shown in Table 5 For oyster tissue no significant difference was found between the found value and the certified mean for uranium at the $P = 0$ 05 level. For the pine needles, low recoveries for both thorium and uranium were observed in comparison with the certified mean, though there was no significant difference between the found value and the bottom of the certified range for both uranium and thorium (i.e 16 ng g^{-1} and 34 ng g^{-1} respectively) at the $P = 0$ 05 level Other workers have reported losses of uranium through the use of porcelain crucibles,[15,16] by adsorption of ^{238}U onto the surface. However, low recoveries could also be the result of analyte losses by volatilisation in the muffle furnace, as by incomplete sample digestion of silicate material. When the lithium metaborate fusion method was used (Table 6) recoveries were within the certified range, probably due to complete digestion of silicates within the pine needle matrix, with no significant difference between the found value and the certified mean for both uranium and thorium at the $P = 0$ 05 level. In order to try and speed up the analysis, the effect of calibrating the analysis by simply flow injecting the standards, rather than depositing them on the column, was investigated. Results are shown in Table 6 and indicate that full recoveries were obtained for both ^{238}U and ^{232}Th When the pre-concentration factor was increased by a factor of 10 (i.e. 5 ml were deposited instead of 0 5 ml) recoveries were still within the certified range, again with no significant difference between the found value and the certified mean for both uranium and thorium at the $P = 0$ 05 level.

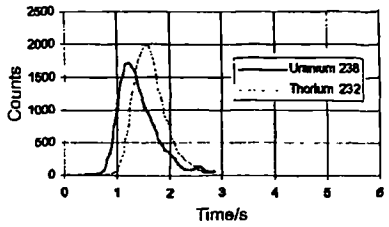

Fig. 3 Vaporisation profiles for ^{238}U (3 pg) and ^{232}Th (30 pg) for ETV-ICP-MS using only argon gas.

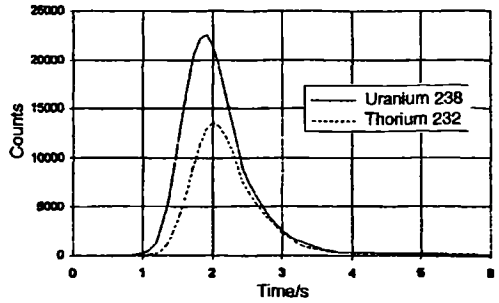

Fig. 4 Vaporisation profiles for ^{238}U (3 pg) and ^{232}Th (3 pg) for ETV-ICP-MS using CHF_3 modifier gas.

ETV–ICP-MS detection

Effect of freon gas, elution profiles and detection limits. Vaporisation profiles for ^{238}U and ^{232}Th with and without freon added during the ashing stage are shown in Figs. 3 and 4. In the absence of freon (Fig. 3) the peaks were approximately 2.5 s wide, and ^{232}Th vaporised slightly later than U. However, when freon was added (Fig. 4), peak height and peak area signals increased by approximately 10 times and 50 times for ^{238}U and ^{232}Th respectively, resulting in much improved detection limits. Other workers have also noted the beneficial effect of freon gas in ETV,[6,17,18] which prevents the formation of refractory carbides on the surface of the graphite tube, however, it is advisable to only introduce the gas during the ashing stage. If freon is introduced during the vaporisation stage, tube lifetimes are reduced substantially.

Instrumental and method detection limits are shown in Table 3 and were determined as before. As for pneumatic nebulization, detection limits were blank limited, so improvements might be expected if the purity of reagents is improved.

Analysis of reference materials. Results for the analysis of water reference materials are shown in Table 4. The samples were analysed after straightforward 10-fold dilution, and after pre-treatment on the column. Low recoveries were obtained for the diluted NASS-4 Open Ocean Sea Water samples without matrix removal on the column, but agreement with the certified value was obtained when the matrix was removed using the column pre-treatment. Similar results were obtained for the SLRS-3 River Water samples regardless of which method was used, reflecting the relative simplicity of this matrix compared to sea water.

Results for the analysis of pine needles reference materials using the lithium metaborate fusion method are shown in Table 6. Results were within the certified range of the reference material.

Conclusions

The determination of ^{238}U and ^{232}Th in certified reference materials was successfully performed in most instances. Low recoveries were observed for the determination of ^{238}U in NASS-4 Open Ocean Sea Water without matrix removal using the column pre-treatment for ETV-ICP-MS, however, with column pre-treatment full recoveries were obtained. Results for the freshwater (SLRS-3) were in good agreement with the indicative value. Agreement with certified values was observed for the determination of ^{238}U and ^{232}Th in NIST 1575 Pine Needles after pre-concentration and matrix elimination after lithium metaborate fusion, and detection by ICP-MS and ETV-ICP-MS. However, losses were apparent when using a dry/wet ashing method. The addition of freon gas to the ETV improved sensitivity for ^{238}U and ^{232}Th 10-fold and 50-fold respectively.

