

UNIVERSIDAD POLITÉCNICA DE CATALUNYA

Departamento de Ingeniería Química

**CHROMATOGRAPHIC SEPARATIONS FOR FISSION PRODUCTS AND
ACTINIDES DETERMINATION BY DIFFERENT ANALYTICAL
TECHNIQUES: MASS SPECTROMETRY AND RADIOMETRY**

Memoria que para optar al título de
DOCTOR EN CIENCIAS
presenta

LORENZO PERNA

BARCELONA, 2003

MARIA BETTI, Profesora Asociada del Departamento de Química y Química Industrial de la Universidad de Pisa y Responsable del Sector de Química Analítica del Instituto de los Elementos Transuránicos (Comisión Europea, Centro Común de Investigación) y JOAN DE PABLO RIBAS, Catedrático del Departamento de Ingeniería Química de la Escuela Técnica Superior de Ingeniería Industrial de Barcelona de la Universidad Politécnica de Catalunya

CERTIFICAN:

Que la presente memoria titulada: **Chromatographic separations for fission products and actinides determination by different analytical techniques: mass spectrometry and radiometry**, ha sido realizada bajo nuestra dirección por Lorenzo Perna, Licenciado en Químicas Industrial (Universidad de Pisa), en el Instituto de los Elementos Transuránicos (CE-CCI) y que constituye su Tesis para optar al Grado de Doctor en Ciencias – Mención Doctor Europeo.

Y para que así conste y tenga los efectos oportunos delante del Departamento de Ingeniería Química de la Universidad Politécnica de Catalunya, firman la presente certificación a 15 de abril de 2003.

Fdo. Dr. Maria Betti

Fdo. Dr. Joan de Pablo Ribas

ABSTRACT

Due to the nuclear testing, reentry and disintegration of nuclear powered satellites, nuclear reactor accidents, uranium nuclear fuel cycle and nuclear weapons production, actinides have been introduced into the environment. Proposed disposal of high-level radioactive waste in mined repositories in geologic formation as well as the storage and disposal of uranium and plutonium from weapons dismantlement are further possible sources for actinide releases to the environment. The mobilization of radionuclides in the environment has been studied for many years with the prime objective of tracing the routes by which they accumulate in the food chain and become available for human consumption. Therefore, it is necessary to have available accurate, reliable and precise analytical methods to determine actinides and fission products in environmental samples as well as their isotopic ratio. These procedures should also be as fast as possible in order to give results in radiological emergency cases to take decision for radiation protection of the environment and human beings.

In this Ph.D. thesis, different kinds of phases for liquid chromatography have been tested to achieve the separation of the interfering elements and isotopes before the mass spectrometry and α -spectrometry measurements. UTEVA and TEVA extraction resin (Eichrom Industries, USA) have been packed in chromatographic column as stationary phases and used for the separation of tri, tetra and hexavalent actinides and for the separation of trivalent lanthanides (La-Eu) and actinides, respectively. IonPac CS5A and CS10 (Dionex, Sunnyvale, USA) ion chromatography column were used for the simultaneous separation of actinide and lanthanides elements and for the actinides separation. The columns were coupled on-line to an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) to solve isobaric interferences between actinide and lanthanide elements and off-line to a α -spectrometer to solve the energy interferences between the analytes. Moreover, an investigation on the use of the UTEVA resin and IonPac Trace Cation Concentrator II column (TCC-II from Dionex, Sunnyvale, USA) as preconcentrator columns for actinide and lanthanide elements has been carried-out.

The analytical measurements have been made by mass spectrometric as well as by radiometric techniques. ICP-MS has been used for the characterization of spent

nuclear fuels in terms of actinides and lanthanides content and burn-up calculation as well as for the determination of the long-lived actinides and lanthanides in environmental samples. α - and γ -spectrometry have been used for ^{241}Am determination in sediments and soils samples. γ -spectrometry and Liquid Scintillation Counting (LSC) have been used to analyze the eluted fractions from on-batch experiments.

The results obtained with the analytical procedures developed, for spent nuclear fuel solutions as well as for environmental samples, were always compared to those obtained by other independent techniques and good agreements have been always achieved.

LIST OF PUBLICATIONS

This thesis is based on the following publications, which will be referred to in the text by their Roman numerals.

- I. L. Perna, J. M. Barrero Moreno, M. Betti and R. Fuoco, **Investigation on the use of UTEVA as stationary phase for chromatographic separation of actinides on-line to inductively coupled plasma mass spectrometry**, *J. Anal. At. Spectrom.*, **16**, 26-31, 2001.
- II. L. Perna, F. Bocci, L. Aldave de las Heras, J. De Pablo and M. Betti, **Studies on the simultaneous separation and determination of lanthanides and actinides by ion chromatography inductively coupled plasma mass spectrometry combined with isotope dilution mass spectrometry**, *J. Anal. At. Spectrom.*, **17**, 1166-1171, 2002.
- III. L. Perna, J. Jernström, L. Aldave de las Heras, J. de Pablo and M. Betti, **Sample clean-up by on-line chromatography for the determination of Am in sediments and soils by alpha spectrometry**, *Analytical Chemistry*, accepted.
- IV. L. Perna, J. Jernström, L. Aldave de las Heras, E. Hrncsek, J. de Pablo and M. Betti, **Characterisation of radioactively contaminated marine sediment core by radiometric and mass spectrometric techniques**, *Journal of Radioanalytical and Nuclear Chemistry*, submitted.

Acknowledgements

This work was carried out during the years 2000-2003 at the Institute for Transuranium Elements (ITU) in the Nuclear Chemistry unit, European Commission, Joint Research Centre in Karlsruhe (Germany) with a grant from the European Commission.

I wish to express my deepest thanks to Prof. Dr. Maria Betti for her support, interest and valuable discussion. It was an honour to work with you. I would also like to thank Dr. Laura Aldave de las Heras who helped me in all stages of the thesis. I gratefully acknowledge Professor Dr. Juan de Pablo, who made it possible for me to study at the Technical University of Catalunya, Dr. Javier Giménez and Mrs. Irene Pérez who helped me with the university bureaucracy.

I am greatly indebted to Dr. Erich Hrncsek, who introduced me to the radiometric methods, and to Mr. Jussi Jernström, who helped me a lot with the laboratory work.

Many thanks to all my colleagues from the Analytical Chemistry Sector who contributed much to this work: Olivier Bildstein, Tanja Huber, Jussi Jernström, Paula Juntunen, Monia Kraiem, Aurélien Pitois, Francesca Schiavo, Gabriele Tamborini and Nadine Steinhübel.

Warmest thanks to Mr Franco Capone and Mrs. Maria Betti who “adopted” me during these three years in Germany.

I would also like to acknowledge Dr. J. Magill, Dr. S. Stürup, Dr. E. Hrncsek, and Dr. S. Becker who revised the thesis.

My deepest thanks to my family and all my friends for their support.

Karlsruhe, April 2003

Lorenzo Perna

TABLE OF CONTENTS

ABSTRACT	i
LIST OF PUBLICATIONS	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
1. INTRODUCTION	1
2. ACTINIDES	6
2.1 Thorium	6
2.1.1 Thorium solution chemistry	7
2.2 Neptunium	8
2.2.1 Neptunium solution chemistry	8
2.3 Uranium	9
2.3.1 Uranium solution chemistry	10
2.4 Plutonium	11
2.4.1 Plutonium solution chemistry	11
2.5 Americium	12
2.5.1 Americium solution chemistry	13
2.6 Curium	13
2.6.1 Curium solution chemistry	13
3. STATIONARY PHASES	15
3.1 Extraction chromatography	15
3.1.1 UTEVA resin	15
3.1.2 TEVA resin	16
3.2 Ion chromatography	17
3.2.1 IonPac CS5A column	17
3.2.2 IonPac CS10 column	18
3.3 Preconcentration	19

3.3.1 IonPac TCC-II column	19
3.3.2 Eichrom resins	19
4. MEASUREMENT TECHNIQUES AND SAMPLE PREPARATIONS	21
4.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	21
4.1.1 Isotopic dilution analysis (IDA)	23
4.1.2 Spent fuel sample preparation	24
4.1.3 Environmental sample preparation for ICP-MS	24
4.2 α -spectrometry	25
4.2.1 α -spectrometry sample preparation	26
4.2.2 Environmental sample preparation for α -spectrometry	27
4.3 ICP-MS and α -spectrometry comparison	27
4.4 γ -spectroscopy	28
4.5 Liquid scintillation counter (LSC)	30
5. RESULT AND DISCUSSIONS	31
5.1 UTEVA resin	31
5.1.1 Optimisation of the oxalic acid concentration	31
5.1.2 Extractant loss	34
5.2 IonPac TCC-II column	35
5.3 TEVA column	38
5.3.1 Behaviour of actinide elements on TEVA column	39
5.3.2 Extraction Mechanism	40
6. CONCLUSIONS	45
7. REFERENCES	47

1 INTRODUCTION

A variety of systems and processes may introduce radioactivity into the environment. Human activities involving nuclear weapons and the nuclear fuel cycle may lead to a significant creation and release of radioactivity¹. Modern nuclear weapons produce radioactivity from the fission, fusion and neutron activation processes². The type and the composition of a nuclear device markedly affect the kinds of radioactivity produced, while the location and size of the detonation determine the quantity of radioactivity released to the biosphere². Atmospheric nuclear weapons testing, conducted from 1945 until 1980, have introduced the majority of the deposited fractions of actinides onto the earth's surface¹.

The nuclear fuel cycle, schematically represented in Figure 1³, includes mining, milling, fuel enrichment, fabrication, reactor operation, spent fuel storage, reprocessing facilities and waste storage. Every single process may lead to the releases of different radionuclides in different amounts into the environment².

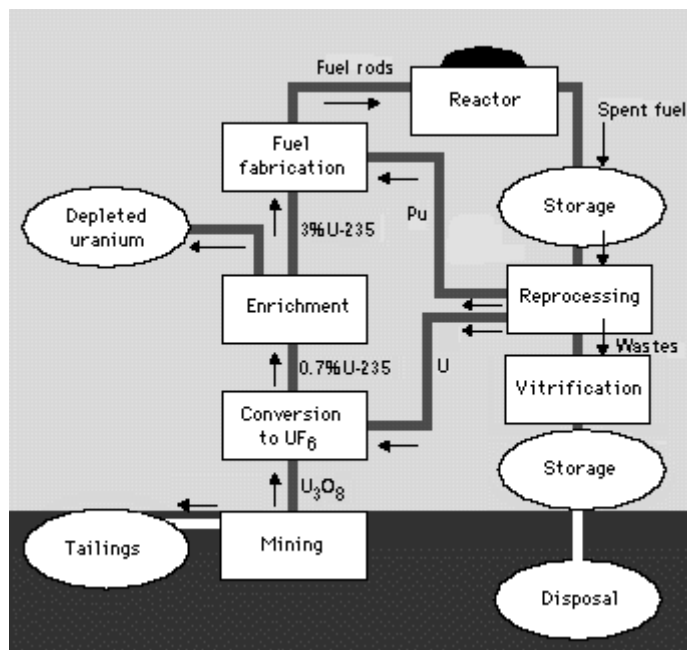


Figure 1. The uranium fuel cycle³.

During the enrichment process of uranium hexafluoride, depleted uranium is obtained as by-product⁴. Depleted uranium, due to its high density which is twice that of lead, has been used in civil and military applications. For instance, it has been used as

counterweights and ballast in aircraft, for radiation shields in medical equipment, as material for containers for transport of radioactive materials as well as in ammunition designed to penetrate armour plate and to reinforce military vehicles, such as tanks. Depleted uranium ammunitions have been used during the Gulf war and the conflicts in Bosnia-Herzegovina as well as in Kosovo. Radiological assessments on the effects of dispersion of uranium into the environment as well as investigations of the chemical- and radio-toxicity of uranium have been carrying out⁴.

Nuclear accidents are other important sources of non-routine releases of radioactivity into the environment. Accidents include an explosion in a waste storage tank, Kyshtym, former USSR (1957), and those involving nuclear reactors at Windscale, UK (1957); Three Mile Island, USA (1978), Chernobyl, former USSR (1986)². Accidental damage to nuclear weapons has resulted in the release of fissile material: Palomares, Spain (1966); Thule, Greenland (1968)⁷. Additional releases have occurred upon re-entry of satellites powered by nuclear sources [629 TBq ²³⁸Pu source], such as SNAP 9-A (1964) [629 TBq ²³⁸Pu source] and Cosmos 954 (1978)⁸.

The determination of long-lived radionuclides, like long-lived fission products and actinides, is of great importance. For instance, the determination of their isotopes is essential in nuclear waste management, due to their long radioactive half-lives, high radiological toxicity and criticality concerns. Moreover actinide isotope determinations are necessary for waste classification purposes⁹. In the environmental radiochemistry, isotope speciation is of relevance in order to study transfer and migration mechanisms related to the geological¹⁰ and cosmic¹¹ samples, including age determinations¹² as well as bioavailability studies^{13,14}.

The burn-up of the nuclear material dispersed in the environment or spent nuclear fuel is an important parameter representative for the energy produced during the reactor irradiation. It is defined as the percentage atomic ratio between the fissioned heavy metal (HM) and the total pre-irradiated HM content. Normally, the fissioned HM content is determined by measuring the ¹⁴⁸Nd content in the spent nuclear fuel solution. ¹⁴⁸Nd has been selected because it is a stable fission product, its fission yield is well known, and because it has a low adsorption cross-section for the thermal neutron. The concentration of this nuclide in the spent fuel is proportional to the total fission number

occurred, from which the burn-up is calculated. This parameter is important also in environmental monitoring since can give information about the source term.^{5,6}.

Nowadays, man made radionuclides constitute an important class of environmental contaminants. Therefore it is very important to have accurate, reliable and precise analytical methods in order to detect radionuclides both in environmental samples, to study their migration mechanism and accumulation as well as for the characterization of spent nuclear fuels which radionuclides can stemm from. Moreover, because the high radio-toxicity of artificial actinide and fission product elements and isotopes, these analytical procedures have to achieve very low detection limits.

Radiometry and mass spectrometry are two powerful and complementary techniques for the determination of concentrations and ratios of actinide isotopes.

Compared to the radiometric methods, mass spectrometric-based instrumental techniques offer the best detection limits for the determination of the long-lived radionuclides¹⁵⁻¹⁹. Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) is at the present the most widely used technique, due to its multi-elemental capability and very low detection limits^{20,21}. Also Isotope Dilution Mass Spectrometric (ID-MS) analysis can be applied to attain very accurate results^{22,23}. Nevertheless, in all mass spectrometers the analytical figures of merit are limited by spectroscopic and non-spectroscopic interferences. Spectroscopic interferences are caused by atomic or molecular ions having the same nominal mass as the analyte isotope of interest. Recently, the use of instruments based on double-focusing mass spectrometers has been proposed in order to overcome such interferences²⁴. In the case of spectroscopic interferences due to isobars of different elements even the high resolution of sector fields is insufficient. In this case a chemical separation of the interfering elements is required before mass spectrometric analysis. The application of chromatographic separation coupled on-line to a mass spectrometric detector is very efficient for this purpose²⁵⁻²⁸. For instance, High Performance Liquid Chromatography (HPLC)-ICP-MS on-line coupling has been applied for the separation of long-lived radionuclides and stable isotopes of lanthanides in a tantalum target from a spallation neutron source irradiated with 800 MeV protons in order to determine the spallation nuclides^{29,30}. Other authors have coupled on-line solid phase extraction chromatography³¹ as well as

chelation ion chromatography³² with sector-field ICP-MS for the determination of trace amounts of actinides in environmental and biological samples.

For the determination by radiometric methods, the separation of the radionuclides as radiochemically pure samples matching the requirements of the applied measurement method (α -spectrometry, liquid scintillation counting (LSC)) is necessary. Determination of americium, plutonium and uranium in environmental samples by alpha spectrometry requires several radiochemical procedures to separate these nuclides from the matrix. The following steps must be performed: conversion of the analytes associated with the matrix into a soluble form, radiochemical separation and preparation of the source for measurement³. Many chemical separation procedures for uranium, plutonium and americium based on anion exchange chromatography³³, solvent extraction³⁴ and extraction chromatography^{35,36} have been investigated in spent fuel and environmental samples. The main difficulties encountered in the analysis of environmental samples regard the preconcentration of radionuclides from a large soil or sediment sample (e.g. 10-20 g) that has a complex chemical composition. Thus the separation of the radionuclides of interest from chemical elements whose concentration in the sample are several orders of magnitude higher than those of the nuclides investigated is necessary. In addition, the applied procedures need a good chemical yield to ascertain the low detection limit necessary for these procedures³⁷.

The research work of this Ph.D. thesis has been focused on the study of actinide and fission product chromatographic behaviors. The prime objective is to achieve the separation of the different elements studied. These elements have been detected by mass spectrometric as well as radiometric techniques. Different kinds of stationary and mobile phases, sample types, sample preparation methods and redox agents were studied.

The UTEVA resin, which is based on the extraction mechanism, has been used for packing chromatographic columns to be coupled on-line with an ICP-MS detector in order to obtain the actinide separations. By this way, the liquid extraction chromatography combines the selectivity and the flexibility of a conventional technique as liquid-liquid extraction with the versatility and simplicity of a chromatographic

column³⁸. The main advantage of all the extraction resins is the high selectivity for analytes.

A commercially available mixed bed anionic/cationic chromatographic column (CS5A) has been used to achieve the simultaneous determination of actinide (Np, U, Pu, Am and Cm) and lanthanide elements. The chromatographic columns were coupled on-line to an ICP-MS. This procedure has been exploited for the characterization of spent nuclear fuels and the results obtained were in good agreement with those obtained using other separation procedures. Moreover, in comparison to the previous developed procedures, the times of analysis and sample handling are drastically reduced.

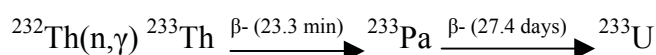
A procedure, based on the combination of different kind of chromatographic mechanisms, has been developed for the Am determination in environmental sample. The method is based on the use of three chromatographic columns. TEVA resin was packed as stationary phase in a chromatographic column to carry out the lanthanides (La-Eu)/trivalent actinides separation. A CS5A column was used to separate Am from lanthanides impurities and other actinides. A trace cation concentrator (TCC-II) column was used to connect the TEVA to the CS5A acting as pre-concentrator column for trivalent ions. The behavior of the columns was studied coupling the chromatograph to an ICP-MS. The chromatographic system has been exploited for sample preparation for α -spectrometry determinations. The procedure has been applied to sediment core samples from Irish Sea.

2 ACTINIDES

The actinide elements include Ac, Th, Pa, U and the transuranium elements Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr. All actinides are radioactive elements. In the actinide element series, the 5f-electron shell is filled, analogous to the 4f shell of the lanthanides³⁹. The chemical similarity between the lanthanides and actinides was recognised nearly 50 years ago. However, there exist differences in the oxidation states⁴⁰. Actinides can exist in many different oxidation states, unlike the lanthanides in aqueous solution exist only in the trivalent state⁴¹. The knowledge of the chemical behavior of the actinide elements in aqueous solution (oxidation states, hydrolysis and complexation) is indispensable during the development of analytical procedure for their determination from complex mixture. In the following paragraphs the nuclear properties and the solution chemistry of the actinide elements studied are briefly described.

2.1 THORIUM

Thorium is widely distributed on the earth's crust and its content is about 12 $\mu\text{g/g}$ ⁴². The element was discovered by Berzelius in 1828 which isolated Th from the black silica (ThSiO_4 : Thorite). In 1898 Curie and Smith, independently, discovered the radioactive properties of Th³⁹. The largest potential use of the element is in nuclear energy. The isotope ^{233}U , which is fissionable with slow neutrons, is formed from ^{232}Th by the following series of nuclear reaction³:



Th has isotopes with masses comprise between 210 and 238⁴³. The ^{229}Th is formed by α -decay of ^{233}U . The most interesting isotopes from the radiochemistry point of view are ^{232}Th (the most stable and abundant in nature), ^{230}Th , ^{229}Th (used as tracer for α -spectrometry) and ^{228}Th . In figure 2 the natural ^{232}Th decay chain is reported.

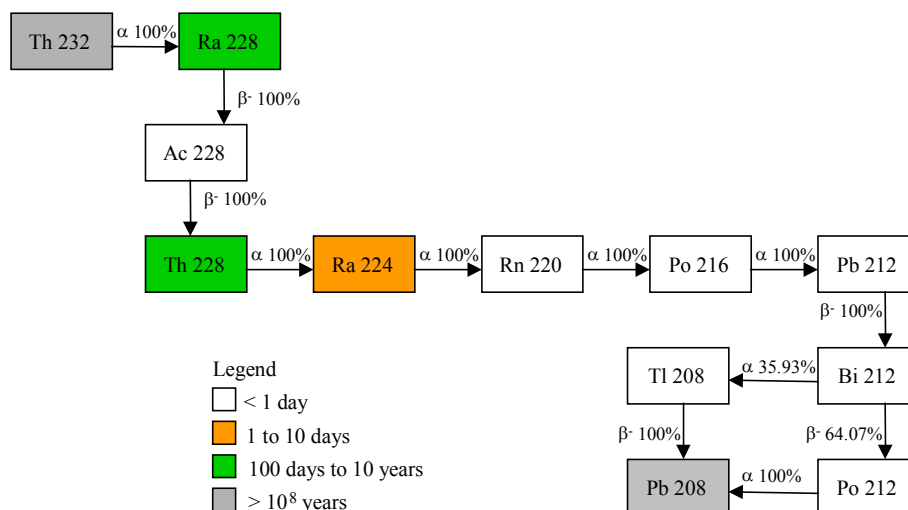


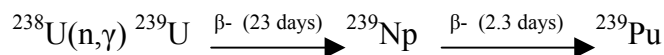
Figure 2. Natural ^{232}Th decay chain.

2.1.1 THORIUM SOLUTION CHEMISTRY

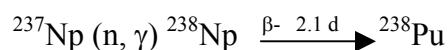
Thorium exhibits in aqueous solution only in the oxidation state IV, independently of the pH and the potential of the solution³⁹. The hydrolysis of Th(IV) is complex. The uncomplexed cation (Th^{4+}) is stable at pH value of 3 or less. Several polymeric hydrolysis products such as $\text{Th}(\text{OH})^{3+}$, $\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_4(\text{OH})_{12}^{4+}$ and $\text{Th}_6(\text{OH})_{15}^{9+}$ have been proposed^{44,45}, the nature of these species is depending on the ionic strength and hydrolysing medium. Thorium shows a strong tendency to form complexes with anions. Evidence exist for complexes with fluoride, bromide, nitrate, chlorate and phosphate. Thorium will form complexes also with most anions of organic acids as formate, acetate, oxalate, malate and citrate³⁹. Some thorium chelates, of considerable practical importance, are those that Th forms with the various organophosphoric acids (monobasic diorganic phosphates, phosphates and phosphonic acids in particular)⁴⁶⁻⁴⁹. The combination of high charge and low extent of hydrolysis makes Th readily adsorbed on cation exchangers. Separations from other cations are thereby facilitated, even when Th is present in trace concentration³⁹. In acid media, Th has been separated from trivalent and divalent cations by cation-exchange⁵⁰. In addition, the absorption of Th from aqueous⁵¹ and non-aqueous⁵² media by anion-exchange resins has been reported.