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Determination of actinide elements at femtogram per gram levels in environmental samples by on-line solid phase extraction and sector-field-inductively coupled plasma-mass spectrometry

Jason B. Truscott[a], Phil Jones[a], Ben E. Fairman[b], E. Hywel Evans[a,*]

[a] *Department of Environmental Sciences, Plymouth Environmental Research Centre, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK*

[b] *LGC, Queens Road, Teddington, Middlesex TW11 0LY, UK*

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Abstract

An on-line solid phase extraction method has been developed for the determination of ^{232}Th, ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Am and ^{243}Am in biological certified reference material using a column containing TRU-Spec™ resin coupled with sector-field inductively coupled plasma-mass spectrometry. Absolute detection limits were 0.7, 0.85, 0.6, and 0.65 fg for ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am, respectively. The ^{239}Pu was determined in NIST Human Liver (963 ± 297 fg g^{-1} compared with a certified value of 848 ± 161 fg g^{-1}) using a dry and wet ashing sample preparation method, and in a spiked cabbage reference material (394 ± 54 fg g^{-1} compared to an indicative value of 467 fg g^{-1}) using microwave digestion. Sequential separation of Pu and U was achieved by on-column reduction of Pu with titanium(III) chloride and elution in 4 M HCl to facilitate the determination of ^{239}Pu in samples containing high levels of ^{238}U, thereby eliminating the interference of $^{238}U^1H^+$ at *m/z* 239. The sequential elution procedure was used to determine ^{239}Pu in NIST human lung (814 ± 55 fg g^{-1} compared with a certified range of 227–951 fg g^{-1}) and NIST Rocky Flats Soil (2423 ± 137 fg g^{-1} compared with a certified value of 3307 ± 248 fg g^{-1}).

Keywords: Uranium; Thorium; Plutonium; Americium; Neptunium; Sector-field inductively coupled plasma-mass spectrometry; Solid phase extraction; Sediments; Biological samples.

1. Introduction

The importance of being able to determine the actinide elements in the environment is highlighted in a recent paper [1] which quotes the mean concentration of man-made ^{239}Pu in the environment to be approaching 10^{-13} g g^{-1} (100 fg g^{-1}) in the surface level [2] of soil. The dangerous level for accumulated Pu in the human body is $\geq 10^{-12}$ g g^{-1} (1000 fg g^{-1}), which highlights the requirement to monitor much lower levels in the surrounding environment in order to evaluate accumulation effects.

Inductively coupled plasma-mass spectrometry (ICP-MS) is ideally suited for the determination of the concentration and isotopic composition of the actinide elements. The principal advantages of advanced ICP-MS instrumentation are speed and sensitivity, with the capability of determining all the actinide elements within a minute, at sub fg ml^{-1} levels without preconcentration. In addition, there is less need

* Corresponding author. Tel. +44-1752-233-040; fax. +44-01752-233-040.
E-mail address: hevans@plymouth.ac.uk (E.H. Evans).

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to separate the actinide elements from each other as there is in α-spectrometry, because this is achieved by the mass spectrometer, hence, the number of sample pre-treatment stages can be reduced. However, it is still necessary to separate the radionuclides from the matrix which may contain elements that will produce polyatomic and or isobaric interferences, and this can achieved using column sequential elution techniques. A number of resins have been used for the preconcentration and separation of the actinides, and recently, a some highly specific chelating resins have become available which are particularly suited to this task. Some extraction procedures and applications of these resins have been addressed by Horwitz [3–6], and earlier work by Crain et al. [7] who quoted 20 fg ml^{-1} detection limits for ^{239}Pu and ^{235}U using TRU-Spec™ resin and a preconcentration step prior to analysis by ICP-MS. Wyse and Fisher [8] have reported a potential 3 fg absolute detection limit for plutonium using ICP-MS and TRU-Spec™ resin, and concluded that results for the determination of ^{239}Pu in urine were comparable to those obtained using α-spectrometry Similarly, ^{230}Th and ^{234}U have been determined in the soil reference material TRM-4 [9] using hydrofluoric acid for sample digestion. Chiappini et al [10] has 1 2 fg detection limits for uranium, using a new high sensitivity ICP-MS instrument [11] and a high-efficiency desolvating nebuliser. More recently, Aldstadt et al. [12] have also reported good results for the determination of ^{238}U by flow injection-ICP-MS using TRU-Spec™ resin. Kim et al. [13] have applied a two-column extraction method with isotope dilution (ID) high resolution (HR) ICP-MS for plutonium isotope determination, achieving detection limits for ^{239}Pu, ^{240}Pu and ^{242}Pu at about 4, 3 and 6 fg ml^{-1}, respectively, when employing a microconcentric nebuliser (MCN-6000®, Cetac Technologies, Omaha, NE)

Previous work undertaken in this laboratory [14,15] has resulted in the successful determination of uranium and thorium in waters and biological matrices using TRU-Spec™ resin for preconcentration and matrix removal prior to analysis by pneumatic nebuliser (PN)-ICP-MS and electrothermal vapourisation-ICP-MS, respectively. Extraction and sequential elution of ^{232}Th, ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Am and ^{243}Am in sediments using TRU-Spec™ resin and coupled to PN-ICP-MS was also demonstrated, indicating the potential for eliminating interferences such as that of $^{238}U^1H^+$ on $^{239}Pu^+$ [14].