2.2 NEPTUNIUM

Neptunium, the first transuranium element identified, was discovered by McMillan and Abelson in 1940, during neutronic irradiation of ^{238}U according to the following reaction³⁹:



Np has several isotopes with atomic masses between 225 and 244⁴³, but only ^{237}Np has a half-life sufficiently long to be measured by mass-spectrometry. In α -spectroscopy the short-lived ^{239}Np is normally employed as a spike. Production of ^{237}Np is becoming important because of the increasing use of ^{238}Pu in batteries for power sources in space vehicles, terrestrial navigation beacons and medical devices². ^{237}Np is the starting material for the production of ^{238}Pu according to the reaction:



2.2.1 NEPTUNIUM SOLUTION CHEMISTRY

In aqueous solution Np exhibits all oxidation states from III to VII⁵³. The stability of these ions may be strongly affected by pH and complexing ligands. In diluted acid solution, in absence of strong redox agents, the most stable oxidation state is V³⁹. Np(III) is produced by electrolysis, in aqueous solution, under inert atmosphere or by hydrogen catalytic reduction⁵⁴. Np in diluted acid solution can be quantitatively stabilised in the tetravalent state with strong reducing agent as Fe^{2+} as well as in the hexavalent state with strong oxidant as Ce(IV) ⁴¹. Differently from the UO_2^+ and PuO_2^+ ions, NpO_2^+ is stable in aqueous solutions. NpO_2^+ disproportionates in Np(IV) and Np(VI) in presence of fluorides or sulphates in strongly acid media³⁹. Hexavalent neptunium is stable in both acid and basic media. Np(VII) can be obtained by Np(IV) oxidation with ozone in alkaline media, Xe(VI, VII) oxygen compounds, hypochloride, hypobromide or by electrolysis on Pt anode⁵³.

Cation exchangers, because of their low selectivity, are normally not employed for the Np separation from other actinide elements³⁹. Np has been quantitatively separated by anion exchangers, using redox reagents in order to convert selectively the actinides in different oxidation states, which were eluted at different elution times⁵⁵⁻⁵⁷.

Np(IV and VI) is quantitatively extracted from nitric aqueous solution by TBP^{36,39} as well as by diamyl amyolphosonate (DAAP)³⁵. Its extraction is hindered by the presence in solution of complexant agents as phosphate, oxalate, fluoride, thiocyanate and sulphate which form stable complexes^{35,36,39}.

2.3 URANIUM

The uranium content in the earth crust is about 2 ppm. It is distributed in three natural isotopes with mass 234, 235 and 238 with a natural abundance of 0.005, 0.720 and 99.275 %, respectively⁵⁸. ²³⁵U is important from the energetic point of view, because of its use in nuclear power reactors (1 kg of ²³⁵U supplies 2 10⁷ kW/h)³⁹. Moreover, from ²³⁵U other important nuclides can be produced. A large number of synthetic isotopes of uranium have been prepared³⁹. The isotope ²³³U is particularly important, because it also undergoes fission with slow neutrons. Some of the other synthetic isotopes have utility as tracer for uranium (β -emitting ²³⁷U, α -emitting ²³²U and ²³³U in mass-spectrometry).

In figure 3 and 4 are reported the two natural decay chains for ²³⁵U and ²³⁸U.

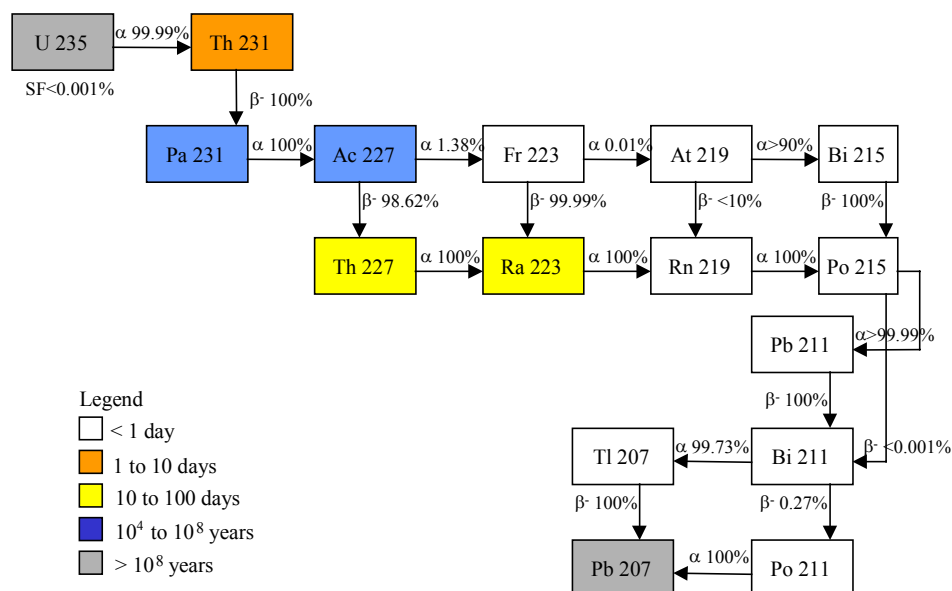


Figure 3. Natural ²³⁵U decay chain.

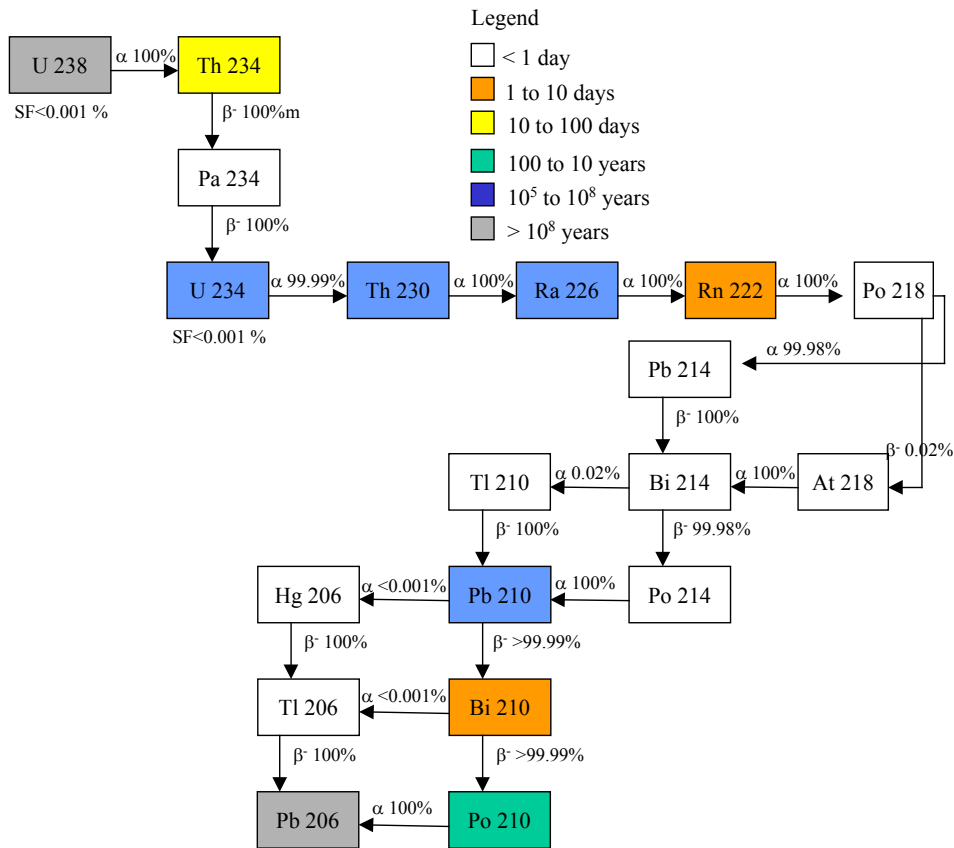
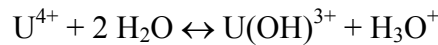


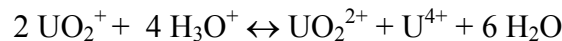
Figure 4. Natural ²³⁸U decay chain.

2.3.1 URANIUM SOLUTION CHEMISTRY

Uranium can be present in solution in four different oxidation states: III, IV, V and VI⁵⁹. U³⁺ ion is stable only in sulphuric, perchloric and halogen acid solutions is otherwise rapidly oxidised to U(IV)⁵⁹. U(IV) in acid solution is present as U⁴⁺ ion; U(IV) salt solutions are acid because the hydrolysis reaction of the U⁴⁺ ions³⁹:



The U⁴⁺ oxidation reaction to UO₂²⁺ in acid solution is slow and it is controlled by the hydroxy complex concentration especially the U(OH)³⁺ ion⁶⁰. U is present in oxidation state V as UO₂⁺, this ion is unstable and it disproportionates to U(IV) and U(VI)⁶¹.

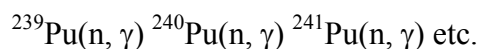


U(VI) is the most stable state for uranium, at pH < 3 U is present in solution as uranyl (UO₂²⁺). For pH > 3 the hydrolysis forms several compound such as [UO₂(OH)]⁺, [(UO₂)₂(OH)₂]²⁺, [(UO₂)₃(OH)₅]⁺, [UO₂(OH)₃]⁻, [UO₂(OH)₂], [(UO₂)₃(OH)₇]⁻ and [(UO₂)₄(OH)₇]⁺.⁶²

Extraction and ion exchange resins can be used to achieve the U separation from the other elements in a single operation. The ion exchangers exploit the capability of U to form anionic complexes with the acid anions (Cl^- , SO_4^{2-} , CO_3^{2-} , CH_3COO^- , SCN^-)⁶³. These anionic complexes are strongly adsorbed from quaternary amine. U can be subsequently eluted from the resin with strong acids^{18,39}. The cationic resins, because their low selectivity, are not widely used for the U separation. Extraction resins have been used for the U isolation in a broad concentration range. The use of complexant and redox agents lead to a pure U fraction⁶³. The most exploited extractant is the TBP, that in concentrated nitric solutions (3-8 M) lead to quantitative recoveries³⁹. Also quaternary amine has been used as extractant in chromatographic resin. The extraction mechanism is analogous to the anion exchange, anionic uranyl complexes are rapidly extracted from the solution to the stationary phase^{39,64,65}. Also strong complexant agent as (1-3)- β diketones and 8-hydroxyquinoline have been tested but the extraction mechanism is strongly depending on the pH and the selectivity is lower compared to TBP and quaternary amine³⁹.

2.4 PLUTONIUM

Plutonium-238 was first produced in 1940 by Seaborg *et al.* by bombarding uranium with deuterons³⁹. ^{239}Pu is the most important plutonium isotope because it is used in nuclear fuel as well as in nuclear weapon. The ^{239}Pu half-life is sufficiently long to permit the preparation of this isotope in large-scale amounts. The higher plutonium isotopes are formed as result of successive neutron capture by the various plutonium isotopes⁶⁶:



The isotopes ^{236}Pu and ^{242}Pu are normally employed as tracers in α -spectrometry, ^{244}Pu is used as tracer in mass-spectrometry.

2.4.1 PLUTONIUM SOLUTION CHEMISTRY

Plutonium may be present in aqueous solution in five oxidation states: III, IV, V, VI and VII. The lower four oxidation states coexist in dilute aqueous solution in substantial quantities⁶⁷. The lowest oxidation state of plutonium is the trivalent cation Pu^{3+} , which has similar behavior to the neodymium in many of its hydrolysi and

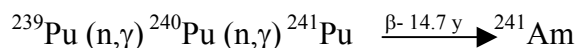
complexation properties³⁹. Pu³⁺ can be oxidized by a variety of oxidants, as nitrite, permanganate and bichromate⁶⁸, to the tetravalent cation Pu⁴⁺. Like other tetravalent cations, it hydrolyzes very easily, forming PuOH³⁺ as the first hydrolysis product and finally the insoluble Pu(OH)₄ (or Pu₂O.*n*H₂O plutonium polymer)³⁹. Oxidation of the tetravalent cation in aqueous solution produces hexavalent plutonium PuO₂²⁺. Careful reduction of PuO₂²⁺ in dilute acids produces pentavalent plutonium PuO₂⁺. This species disproportionates into a mixture of oxidation states⁶⁷. Pu(VII) can be obtained in diluted alkali solution by ozonization, anodic oxidation and treatment with peroxodisulfate⁶⁷.

All the Pu oxidation states are retained from aqueous solution on the cationic exchangers³⁹. Pu(IV) as well as Pu(VI) form anionic complexes in hydrochloric solutions, these complexes are retained on anionic exchanger resins. Pu(IV) in concentrated nitric solution forms an hexa-nitrate complex [Pu(NO₃)₆]²⁻ that is also retained in anionic resins. Therefore, both types of exchangers can be used for the Pu separation from actinide and lanthanide elements⁶⁶.

Pu can be easily extracted from pure nitric solution. However, the extraction is hindered by the presence in solution of complexant agents as phosphate, oxalate, fluoride and sulphate³⁹. Moreover, Pu is usually extracted together with other actinide elements. Since, according to the oxidation state, Pu has a different value of the repartition coefficient on the extraction resin, its isolation from other actinides can be achieved changing its oxidation state in the aqueous solution as well as in the stationary phase^{64,65,69}.

2.5 AMERICIUM

Americium was discovered by Seaborg *et al.* in 1944. The reaction used was:



This reaction is still the best source of the pure ²⁴¹Am available today³⁹. ²⁴¹Am is an alpha emitter with half-life of 433 years. Americium has several isotopes with atomic mass between 231 and 249⁴³. The longest-lived americium isotope is ²⁴³Am (7380 years), it is normally employed as tracers in mass-spectrometry as well as in alpha spectrometry.

2.5.1 AMERICIUM SOLUTION CHEMISTRY

Americium in aqueous solution can be present in the oxidation states III, IV, V and VI³⁹. Am³⁺ is the most stable cation in aqueous solution, it hydrolyzes very easily, forming AmOH⁺ as first hydrolysis product and then Am(OH)₂⁺ and Am(OH)₃⁶². The tetravalent Am is unstable in non-complexing acid solutions and reduction of Am(IV) to Am(III) occurs spontaneously because the α -radiation effects³⁹. This effect has been reported also for Am(V and VI). In nitric solution Am(IV and V) disproportionates in Am(III) and Am(VI)⁴¹.

Am(III) forms thiocyanate complexes in concentrated thiocyanate solutions⁷⁰. These complexes are sorbed on anion-exchange resins⁷¹⁻⁷⁵. Cation-exchangers sorb strongly Am³⁺ from diluted acid solutions⁷⁶. This property has been exploited for the concentration of Am³⁺ from dilute acid solutions. Am can be extracted by the TBP from aqueous solution together with other actinides. The distribution coefficient values for Am are from 1 to 3 orders of magnitude lower compared to other actinide elements. This property is exploited for its separation^{64,65}.

2.6 CURIUM

The first curium isotope, ²⁴²Cm, was prepared by Seaborg *et al*, in 1944, by cyclotron alpha bombardment of ²³⁹Pu³⁹. Curium has 20 isotopes, all radioactive, with mass ranges from 233 to 252⁴³. The most common isotopes are the ²⁴²Cm and ²⁴⁴Cm, both have been used in radionuclide batteries as power source for space and medical applications². The isotope ²⁴⁸Cm has the highest half-life (3.4 10⁵ years) and it is used as a mass-spectrometry tracer. The short-lived ²⁴³Cm is normally employed as tracer in α -spectrometry.

2.6.1 CURIUM SOLUTION CHEMISTRY

The most important chemical characteristic that distinguishes curium from lighter actinides is the great stability of the oxidation state (III) with respect to oxidation or reduction³⁹. The stability of Cm(III) has been attributed to the relative stability of the half-filled (5f⁷) configuration⁷⁷. The predominance of the oxidation states (III) causes a chemical resemblance to lanthanides. The fluoride, oxalate, phosphate, iodate and hydroxide are essentially water-insoluble and the chloride, perchlorate, nitrate and sulfate are water soluble³⁹. In contrast to Am, the oxidation of

Cm(III) to Cm(IV) is achieved only with very strong oxidising agents⁷⁸⁻⁸⁰. Cm³⁺, as Am³⁺, can be separated from other actinides by cationic exchangers²⁷. It is also possible to separate Cm with anionic exchangers thanks to the capability of Cm to form anionic complexes with nitrate⁸², thiocyanate^{75,83} and oxalate ions⁸⁴. Separation of Am and Cm can be achieved, by cation exchange resins, using a tartrate solution as eluent⁸⁵. Cm is also extracted by TBP in concentrated nitric and hydrochloric solution. Its separation from Am and lanthanides can be achieved in 10-16 M HNO₃, in this condition the Cm distribution coefficient values are relatively higher compared to the other trivalent ions^{64,65,86}.

3 STATIONARY PHASES

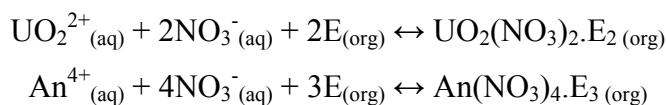
Two different kinds of liquid chromatography have been studied: extraction and ion chromatography. In the following paragraphs the principal characteristics of the two kinds of chromatography together with the description of the stationary phases used are reported.

3.1 EXTRACTION CHROMATOGRAPHY

The extraction chromatography combines the selectivity and the flexibility of a conventional technique as the liquid-liquid extraction with the versatility and the simplicity of a chromatographic column. In this kind of chromatography, the stationary phase consists of an organic complexant that is supported by a porous substrate. The solute retention proceeds from its tendency to form stable complexes with the organic compound sorbed on the surface of the porous substrate. The solute distribution coefficients are often derived, with good results, from the existing data of equivalent systems of liquid-liquid extraction³⁸.

3.1.1 UTEVA RESIN

The UTEVA-Spec. [*Uranium and Tetravalent Actinide Specific*] (Eichrom Industries, USA) is a resin for extraction chromatography. It is able to separate and concentrate uranium and tetravalent actinides from aqueous solutions. The extractant, *diamyl amyolphosphonate* (DAAP), is sorbed on the particles of the porous substrate, Amberlite™ XAD-7 or Amberchrom™ CG-71. The retention or more properly the extraction of the actinides is driven by the formation of the mixed complexes between nitrate or chloride ions, DAAP and actinides³⁵. The formation of these complexes is driven by the concentration of the nitrate or chloride ions in the sample solution. Mason and Griffin, studying the distribution ratio dependency of tetra and hexavalent actinides between a solution of DAAP-dodecane (indicated below as E) and nitric acid, concluded that the extraction proceed by the following reaction⁸⁷⁻⁸⁸:



Other studies demonstrated, according to the reaction described, that the uptake of uranium increases with increasing nitric acid concentration. The nitric and

hydrochloric acid dependency on the capacity factor for actinide ions on UTEVA resin was published by Horwitz *et al*³⁵. The uptake of tetravalent and hexavalent actinides is similar and the sorbed actinides can be eluted from the resin with dilute nitric acid. The addition of a complexant agent to the acid solution, drastically reduces the capacity factors of the actinide ions. The effect of some complexant agents on the actinide capacity factors is described by Horwitz *et al*³⁵. Most of the mono-, di- and trivalent metal ions (e.g. Li, Al, Ca, Am and Cm) are not retained when the concentration of the nitric acid is lower than 6 M³⁵.

UTEVA resin has been applied to a variety of analysis: uranium measurements in environmental samples^{34,89,90}, clean-up of uranium content in samples prior the analysis of other elements⁹¹, sequential determination of uranium, plutonium and americium⁶⁹, measurement of actinides in urine⁹² and in high level waste^{69,93}. In all this procedures the UTEVA resin was always used for the on-batch separations. In this study the use of UTEVA as stationary phase for on-line determination by ICP-MS was investigated [Publication I].

3.1.2 TEVA RESIN

The active component of the TEVA resin (Eichrom Industries, USA) is an aliphatic quaternary amine. As such, it has properties similar to those of typical strong anion exchange resins. However, because the functional groups are in a liquid form, rather than fixed to a polymer backbone, these groups have greater mobility to coordinate around target anions. This means that the uptake of these ions is generally higher at much low acid concentration⁶⁴. TEVA resin provides a simple and effective method for the separation and preconcentration of tetravalent actinides from aqueous solution. Tetravalent plutonium and neptunium are efficiently sorbed from a wide range of nitric and hydrochloric acid concentration⁹⁴. Similarly, thorium is strongly sorbed from nitric acid solution. Under the same conditions, many commonly encountered cations as alkali, alkaline earths, transition metals and fission products are essentially not retained by the resin. The complete behavior of actinide ions in nitric and hydrochloric media has been described by Horwitz *et al*⁶⁴.

TEVA resin has been exploited for technetium analysis⁹⁵⁻⁹⁶, measurement of the tetravalent actinides^{94,97} and separation of trivalent actinides from lanthanides^{71, 98}. In

this Ph.D. thesis the TEVA resin has been packed as a stationary phases in analytical chromatographic column to carry out the lanthanides (La-Eu)/trivalent actinides separation in order to obtain a radiochemically pure fraction of Am [Publication III, IV].

3.2 ION CHROMATOGRAPHY

Ion exchangers are the most widely used stationary phase in ion chromatography. An ion exchanger comprises three important elements: an insoluble matrix, which may be organic or inorganic; fixed ionic sites, either attached to or as an integral part of the matrix; and, associated with these fixed sites, an equivalent amount of ions of charge opposite to that of the fixed sites. The ions with opposite charge are mobile throughout the ion exchanger and most importantly have the ability to exchange with others of the same charge when placed in contact with a solution containing them⁹⁹.

3.2.1 IONPAC CS5A COLUMN

The IonPac CS5A (Dionex, Sunnyvale, USA) is a mixed cation/anionic exchanger. It has been exploited to separate a broad range of chelated metal complexes by anion chromatography as heavy and transition metals and rare earth. The CS5A column is based on a surface-sulfonated polystyrene/divinylbenzene substrate with a particle size of 13 μm and a degree of crosslinking of about 2 %¹⁰⁰. It is a microporous, hydrophobic resin core that has been agglomerated with totally permeable latex particles (150 nm) that are completely aminated¹⁰⁰. The latex particles carry the actual anion exchange function, an alkanol quaternary ammonium group. A schematic representation of this kind of support is given in Figure 5¹⁰¹.

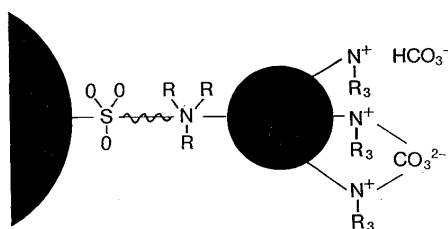


Figure 5: Representation of the CS5A stationary phase¹⁰¹.

The nature of the cross-linked polymeric structure of the packing material makes CS5A column compatible with pH 0-14 eluents which is of particular important for anion exchange¹⁰¹. In this Ph.D. thesis, IonPac CS5A has been used for the determination of lanthanides in spent nuclear fuels as well as for the simultaneous separation and determination of actinide and lanthanide elements [Publication II].

3.2.2 IONPAC CS10 COLUMN

The IonPac CS10 (Dionex, Sunnyvale, USA) is a latex cation exchanger normally employed for the simultaneous analysis of alkali and alkaline-earth metals and for actinide determinations. Its support material is composed of a highly cross-linked ethylvinylbenzene/divinylbenzene copolymer with a particle size of 8 μm ¹⁰². This support is manufactured as follow: at the time of polymerisation, the individual particles are furnished with a reactive surface to which a monolayer of a fully aminated colloidal polymer particle is covalently bound¹⁰¹. A schematic representation of this kind of support is given in Figure 6.

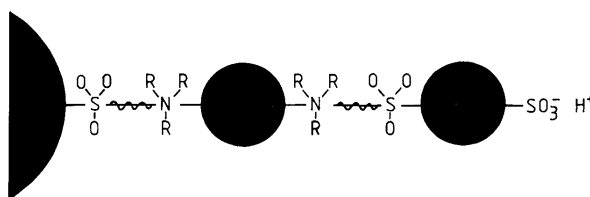


Figure 6: Representation of the CS10 stationary phase¹⁰¹.

However, the fully aminated polymer particles act only as anchor groups for the second layer of latex beads, carrying the actual exchange function in form of sulfonate groups. The covalent bond of the latex beads to the support material provides a high mechanical and chemical stability for this stationary phase and allows operating with a higher flow rate without a significant decrease of the separation efficiency¹⁰¹. In this Ph.D. thesis the IonPac CS10 has been used for the determination of actinides in spent fuel solutions [Publications I and II].

3.3 PRECONCENTRATION PHASES

The actinide elements are normally released into the environment at very low concentration levels. Due to their high toxicity it is very important to develop analytical procedures able to pre-concentrate them from the matrix reaching lower detection limits. Several methods based on ion chromatography¹⁰³⁻¹⁰⁵, liquid-liquid extraction¹⁰⁶, selective precipitation¹⁰⁷, extraction chromatography¹⁰⁸ or a combination of these techniques¹⁰⁹ have been reported in the literature. Between those, the selective precipitation method is not effective in case of trace and ultra trace analysis. Liquid-liquid extraction produces large volumes of organic waste and is very time consuming³⁹. Nowadays, Eichrom and Dionex have developed stationary phases, for extraction and ion chromatography respectively, which are able to uptake different kinds of ions from diluted aqueous solutions, appropriate for preconcentration purposes.

3.3.1 IONPAC TCC-II COLUMN

The IonPac Trace Cation Concentrator (TCC-II from Dionex, Sunnyvale, USA) is packed with a styrene/divinylbenzene copolymer that is surface sulfonated. The high degree of crosslinking yields to a high physical rigidity of this resin and allows the TCC-II to be used with flow rates up to 3 ml/min and pressures of 4000 psi¹¹⁰. The function of the TCC-II is to strip trivalent, tetravalent and hexavalent ions from a measured volume of a relatively clean aqueous sample matrix. This process concentrates the desired analyte species onto the TCC-II leading to a lowering of detection limits by 2-5 orders of magnitude. The advantage of the TCC-II is the capability of performing routine trace analyses without extensive and laborious sample pretreatment¹¹⁰. The TCC-II has been used in this Ph.D. thesis for the trivalent ions concentration before their separation on the CS5A column [Publication III, IV].

3.3.2 EICHROM RESINS

All the Eichrom resins hold a highly selective extraction agent, normally employed for the treatment of nuclear waste in reprocessing plants, adsorbed on a inert substrate. These resins are able to uptake selectively tri, tetra and hexavalent actinides from aqueous solutions. In the on-batch preconcentration procedure the sample solution is loaded in a 2 ml Teflon column with a flow rate of 0.5 ml/min. The actinides are

extracted from the agent present on the stationary phase and are consequently eluted with few millilitres of an appropriate eluent. This procedure leads to a pre-concentration factor of 10-100. In this Ph.D. thesis UTEVA resin has been used for the simultaneous pre-concentration and separation of actinides [Publication I].

4 MEASUREMENT TECHNIQUES AND SAMPLE PREPARATION

All the analytical procedures reported in this Ph.D. thesis, have been basically developed by the use of ICP-MS [Publications I, II and III]. Due to the very small americium concentration in sediment samples [mBq/g or fg/g] its measurements have been performed by α - and γ -spectrometry [Publications III and IV]. Liquid scintillation counting (LSC) and γ -spectrometry were used to analyze the liquid fractions from on-batch experiments. The instrumentation used along with the sample preparation necessary are below briefly described.

4.1 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

An Elan 5000 ICP-MS instrument (Perkin Elmer SCIEX, Thornhill, Ontario, Canada) modified to handle radioactive samples in a glove-box was used^{111,112}. In Figure 7 a photograph of the glove-box ICP-MS system is shown.

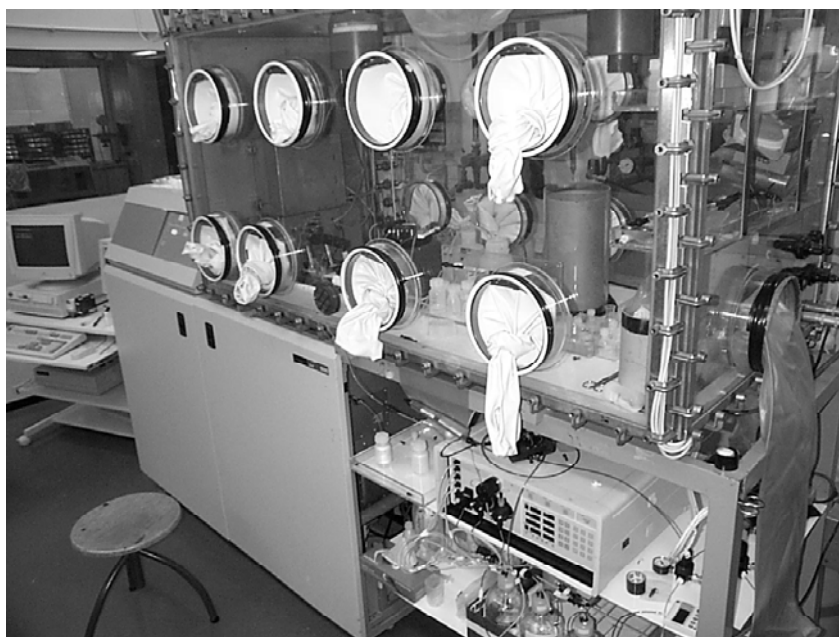


Figure 7. A glove box ICP-MS system installed in the hot laboratory.

The glove-box is constituted of a metallic structure with polycarbonate walls, which shield the α - and β -radiation coming from the samples. The ICP-MS has been coupled with a GP 50 Dionex (Sunnyvale, CA, USA) chromatograph located outside the glove-

box. A pneumatically activated four ways high pressure valve Dionex (Sunnyvale, CA, USA), located inside the glove-box, was used for sample injection into the analytical column, which was finally connected directly to the cross-flow nebulizer. An injection valve along with the analytical columns, to be used with inactive samples, was also installed outside the glove-box. In this case, the effluent from the analytical column entered the glove-box by a small tube through a filter and was connected directly to the nebulizer. Different loops (50, 100, 250 μ l) were used for the measurements. To carry out the on-line sample preconcentration, the valve was modified as described in the publication I. Helium gas was used for degassing the eluents and to activate the injection valve from the chromatograph automatically. The waste from the spray chamber was pumped out with a two ways peristaltic pump (Gilson, Villiersle-Bel, France) and stored inside the glove-box. All gas inlets into the glove-box were provided with stainless steel filters (3 μ m pore size)¹¹³. The interface between the plasma and the mass spectrometer was placed on the outside of the glove-box and connected to the glove-box frame with a water-cooled flange provided with O-rings and fixed in front of the interface. The plasma torch, spray chamber, nebulizer and Tesla igniter were mounted on a moving rail in order to facilitate the maintenance of the plasma source¹¹⁴. Figure 8 shows a diagram of the glove-box ICP-MS system.

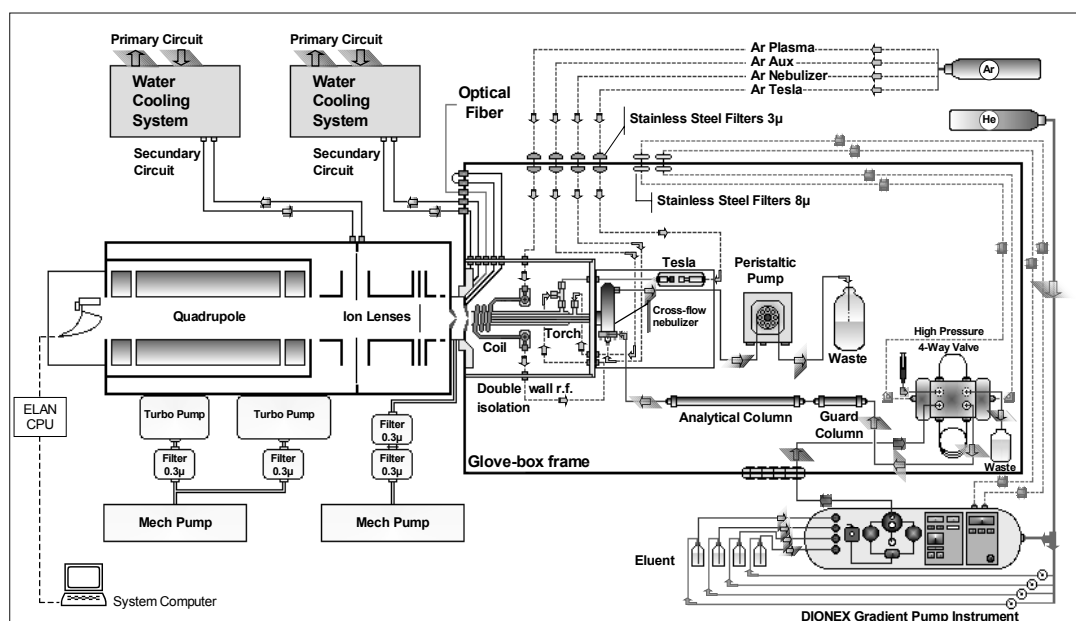


Figure 8. A schematic diagram of the glove-box ICP-MS.

The operation conditions of the ICP-MS were changed according to the nature of the analytes measured. The optimizations have been done by the use of 10 pg/g standard solutions and are reported in the publications I, II and III.

4.1.1 ISOTOPIC DILUTION ANALYSIS (IDA)

Mass spectrometry is a very sensitive method, but highly accurate and precise results can be obtained only with the isotopic dilution technique¹¹⁵. The application of isotopic dilution to mass spectrometry enables to obtain very precise results even for determinations at ultra-trace levels¹¹⁶.

The principle of IDA involves the measurement of the change in isotopic ratio when a known quantity of a spike isotope, normally a stable or long-lived isotope, is added to the sample. From the certified and/or measured isotope abundances both in the sample, the spike and in the mixture, the concentration of the element in the sample can be calculated¹¹⁵⁻¹¹⁷. Obviously the element should be present under the same chemical form in the sample and in the spike¹¹⁸. To attain high precision on the quantitative determination of the sample, a proper choice of the sample to spike ratio has to be made. This implies the estimation of the unknown analyte in the sample. Moreover, in all the analysis measurements of blank solutions have to be performed. In this Ph.D. thesis the IDA has been applied for the determination of Nd, Cm, Am, U and Pu. [Publications II]. The equation used¹¹⁷ was:

$$C_S = C_{Sp} \times \left(\frac{W_{Sp}}{W_S} \right) \times \left(\frac{Aw_S}{Aw_{Sp}} \right) \times \left(\frac{A_{Sp}^a}{A_S^b} \right) \times \left(\frac{R_M - R_{Sp}}{1 - R_M \times R_S} \right)$$

Where C_S is the unknown concentration of the element in the sample (S) and C_{Sp} the concentration of the element in the spike (Sp). W_S and W_{Sp} are the weights taken from the sample and spike, respectively. Aw_S and Aw_{Sp} are the elemental atomic weights in the sample and spike, respectively. A_{Sp}^a is the isotope abundance (At%) of the reference isotope in the spike (isotope a) and A_S^b is the isotope abundance (At%) of the reference isotope in the sample (isotope b). R_M and R_{Sp} are the atomic ratios (isotope b/isotope a) in the mixture and spike respectively and R_S is the atomic ratio (isotope a/isotope b) in the sample¹¹⁷.

4.1.2 SPENT FUEL SAMPLE PREPARATION

The dissolutions of the spent nuclear fuels were made in the hot-cell facilities installed at EU-JRC-ITU (Figure 9). This kind of facilities are shielded from γ and neutron radiation with a lead wall which allowed to work with high radioactive samples, as the spent fuels. The manipulation of the sample, inside the hot-cell, is performed by the use of master-slave telemanipulators.

Fuels pellets (*ca.* 30 g) of spent nuclear fuels were dissolved in 7 M HNO_3 in a hot-cell facility by refluxing and the resulting solution was diluted with 4 M HNO_3 . A second dilution by mass was performed using 1 M HNO_3 , and 5 ml of this solution containing about 100 μg of fuel per gram of solution were transferred into a glove-box for further dilution and spiking. The final samples were then introduced in the ICP-MS glove-box to perform direct as well as HPLC-ICP-MS analyses.



Figure 9: Hot-cell facility installed at EC-JRC-ITU.

4.1.3 ENVIRONMENTAL SAMPLE PREPARATION FOR ICP-MS

The certified sediments IAEA 135 and NIST SRM4355 were analyzed by ICP-MS. The total dissolution of the samples was performed by means of a microwave digester (Alabo, Perkin Elmer, Germany) and ultra-pure acids. Two different rotors were employed for sample dissolution (6MF100, Alabo, Perkin Elmer, Germany) and sample concentration and HF evaporation (6EVAP Alabo, Perkin Elmer, Germany). 4 ml HNO_3 (30 % v/v) and 6 ml HF (48 % v/v) for each gram of sample were added to

the solid sample before starting the dissolution. Dissolved samples were diluted with 1 M nitric acid and different aliquots were prepared. An aliquot was introduced in the glove-box and known amounts of actinides were added before the analysis by ICP-MS [Publication I, II]. Other aliquots were used for the determination of lanthanides without adding active spikes [Publication II].

4.2 α -SPECTROMETRY

When a nuclear particle enters a detector it produces excitation and ionization, both of which can be used for detection. In an α -detector the α -particles create electron-hole pairs, which are separated in the electrical field and collected on their respective contacts. A charge-sensitive preamplifier generates a pulse with amplitude proportional to the incident α -energy. A vacuum is applied between the detector and the radiation source, so that the α -particle energy loss will be minimized¹¹⁹.

α -measurements were performed with an OCTÊTE™ PC (EG&G Ortec) with ULTRA ion-implanted silicon detectors with an active area of 450 mm¹²⁰. These detectors can be cleaned easily, they have a thin and rug front contact, very good energy resolution, low electronic noise, high geometric efficiency and the surface is hard-wearing. Energy and efficiency calibrations were made with a certified mixed nuclide source (GM810 AEA Technology). Measurements were evaluated with MAESTRO for Windows software (EG&G Ortec) [Publication III, IV].

The efficiency of the α -detectors depends on measurement distance between the sample and the detector¹¹⁹. The most contaminated samples were measured at the distance of 15 mm with an efficiency of 7.8 %. In case of less contaminated samples a shorter distance (3 mm) was used and the efficiency was 33.2 %. The counting time varied between 80000 and 200000 s depending of the sample activity. In figure 10 an example of the α -chambers used are shown. As can be seen in the chambers the distance between sample and detector can be changed according to the sample activity.



Figure 10. α -spectrometer sample chambers.

4.2.1 α -SPECTROMETRY SAMPLE PREPARATION

Sample preparation must convert the raw sample into a form that is suitable for α -spectrometry. This implies two requirements for the preparation:

1. Chemical separation of elements that would produce chemical or radiochemical interferences
2. Production of a thin sample layer

As consequence, Th and Pu have to be chemically separated from Am before the sample preparation. For ^{241}Am at 5.49 MeV the major interferences are ^{238}Pu (5.50 MeV) and ^{228}Th (5.42 MeV). The presence of ^{238}Pu in the Am fraction can be easily detected from the peaks of $^{239(40)}\text{Pu}$ (5.16 MeV) and that of the tracer ^{242}Pu (4.90 MeV). ^{228}Th can be detected from the presence of the peaks of its shorted lived daughter nuclides ^{224}Ra (5.68 MeV), ^{220}Rn (6.29 MeV), ^{216}Po (6.78 MeV), ^{212}Bi (6.09 and 6.05 MeV) and ^{212}Po (8.79 MeV).

Due to their large size, α particles do not penetrate matter deeply (*ca.* $30\mu\text{m}^4$) therefore is necessary to produce the α samples in a very thin layer. Co-precipitation followed by filtration is a fast method used to prepare samples for α -spectrometry. Basically, the method provides for the coprecipitation of the nuclides of interest as either a hydroxide or a fluoride using neodymium as a carrier to produce an extremely finely divided precipitate, which is deposited by filtration over a substrate of neodymium fluoride¹¹⁹. The sample is prepared by filtering the substrate solution

(neodymium fluoride) through a 0.1 μm membrane filter. These very finely divided precipitates plug the filter and provide a very smooth and nearly impenetrable surface upon which the coprecipitated (with neodymium fluoride) americium lies.

4.2.2 ENVIRONMENTAL SAMPLE PREPARATION FOR α -SPECTROMETRY

The transuranium elements were leached from the environmental samples as well as the certified sediment (IAEA 135) and soil (NIST SRM4353A) using the following procedure. Samples were dried at 105 °C for 24 hours and ashed at 450 °C for 8 hours. After addition of the appropriate amount of tracer solution, a 0.25-5 g aliquot of the sample was leached on a hot plate for 4 hours with 200 ml 7.2 M HNO_3 . After leaching, the solution was filtered with Schleicher & Schuell 589³™ blue ribbon ashless filter paper. An oxalate coprecipitation has been applied in order to concentrate and purify americium from the majority of leached matrix constituents. For this purpose 1 g of oxalic acid per gram of sample leached was added to the leached solution. Calcium chloride was added to ensure the presence of Ca^{2+} ions in the solution. The pH of the solution was slowly increased to pH 2-3 with NH_3 (25 % w/w) under magnetic stirring. After filtration the filtrate was discharged and the filter was ashed in a oven for 10 hours at 850 °C. The residue was dissolved and fumed in HNO_3 (65 % w/w). After evaporation to dryness the residue was fumed with 0.1 M HCOOH and then a 10 ml of a 2 M NH_4SCN in 0.1 M HCOOH were added to the sample.

4.3 ICP-MS AND α -SPECTROMETRY COMPARISON

ICP-MS and α -spectrometry are two powerful and complementary techniques for the determination of concentrations and ratios of actinide isotopes. The main difference between the two techniques is that α -spectrometers are sensible to the α particles emitted from the samples, instead ICP-MS is sensible to the number of ions of analyte that arrived to the detector. In figure 11 a comparison between the detection limit, expressed in activity (Bq) as absolute detection limit, of three different ICP-MS and α -spectrometry (the detection limit is given for 4000-minutes measurement period) on standard solution is shown ¹²¹. In the figure it is assumed that the absolute detection limit for alpha spectrometry and liquid scintillation counting is about 1.7×10^{-4} Bq. As can be seen, until the new high resolution ICP-MS were not commercially available, the

α -spectrometers had the best detection limits for short-lived nuclides, with half-life less than 2×10^4 years. With the new generation of high resolution ICP-MS, this limit is decreases down to 400 years and down to 20 years for ICP-MS Axiom¹²¹. Consequently, ICP-MS can be even exploited for the determination of short-lived nuclides at ppq (10^{-12} g/kg) level.

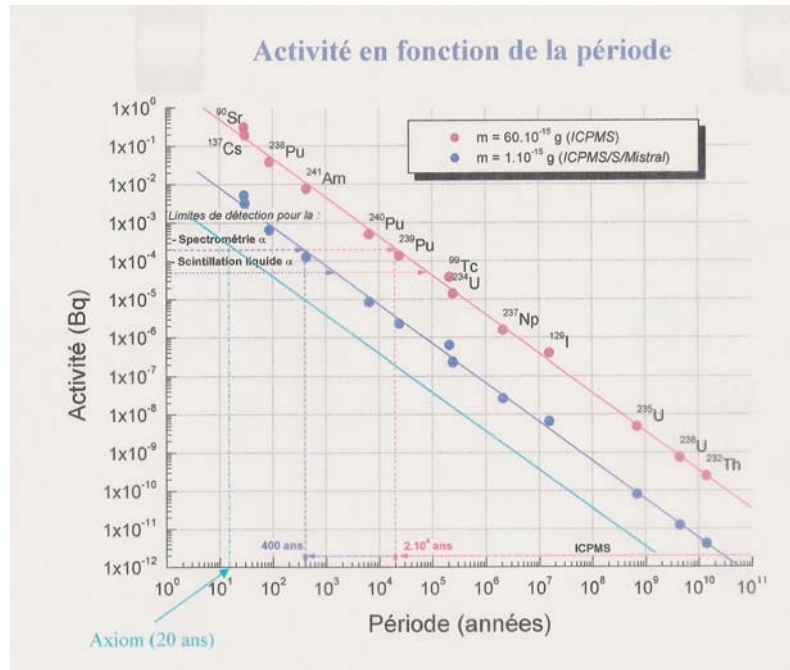


Figure 11: Detection limit comparison between ICP-MS, HR-ICP-MS and α -spectrometry¹²¹.

In table 1 the principle differences between the two techniques are reported.

Table 1: Main differences between α -spectrometry and ICP-MS¹²¹.

ICP-MS	α -Spectrometry
Complex and expensive	Simple and cheap
Expensive maintenance	Cheap maintenance
Qualified staff	Qualified staff
Able to measure all isotopic ratios ($^{240}\text{Pu}/^{239}\text{Pu}$)	Not all isotopic ratios can be measure (no $^{240}\text{Pu}/^{239}\text{Pu}$)
Rapid measurements (minutes)	Longer measurements time (days)
Isobaric interferences	Spectroscopic interferences
Lower detection limit for $T_{1/2} < 500$ years	
Measurement of stable isotopes	

4.4 γ -SPECTROMETRY

γ -ray spectra can be measured with very high precision using semiconductor detectors like HPGe. γ -Spectrometry is very suitable for determination of low

concentrations of both natural uranium and thorium series, K-40 and artificial isotopes like cesium-137 and other fission products. The high-resolution γ -spectrometry gives fast and reliable results for many isotopes as they have γ lines in the 150-1500 keV region¹¹⁹. Problems can come from the probability of the γ decay that for actinides can be low. The actinide nuclides that can be easily detected are ^{241}Am , ^{235}U , $^{228,234}\text{Th}$, $^{241,242,244}\text{Cm}$ (when >2 kBq).