Considering the speed and simplicity of using a TRU-Spec™ single column extraction method, the work laid out in this paper demonstrates a refining of the separation procedures tailored to eliminate the problems associated with polyatomic and isobaric interferences and increase sample throughput

2. Experimental

2.1. Instrumentation

All analyses were performed using a SF-ICP-MS (Element 1, Finnigan-MAT) interfaced with a flow injection sample injection system, shown in Fig 1 Data

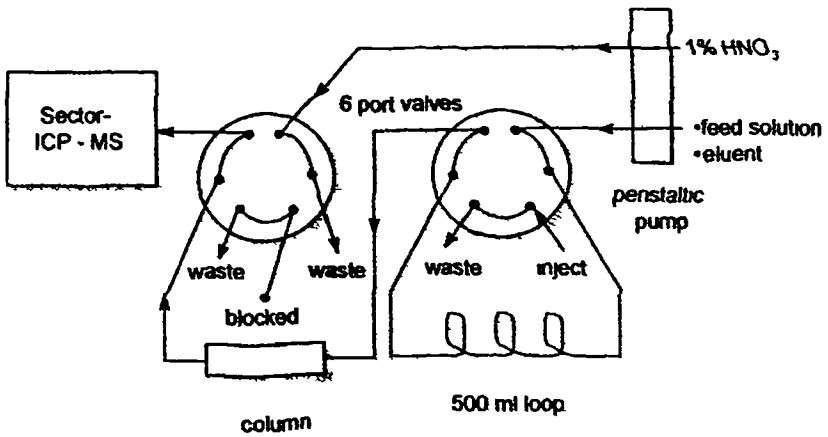

Fig 1. Schematic diagram of the flow injection manifold interface with the SF-ICP-MS instrument

Table 1
Operating conditions for Finnigan MAT sector-field-ICP-MS

Forward power (W)	1100
Plasma gas (l min^{-1})	14 0
Auxillary gas (l min^{-1})	0 9
Nebuliser gas (l min^{-1})	1 1
Sample flow (ml min^{-1})	0 5–2
Torch	Fassel (quartz)
Nebuliser	Concentric MicroMist (quartz)
Spray chamber	Scott type (quartz)
Interface	
Sampler	Ni
Skimmer	Ni
Mass spectrometer	
Ion masses (*m/z*)	^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{237}Np, ^{238}U, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{243}Am
Data acquisition	
Dead time (ns)	25
Points per peak	25
Dwell time (ms)	30
Time-slice duration (s)	1

were acquired in the transient peak hopping mode, which allows time resolved monitoring of multiple isotopes. The operating conditions used are shown in Table 1.

2 2. Analytical columns

Columns were prepared using TRU-Spec™ resin (50–100 μm, Eichrom, Paris), dry packed into PEEK columns of 4 mm i d. and 50 mm length (Dionex UK *Ltd.*, Camberley, Surrey, UK). When not in use, the columns were filled with 2 M HNO_3, and prior to use they were washed with successive portions of 0.1 M ammonium hydrogenoxalate and 2 M HNO_3 at a flow rate of 0.5 ml min^{-1} for 6 min, and finally 1 ml of column feed solution.

2 3. Reagents

All solutions were prepared using analytical grade reagents and distilled deionised water (DDW, Ultra Pure Water, Elgastat Maxima, Elga Ltd , Bucks, UK) The following analytical reagents were prepared as detailed previously [14,15]: 2 M nitric acid (Aristar, BDH, Poole, UK), 0 1 M ammonium hydrogenoxalate eluting solution (Fisons Scientific Equipment, Loughborough, UK); 0. 5 M aluminium nitrate dissolved in 2 M nitric acid (Analytical Grade, Fisher Scientific, UK) column feed solution; off-column reducing solution prepared from 0.3 g of ammonium iron(II) sulphate and 0.3 g of sodium formaldehyde sulfoxylate dissolved in 10 ml of 2 M HNO_3 In addition, an on-column reducing solution was prepared from titanium(III) chloride >10% w/v solution in concentrated HCl (Aldrich, Gillingham, Dorset, UK) to produce a final solution of 0.006 M $TiCl_3$ in 4 M HCl

A mixed standard solution of ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am, was prepared by boiling to dryness in nitric acid then reduction with off-column reducing solution in order to ensure that the analytes were in the correct oxidation states to be retained on the column, as described previously [14]

2.4. Sample preparation

The certified reference materials (CRMs) NIST 4352 Human Liver and NIST 4351 human lung (National Institute of Science and Technology, Gaithersburg, MD) were subjected to a dry and wet ashing procedure as described previously [14,15]. Approximately 10 g portions of the human liver were used, however, it was necessary to digest the whole sample of human lung (approximately 45 g), as required by the certificate, due to inhomogeneity caused by the presence of "hot particles".

Samples (0 5 g) of dried and homogenised cabbage (Ministry of Agriculture, Food and Fisheries, UK) which had been spiked with ^{239}Pu were treated using a microwave digestion procedure The samples were measured into microwave 'bombs', 4 ml of concentrated HNO_3 acid and 1 ml of concentrated HCl were added, and the bombs were irradiated in the microwave digester (Perkin-Elmer Paar Physica Multiwave Sample Preparation System), for 5 min at 500 W and 15 min at 800 W. Samples were quantitatively transferred into clean vials and made up to a known weight with approximately 6 g of 2 M HNO_3 and 0.3 ml of off-column reducing solution.

Samples of the CRMs NIST 4350B River Sediment (10 g) and NIST 4253 Rocky Flats Soil No. 1 (6 g) were ashed in a muffle furnace, then leached with concentrated nitric acid as described previously [14]

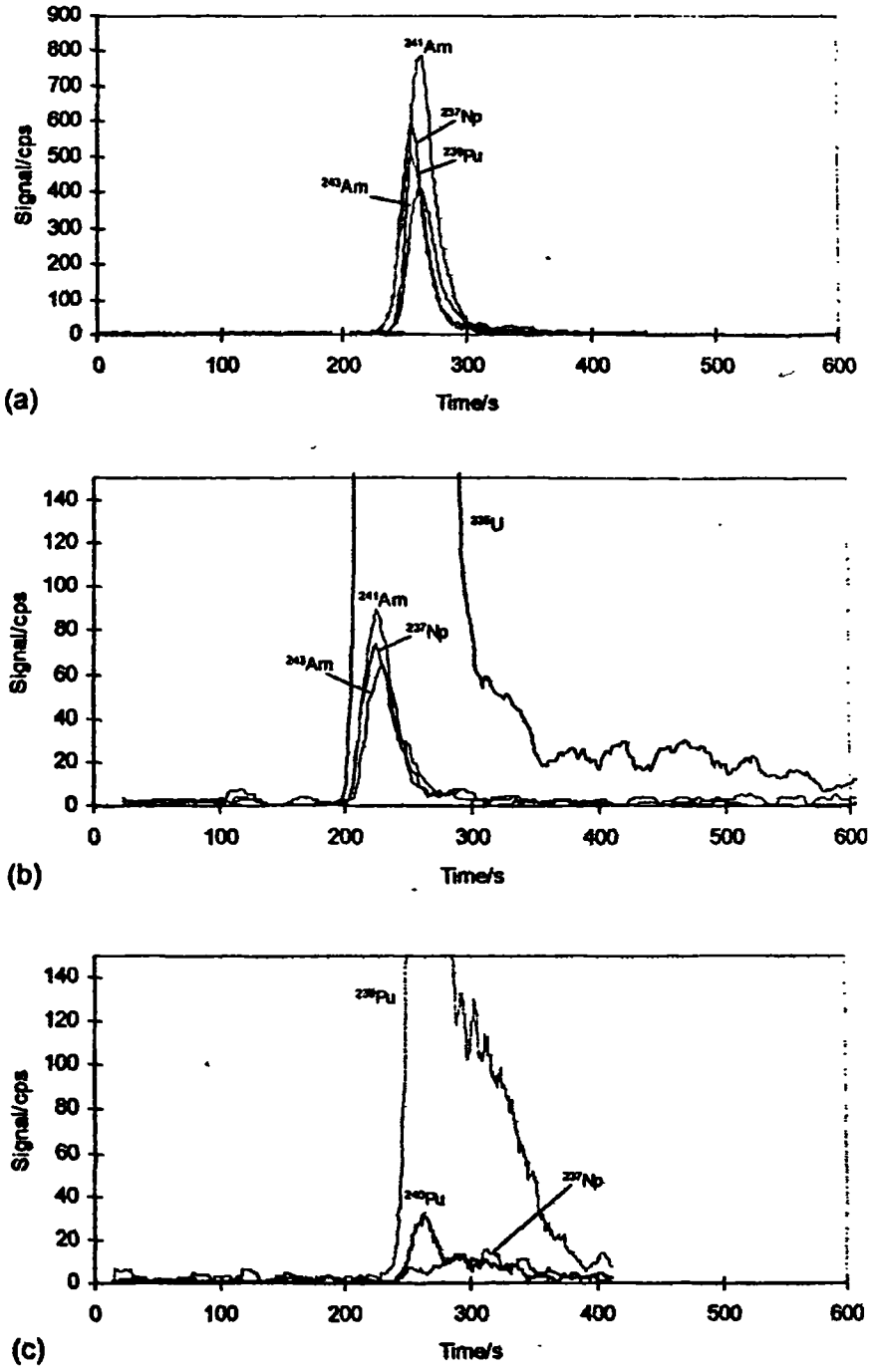

Fig. 2. Elution profiles obtained after deposition on TRU-Spec™ resin and using SF-ICP-MS detection: (a) 0.5 ml of a 70 fg g^{-1} solution; (b) 50 ml of a 200 ag g^{-1} solution; (c) 0.5 ml of a digest of NIST 4352 Human Liver.