The Compton Suppression γ -spectrometer used in this Ph.D. thesis consisted of a high purity germanium detector (HPGe) coaxial detector (EG&G Ortec) with 52 % efficiency and a diameter of 83 mm. The resolution is 1.83 keV at 1332.5 keV (^{60}Co). For reduction of the external radiation a multiple-layer passive shielding is used. The detector was connected to a digital acquisition module (DSPEC, EG&G Ortec). The HPGe-detector was coupled in anti-coincidence with a solid scintillation detector (NaI(Tl)) to enhance low level radioactivity measurements by reduction of the Compton background¹²². This particularly configuration, for low level measurement, is shown in figure 12. γ -spectrometry has been used to measure the ^{241}Am activity in environmental samples [Publication III, IV].



Figure 12: The γ -spectrometry sample chamber used.

4.5 LIQUID SCINTILLATION COUNTER (LSC)

An ultra low level liquid scintillation counter Quantulus 1220 (Wallac Oy, Finland) was used to analyze the elution fractions when on-batch experiments were performed. The counter is equipped with a passive, heavy lead shielding and an active guard. It consists of a stainless steel tank, which surrounds the measurement chamber, filled with a mineral oil based scintillation cocktail and viewed by photomultipliers. Any event detected simultaneously in the guard and in the sample is rejected, which reduce the background to extremely low values¹¹⁹. The system is also equipped with a pulse shape analyzer (PSA) which allows discrimination between α and β pulses. The counting efficiency for α emitters by liquid scintillation is 100 %.

5 RESULTS AND DISCUSSION

The majority of the results obtained during this Ph.D. thesis are presented and discussed in detail in the publications [I-IV]. Some additional findings are presented here as complement.

5.1 UTEVA RESIN

The UTEVA resin has been used to develop a new analytical procedure for the determination of U, Th, Np and Pu isotopes in spent nuclear fuel solutions as well as in environmental samples [Publication I]. The UTEVA resin can be used to separate tri, tetra and hexavalent actinides. The resin, which consists of particles with an external diameter of 100-150 μm , has been packed as a stationary phases in chromatographic columns of length of 50 mm and of 4 mm internal diameter. The column was coupled on-line to an ICP-MS.

5.1.1 Optimization of the oxalic acid concentration

Trivalent actinides such Am^{3+} and Cm^{3+} as well as trivalent lanthanide ions, are not retained in the UTEVA column in diluted acid solution and are eluted at the dead time of the column. This behavior of the trivalent ions does not permit their analytical determination under this conditions but allows the isobaric interferences at the masses 240, 241, 242, 244 between Am, Cm and Pu isotopes to be resolved. Hexavalent uranium and tetravalent Th, Pu and Np show in nitric solution very high values of the distribution coefficients. These values decrease very rapidly if the acid concentration is decreased. This behavior has been exploited for tetra and hexavalent actinides elution from UTEVA resin performed with diluted hydrochloric solution. Th, Np and Pu isotopes can be eluted with 2 M HCl. For the hexavalent uranium elution it is necessary to use a more diluted solution as 0.025 M HCl. In Figure 13 the chromatogram obtained for a solution in 3 M HNO_3 containing 50 ng/g of Th, Np, U, Pu and 10 ng/g of Am, after previous redox reaction with the Mohr's salt and sodium nitrite is shown. As can be seen, the trivalent Am is eluted at the dead time of the system unlike Th, Np, Pu and U which are eluted in sequence in a total time of 500 s. The resolution between Th, Np

and Pu peaks relative to that of U, can be increased by adding oxalic acid to the 2 M HCl eluent solution.

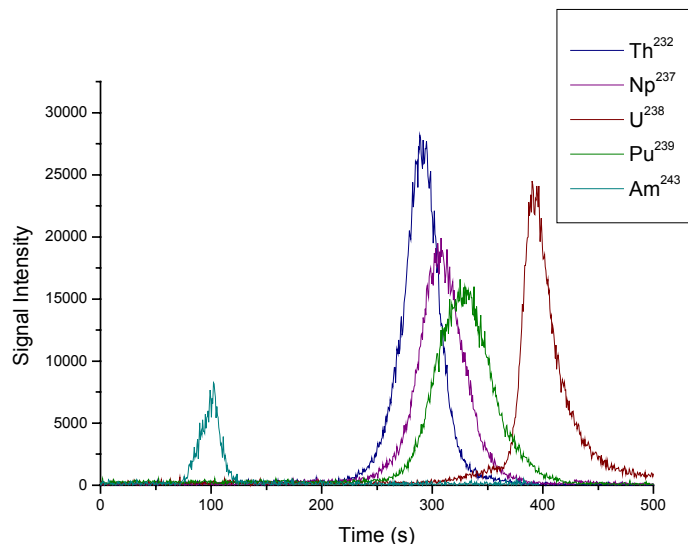


Figura 13. Chromatogram of a solution containing Th, Np, Pu and U (50 ng/g of each) and Am (10 ng/g), obtained using UTEVA column, 2 M and 0.025 M HCl as eluent. Detector ICP-MS.

The oxalic acid varies the repartition constant of the tetra and hexavalent actinides according to the value of the formation constant for the different complexes. In table 2 the values of the complex formation constants between oxalic acid and selected actinides are reported³⁹. As can be seen, the constant values for the hexavalent uranium are 2-4 orders of magnitudes lower respect to the Th, Np and Pu values.

Table 2. Complex formation values of selected actinides with oxalic acid (Ionic Strength 1M)³⁹.

Element	Log K ₁	Log K ₂	Log K ₃	Log K ₄
Th (IV)	8.23	8.54	6	4.4
Np (IV)	7.47	6.2	5.68	-
Pu (IV)	8.74	8.17	6.48	4.09
U (VI)	4.63	4.05	3.31	-

Oxalic acid with concentration range of 0.02-0.1 M was added to the 2 M HCl eluent in order to achieve a reduction of the retention times of Th, Np and Pu. All the measurements have been carried-out using the same elution program reported on the publication I and samples containing 50 ng/g of actinides in 3 M HNO₃ after reaction

with Mohr's salt and sodium nitrite. Figures 14-18 show the elution profile of Th, Np, Pu and U in function of the eluent composition.

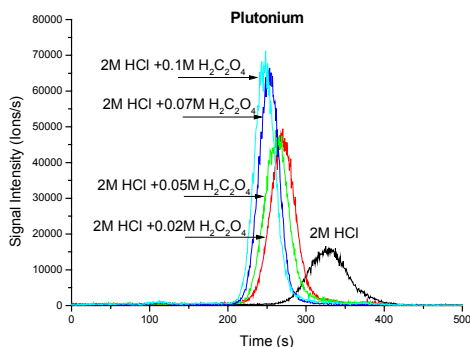


Figure 14. Pu elution time variation in function of the oxalic acid concentration in the eluent.

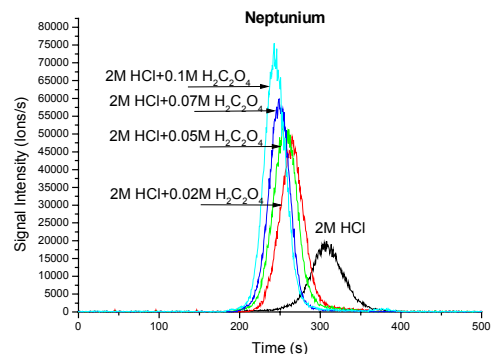


Figure 15. Np elution time variation in function of the oxalic acid concentration in the eluent.

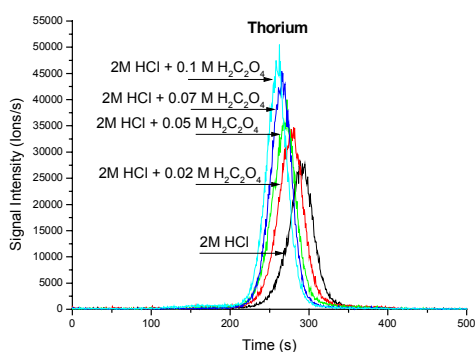


Figure 16. Th elution time variation in function of the oxalic acid concentration in the eluent.

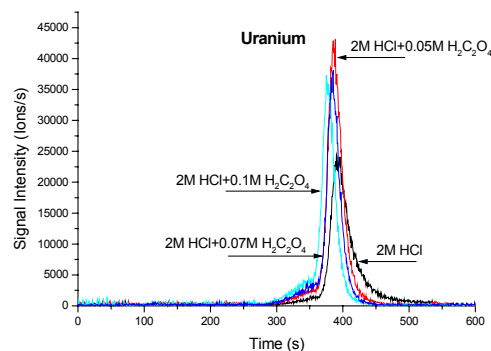


Figure 17. U elution time variation in function of the oxalic acid concentration in the eluent.

As can be seen from figures 14 to 17, the elution time for the tetravalent actinides decreases significantly with the increase of the oxalic acid concentration in the eluent. For the uranium the reduction of the elution time is not so evident because its elution has been made with 0.025 M HCl without addition of oxalic acid. Concentrations of oxalic acid higher than 0.1 M have not been tested in order to avoid problem of salt depositions on the cone as well as on the skimmer of the instrument. In figure 18 the chromatograms obtained for a sample solution containing U, Th, Np, Pu and Am using an oxalic acid concentration of 0.1 M in the 2 M HCl eluent are reported. As can be seen, Th, Pu and Np peaks are completely separated from the U.

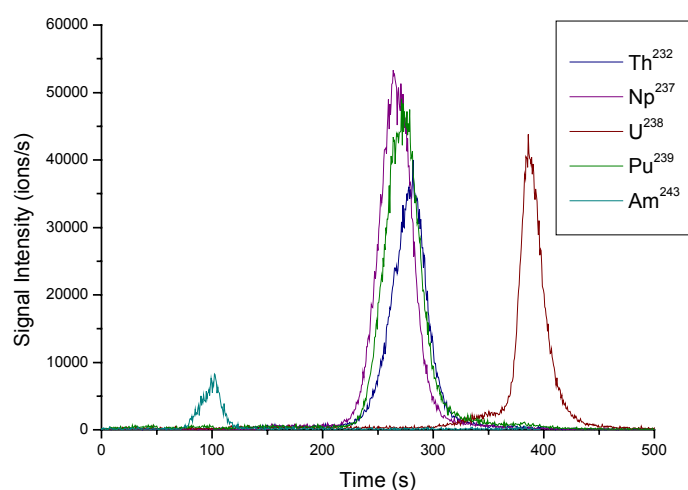


Figure 18. Chromatogram of a solution containing Am^{243} , Np^{237} , U^{238} , Th^{232} and Pu^{239} obtained according to the procedure developed [Publication I].

5.1.2 EXTRACTANT LOSS

In the UTEVA resin the extractant (DAAP) is not covalently bonded on the support (Amberlite) but it is only adsorbed on it. This property determines a higher mobility of the extractant to coordinate the actinide cations as well as the loss of the extractant during the subsequent elution runs. As consequence, a lower retention for actinide elements is achieved and a smaller area of the chromatographic peaks is obtained. The figures 19-21 show this effect on the peaks of U, Np and Th. The chromatograms were obtained analyzing several times the sample solution and applying the same elution program.

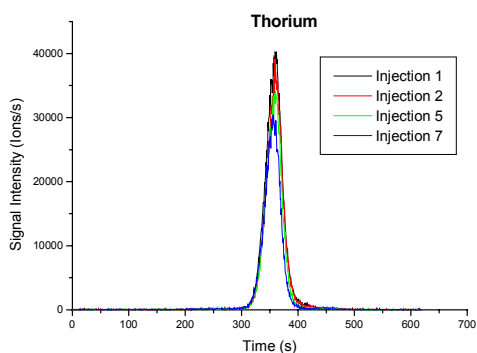


Figure 19. Effect of the extractant losses from the UTEVA resin on the Th peak highs.

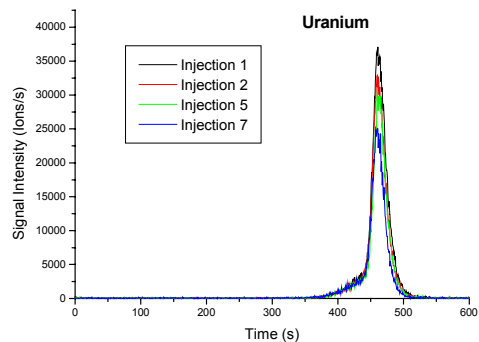


Figure 20. Effect of the extractant losses from the UTEVA resin on the U peak highs.

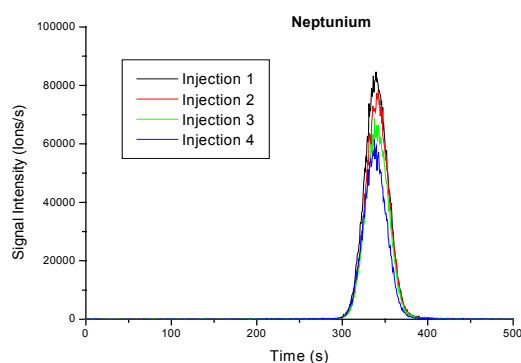


Figure 21. Effect of the extractant losses from the UTEVA resin on the Np peak highs.

The loss of the extractant from the resin leads to an inability of the UTEVA resin to preconcentrate sample volumes higher than 10-20 ml.

From the analytical point of view this problem can be easily overcome by adding a spike to the sample solution as internal standard. In the publication I, all the calibration curves were obtained reporting the ratio between the area of the analyte and the relative spike added *versus* the ratio of the concentrations. For Np, since no spike is available due to the fact that ^{237}Np is the only long-lived isotope that can be measured with the ICP-MS, the calibration curve was obtained using ^{233}U as spike.

5.2 IONPAC TCC-2 COLUMN

IonPac TCC-II column (Dionex, Sunnyvale, USA) has been used in the procedure for the sample clean-up by on-line chromatography for the determination of Am in sediments and soils by α -spectrometry [Publication III and IV]. Moreover, TCC-II column has been also studied for the preconcentration of lanthanides from acid solution media. The trivalent lanthanides were concentrated on a TCC-II column, then eluted on-line to a CS5 column for their chromatographic separation, and detected by ICP-MS. By this way, the detection limits for the analytes can be lowered by 2-3 orders of magnitude.

In comparison to the UTEVA column, the sample volume loaded in the TCC-II column can be higher without any loss of the analytes. The study on this resin has been performed using 40 ml of sample solution containing selected lanthanides (La-Tb) in 1% nitric acid. In order to load the 40 ml on the TCC-II column the tube from the pump pistons was directly connected to the sample bottle. In this way the chromatograph

pumps the sample into the column instead of the eluent. The flow direction in the column during the preconcentration was opposite to the eluent flow. This configuration concentrated the cations in a compact band at the bottom of the TCC-II. When the eluent (0.1 M oxalic acid in 0.19 M LiOH) was injected in the column, all the ions were rapidly eluted off the TCC-II and injected onto the guard and analytical column (CG5A and CS5A). If the sample is loaded on the TCC-II column in the same flow direction as the eluent flow, the cations are concentrated at the head of the column rather than at the bottom. When the eluent is injected, the cations begin the chromatographic separation on the concentrator before reaching the guard and the analytical column. Figure 22 shows a chromatogram of a 40 ml solution containing 60 pg/ml (ppt) of lanthanides (La-Gd) and 30 pg/ml Tb, obtained applying the on-line preconcentration in the TCC-II and the separation in the CS5A column.

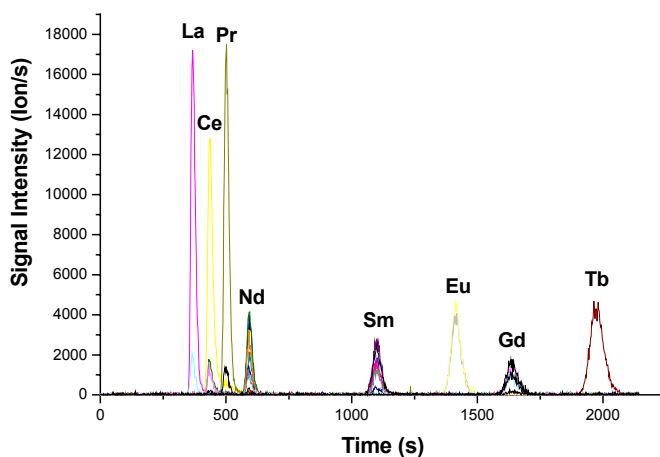


Figure 22: Chromatogram of a solution containing 60 pg/ml of La-Gd and 30 pg/ml of Tb in 1% nitric acid, obtained performing the 40 ml sample preconcentration in the TCC-II column and the separation in the CS5A, eluent 0.1 M oxalic acid in 0.19 M LiOH, detector ICP-MS.

In order to evaluate the linear dynamic range for the lanthanide elements, solutions containing different concentration varying between 5 – 120 pg/ml (ppt) were analyzed. For each value of concentration, three measurements were performed. In all the sample solutions 30 ng/ml of ^{159}Tb were added as internal standard. The calibration curves were obtained by plotting the ratio between the peak area of the analyte and the ^{159}Tb versus the concentration ratio. In table 3 the calibration curve parameters for selected La, Ce, Pr, Nd, Sm, Eu and Gd isotopes are reported.

Table 3: Calibration curve parameters for lanthanide preconcentration in a TCC-II column.

<i>Element</i>	<i>Calibration Curve</i>
¹³⁹ La	Y=1.1149 x - 0.0794 R ² = 0.9925
¹⁴⁰ Ce	Y=1.0667 x + 0.0064 R ² = 0.9992
¹⁴¹ Pr	Y=1.1853 x -0.0508 R ² =0.9992
¹⁴⁴ Nd	Y=1.1332 x + 0.0013 R ² =0.9994
¹⁵² Sm	Y=0.3854 x - 0.0083 R ² = 0.9996
¹⁵³ Eu	Y = 1.019 x + 0.0216 R ² = 0.9994
¹⁵⁸ Gd	Y = 0.9046 x + 0.011 R ² = 0.9989

Experiments were made also preparing the sample solution in different acid concentration. Sample solutions prepared in 2 M, 1 M, 0.5 M and 0.25 M hydrochloric acid were tested. The solution prepared in 0.5 M and 0.25 M were successfully preconcentrated in the TCC-II column. For those prepared in 2 M and 1 M HCl no preconcentration on the column could be attained.

The behavior of Am and Cm on the TCC-2 column is similar to those of trivalent lanthanides, as discussed in the publication III. The qualitative results obtained for Np, U, Th and Pu are here presented. Synthetic solutions, each containing either ²²⁹Th or ²⁴²Pu or ²³²U or ²³⁷Np as single isotope in 0.25 M HCl were preconcentrated on the TCC-II column. The elutions were performed with 0.1 M oxalic acid in 0.19 M LiOH and 2 M HNO₃. In the ²⁴²Pu sample solution, some drops of TiCl₃ were added in order to reduce Pu to Pu(III). Each sample solution containing between 1 to 5 Bq of the selected actinides was loaded in a 500 µl loop. The loop was connected to bottom of the column and 5 ml of 0.25 M HCl was used for the retention of the element. Also in this experiment the flow direction in the column during the preconcentration was opposite to the eluent flow. The effluent from the column was collected in different fractions and analyzed by LSC. The results are shown in Figure 22 (A,B,C,D). During the preconcentration step, Pu and Np were not completely retained in the column, and were detected in the first fraction. The Np behavior could be explained hypothesizing that the element in solution is principally present as Np(V) which is not retained in the column. Pu in solution, after reaction with TiCl₃, should be quantitatively reduced to Pu³⁺, which is retained in the TCC-II column. Probably the Pu reduction was not complete and some Pu(V) was still present in the sample solution. Pu(V), as Np(V), is not retained in the column. The hexavalent U and the tetravalent Th were retained on the TCC-II column.