2 5 Procedure

Two analytical procedures were adopted depending on whether it was necessary to elute the analytes simultaneously or sequentially.

2.5 1. Simultaneous analyte elution

Standard solutions were introduced in duplicate by flow injection through a 500-μl injection loop on a six port valve (Model 9010, Rheodyne, Cotati, CA), into a carrier stream of 0.1 M ammonium hydrogenoxalate solution at a flow rate of approximately 0 5 ml min^{-1}, so that the analytes passed through the column without retention. Prior to deposition, approximately 0 5 ml of off-column reducing solution was added to each 10 ml of sample. Sample solutions were deposited in a carrier stream of either column feed solution or 2 M HNO_3 at a flow rate of approximately 0.5 ml min^{-1} for 1 min. During deposition, the outlet from the column was diverted to waste. The column was then rinsed with 1 75 ml of 2 M HNO_3 to remove any residual column feed solution, diverted back to the ICP-MS instrument and the analytes eluted with 0.1 M ammonium hydrogenoxalate After elution, the column was diverted away from the spectrometer and flushed with 1 ml of column feed solution or 2 M HNO_3 to remove residual ammonium hydrogenoxalate prior to further deposition.

2 5.2. Sequential analyte elution

The procedure was the same as above except that both standard and sample solution were deposited onto the column in a carrier stream of the column feed solution Americium and plutonium were eluted with a solution of 0 006 M titanium(III) chloride in 4 M HCl, then the other analytes were eluted with 0 1 M ammonium hydrogenoxalate.

Table 2
Instrumental detection limits for the actinide elements in 0 1 M ammonium hydrogenoxalate (500 μl injections for SF-ICP-MS)

Element	Sensitivity (cps fg^{-1})	R^2	Detection limit	
			Relative ($fg\,g^{-1}$)	Absolute (fg)
^{237}Np	336	0 9995	1 4	0 70
^{239}Pu	287	1 0000	1 7	0 85
^{241}Am	487	0 9992	1.2	0 60
^{243}Am	280	0 9996	1.3	0.65

3. Results and discussion

3.1. Figures of merit

Elution peaks for 35 fg depositions of ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am with 0 1 M ammonium hydrogenoxalate are shown in Fig 2a. Instrumental detection limits for ^{237}Np, ^{239}Pu, ^{241}Am and ^{243}Am are shown in Table 2, with absolute detection limits as low as 0 6 fg for ^{241}Am. In order to reduce detection limits further a preconcentration step was included, such that 50 ml of an approximately 200 attogram (ag) ml^{-1} solution of ^{239}Pu, ^{237}Np, ^{241}Am, and ^{243}Am in 2 M HNO_3 was deposited onto the column, eluted (Fig. 2b), and recoveries calculated relative to a 500-μl injection volume Mean recoveries for duplicate preconcentrations were 93, 62, and 54% for ^{237}Np, ^{241}Am, and ^{243}Am, respectively. Excellent recoveries were obtained for the relatively well

Table 3
Results for the determination of ^{239}Pu and ^{237}Np in certified reference materials with simultaneous analyte elution

Material	Certified value ($fg\,g^{-1}$) ^{239}Pu	Concentration found ($fg\,g^{-1}$)	
		^{239}Pu	^{237}Np
NIST 4352 Human Liver	848[a] ± 161[b]	963 ± 596[c]	35 ± 24[c]
MAFF Spiked Cabbage	467[d]	394 ± 108[e]	

[a] Assuming 10% of activity due to ^{240}Pu.
[b] 95% confidence
[c] 95% confidence, $n = 4$, one injection.
[d] Indicative value,
[e] 95% confidence, $n = 2$, three injections

Table 4
Possible polyatomic interferences formed in the plasma

	m/z
^{230}Th polyatomic interferences	
$^{190}Os^{40}Ar$	229 92084
$^{190}Pt^{40}Ar$	229 92232
$^{190}Os^{38}Ar$	229 92422
$^{193}Ir^{37}Cl$	229 92884
$^{194}Pt^{36}Ar$	229 93023
$^{194}Au^{33}S$	229 93802
$^{195}Pt^{35}Cl$	229 93364
$^{196}Pt^{34}S$	229.93282
$^{198}Hg^{32}S$	229 93883
$^{198}Pt^{32}S$	229 93995
$^{199}Hg^{31}P$	229 94203
^{232}Th polyatomic interferences	
$^{201}Hg^{31}P$	231 94405
$^{200}Hg^{32}S$	231 94039
$^{199}Hg^{33}S$	231 93973
$^{198}Hg^{34}S$	231 93575
$^{198}Pt^{34}S$	231.93463
$^{197}Au^{35}Cl$	231 93069
$^{196}Pt^{36}Ar$	231 93250
$^{195}Pt^{37}Cl$	231 93541
$^{194}Pt^{38}Ar$	231 92541
$^{192}Pt^{40}Ar$	231 92343
$^{192}Os^{40}Ar$	231 92387
^{234}U polyatomic interferences	
$^{232}Th^{2}H$	234 05215
$^{203}Tl^{31}P$	233 94610
$^{202}Hg^{32}S$	233 94270
$^{201}Hg^{33}S$	233 94175
$^{200}Hg^{34}S$	233 93619
$^{199}Hg^{35}Cl$	233 93712
$^{198}Hg^{36}Ar$	233 93431
$^{198}Pt^{36}Ar$	233 93543
$^{197}Au^{37}Cl$	233 93246
$^{196}Pt^{38}Ar$	233 92768
$^{194}Pt^{40}Ar$	233 92506
^{235}U polyatomic interferences	
$^{204}Pb^{31}P$	234.94680
$^{204}Hg^{31}P$	234.94724
$^{203}Tl^{32}S$	234 94441
$^{202}Hg^{33}S$	234 94209
$^{201}Hg^{34}S$	234 93816
$^{200}Hg^{35}Cl$	234 93717
$^{199}Hg^{36}Ar$	234 93582
$^{198}Hg^{37}Cl$	234 93266
$^{198}Pt^{37}Cl$	234.93378
$^{197}Au^{38}Ar$	234 92929
$^{195}Pt^{40}Ar$	234 92717
^{237}Np polyatomic interferences	
$^{205}Pb^{31}P$	236 94822
$^{205}Tl^{32}S$	236 94648
$^{204}Pb^{33}S$	236 94450
$^{204}Hg^{33}S$	236 94494

Table 4 (*Continued*)

	m/z
$^{203}Tl^{34}S$	236.94021
$^{202}Hg^{35}Cl$	236 93948
$^{201}Hg^{36}Ar$	236 93784
$^{200}Hg^{37}Cl$	236 93422
$^{199}Hg^{38}Ar$	236 93100
$^{197}Au^{40}Ar$	236 92894
^{238}U polyatomic interferences	
$^{207}Pb^{31}P$	237 94965
$^{206}Pb^{32}S$	237 94653
$^{205}Tl^{33}S$	237 94587
$^{204}Pb^{34}S$	237 94091
$^{204}Hg^{34}S$	237 94135
$^{203}Tl^{35}Cl$	237 94119
$^{202}Hg^{36}Ar$	237 93818
$^{201}Hg^{37}Cl$	237 93619
$^{200}Hg^{38}Ar$	237 93105
$^{198}Hg^{40}Ar$	237 92914
$^{198}Pt^{40}Ar$	237.93026
^{239}Pu polyatomic interferences	
$^{238}U^{1}H$	239 05862
$^{208}Pb^{31}P$	238 95040
$^{207}Pb^{32}S$	238 94796
$^{206}Pb^{33}S$	238.94592
$^{204}Hg^{35}Cl$	238 94233
$^{205}Tl^{34}S$	238.94228
$^{204}Pb^{35}Cl$	238 94189
$^{203}Tl^{36}Ar$	238 93989
$^{202}Hg^{37}Cl$	238 93653
$^{201}Hg^{38}Ar$	238 93302
$^{199}Hg^{40}Ar$	238 93065
^{240}Pu polyatomic interferences	
$^{238}U^{2}H$	240 06489
$^{209}Bi^{31}P$	239 95415
$^{208}Pb^{32}S$	239 94871
$^{207}Pb^{33}S$	239 94735
$^{206}Pb^{34}S$	239 94233
$^{205}Tl^{35}Cl$	239 94326
$^{204}Pb^{36}Ar$	239 93406
$^{204}Hg^{36}Ar$	239 94103
$^{203}Tl^{37}Cl$	239 93824
$^{202}Hg^{38}Ar$	239.93336
$^{200}Hg^{40}Ar$	239 93070
^{241}Am polyatomic interferences	
$^{209}Bi^{32}S$	240 95246
$^{208}Pb^{33}S$	240 94810
$^{207}Pb^{34}S$	240 94376
$^{206}Pb^{35}Cl$	240 94331
$^{205}Tl^{36}Ar$	240 94196
$^{205}Tl^{36}S$	240 94149
$^{204}Pb^{37}Cl$	240 93894
$^{204}Hg^{37}Cl$	240 93938
$^{203}Tl^{38}Ar$	240 93507
$^{201}Hg^{40}Ar$	240 93267