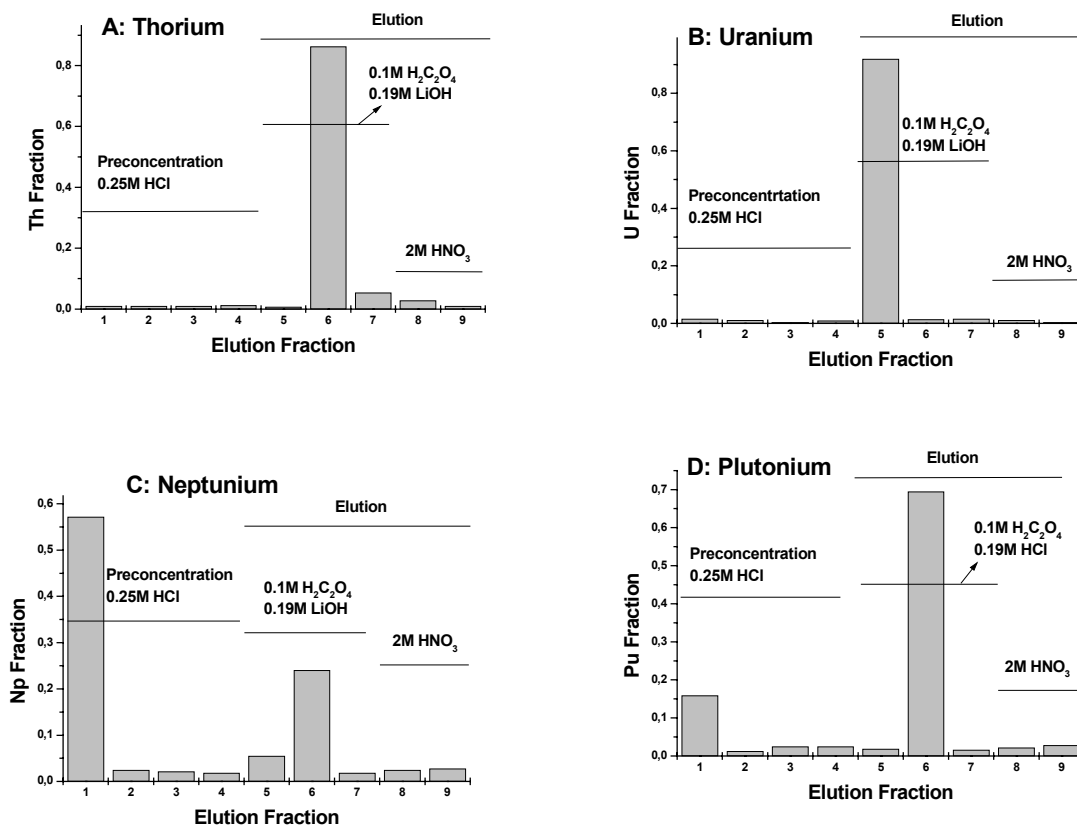


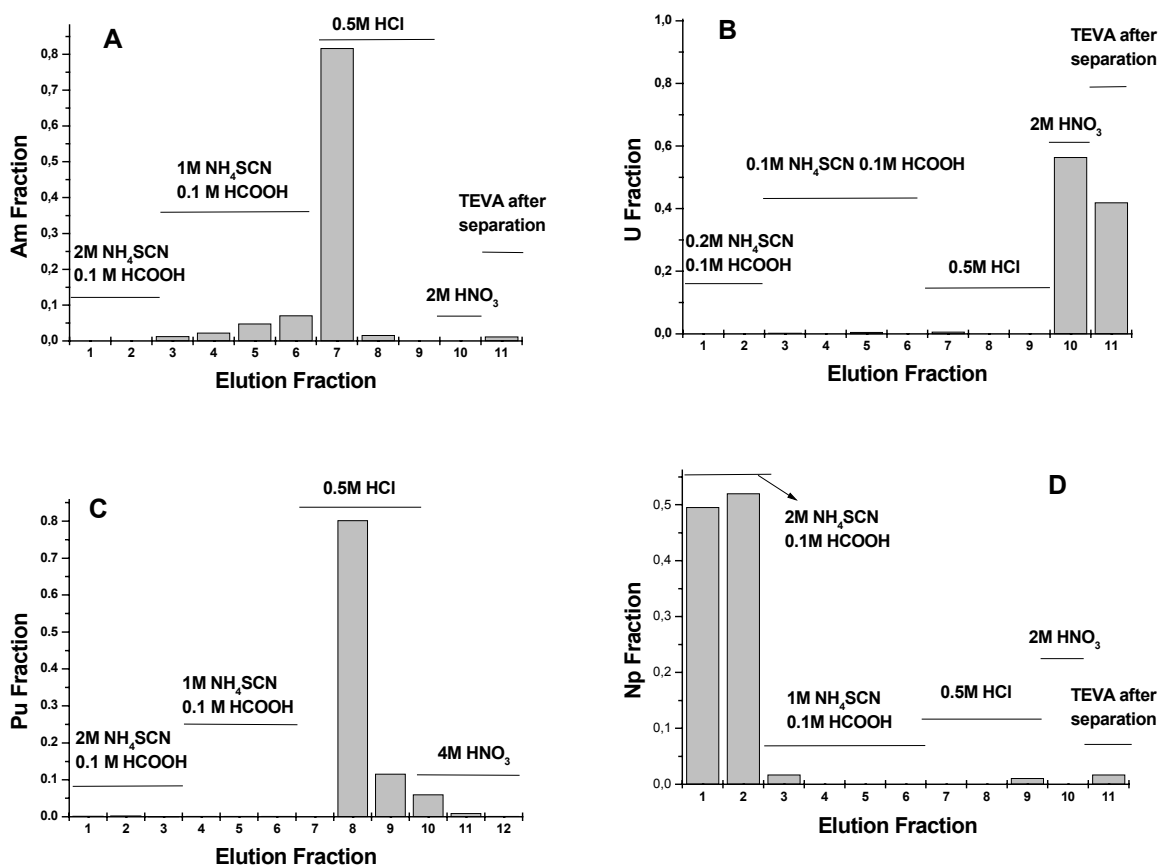
Figure 22. Actinide elution profiles in TCC-II column. **A:** Thorium, **B:** Uranium, **C:** Neptunium, **D:** Plutonium. **Preconcentration:** Fr. 1: 2ml 0.25 HCl, Fr. 2, 3, 4: 1ml 0.25 M HCl; **Elution:** Fr. 5: 1 ml 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ in 0.19 M LiOH, Fr. 6, 7: 2 ml 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ in 0.19 M LiOH; Fr. 8: 2 ml 2 M HNO_3 , Fr. 9: 3 ml 2 M HNO_3 . Fractions analyzed by LSC.

5.3 TEVA COLUMN

TEVA resin has been used to separate lanthanides (La-Eu) from trivalent actinides (Am and Cm) in formic acid/thiocyanate solution. The resin, which consists of particles with an external diameter of 100-150 μm , has been packed as a stationary phases in chromatographic columns of length of 250 mm and of 4 mm internal diameter and connected on-line to the chromatograph and to a columns (TCC-II and CS5A) system. The chromatographic system has been exploited to isolate the Am isotopes from soil and sediment samples. The Am fraction was used to prepare the samples for α -spectrometry measurement [publications III and IV].

5.3.1 BEHAVIOR OF ACTINIDE ELEMENTS ON TEVA RESIN

In order to understand the behavior of actinide elements in thiocyanate solutions, on-batch experiments with TEVA resin were performed. Synthetic solutions prepared in 2 M NH₄SCN/0.1 M HCOOH, containing Np²³⁷, Pu²³⁸, Am²⁴¹, U²³⁵ and Th²²⁹ were used for on-batch experiments. For this purpose, TEVA columns of 1ml volume were employed. The elution has been normally carried out with 2 ml of 2 M NH₄SCN/0.1 M HCOOH, 4 ml of 1 M NH₄SCN/0.1 M HCOOH, 3 ml 0.5 M HCl, and 1 ml of 2 M HNO₃. The fractions (1ml) and the used resin were analyzed by γ -spectrometry. The results obtained are shown in figures 23(A, B, C, D, E).



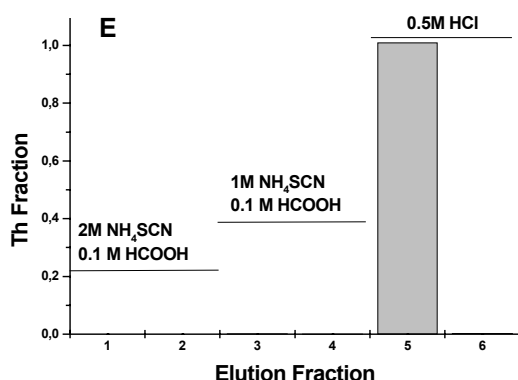


Figure 23. Actinide elution profiles in TEVA column. **A:** Americium; **B:** Uranium; **C:** Plutonium; **D:** Neptunium, **E:** Thorium. Elution: 2ml of 2M NH₄SCN in 0.1M HCOOH, 4ml of 2M NH₄SCN in 0.1M HCOOH, 3 ml 0.5M HCl and 1 ml of 2M HNO₃. Fractions analyzed by γ -spectrometry.

As can be seen from the figures, Np is the only actinide element not retained in the TEVA column. This element is probably present in solution as Np(V), which is not extracted from the resin under this condition. U(VI) was strongly absorbed in the TEVA column and its partial elution from the resin was achieved using 2 M HNO₃ as eluent. Th (IV) is quantitatively eluted together with Am (III) in the 0.5 M HCl fraction.

Performing experiment for Am, its partial elution (*ca.* 15%) was observed when 1 M NH₄SCN/0.1 M HCOOH was used as eluent. It has been calculated that the major part of Am (*ca.* 83 %) was retained in the TEVA column and eluted in the hydrochloric fractions. This data were used to calculate the americium distribution ratio between the aqueous and the organic phase (paragraph 5.3.3).

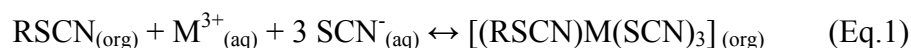
5.3.2 EXTRACTION MECHANISM

The use of TEVA for the extraction of trivalent actinides and separation from lanthanides (La-Eu) has been reported, using nitrate solutions as aqueous phase⁷⁴. It was found out that trivalent actinides and lanthanides are efficiently extracted only in presence of high concentrations of salting out agents and at very low aqueous acidity. Also, very low Am/Eu separation factors were reported⁷¹. Much higher Am/Eu separation factors are achieved when extracting the metal species with TEVA from thiocyanate medium^{71,98,124,125}. The reason for the higher separation factors achievable in thiocyanate solutions is to be related to the tendency of the thiocyanate ligand to form

inner sphere complexes more readily with actinides than with lanthanides⁷⁷ and to the fact that ions with 5f electrons preferentially bond to soft donor ligands^{41,71}.

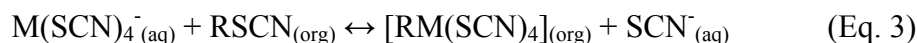
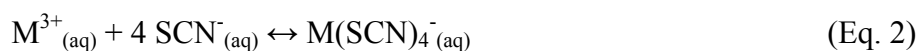
Different equations have been proposed to describe the equilibrium between the aqueous and the organic phase during the extraction by TEVA resin.

The extraction of trivalent actinide or lanthanide metal ions (M^{3+}) by an organic solution of quaternary amine, in thiocyanate form (RSCN), can be formally represented by the following equilibrium⁷¹:



Where R is quaternary amine, (org) and (aq) indicate the organic and the aqueous phase respectively.

The equilibrium could be also written as an anion exchange:



It has to be pointed out that the equilibrium 1 has been written as an additional reaction and not as an ion-exchange reaction involving $M(SCN)_4^{-}$. From a formal point of view there is no difference between both alternatives, since the final form of the expression describing the combined aqueous complexation and extraction would be the same⁷¹.

When considering chromatographic separations, two different equilibria have to be taken into account: that in the sample solution and that of the sample solution together with the stationary phase. Taking into account the Am-thiocyanate complex formation constants reviewed by R.J. Silva *et al.*⁷⁰ and performing theoretic calculations with the program Chess/Jchess ver. 3.0 it has been calculated that the presence of the anionic species $Am(SCN)_4^{-}$ in the sample solution (2 M NH_4SCN and 0.1 M $HCOOH$) is negligible.

When the stationary phase is also considered, the equilibrium in the aqueous phase becomes dynamic. The distribution of some species between the aqueous and organic phase or the anionic-exchange of the thiocyanate complexes, at the interface between the two phases, becomes the driving force of the mechanisms and shifts the aqueous equilibrium to the formation of certain complexes. The first mechanism (Eq.1) takes into account the formation of the neutral species $M(SCN)_3$ in the aqueous solution, its

subsequent distribution between aqueous and organic phase and the formation of the complex in the organic phase. On the other hand, in the second mechanism (Eq. 2 and 3), the formation of the anionic species in the aqueous solution and its subsequent anion-exchange at the interface between the two phases is considered. For ionic species the distribution coefficient values between aqueous and organic phase are normally very high. Therefore, the ionic species are predominantly present in the aqueous phase. Since in the TEVA resin the particle diameter is about 100-150 μm , the interface between the organic and the aqueous phase can be considered very large.

The tendency of thiocyanate ligand to form inner sphere complexes more readily with actinides than lanthanides is the reason for the high separation factors achieved⁷⁷. The inner sphere complexes are characterized by a higher stability compared to the outer sphere ones and consequently they have higher formation constant values. Moreover, the water coordination sphere of the inner sphere complexes is partially destroyed leading to a higher hydrophobicity of the complex and then to lower distribution ratios between aqueous and organic phase⁷¹.

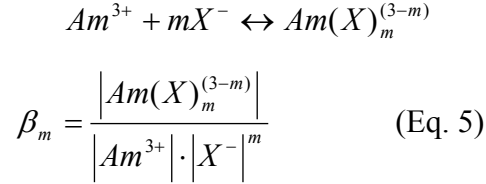
The separation of trivalent lanthanides/actinides in thiocyanate media by quaternary amine works efficiently also if it is performed by liquid-liquid extraction. The extraction mechanism (Eq.1) is partially confirmed by the liquid-liquid extraction data. Moreover, it has been reported in literature, that the extracted predominant species in thiocyanate media, with quaternary amine was always the neutral species $\text{M}(\text{SCN})_3$ ^{4,74,123}. Khopkar and Narayanankutty¹²⁶ reported about the synergic extraction effects, mixing a quaternary amine with three different organophosphorous, for the extraction of $\text{M}(\text{SCN})_3$. Therefore, it can be concluded that the separation mechanism of trivalent lanthanides (La-Eu)/ actinides in thiocyanate solution by TEVA resin, should involve the extraction of the neutral species $\text{M}(\text{SCN})_3$.

In the present experimental conditions the Am distribution ratio in the two phases has been calculated applying the Equation 1 related to the extraction mechanism.

The concentration of the Am in the organic phase can be calculated from the following equation:

$$\text{Am}_{(\text{org})} = [(\text{RSCN})\text{Am}(\text{SCN})_3]_{(\text{org})} = [\text{Am}^{3+}]_{(\text{aq})} \times K_1 \times [\text{SCN}^-]_{(\text{aq})}^3 \times [\text{RSCN}]_{(\text{org})} \text{ (Eq.4)}$$

For the calculation of the Am^{3+} concentration in aqueous solution all the aqueous equilibria (hydrolysis and pH, thiocyanate and formate complexation) have been taken into account. The reaction between the Am^{3+} ions and a generic complexant X^- can be written as:



From the Eq. 5, the Am^{3+} concentration in the aqueous phases can be written as:

$$[Am]_{(aq)} = [Am^{3+}] \times \left(1 + \sum_i \beta_i \times [HCOO^-]^i + \sum_j \beta_j [SCN^-]^j + \sum_k \beta_k [OH^-]^k \right) \quad (\text{Eq. 6})$$

The Am distribution ratio D is defined as:

$$D = \frac{[Am]_{(org)}}{[Am]_{(aq)}} \quad (\text{Eq. 7})$$

Substituting the Eq. 4 and 6 in the Eq. 7:

$$D = \frac{K_1 \times [SCN^-]^3 \times [RSCN]_{(org)}}{1 + \sum_i \beta_i \times [HCOO^-]^i + \sum_j \beta_j \times [SCN^-]^j + \sum_k \beta_k \times [OH^-]^k} \quad (\text{Eq. 8})$$

At pH 2.38, in presence of a much lower concentration of formate than thiocyanate anions as in our experiment condition, and the on the basis of the values of the β_j and β_i constants for Am [$\beta_1^{SCN} = 1.3 \cdot 10^7$; $\beta_1^{HCOO} = 14.1 \cdot 10^7$, $\beta_2^{HCOO} = 34.7 \cdot 10^7$], the effect of the thiocyanate concentration is largely predominant in determining the value of D.

Using the K_1 experimental value of 990 given by Chiarizia *et al*⁷¹, the value of D calculated for a concentration of $\text{SCN}^- = 1 \text{ M}$ and $\text{HCOOH} = 0.1 \text{ M}$ resulted to be $D=3.6$. This value is in agreement with that calculated by Chiarizia *et al*⁷¹ of *ca* 4.

6 CONCLUSION

UTEVA resin based on the extraction mechanism has been used as a stationary phase in chromatographic columns coupled on-line with an ICP-MS detector. The advantage of this column is its selectivity for actinides. The addition of a complexing agent as oxalic acid to the eluent improves the separation between the tetra and hexavalent actinides. The possibility of performing the on-line preconcentration and separation using the same column is a very important feature.

IC-ID-ICP-MS has been exploited for the simultaneous determination of fission products (lanthanides) and actinides (Np, U, Pu, Am and Cm) using a mixed bed anionic/cationic exchange column. In comparison to the previous developed procedures, the time of analysis and sample handling are drastically reduced. The use of 0.2 M sodium nitrite permits the stabilisation of Np and Pu in the oxidation state IV to be completed after 10 min of reaction. In addition, the advantages of the procedure are the large differences in the retention times of Np and Pu from U, and the possibility of resolving Am from Cm.

The stationary phase of the IonPac TCC-II column has been proved to be the most appropriate for the preconcentration of hexa, tetra and trivalent actinides and lanthanides. Compared to the Eichrom resins, larger sample volumes (up to 40 ml) can be loaded onto the column without reaching the breakthrough volume.

HPLC has been exploited for the chemical purification of environmental samples for the α -spectrometry determination of Am. In comparison with the on-batch separation procedures the time of analysis and sample handling are drastically reduced. Moreover, cross contamination of the sample can be avoided respect to the batch separation procedures. An advantage is that in case of large number of samples the system can be automated.

The separation mechanism of trivalent lanthanides (La-Eu)/actinides in thiocyanate solution by TEVA resin, involves the extraction of the neutral species

$M(SCN)_3$. As for Am, the distribution ratio between the organic and the aqueous phase has been calculated and it resulted in good agreement with that reported by other authors.

All the procedures developed have been applied to real samples (spent nuclear fuel solutions either environmental samples). The results obtained were always in agreement with those obtained applying the previous developed methods.

7 REFERENCES

- 1 M. Betti, *Microchemical Journal*, **67**, 363, 2000.
- 2 F. Waren and R. Harrison, *Radioecology after Chernobyl*, John Wiley and Sons, New York, 1993.
- 3 D. Solatie, *Development and comparison of analytical methods for the determination of uranium and plutonium in spent fuel and environmental samples*, University of Helsinki, Report Series in Radiochemistry 19/2002.
- 4 M. Betti, *J. Environ. Radioactivity*, **64(2)**, 113, 2003.
- 5 L. Koch, G. Cottone and M. W. Geerlings, *Radiochim. Acta*, **10**, 122, 1968.
- 6 M. Betti, J. M. Barrero Moreno, L. Koch, P. Peerani and E. Toscano, Comparison of IC-ICP-MS with TIMS for the determination of Neodymium isotopes for the burn-up calculation of spent nuclear fuel, Poster presented at 2000 Winter Conference on Plasma Spectrochemistry, 10-15 January 2000.
- 7 I. A. Croudace, P. Warwick, R. Taylor and S. Dee, *Anal. Chim. Acta*, **371**, 217, 1998.
- 8 R. J. Silva and H. Nitsche, *Radiochimica Acta*, **70/71**, 377, 1995.
- 9 R. L. Murray, *Understanding Radioactive Waste*, 4th edn., Battelle Press, 1994.
- 10 J. Hoefs, *Stable Isotopes Geochemistry*, Springer, Berlin, 1987.
- 11 M. Shima, *Geochim. Cosmochim. Acta*, **50**, 577, 1986.
- 12 G. Faure, *Principle of Isotope Geology*, Wiley, New York, 1986.
- 13 F. A. Mellon and B. Sandström, *Stable Isotope in Human Nutrition*, Academic Press, London, 1996.
- 14 L. Skipperud, D. Oughton and B. Salbu, *Sci. Total Environ.*, **257**, 81, 2000.
- 15 J. S. Crain, *At. Spectrosc. Perspectives*, **11(2)**, 30, 1996.
- 16 J. S. Becker and H.-J. Dietze, *Adv. Mass Spectrom.*, **14**, 681, 1998.
- 17 C. K. Kim, R. Seki, S. Morita, S. Yamasaki, A. Tsumura, Y. Igarashi and M. Yamamoto, *J. Anal. At. Spectrom.*, **6**, 205, 1991.
- 18 D. Solatie, P. Carbol, M. Betti, F. Bocci, T. Hiernaut, V. V. Rondinella and J. Cobos, *Fresenius' J. Anal. Chem.*, **368**, 88, 2000.
- 19 J. S. Becker and H.-J. Dietze, in *The Encyclopedia of Analytical Chemistry*, Ed. R. A. Meyers, John Wiley and Sons, 12947, 2000.
- 20 K. E. Jarvis, A. L. Gray and R. S. Houk, *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Blackie Academic and Professional, London, 1997.
- 21 A. Montaser, *Inductively Coupled Plasma Mass Spectrometry*, Wiley-VCH, New York, 1998,
- 22 K. G. Heumann, *Int. J. Mass. Spectrom. Ion Pro.*, **118(119)**, 575, 1992,
- 23 J. I. Garcia Alonso, *Anal. Chim. Acta*, **312**, 57, 1995.
- 24 N. Jakubowsky, L. Moens and F. Vanhaecke, *Spectrochim. Acta, Part B*, **53**, 1739, 1998.
- 25 J. S. Becker, R. S. Soman, K. L. Sutton, J. A. Caruso and H.-J. Dietze, *J. Anal. At. Spectrom.*, **14**, 933, 1999.

- 26 M. Betti, *J. Chromatogr. A*, **789**, 369, 1997.
- 27 J. M. Barrero Moreno, M. Betti and G. Nicolau, *J. Anal. At. Spectrom.*, **14**, 875, 1999.
- 28 J. M. Barrero Moreno, M. Betti and J. I. Garcia Alonso, *J. Anal. At. Spectrom.*, **12**, 355, 1997.
- 29 J. S. Becker, G. Küppers, F. Carsughi, W. Kerl, W. Schall, F. Ullmaier and H.-J. Dietze, *Ber. Forschungszentrum Jülich*, **3272**, 143, 1996.
- 30 W. Kerl, J. S. Becker, W. Dannecker and H.-J. Dietze, *Fresenius' J. Anal. Chem.*, **11**, 433, 1998.
- 31 J. B. Truscott, P. Jones, B. E. Fairman and E. H. Evans, *Anal. Chim. Acta*, **433**, 245, 2001.
- 32 J. B. Truscott, P. Jones, B. E. Fairman and E. H. Evans, *J. Chromatogr. A*, **928**, 91, 2001.
- 33 A. Yamato, *J. Radioanal. Chem.*, **75**, 265, 1982.
- 34 E. P. Horwitz, R. Chiarizia, H. Diamond, R. C. Gatrone, S. D. Alexandratos, A. Q. Trochimczuk, D. N. Crick, *Solvent Extraction and Ion Exchange*, **11**, 943, 1993.
- 35 E. P. Horwitz, M. L. Dietz, R. Chiarizia, H. Diamond, *Analytica Chimica Acta*, **266**, 25, 1992.
- 36 E. P. Horwitz, R. Chiarizia, M. L. Dietz, H. Diamond, *Analytica Chimica Acta*, **281**, 361, 1993.
- 37 E. Hrneck, Development of analytical techniques for the identification and verification of radioactive traces from emissions, discharges and wastes during nuclear activities, JRC-ITU Technical Note 2001/20, 2001.
- 38 W. A. Abbasi and M. Streat, *J. Radioanal. Nucl. Chem., Letters*, **2**, 163, 1994.
- 39 J. J. Katz, G. T. Seaborg, L. R. Morss, *The Chemistry of the Actinide Elements*, Second Edition, Chapman & Hall, New York, Vol. 1 and 2, 1986.
- 40 G. T. Seaborg, *Radiochim. Acta*, **61**, 115, 1993.
- 41 A. D. Jones and G. R. Choppin, *Actinides Reviews*, **1**, 311, 1969.
- 42 V. M. Goldschmidt, *Geochemistry*, Oxford University Press, 1954.
- 43 J. Magill, *Nuclides.net An Integrated Environment for Computations on Radionuclides and their Radiation*, Springer-Verlag Berlin Heidelberg New York, 2003.
- 44 N. A. Milic and T. M. Suranji, *Can. J. Chem.*, **60**, 1298, 1982.
- 45 P. L. Brown, J. Ellis and R. N. Sylva, *J. Chem. Soc. Dalton Trans*, **31**, 1983.
- 46 D. F. Peppard and G. W. Mason, *Nucl. Sci. Eng.*, **16**, 382, 1963.
- 47 A. D. Banavali *et al*, *Radioactivity and Radiochemistry*, **6(3)**, 26, 1995.
- 48 J. C. Butterworth, *The Science of the Total Environment*, **173/ 174**, 293, 1995.
- 49 K. Bunzl and W. Kracke, *J. of Radioanalytical and Nuclear Chemistry, Letters*, **186(5)**, 401, 1994.
- 50 L. C. T. Eusebius, A. K. Ghose and A. K. Dey, *Sep. Sci. Technol.*, **17**, 717, 1982.
- 51 T. Kiriya and R. Kuroda, *Anal. Chim. Acta*, **101**, 207, 1978.
- 52 P. C. Mayankutty, B. L. Jangida and M. Sundaresam, *Sep. Sci. Technol.*, **17**, 1327, 1982.
- 53 L. Gmelin, *Gmelin Handbuch der Anorganischen Chemie*, Bands, Teil **A2**, 1974.
- 54 E. Martelli and L. G. Sillen, *Stability constant of metal ion complexes*, Spec. Publ., **17**, London 1964.
- 55 D. Cojeticamin, S. Ratkovic, *J. Chromatog.*, **46**, 326, 1970.
- 56 E. A. C. Crouch and G. B. Cook, *J. Inorg. Nucl. Chem.*, **2**, 223, 1966.