Table 4 (*Continued*)

	m/z
^{243}Am polyatomic interferences	
$^{209}Bi^{34}S$	242.94826
$^{208}Pb^{35}Cl$	242.94549
$^{207}Pb^{36}Ar$	242.94344
$^{206}Pb^{37}Cl$	242.94036
$^{205}Tl^{38}Ar$	242.93714
$^{203}Tl^{40}Ar$	242.93472

retained Np species, but low recoveries were observed for Am species, which are less well retained on the column. In the work shown here, the analytes were deposited from 2 M HNO_3, so it should be possible to improve recovery using $Al(NO_3)_3$ + 2 M HNO_3 as the feed solution, which increases the breakthrough capacity; however, this will also increase the blank signal. It was not possible to determine the recovery for ^{239}Pu due to an interference caused by $^{238}U^1H^+$ at *m/z* 239 which arose because the 2 M nitric acid contained sufficient ^{238}U to interfere It is clear from the elution profiles shown in Fig 2b that detection limits of well below 200 ag ml^{-1} should be possible using preconcentration.

3 2 *Analysis of reference materials*

Results for the determination of ^{239}Pu and ^{237}Np in NIST 4352 Human Liver and MAFF Spiked Cabbage are given in Table 3. The concentrations of ^{239}Pu were within the certified range (human liver) or encompassed the indicative value (cabbage). In the case of the human liver sample, the certified value was quoted as activity due to ^{239}Pu+^{240}Pu, so it was necessary to calculate the concentration of ^{239}Pu by assuming that 6% of the activity was due to ^{240}Pu Measurable quantities of ^{237}Np were found in the human liver sample, but the sample is not certified for this element. A typical elution curve for ^{239}Pu in the NIST human liver sample is shown in Fig 2c. As can be seen, ^{239}Pu eluted completely over a period of 160 s within 220 s of injection.

An attempt was also made to determine ^{239}Pu in NIST River Sediment using simultaneous analyte elution, however, this resulted in a gross overestimation of ^{239}Pu concentration, possibly as a result of $^{238}U^1H^+$ interference due to the relatively high concentration of ^{238}U in the sample. Ironically, the problem of polyatomic ion interferences is even more pronounced when using SF-ICP-MS for sub-fg determinations in unit mass resolution mode because polyatomic ions which would not normally be observed using a quadrupole ICP-MS can cause significant interferences with highly sensitive SF-ICP-MS For example, it was found that platinum skimmer and sampler cones resulted in the formation of platinum-argon species (e g $^{190}Pt^{40}Ar$ or $^{194}Pt^{36}Ar$) at *m/z* 230, which interfere with ^{230}Th determination The platinum–argon polyatomic ions caused count rates of approximately 100 cps at ^{232}Th, ^{234}U, ^{235}U and ^{238}U, particularly when using high concentrations of HCl or HNO_3, and the interferences were reduced to <3 cps when Ni cones were used. Environmental samples often contain relatively high (relative to analyte concentration) levels of other elements which give rise to polyatomic species (e g phosphorus, sulphur, chlorine, lead and osmium) when combined with each other or with argon. Some of the potential polyatomic interferences that can arise are shown in Table 4, and these clearly illustrate the necessity to separate the matrix from the analyte The particular problem encountered in this work was the interference due to $^{238}U^1H^+$ on ^{239}Pu, so a sequential elution method was used to separate these two elements.

3 3 *Sequential analyte elution*

Separation of the actinide elements using the sequential elution method is shown in Fig 3. A titanium(III) chloride solution was used to reduce Pu to Pu(III) [16], which is not well retained and was eluted in the 4 M HCl. This procedure normally requires fixing Pu as Pu(IV) using sodium nitrite, but this was found to be unnecessary in this case. Americium, which is usually found only as Am(III), was also eluted in the $TiCl_3$/4 M HCl fraction but Th, U and Np were retained on the column as Th(IV), U(VI) and Np(IV), respectively, and subsequently eluted using 0 1 M ammonium hydrogenoxalate. If an additional separation of Th and Np from U is required (not shown), this can be achieved using a solution of 1 M HCl + 0 03 M oxalic acid [14], leaving U to be eluted with 0 1 M ammonium hydrogenoxalate.