- 57 I. M. Kolthoff, P. J. Elvin and E. B. Sandell, *Treatise on analytical chemistry*, **9**, Pt.II, New York 1962.
- 58 N. E. Holden, *Pure Appl. Chem.*, **52**, 2371, 1979.
- 59 L. Gmelin, *Gmelin Handbook of Inorganic Chemistry*, U Suppl., Vol. **D1**, 1984.
- 60 *Analytical Chemistry of Uranium*, Israel Program for Scientific Translations, Jerusalem, 1963.
- 61 K. A. Kraus, F. Nelson, G. L. Johnson, *J. Am. Chem. Soc.*, **71**, 2510, 1949.
- 62 F. J. Giménez Izquierdo, Establecimiento de los parámetros cinético y termodinámico que rigen la disolución del dióxido de uranio en medios de elevada fuerza iónica. Extrapolación al comportamiento del combustible nuclear gastado en un repositorio salino, Academic dissertation, Technical University of Catalunya, Barcelona (Spain), 1996.
- 63 L. Gmelin, *Gmelin Handbook of Inorganic Chemistry*, U Suppl., Vol. **A7**, 1982.
- 64 E. P. Horwitz, M. L. Dietz, R. Chiarizia, H. Diamond, S. L. Maxwell III, M. R. Nelson, *Anal. Chim. Acta*, **310**, 63, 1995.
- 65 E. P. Horwitz, R. Chiarizia and M. L. Dietz, *Solvent Extr. Ion Exch.*, **10**, 313, 1992.
- 66 O. J. Wick, *Plutonium Handbook A Guide to the Technology*, Gordon & Breach, New York (1980).
- 67 M.S. Milykova, N.I. Gusev, I. G. Sentyurin and I. S. Sklyarenko, *Analytical Chemistry of Plutonium*, Ann Arbor-Humphrey Science Publishers, Ann Arbor, London 1969.
- 68 L. Gmelin, *Gmelin Handbuch der Anorganischen Chemie*, Transurane **D1**, 1975.
- 69 D. Solatie, P. Carbol, P. Peerani and M. Betti, *Radiochim. Acta*, **89**, 551, 2001.
- 70 R. J. Silva, G. Bidoglio, M. H. Rand, P. B. Robouch, H. Wanner and I. Puigdomenech, *Chemical Thermodynamics of Americium* in *Chemical Thermodynamics 2*, Elsevier Amsterdam Lausanne New York Oxford Shannon Tokyo 1995.
- 71 R. Chiarizia, R. C. Gatrone and E. P. Horwitz, *Solv. Extr. Ion Exch.*, **13(4)**, 615, 1995.
- 72 E. Hrnccek and K. Irlweck, *Determination of Am and Pu in Contaminated Soil Samples in Environmental Radiochemical Analysis*, Ed. G. W. A. Newton, The Royal Society of Chemistry, Cambridge, 1999.
- 73 J. P. Surls and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **4**, 62, 1957.
- 74 W. F. Kinard and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **36**, 1131, 1974.
- 75 P. K. Khopkar and J. N. Mathur, *J. Inorg. Nucl. Chem.*, **36**, 3819, 1974.
- 76 W. H. Hale and J. T. Corwe, *J. Inorg. Nucl. Chem.*, **5**, 363, 1969.
- 77 G. R. Choppin and J. Kettels, *J. Inorg. Nucl. Chem.*, **27**, 1965.
- 78 K. W. Bagnall, *Coord. Chem. Rev.*, **2**, 145, 1967.
- 79 M. Pages and R. Demichelis, *C. R. Acad. Sci. Paris C*, **253**, 938, 1966.
- 80 B. F. Myasoedov and I. A. Lebedev, *Radiochem. Radioanal. Chem. Lett.*, **14**, 131, 1974.
- 81 J. M. Barrero Moreno, M. Betti and J. I. Garcia Alonso, *J. Anal. At. Spectr.*, **12**, 335, 1997.
- 82 E.P. Horwitz, C. A. A. Bloomquist, L. J. Sauro and D.J. Henderson, *J. Inorg. Nucl. Chem.*, **28**, 2313, 1966.
- 83 E.K. Hulet, R. G. Gutmacher and M. S. Coops, *J. Inorg. Nucl. Chem.*, **17**, 350, 1961.

- 84 L. Perna, F. Bocci, L. Aldave de las Heras, J. de Pablo and M. Betti, *J. Anal. At. Spectr.*, **17**, 1166, 2002.
- 85 R. A. Glass, *J. Am. Chem. Soc.*, **77**, 807, 1955.
- 86 D. F. Peppard and P. R. Gray, *U. S. Patent 2*, **683**, 685, 1954.
- 87 G. W. Mason and H. E. Griffin in Actinide Separations, Eds. J. D. Navratil and W. W. Schulz, American Chemistry Society, Washington D.C., USA.
- 88 *Eichrom Analytical Products Description*, Eichrom Industries Inc., Darien, USA, 1995.
- 89 A. G. Adriaens, J. D. Fasset, W. R. Kelly, D. S. Simons and F. C. Adams, *Anal. Chem.*, **64**, 2945, 1992.
- 90 M. Agarande et al, *17th Annual Esarda Conference*, CEC, JRC-IRMM, 1994.
- 91 K. P. Carney, *J. Of Radioanal. And Nucl. Chem.*, Articles, **194**, 41, 1995.
- 92 R. Langston, S. Nguyen, T. Simpson, *41st Annual Conference on Bioassay, Analytical and Environmental Radiochemistry*, Boston, MA, 1995.
- 93 C. Apostolidis, R. Molinet, P. Richir, M. Ougier and K. Mayer, *Radiochim. Acta*, **83**, 21, 1998.
- 94 K. Bunzl and W. Kracke, *J. of Radioanalytical and Nuclear Chemistry, Letters*, **186(5)**, 401, 1994.
- 95 A. D. Banavali et al, *Radioactivity and Radiochemistry*, **6(3)**, 26, 1995.
- 96 J. C. Butterworth, *The Science of the Total Environment*, **173/ 174**, 293, 1995.
- 97 J. C. Harduin et al, *Radioprotection*, **31(2)**, 229, 1996.
- 98 M. Pimpl and R. H. Higgy, *J. of Radioanalytical and Nuclear Chemistry*, **248(3)**, 537, 2001.
- 99 H. Small, *Ion chromatography*, Modern Analytical Chemistry, Series Ed. D. Hercules, Plenum Press New York and London, 1989.
- 100 *Installation instructions and troubleshooting guide for Ion Pac CS5*. Dionex Corporation Document N. 032558, 1998.
- 101 J. Weiss, *Ion Chromatography*, 2nd Edition, VCH Weinheim, 1995.
- 102 *Installation instructions and troubleshooting guide for Ion Pac CS10*. Dionex Corporation Document N. 034341, 1998.
- 103 Gmelin Handbook of Inorganic Chemistry, Uranium Supplement, **D4**, *Cation-exchange and Chromatography*, Springer-Uerlag, Berlin, 1983.
- 104 J. Korkisch, *Handbook of Ion-Exchange Resins: Their application in inorganic analytical chemistry*, **Vol. 2**, CRC Press, Boca Raton, Fl, 1989.
- 105 G. H. Coleman, *The radiochemistry of plutonium*, National Academy of Sciences, Springfield, VA, 1965.
- 106 T. Sekine and Y. Hasegawa, *Solvent Extraction Chemistry: Fundamental and Application*, Marcel Dekker, New York, 1977.
- 107 J. C. Vaselsky, P. C. Kiel and N. Sezginer, *J. Radioanal. Chem.*, **21**, 97, 1974.
- 108 T. Braun and G. Ghersini, *Extraction Chromatography*, Elsevier, New York, 1975.
- 109 C. W. Sill, K. W. Puphal and F. D. Hindman, *Anal. Chem.*, **46**, 1725, 1974.

- 110 *Installation instructions and troubleshooting guide for Ion Pac TCC-II*. Dionex Corporation Document N. 034466, 1998.
- 111 M. Betti, J. I. Garcia Alonso, Ph. Arbore and L. Koch, in *Applications of Plasma Source Mass Spectrometry II*, Eds. G. Holland, A. N. Eaton, Royal Society of Chemistry, Cambridge, p.205, 1993.
- 112 J. I. Garcia Alonso, M. Betti, Ph. Arbore, L. Koch and H. Wiesmann, paper presented at European Winter Conference on Plasma Spectrochemistry, Granada, Spain, 10-15 January 1993.
- 113 J. I. Garcia Alonso, D. Thoby-Schultzendorff, B. Giovannone, L. Koch and H. Wiesmann, *J. Anal. At. Spectrom.*, **62**, 71, 1993.
- 114 J. I. Garcia Alonso, F. Sena, Ph. Arbore, M. Betti and L. Koch, *J. Anal. At. Spectrom.*, **10**, 381, 1995.
- 115 P. J. De Bièvre and G. H. Hebus, *Nuclear instruments and methods*, **32**, 224, 1965.
- 116 K. G. Heumann, *Isotope Dilution Mass Spectrometry in Inorganic Mass Spectrometry*, Eds F. Adams, R.G. Gijbels, Van Grieken, John Wiley and Sons.
- 117 J. I. Garcia Alonso, *Anal. Chim. Acta*, **312**, 57, 1995.
- 118 P. J. De Bièvre, *Fresenius J. Anal. Chem*, **337**, 766, 1990.
- 119 M. F. L'Annunziata, *Handbook of radioactive analysis*, Academic Press, San Diego, CA, USA, 1998.
- 120 E. Hrncsek, Development of analytical techniques for identification and verification for radioactive traces from emissions, discharge and wastes during nuclear activities, European Commission-JRC-Institute for Transuranium Elements, Technical Note 05/2002.
- 121 R. Chiappini, J.-M. Taillade and F. Pointurier, *Low level plutonium and uranium isotopic ratio measurements using high-sensitivity ICP-MS*, Esarda Proceedings, Geel (Belgium), 25-27 February 1997.
- 122 P. Peerani, P. Carbol, E. Hrncsek, M. Betti, *Nucl. Instrum. Meth. Phys. Res. A*, **482**, 42, 2002.
- 123 H. D. Harmor, J. R. Peterson, J. T. Bell and W. J. McDowell, *J. Inorg. Nucl. Chem.*, **34**, 1711, 1972.
- 124 R. Chiarizia, P. R. Danesi, G. Scibona and L. Magon, *J. Inorg. Nucl. Chem.*, **35**, 3595, 1973.
- 125 E. P. Horwitz and C. A. A. Bloomquist, *J. of Chromatogr. Sci.*, **12**, 200, 1974.
- 126 P. K. Khopkar and P. Narayanankutty, *J. Inorg. Nucl. Chem.*, **34**, 3233, 1972.

Investigation on the use of UTEVA as a stationary phase for chromatographic separation of actinides on-line to inductively coupled plasma mass spectrometry

Lorenzo Perna,^{a,b} Maria Betti,^{*b} Josepha Maria Barrero Moreno^{†b} and Roger Fuoco^a

^aUniversità degli Studi di Pisa, Department of Chemistry Industrial Chemistry, Via Risorgimento 35, 56126 Pisa, Italy

^bEuropean Commission JRC, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany

www.rsc.org/jaas

Received 4th September 2000, Accepted 20th November 2000

First published as an Advance Article on the web 15th December 2000

A method based on the use of the UTEVA-Spec. Eichrom resin as the stationary chromatographic phase is described. The column was coupled on-line to an ICP-MS detector for the determination of actinides. The method is compared with one based on the use of commercially available cation-exchange stationary phases. The analytical procedure was validated by the use of certified reference materials as well as by other independent analytical techniques. It was demonstrated that the UTEVA-Spec. column can be used at the same time as a pre-concentration column, as well as a chromatographic column, lowering the detection limit of analysis down to a few pg g^{-1} .

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has become one of the most successful methods in atomic spectroscopy, owing to its high detection power and true multi-elemental capability. Nevertheless, the analytical figures of merit are limited by spectroscopic and non-spectroscopic interference. Spectroscopic interferences are caused by atomic or molecular ions having the same nominal mass as the analyte isotope of interest. Recently, the use of ICP-MS instruments based on double-focusing sector field mass spectrometers (ICP-SFMS) has been proposed in order to overcome such interferences.¹

Quadrupole and sector ICP-MS are very intensively exploited for the determination of longer lived radioisotopes.²⁻⁴

In the case of the spectroscopic interferences due to isobars of different elements, for example, those for transuranium elements or fission products (Table 1), even the resolution of sector field ICP-MS is insufficient. In these cases a chemical separation of the elements is necessary. In our laboratory, the use of a chromatographic separations system coupled on-line to an ICP-MS quadrupole instrument has been exploited for the determination of the complete inventory of fission products and actinides in solutions of spent nuclear fuel as well as in environmental samples.⁵⁻⁷ The chromatographic phases used consisted of commercially available columns from Dionex and the separation mechanisms were based on cation exchange. Automated radiochemical separation based on the use of Eichrom resins has been recently revised.⁸ The use of UTEVA-Spec. has also been investigated for the separation on-batch of U and Pu from fission product and minor actinides before their measurements by thermal ionization mass spectrometry (TIMS).⁹ In this paper we investigated the use of UTEVA-Spec. as a stationary chromatographic phase coupled on-line with ICP-MS. A method based on extraction chromatography for the simultaneous determinations for Th, Np, U and Pu isotopes was developed. Interferences from Am and Cm could

be avoided by exploiting their elution in the dead volume of the column.

The method has been compared with that based on the use of the CS10 (Dionex) column for the separation of Np, U and Pu.⁶

Experimental

Instrumentation

An Elan 5000 (Perkin-Elmer SCIEX, Thornhill, Ontario, Canada) ICP-MS instrument was modified for installation in a glove-box as described elsewhere.^{10,11} The eluent from the Dionex 4500I (Sunnyvale, CA USA) gradient high-performance liquid chromatographic (HPLC) pump passed inside the box through a Dionex CG2 guard column, which was used only as a security column (*i.e.*, to prevent any liquid flow from the box to the outside). After the inlet, a pneumatically activated four-way high-pressure valve was used for injection prior to separation on the column, which was finally connected directly to the cross-flow nebulizer. Helium gas was used for degassing the eluents and to activate the injection valve from the HPLC pump automatically. The waste from the spray chamber was pumped out with a two-way peristaltic pump

Table 1 List of the more common isobaric interferences for transuranium elements and fission products

Mass	Elements
134	Cs–Ba
135	Cs–Ba
137	Cs–Ba
144	Ce–Nd
147	Pm–Sm
151	Sm–Eu
155	Eu–Gd
232	Th–U
238	U–Pu
241	Am–Pu
242	Pu–Cm
243	Am–Cm

[†]Present address: European Commission, JRC, Institute for Health and Consumer Protection, TP 260, 21020 Ispra, Italy

(Gilson, Villiers-le-Bel, France) and stored inside the glove-box.

Reagents and materials

Natural element standards (^{232}Th , ^{238}U) were obtained from SPEX (Grasbrunn, Germany) as $1000\ \mu\text{g ml}^{-1}$ stock standard solutions and diluted as necessary with 3 M nitric acid. Enriched isotopes ^{243}Am , ^{248}Cm and ^{230}Th from Amersham (Braunschweig, Germany), a certified enriched ^{233}U from IRMM (Geel, Belgium), and a ^{237}Np standard from Los Alamos National Laboratory (Los Alamos, NM, USA) were used. Certified enriched ^{244}Pu and certified ^{238}Pu and ^{239}Pu standards were obtained from the New Brunswick Laboratory (Argonne, IL, USA) and National Institute of Standards and Technology (Gaithersburg, MD, USA), respectively. UTEVA-Spec. resin (100–150 μm) from Eichrom Inc. was used.

Nitric acid and hydrochloric acid were Suprapur grade from Merck (Darmstadt, Germany). Oxalic acid, ascorbic acid, hydrogen peroxide, sodium nitrite, sodium sulfite, hydroxylamine and Mohr's salt $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ were obtained from Merck (Darmstadt, Germany). Water purified in a Milli-Q system (Millipore, Eschborn, Germany) was used throughout.

All standard solutions, spikes and sample were prepared by dilution by mass in polyethylene bottles. Radioactive samples and standards were treated in a glove-box.

A sediment reference sample, IAEA 135, certified for ^{232}Th was used. The sample was prepared in a clean laboratory (class 10-100) using a microwave digester (Gesa 301, Prolabo, France).

Column preparation

The UTEVA-Spec., TRU and TEVA resins from Eichrom were used to pack the chromatographic analytical columns to be connected on-line to an ICP-MS detector. For this purpose columns of length of 5 cm and 4 mm internal diameter were used.

In particular the UTEVA-Spec. resin, exploited in this investigation, consisted of particles with an external diameter of 100–150 μm .

Quantification procedures

The samples, spiked sample and spikes were injected into the chromatographic system. Integration of chromatographic peaks was performed using the software package Origin[®] (Microcal Software Inc., Northampton, MA, USA). Quantitative results based on peak areas were obtained by isotope dilution analysis as well as the standard additions method.

Procedures for separation and pre-concentration

For the normal sample injection in the chromatographic column, a four-way valve as shown in Fig. 1A was used. In the standard configuration, when the valve is in the off position, the syringe in position (3) that fills up the loop (4–8), is used for sample injection. The eluent enters in position (5), flows through the loop (8–4) that contains the sample and flows to the chromatographic column through the exit (1), and then to the ICP-MS instrument.

To carry out the on-line pre-concentration of the actinides, the system was modified as follows (Fig. 1B): when the valve is closed (off), the sample solution is loaded onto the column (4–8) by a two-way peristaltic pump. In this way the actinides are retained on the column, while the matrix flows to waste (7). The eluent enters in (5), flows through the connection tube and exits at (1), and then goes directly to the ICP-MS instrument. When the pre-concentration operation is finished, the valve is

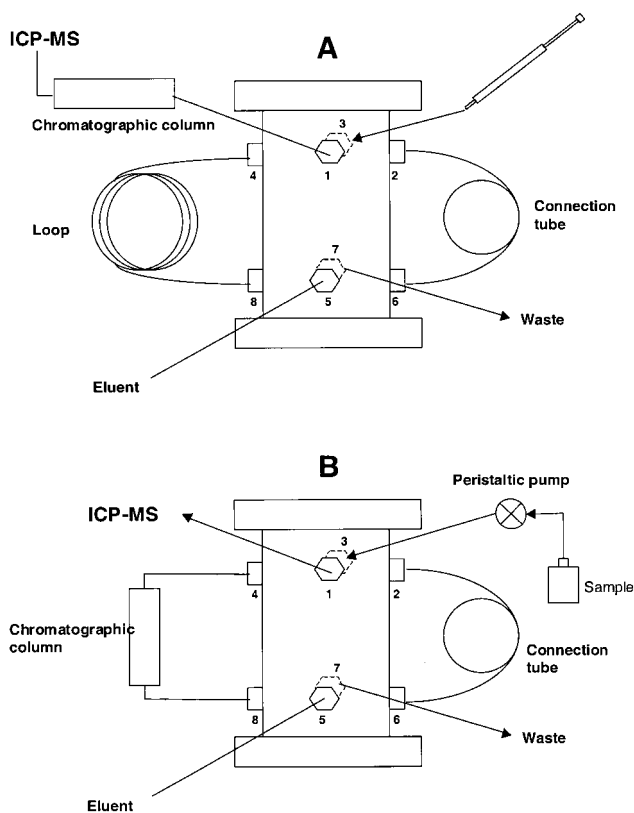


Fig. 1 Four-way valve configuration for chromatographic separation on UTEVA-Spec: A, normal chromatographic elution and B, on-line pre-concentration and successive chromatographic separation.

opened and the eluent flows through the chromatographic column (8–4), exits at (1) and goes to the ICP-MS instrument.

Results and discussion

Hydrochloric or nitric acids (more than 2 M) are normally employed in order to retain actinides on the UTEVA-Spec. resin.¹² According to the sample's acidity, Np and Pu can be present in solution in different oxidation states. In fact, Pu can be present as Pu(III), Pu(IV) and Pu(VI), and Np as Np(IV), Np(V) and Np(VI). Since our interest is in performing quantitative determinations of the total elements and not to study their speciation, it was necessary to have them in a single oxidation state. Nevertheless, it has been observed that this resin is very appropriate for performing speciation of actinides and further research is on going in this direction. For both, the oxidation state IV was the choice. This was because: (1) Pu(III) and Np(V) are not retained on the UTEVA-Spec.; and (2) Np(VI) and Pu(VI) have the same elution time as U(VI), and therefore the isobaric interference at mass 238 between U and Pu cannot be resolved. Moreover high concentrations of ^{238}U cause interference on Np determination at mass 237.^{5,6}

In order to obtain Pu and Np in the oxidation state IV, different redox agents were tested; reported in Table 2 along with the oxidation states obtained by their use for both Pu and Np. Among the different agents studied, as can be seen from the Table 2, only hydrogen peroxide is capable of giving both elements in the oxidation state (IV). Nevertheless, the procedure employing hydrogen peroxide is quite complicated and it is necessary to bring the solution to the boiling point; a potential hazard when performed in a glove-box on radioactive samples. In view of this, it was decided to employ another procedure consisting of the combined use of two redox agents. According to this procedure, the Mohr's salt was used in order to convert all Np to the Np(IV). The Pu was converted to Pu(III). After

Table 2 Different redox reagents and relevant oxidation states of Np and Pu

Redox agent	Plutonium	Neptunium
Ammonium and iron (ii) sulfate.	III	IV
Sodium sulfite	III and IV	IV and V
Hydrogen peroxide	IV	IV
Sodium nitrite	IV	IV and V
Ascorbic acid	III	IV

4 min, which is the necessary time to complete the reaction to obtain all Np in the oxidation state (iv), sodium nitrite is added in order to oxidise the Pu(III) to Pu(IV). This procedure is less complicated, but sensitive to the reaction time. In Fig. 2(a) and (b) the kinetic of the reaction after addition of sodium nitrite to the sample treated with Mohr's salt is reported. A solution containing 50 ng g⁻¹ of Np and Pu was analyzed at different times using the UTEVA Spec. resin in the chromatographic column coupled on-line to the ICP-MS detector. As can be seen, after 10 min of reaction with sodium nitrite, the oxidation to state iv is complete for both the analytes.

Table 3 Chromatographic elution program

Step	Time/ min	Flux/ ml min ⁻¹	Eluent	Valve position	Analytical process
1	0.0	0.5	HNO ₃ , 3 M	Off	Column precondition
2	0.4	0.5	HNO ₃ , 3 M	On	Sample Injection and elements retention
3	1.7	1	HCl, 2 M	On	Th, Np and Pu elution
4	5.0	1	HCl, 0.025 M	On	U elution
5	8.6	1	HNO ₃ , 3 M	Off	Column precondition

Retention and elution of actinides on UTEVA-Spec

U(vi), Np(iv), Pu(iv), and Th(iv) have a high value for the coefficient of distribution on the UTEVA-Spec. in 3 M nitric acid.¹² On the other hand, the three-valent actinides are not retained under these conditions independently of the concentration of the nitric or hydrochloric acid solution.¹² Consequently, Am(III) and Cm(III) are eluted at the dead time of the chromatographic system, thus avoiding isobaric interferences with Pu. When using 2 M hydrochloric acid solution, the distribution coefficient of the tetra- and hexavalent actinides

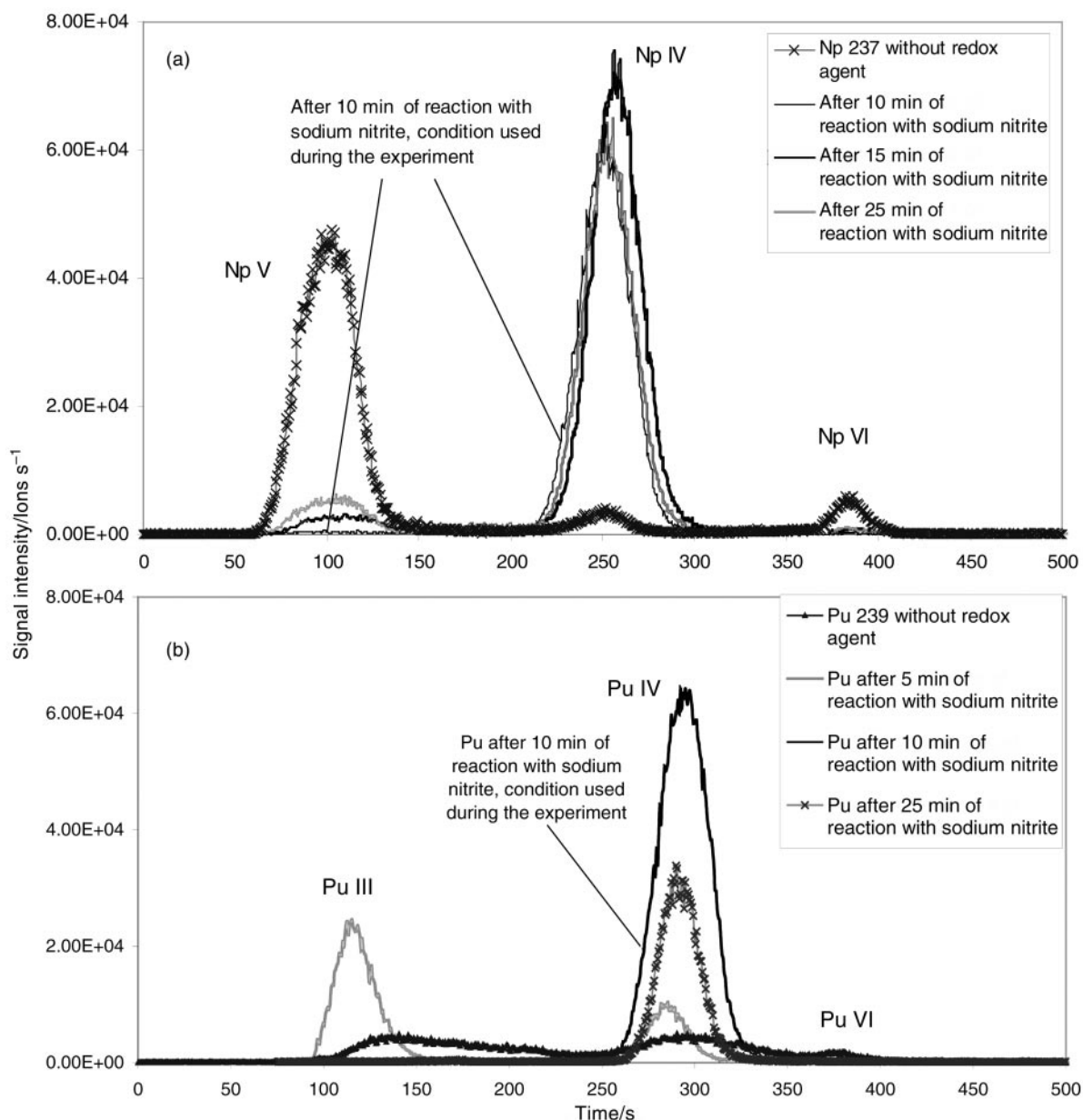


Fig. 2 (a) Kinetic of reaction of ²³⁷Np with sodium nitrite (redox agent) and (b) kinetic of reaction of ²³⁹Pu with sodium nitrite (redox agent).

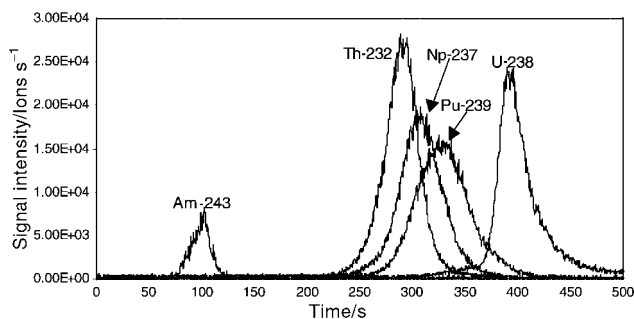


Fig. 3 Chromatogram of a solution containing Th, Np, Pu and U (50 ng g^{-1} of each) and Am (10 ng g^{-1}), obtained according to the elution conditions of Table 3.

decreases very rapidly. At this concentration of hydrochloric acid, Th, Pu and Np can be eluted. For U it is necessary to use a more diluted solution, e.g., 0.025 M hydrochloric acid. In Table 3, the chromatographic conditions utilized for the separation of U, Np, Pu and Th from the UTEVA-Spec. are reported. The concentration of the hydrochloric acid was changed after 5 min to 0.025 M in order to elute the U. In Fig. 3, the chromatogram obtained for a solution 3 M HNO_3 containing 50 ng g^{-1} of Th, Np, U and Pu, and 10 ng g^{-1} of Am, after a previous redox reaction with Mohr's salt and sodium nitrite, is reported. As can be seen, Am is eluted in the void volume of the column, and Th, Np, Pu and U are eluted in sequence in a total time of 500 s.

Use of a complexing agent (oxalic acid) in the eluent solution

The resolution between the peaks of Th, Np and Pu, relative to that of U, can be increased by adding oxalic acid in the eluent solution consisting of hydrochloric acid. The oxalic acid can vary, in different ways, the constant of repartition of the tetra- and hexavalent actinides according to the value of the constant of formation for the different complexes.¹³ Oxalic acid with a concentration range of 0.02–0.1 M was added to the 2 M hydrochloric acid solution. To avoid problems of carbon deposition on the torch and on the cone of the instrument, the maximum concentration of oxalic acid that can be used is 0.1 M. Fig. 4 shows the chromatogram obtained for one solution containing 50 ng g^{-1} of Th, U, Np and Pu, and 10 ng g^{-1} of Am, according to the elution program reported in Table 3. The only change was the presence of 0.1 molar oxalic acid in the solution of 2 M hydrochloric acid in step 3. As can be seen in Fig. 4, the separation of U from the other analytes is improved.

Linear dynamic range

In order to evaluate the linear dynamic range for the different analytes, solutions containing different concentrations varying

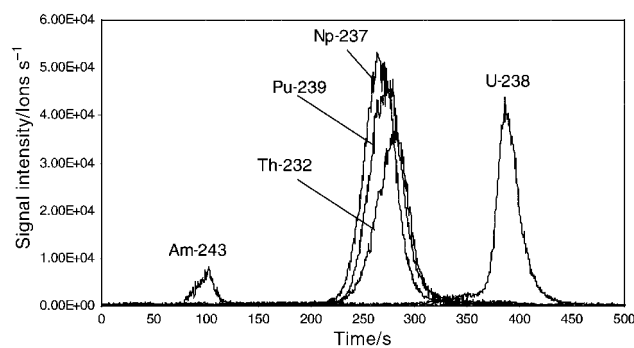


Fig. 4 Chromatogram of a solution containing Th, Np, Pu and U (50 ng g^{-1} of each) and Am (10 ng g^{-1}) adding 0.1 M oxalic acid to the eluent at step 3 of Table 3.

between 10 and 100 ng g^{-1} were analyzed. For each value of concentration, two measurements were performed. A decrease in the peak areas was observed due to the loss of the extractant adsorbed on the inert support during subsequent elution runs. For this reason it was decided to add ^{230}Th , ^{233}U and ^{244}Pu to the sample as internal standards. All the calibration curves were obtained by using the ratio between the area of the analyte and the relative spike added to the sample versus the ratio of the concentration between the analyte and the spike. For Np, since no spike is available due to the fact that ^{237}Np is the only long-lived isotope that can be used with an ICP-MS, the calibration curve was obtained using the spike applied for the U determination. For all four analytes the parameters of the calibration curves, calculated by means of the method of linear regression had $r^2 = 0.999$.

Detection limit and precision

The detection limit was calculated by means of repeated measurements of the blank. The blank was constituted by a solution of Mohr's Salt (0.1 M) and sodium nitrite (0.2 M) in HNO_3 (3 M). Assuming that the minimum detectable is equal to three times the standard deviation of the measured signal of the blank, it was possible to calculate the detection limit. Using our experimental conditions the detection limit was typically equal to 0.7 ng g^{-1} . The precision, based on the relative standard deviation of the peak area calculated on the basis of seven repeated measurements, was always less than 2% for the concentration range 10– 100 ng g^{-1} .

Validation of the analytical procedure

In order to validate the analytical procedure, two different reference materials were analyzed. One consisted of one sediment (IAEA 135) certified for the Th content, and the other one was a sample analyzed for ^{238}U and ^{238}Pu by several analytical techniques.¹⁴

The certified sediment was treated in a clean laboratory class 10-100. The dissolution was performed by means of a digester operating with microwaves, and ultra pure acid. After that, the sample solution was introduced into a glove-box and ^{237}Np was added in known amounts in order to validate the procedure for this element. The amount of Np added was of the same order of magnitude as the other actinides in the sample solution (several ng g^{-1}). Four different aliquots were prepared from this sample solution. For each of the four aliquots, ^{233}U and ^{230}Th were added in a concentration equal to 10 ng g^{-1} for isotope dilution analysis. In the other three aliquots, increasing amounts of ^{238}U , ^{232}Th and ^{237}Np were added in order to calculate the concentration of the three elements by means of the standard additions method. All solutions were analyzed with chromatographic separation using UTEVA-Spec. and ICP-MS. For all aliquots, the reaction with Mohr's salt and sodium nitrite was performed. A $250 \mu\text{l}$ sample was injected onto the column. In Fig. 5 a typical chromatogram is reported. The appearance of a

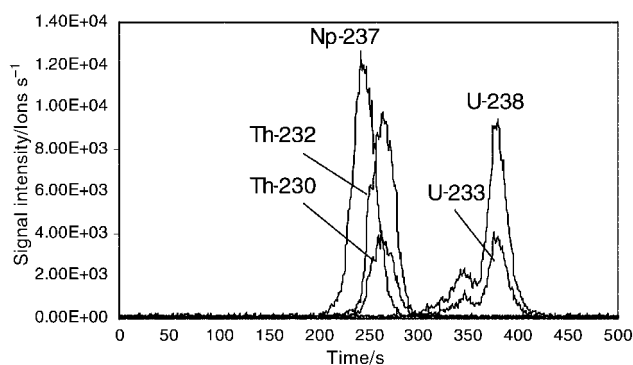


Fig. 5 Chromatogram obtained for the sample IAEA 135.

Table 4 Parameters of the calibration curve. Experimental and expected values, together with interval confidence at 95% for $n=3$, obtained for the IAEA 135 sample

Element	Calibration curve	Experimental values/ng g ⁻¹	Expected values/ng g ⁻¹
²³² Th	$y=0.66x+1.34$ $r^2=0.999$	202 ± 5.6	215 ± 11^a
²³⁸ U	$y=0.69x+0.80$ $r^2=0.999_0$	100 ± 3.4	105^b
²³⁷ Np	$y=0.91x+3.32$ $r^2=0.999_1$	325 ± 8.4	337^c

^aCertificate value. ^bRecommended value. ^cAdded to the sample.

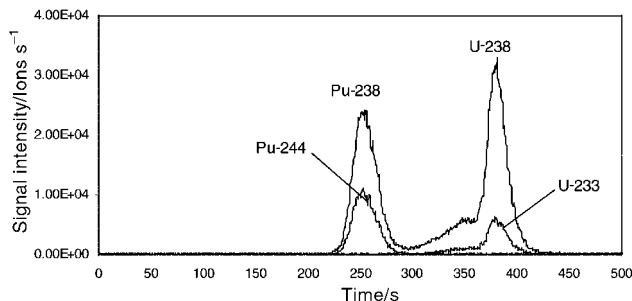


Fig. 6 Chromatogram obtained for the leaching solution.

peak at 300 s is imputed to the change in the eluent at this time (*c.f.*, Table 3 step 4). This peak shape does not influence the quantitative determination of U because it is reproducible in the chromatograms of the spiked samples.

In Table 4 the parameters of the calibration curves obtained for the different samples are reported together with the experimental values, expected values and certified values in terms of concentration. As can be seen, the experimental values are in good agreement with the expected values.

The second sample analyzed for the validation of the analytical procedure consisted of a leaching solution containing ²³⁸U and ²³⁸Pu. This sample was previously analyzed in the laboratory by several analytical procedures based on independent techniques.¹⁴ Also, for the calculation of the concentration, the method of internal standard additions was performed. The same experimental conditions used for the analysis of the sample IAEA 135 were also used for the analysis of this leaching solution. In Fig. 6 the chromatogram obtained for this solution is reported. In Table 5 are reported the parameters relative to the calibration curve obtained for ²³⁸U and ²³⁸Pu, together with the concentrations obtained *versus* the expected concentrations, according to the other measurements performed in the laboratory. Moreover, the same leaching solution was also analyzed using a method developed in the laboratory based on oxidation with silver oxide and chromatographic elution with DAP (40 mM) in HNO₃ (0.6 M) on IonPac CS10.⁶ The results are also compared in Table 5. As can be seen they are all in good agreement. However the accuracy, at least for ²³⁸U, is better when using UTEVA-Spec. than the CS10 column. In the case of UTEVA-Spec., the chromatography based on the extraction mechanism improves the efficiency of

Table 5 Calibration curve parameters relative to ²³⁸U and ²³⁸Pu, obtained by the standard additions method: measured and expected values, together with standard deviation, for the ²³⁸Pu and ²³⁸U determination in a leaching solution by UTEVA-Spec. and CS10 columns

Element	Calibration curve	UTEVA value/ng g ⁻¹	Expected value/ng g ⁻¹	CS 10 value/ng g ⁻¹
²³⁸ Pu	$y=0.94x+0.76$ $r^2=0.999_1$	90 ± 2	92 ± 2	91 ± 2
²³⁸ U	$y=0.74x+0.79$ $r^2=0.99_3$	19.9 ± 0.4	20 ± 1	21 ± 1

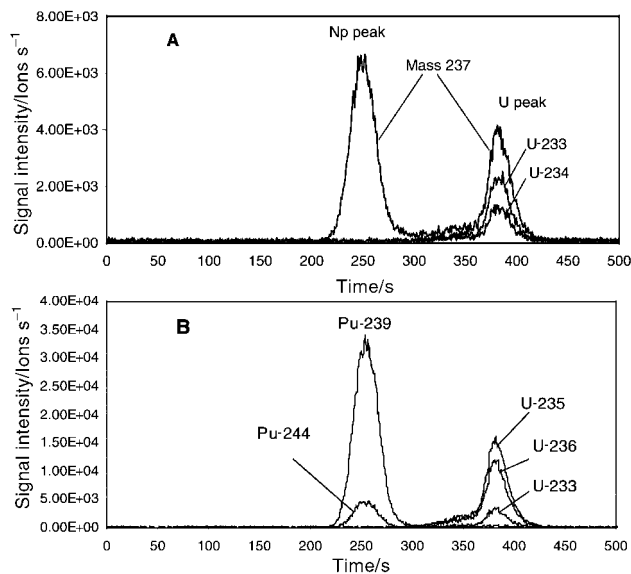


Fig. 7 Chromatogram obtained for a spent fuel solution. A, Separation Np/U. The peak relevant to U at mass 237 is due to the interference of ²³⁸U on ²³⁷Np. The others U isotopes are also present. B, Separation Pu/U.

elution with respect to that based on a cation-exchange mechanism.

Real samples

To verify the feasibility of the application of the proposed analytical procedure to a real sample, Np, U and Pu were determined for an irradiated nuclear fuel sample, which was dissolved in a hot cell following the standard procedure.¹⁵

The quantity of Np, U and Pu was measured according to the standard additions method. Fig. 7A shows a typical chromatogram for Np determination. The peak relevant to U found by scanning mass 237 is due to the interference of ²³⁸U on ²³⁷Np and is a good example of the need of a chromatographic separation between U and Np for samples of high U concentration.

The parameters for the Np calibration curve are: $y=1.06x+1.39$, $r^2=0.999_7$. Calculation of Np concentration, according to the above mentioned parameters, gives 13.2 ± 0.2 ng g⁻¹.

Fig. 7B shows the chromatogram relative to ²³⁹Pu and ²³⁵U determination in the diluted solution. Table 6 reports the calculated concentrations, referred to the diluted spent fuel solution analysed, for ²³⁵U and ²³⁹Pu as well as the total U and Pu concentrations, obtained by the analytical procedure proposed as well as by TIMS.

In order to obtain the isotopic composition for the irradiated fuel solution, Pu and U isotopes were measured. The values in weight % are reported in Table 7 and are in agreement with those obtained by isotope dilution thermal ionization mass spectrometry after chemical separation of U and Pu.

Table 6 ²³⁵U and ²³⁹Pu concentrations, together with the standard deviations, in the diluted solution, obtained by the analytical procedure proposed and by TIMS

Element	Analyzed solution concentration	
	Proposed analytical procedure	TIMS
²³⁵ U	69 ± 2 ng g ⁻¹	67.2 ± 0.6 ng g ⁻¹
²³⁹ Pu	90 ± 2 ng g ⁻¹	94.7 ± 0.5 ng g ⁻¹
U _{total}	10 ± 1 µg g ⁻¹	10.5 ± 0.3 µg g ⁻¹
Pu _{total}	0.18 ± 0.02 µg g ⁻¹	0.18 ± 0.01 µg g ⁻¹

Table 7 Pu and U isotopic composition obtained from an irradiated nuclear fuel, analyzed by the analytical procedure proposed and by TIMS

Isotope	Weight (%)		Isotope	Weight (%)	
	Proposed analytical procedure	TIMS		Proposed analytical procedure	TIMS
²³⁸ Pu	3.1±0.5	3.4±0.4	²³⁴ U	0.03±0.01	0.014±0.005
²³⁹ Pu	50±7	51.3±3.6	²³⁵ U	0.7±0.1	0.64±0.05
²⁴⁰ Pu	24±3	23.2±1.9	²³⁶ U	0.7±0.1	0.60±0.05
²⁴¹ Pu	14±2	13.5±0.7	²³⁸ U	98.5±1.4	98.7±0.9
²⁴² Pu	9±1	8.4±0.5			

Pre-concentration

To lower the analytical procedure detection limit down to the pg g^{-1} level, the chromatograph–valve–column–ICP-MS system was modified to carry out an on-line pre-concentration of an actinide aqueous solution. The scheme shown in Fig. 1 is used.

In this way a pre-concentration factor that is proportional to the sample volume flowing through the column is obtained. The advantage is evident when very dilute aqueous solutions have to be analysed. Fig. 8A shows a chromatogram of a waste solution from a uranium enrichment plant. The concentration was about 1 ng g^{-1} , and the chromatogram was obtained with the methodology proposed with the standard configuration. As can be seen, the analytical signal is very disturbed with a low signal-to-noise ratio, and, in this condition, it is difficult to determinate the concentration. Fig. 8B shows the chromatogram of 5 ml of the same solution, analyzed with the

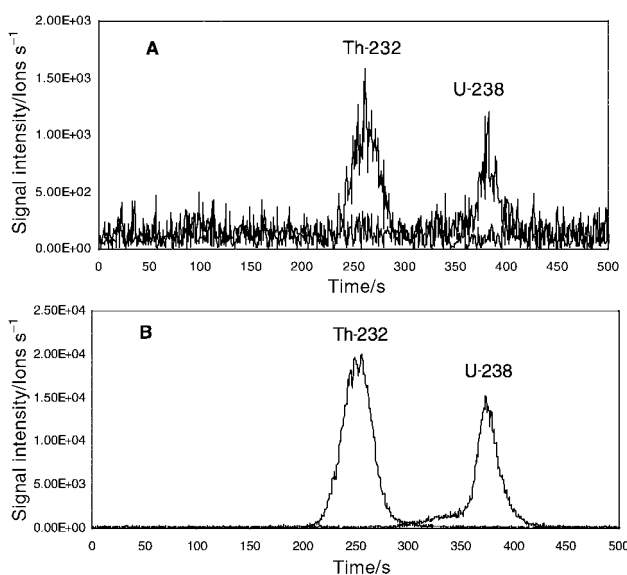


Fig. 8 Chromatogram obtained for a waste solution containing 1 ng g^{-1} of Th and U, respectively: A, without on-line pre-concentration and B, with on-line pre-concentration.

preconcentration system described above. In both the measurements the same eluents and conditions were used. In the second case a larger signal-to-noise ratio was obtained and consequently the concentration calculated has a lower error.