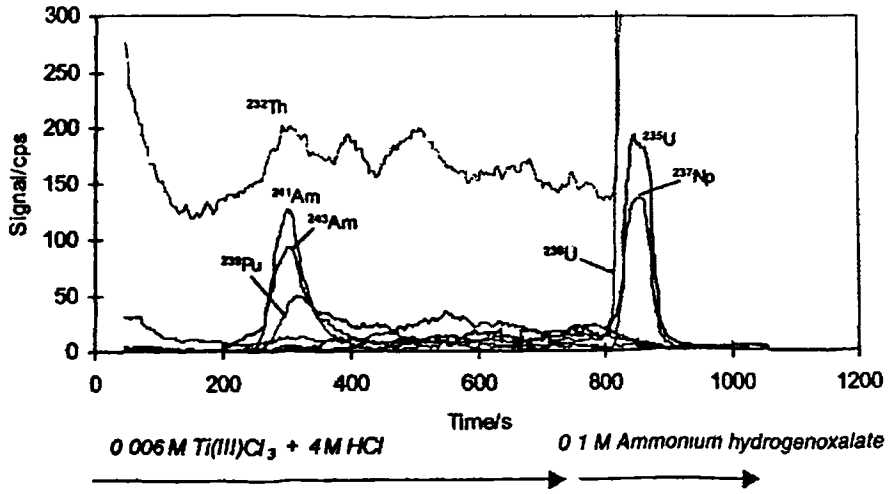

Fig. 3 Sequential elution of approximately 100 fg of each of the actinides using SF-ICP-MS detection

Results for the determination of ^{239}Pu in NIST 4351 Human Lung and NIST 4353 Rocky Flats Soil (No 1) are shown in Table 5. In the case of the human lung, the concentration found for ^{239}Pu fell within the certified range, but slightly low recoveries were observed for the rocky flats soil. In the latter case, the low recoveries could have been due to incomplete leaching because the certificate states that approximately 8% of the Pu resists HNO_3 leaching. Another possible explanation is that column breakthrough occurred because 6 g aliquots of the digested

Table 5
Results for the determination of ^{239}Pu in certified reference materials with sequential analyte elution

Material	Certified value[a] ($fg\,g^{-1}$)	Found[a] ($fg\,g^{-1}$)
NIST 4351 Human Lung	453 (227-951)[b]	814 ± 110[c]
NIST 4353 Rocky Flats Soil	3307 ± 248[d]	2423 ± 272[e]

[a] Assuming 6% of activity due to ^{240}Pu.
[b] Certificate states 453 with an uncertainty of +110 to −50%
[c] 95% confidence, $n = 1$, three injections.
[d] Certificate states 7.5% uncertainty
[e] 95% confidence, $n = 3$, one injection

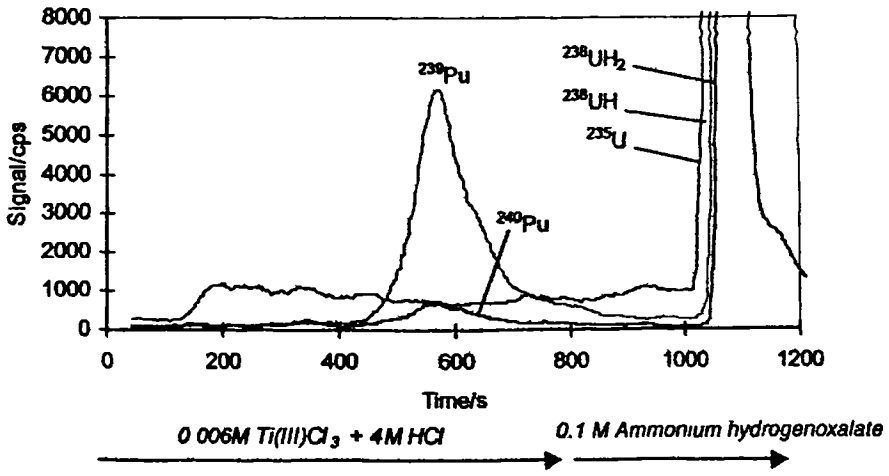

Fig 4 Separation of Pu from U in NIST Rock Flats soil CRM using $TiCl_3$ reduction

soil were preconcentrated onto the column rather than deposited from a 0.5 ml loop. One problem that was encountered was a change in elution time for ^{239}Pu in the sediment leach compared to the standard. This is illustrated in Fig. 4, which shows that ^{239}Pu started to elute at about 450 s, but at 225 s in the standard (Fig. 3). This was thought to be caused by the much higher acidity of the sample due to the leaching procedure, which improved retention on the column.

4. Conclusions

Solid phase extraction, using TRU-Spec™ resin, coupled with SF-ICP-MS has been successfully used for the determination of actinides in environmental samples, with limits of detection of the order of $2\,fg\,g^{-1}$. There is potential for obtaining detection limits less than $152\,ag\,ml^{-1}$ by using preconcentration. The technique has been successfully applied for the determination of ^{239}Pu in biological CRMs and reference materials, however, it was not possible to determine ^{239}Pu in sediments due to the co-elution of ^{238}U and associated interference due to $^{238}U^1H^+$ at m/z 239. In order to overcome this interference, a sequential elution procedure was applied to separate Pu and U, so that the interference-free determination of ^{239}Pu in human lung and soil was possible.

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