Conclusion

The UTEVA-Spec. resin based on the extraction mechanism can be used for packing chromatographic columns to be used on-line with an ICP-MS detector. The advantage of this column is the selectivity for actinides. By adding a complexing agent such as oxalic acid to the 2 M hydrochloric acid eluent solution, the separation between uranium and the other actinides is improved. Therefore the method is applicable to samples containing a large amount of uranium. Of particular interest is the possibility of performing on-line pre-concentration, using the same column both for pre-concentration and chromatographic separation. Moreover the method can be exploited to perform speciation studies of actinides.

Acknowledgements

Maria Betti and Roger Fuoco dedicate this paper to Prof. P. Papoff on the occasion of his 80th birthday. The authors thank Dr C. Apostolidis for useful discussions.

References

- 1 N. Jakubowsky, L. Moens and F. Vanhaecke, *Spectrochim. Acta, Part B*, 1998, **53**, 1739.
- 2 J. S. Becker, R. S. Soman, K. L. Sutton, J. A. Caruso and H. J. Dietze, *J. Anal. At. Spectrom.*, 1999, **14**, 933.
- 3 J. S. Becker, H. J. Dietze, J. A. McLean and A. Montaser, *Anal. Chem.*, 1999, **15**, 3077.
- 4 J. S. Becker and H. J. Dietze, *J. Anal. At. Spectrom.*, 1999, **14**, 1493.
- 5 M. Betti, *J. Chromatogr. A*, 1997, **789**, 369.
- 6 J. M. Barrero Moreno, M. Betti and J. I. García Alonso, *J. Anal. At. Spectrom.*, 1997, **12**, 355.
- 7 J. M. Barrero Moreno, M. Betti and G. Nicolaou, *J. Anal. At. Spectrom.*, 1999, **14**, 875.
- 8 J. W. Grate and O. B. Egorov, *Anal. Chem.*, 1998, **70**, 3920.
- 9 C. Apostolidis, R. Molinet, P. Richir, M. Ougier and K. Mayer, *Radiochim. Acta*, 1998, **83**, 21.
- 10 J. I. García Alonso, F. Sena, Ph. Arboré, M. Betti and L. Koch, *J. Anal. At. Spectrom.*, 1995, **10**, 381.
- 11 M. Betti, J. I. García Alonso, Ph. Arboré, L. Koch and T. Sato, in *Application of Plasma Source Mass Spectrometry*, ed. G. Holland and N. Eaton, Royal Society of Chemistry, London, 1993, p. 205.
- 12 E. P. Horwitz, M. L. Dietz, R. Chiarizia, H. Diamond, A. M. Esslign and D. Graczyk, *Anal. Chim. Acta*, 1992, **266**, 25.
- 13 J. J. Katz, G. T. Seaborg and L. R. Moor, *The Chemistry of Actinide Elements*, Chapman and Hall, London, New York, 1986, vol. 2, p. 1497.
- 14 D. Solatie, P. Carbol, M. Betti, F. Bocci, T. Hiernaut, V. Rondinella and J. Cobos, *Fresenius' J. Anal. Chem.*, 2000, **368**, 88.
- 15 J. M. Barrero Moreno, J. I. García Alonso, Ph. Arboré, G. Nicolaou and L. Koch, *J. Anal. At. Spectrom.*, 1996, **11**, 929.

Studies on simultaneous separation and determination of lanthanides and actinides by ion chromatography inductively coupled plasma mass spectrometry combined with isotope dilution mass spectrometry†

L. Perna,^{a,b} F. Bocci,^a L. Aldave de las Heras,^a J. De Pablo^b and M. Betti*^a

^aEuropean Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany

^bUniversidad Politecnica de Catalunya, Chemical Engineering Department, Av. Diagonal 647, 08028 Barcelona, Spain

Received 8th March 2002, Accepted 24th April 2002

First published as an Advance Article on the web 6th June 2002

A procedure for the simultaneous separation and determination of fission products (lanthanides) and actinides (Pu, Np, U, Am and Cm) is described. The method is based on the use of an anionic/cationic mixed bed chromatographic column (CS5A, Dionex), coupled on-line to an ICP-MS detector. Optimisation of the parameters was carried out with standard solutions containing actinides and lanthanides at the 50 ng ml⁻¹ concentration level. The effects of different oxidising/reducing agents as well as different mobile phases on the intensity and position of the chromatographic peaks were investigated. The analytical procedure was validated by the use of certified materials as well as by other independent techniques. Analytical figures of merit resulting from the procedure were compared with those obtained using other commercially available ion-exchange stationary phases. The procedure developed was applied to the inventory of spent nuclear fuel samples. Detection limits of 0.25 ng ml⁻¹ and 0.45 ng ml⁻¹ were obtained for lanthanides and actinides, respectively. Analytical precision was typical better than 5% over seven repeated measurements.

Introduction

Radionuclides can be introduced into the environment through a variety of systems and processes.^{1–3} Their mobilisation in the environment has been studied for many years, with the prime objective of tracing the routes by which they accumulate in the food chain and become available for human consumption.

The determination of long-lived radionuclides, like fission products and actinides, is of great importance. For instance, the determination of their isotopes is essential in nuclear waste management, due to their long radioactive half-lives, high radiological toxicity and criticality concerns. Moreover, actinide isotope determinations are necessary for waste classification purposes.⁴ In environmental radiochemistry, isotope speciation is of relevance in order to study transfer/migration mechanisms related to geological⁵ and cosmic⁶ samples, including age determinations⁷ as well as bioavailability studies.^{8,9}

In the majority of these investigations it is necessary to obtain the complete inventory of fission products and actinides. Compared to radiometric methods, mass spectrometric-based instrumental techniques offer the best detection limits for the determination of the long-lived radionuclides.^{10–14} ICP-MS is at present the most widely used technique, due to its multi-elemental capability and very low detection limits.^{15,16} Also, isotope dilution mass spectrometric (IDMS) analysis can be applied to attain very accurate results.^{17,18}

However, a problem that is difficult to solve in the determination of long-lived radionuclides is the isobaric interference of certain elements.^{19,20} Therefore, for the determination of long-lived radionuclides, a chemical separation of interfering elements is required before mass spectrometric analysis. The application of chromatographic separation coupled on-line to a

mass spectrometric detector is very efficient for this purpose.²¹ For instance, HPLC-ICP-MS on-line coupling has been applied for the separation of long-lived radionuclides and stable isotopes of lanthanides in a tantalum target from a spallation neutron source irradiated with 800 MeV protons^{22,23} in order to determine the spallation nuclides. The same authors also proposed the on-line coupling of capillary electrophoresis with ICP-MS.¹⁴ This approach reduces the sample volume further from the µl range using HPLC-ICP-MS to the nl range, which is very interesting when high-radioactive solutions have to be characterised. Other authors have coupled on-line solid phase extraction chromatography²⁴ as well as chelation ion chromatography²⁵ with sector-field ICP-MS for the determination of trace amounts of actinides in environmental and biological samples.

ICP-MS in connection with chromatographic separation techniques will play an important role in the future for making element speciation methods more capable of routine analysis. IDMS is the only method able to prove possible transformations of the element species during the analytical procedure.^{26–28} Therefore, with respect to quality assurance of element speciation, IDMS is the candidate method to become a routine tool in analytical chemistry.

In our laboratory HPLC has been coupled on-line to ICP-MS.²⁹ Methodologies based on HPLC-ID-ICP-MS for the inventory of fission products^{30–33} as well as of actinides^{20,34} have been developed and applied to nuclear and environmental samples. However, an analytical procedure providing both the complete inventory of fission products and actinides at the same time has not been yet evaluated.

In this paper a method for the complete inventory of fission products and actinides, based on the use of an anionic/cationic mixed bed chromatographic column coupled on-line to an ICP-MS detector and combined with IDMS, is described. The results obtained for the simultaneous separation and

†Presented at the 2002 Winter Conference on Plasma Spectrochemistry, Scottsdale, AZ, USA, January 6–12, 2002.

determination of lanthanides (fission products from mass 139–160) and actinides (Pu, Np, U, Am and Cm) are reported in terms of accuracy, precision and dynamic range. The method is compared with those previously developed.

Experimental

Instrumentation

An Elan 5000 ICP-MS instrument (PerkinElmer SCIEX, Thornhill, Ontario, Canada), modified to handle radioactive samples in a glove-box and coupled with a GP50 high-pressure chromatographic pump (Dionex, Sunnyvale, CA, USA), was used. Details of the instrumental set-up have been published previously.²⁹ The Dionex high-pressure pump was located outside the glove-box while the four-ways injection valve (Dionex, Part No 42766, 250 µl loop), guard column and analytical column were placed inside the glove-box.³⁰ The effluent from the chromatographic column was directed to a cross-flow nebulizer. A two-way peristaltic pump (Gilson, Villiers-le-Bel, France) was used to carry the waste to a vessel inside the glove-box. Standard plasma and ion lens operating conditions are summarized in Table 1. A microwave digester (Alabo, PerkinElmer, Germany) was used for the preparation of the certified sample, SRM 4355. A rotor 6MF100 and an evaporation rotor 6EVAP were employed for sample decomposition and sample concentration, as well as for HF evaporation, respectively.

Reagents and materials

Lanthanide and actinide separations were performed using Dionex CS5A and CG5A mixed bed columns. The eluent consisted of a mixture of 100 mmol l⁻¹ oxalic acid and 190 mmol l⁻¹ lithium hydroxide (Suprapur grade, Merck, Darmstadt, Germany) and of 2 mol l⁻¹ hydrochloric acid, (Suprapur grade, Merck).

Natural element standards (La, Ce, Pr, Nd, Sm, Eu, Gd) were obtained from SPEX (Grasbrunn, Germany) as 1000 µg ml⁻¹ stock standard solutions and diluted as necessary with 1% nitric acid. Certified enriched isotopes ²⁴³Am, ²⁴²Pu, ²⁴⁸Cm and ²³⁷Np were obtained from the "D.I. Mendeleev" Institute for Metrology (St. Petersburg, Russia). A certified enriched ²³³U and ²⁴⁴Pu was obtained from IRMM (Geel, Belgium) and a certified enriched ¹⁵⁰Nd was obtained from Oak Ridge National Laboratory (USA). Nitric acid and hydrochloric acid were Suprapur grade from Merck.

Water purified in a Milli-Q system (Millipore, Eschborn, Germany) was used throughout.

All standard solutions, spikes and samples were prepared by dilution by mass in polyethylene bottles previously cleaned according to a procedure for trace element analysis.³⁵

Table 1 ICP-MS operating conditions

<i>ICP ion source—</i>	
Rf power	1045 W
Cooling Ar flow rate	15.0 l min ⁻¹
Nebuliser Ar flow rate	0.98 l min ⁻¹
Auxiliary Ar flow rate	0.9 l min ⁻¹
<i>Lens voltage—</i>	
Einzel lens E1	70
Bessel box B	76
Photon stop S2	2
Bessel box P	45
<i>Data acquisition—</i>	
Dwell time	100 ms
Replicate time	100 ms
Scan mode	Peak hop
Reading per replicate	1
Sweeps per replicate	1

Radioactive samples and standards were treated in a glove-box. A sediment reference sample, SRM4355 from NIST, was used for the validation of the proposed analytical procedure.

Experimental procedures

Optimisation of the variables affecting the separation

The sample, treated with an oxidising/reducing agent for 5–15 min, was injected through a pneumatic four-way valve onto the analytical column. The eluents, in isocratic mode, supplied by the high-pressure pump reached the column and carried the sample to the nebulizer. This was the general procedure used to test different redox reagents and the acidity of different samples. In all instances the resolution and the recovery were calculated. The area ratios after IC separation were also calculated and compared with those obtained without separation.

Sample preparation

Spent nuclear fuel samples. Fuel pellets (*ca.* 30 g) of spent nuclear fuels were dissolved (in duplicate) in 7 M HNO₃ in a hot-cell facility by refluxing and the resulting solution was diluted with 4 M HNO₃. A second dilution by mass was performed using 1 M HNO₃, and 5 ml of these solutions containing about 100 µg of fuel per gram of solution were transferred into a glove-box for further dilution and spiking. A solution containing natural La, Ce, Pr, Nd, Sm, Eu, Gd and ²³³U, ²⁴²Pu, ²³⁷Np, ²⁴³Am and ²⁴⁸Cm was prepared by measuring aliquots by mass in the glove-box in order to spike the sample for analysis.³¹

Certified sediment sample. The total dissolution of two different aliquots of the certified sediment SRM4355 from NIST was performed by means of a microwave digester and ultra-pure acid by applying the programme reported in Table 2. Before starting the process, 4 ml HNO₃ (65% v/v), 10 ml HCl (30% v/v) and 6 ml HF (48% v/v) for each gram of sample were added to the samples. Dissolved samples were diluted with 1 M nitric acid, introduced into a glove-box and ²⁴⁴Pu, ²³⁷Np, ²⁴³Am and ²⁴⁸Cm were added in known amounts in order to validate the procedure for these elements.

Optimisation of the isotope dilution procedure

In order to optimise the spike addition, the concentrations of the isotopes present in the spent fuel solution were determined semi-quantitatively based on the response curve of the instrument.³⁰ For this purpose, solutions containing Tb and Th were added at concentration levels of about 50 ng ml⁻¹. Tb was used to estimate the amount of lanthanides and Th was added to calculate the amount of actinides. Mass spectra were measured for all samples in the range 139–160 u for lanthanides and 230–250 u for actinides using the standard operating conditions. The isotopic dilution analysis was performed for Nd, Am, Pu, U and Cm using spikes ¹⁵⁰Nd, ²⁴³Am, ²⁴⁴Pu, ²³³U and ²⁴⁸Cm. The ratios between the spikes and analytes were usually 1:1. The isotopes used as references in the samples were ¹⁴⁴Nd,

Table 2 Microwave programme applied for the dissolution of SRM 4355

Power/W	Time/min	Process
1000	25	Dissolution
1000 → 0	35	
0 → 400	4	Concentration
400	10	
400 → 0	8	
0 → 400	5	Evaporation HF
400	5	
400 → 0	8	

²⁴¹Am, ^{240,241,242}Pu, ^{235,238}U and ²⁴⁴Cm. The other lanthanides and Np were quantified on the basis of the standard additions method.

Quantification procedures

The samples, spiked samples and spike solutions were injected into the chromatograph consecutively. Detection was carried out by scanning at 1 point per u with a 0.1 s integration time per point and approximately 2.5 s per scan. The data were transferred to a personal computer for further treatment. Integration of chromatographic peaks was performed using the software package Origin[®] (Microcal Software Inc., Northampton, MA, USA). Quantitative results based on peak areas were obtained by isotope dilution analysis as well as the standard additions method.

Results and discussion

Oxidising/reducing agents

In acidic aqueous solution, the entire lanthanide series and Am, Cm and U are present in the solution in a single oxidation state; however, Np and Pu can be present in different oxidation states. In fact, Pu is present as Pu(III), Pu(IV), Pu(V) and Pu(VI) and Np as Np(IV), Np(V) and Np(VI).^{36–38} Since the aim of this investigation was to perform quantitative determinations of the total elements and not to study their speciation, it was necessary to convert the elements into a single oxidation state. For this purpose different redox agents in different acid media were tested, using 100 mM oxalic acid–190 mM lithium hydroxide and 2 M hydrochloric acid as eluents. Table 3 summarises the results obtained. As can be seen, among the different agents studied, only hydrogen peroxide and sodium nitrite can transform both elements into the oxidation state (IV). As already reported,²⁰ the procedure employing hydrogen peroxide is more laborious and hazardous compared with that employing sodium nitrite. Therefore, 0.2 M sodium nitrite was added to the samples prepared in 1 M nitric acid, and the total conversion was obtained in 10 min.

In a previous study³³ silver oxide was used to obtain Np and Pu in the oxidation state (VI). Under those experimental conditions, the oxidation state was stable since the eluent was 0.6 M nitric acid. In the present investigation, a pH of 4.8 for the eluent cannot stabilise the Np and Pu in the oxidised form.

Linear dynamic range

The simultaneous separation of actinide and lanthanide elements was achieved with the proposed analytical procedure using 100 mM oxalic acid–190 mM LiOH and 2 M HCl,

according to the chromatographic programme reported in Table 4. The separation was performed on a Dionex CS5A mixed bed column. In all the samples, 0.2 M sodium nitrite was added and the chromatographic injection was performed after 10 min of reaction. The sample loop used was typically 250 µl. In order to evaluate the linear dynamic range for the different analytes, solutions containing different concentration varying between 1 and 120 ng ml⁻¹ were analysed. For each value of concentration, three measurements were performed. All the sample solutions were spiked with ¹⁵⁰Nd, ²³³U and ²⁴⁴Pu as internal standards. The calibration curves were obtained by plotting the ratio between the area of the analyte and the relative spike added to the sample *versus* the concentration ratio. ¹⁵⁰Nd, ²⁴⁴Pu and ²³³U were used to evaluate the linear dynamic range of lanthanides, actinides and uranium, respectively. For all analytes the regression factor of the calibration curve, calculated by means of the method of linear regression, was typically $r^2 = 0.999$.

Detection limit and precision

The detection limit was calculated by means of repeated measurements of the blank. The blank consisted of a solution of 0.2 M sodium nitrite in 1 M nitric acid. Assuming that the minimum amount detectable is equal to three times the standard deviation of the measured signal of the blank, it was possible to calculate that the detection limit in these experimental conditions was typically 0.25 ng ml⁻¹ for lanthanides and 0.45 ng ml⁻¹ for actinides. The precision, based on the relative standard deviation of the peak area and calculated on the basis of seven repeated measurements, was always less than 5% over the entire concentration range tested.

The detection limits achievable with the IC-ICP-MS are worse than those attained when the sample is directly injected into the ICP-MS (10–100 pg ml⁻¹). This fact might be due to the high salinity of the eluent media used. However, 1 M hydrochloric acid and 1% nitric acid were used between each injection and no decrease in sensitivity was observed. Therefore, this worse detection limit might stem directly from the inherent inability of the pneumatic nebulizer used in ICP systems to equilibrate to the rapidly changing concentration of the analyte that is eluted from the ion chromatograph in a very small volume, since such nebulizers typically have large internal volumes.³⁰ The use of an MCN nebulizer might help in decreasing the detection limit.

Validation of the analytical procedure

In order to validate the analytical procedure, the certified sediment SRM4355 was analysed. Due to the different

Table 3 Different redox reagents and relevant oxidation states of Np and Pu

Redox reagent	Reaction time	Redox agent concentration	Plutonium	Neptunium
Ammonium and iron (II) sulfate	10 and 15 min	0.2 M	III, IV	IV, V
Sodium nitrite	10 min	0.2 M	IV	IV
Silver oxide	5 and 10 min	2.5 mg	IV, V, VI	IV, V
Hydrogen peroxide	—	30%	IV	IV
Hydroxylamine	10 and 15 min	0.1 M	III, IV, V	IV, V

Table 4 Chromatographic elution programme

Step	Time/min	Flow rate/ml min ⁻¹	Eluent	Analytical process
1	0.0	1	100 mM oxalic acid and LiOH 190 mM	Washing
2	0.4	1	100 mM oxalic acid and LiOH 190 mM	Sample injection, actinides and lanthanides elution
3	27.5	1	2 M HCl (70%)–100 mM oxalic acid and LiOH 190 mM (30%)	U elution

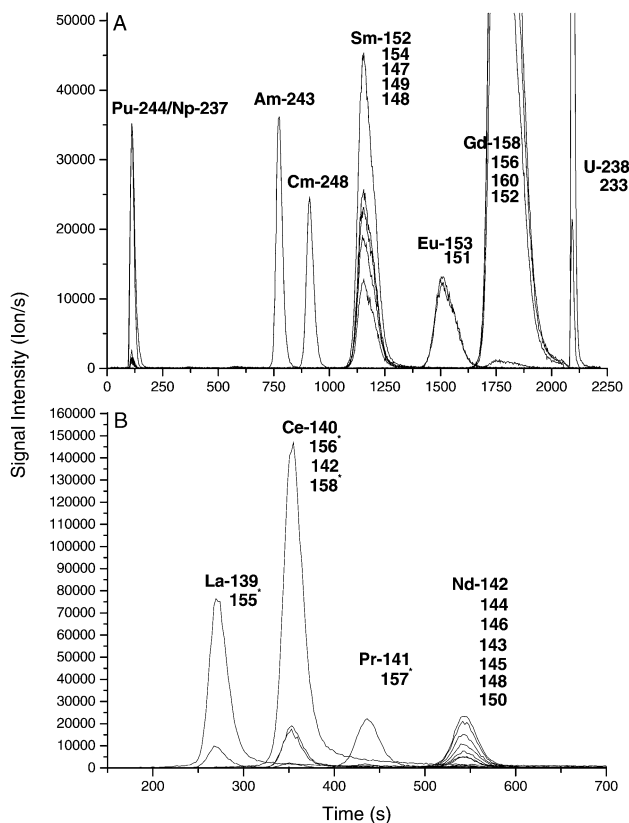


Fig. 1 A, Typical chromatogram obtained with the proposed analytical procedure for SRM 4355. The isotopes are listed in decreasing signal intensity order. B, Typical chromatogram obtained with the proposed analytical procedure for SRM 4355. The isotopes marked with (*) are relevant to the oxides of the element. The isotopes are listed in decreasing signal intensity order.

lanthanide concentration levels in the SRM 4355, two different amounts of sample were dissolved. One was used for La, Ce, Pr and Nd and the other for Sm, Eu, Gd, U, Np, Pu, Am and Cm determinations. From each sample solution, four different aliquots were prepared. Both standard additions and isotopic dilution analysis were performed during the validation of the analytical procedure, as described under "Optimisation of the isotope dilution procedure".

All aliquots were analysed with chromatographic separation using a CS5A column coupled on-line to an ICP-MS, and the chromatographic programme is shown in Table 4. For all the aliquots, a reaction with sodium nitrite was performed for 10 min. A 250 μ l sample-loop was used. In Fig. 1 A and B two typical chromatograms obtained for the two different aliquots are shown. In Table 5, the experimental values are compared

Table 5 Experimental and expected values (ng ml^{-1}), together with confidence interval at 95% for $n = 3$, obtained for the certified sample SRM 4355

Isotope	Experimental values	Expected values
La 139	39.9 ± 0.4	40.2^a
Ce 140	76.2 ± 0.7	75.6^a
Pr 141	7.3 ± 0.3	7.2^b
Nd 144	10.4 ± 0.3	10.2^a
Nd 146	7.5 ± 0.3	7.4^a
Sm 147	14.4 ± 0.3	14.2^a
Sm 149	12.9 ± 0.2	13.1^a
Eu 153	11.1 ± 0.4	10.8^a
Gd 154	13.5 ± 0.3	13.2^b
U 238	10.0 ± 0.2	9.9^a
Np 237	15.8 ± 0.4	16.0^c
Pu 244	15.6 ± 0.4	16.0^c
Am 243	16.3 ± 0.3	16.1^c
Cm 248	16.1 ± 0.3	15.9^c

^aCertified values after sample treatments. ^bRecommended values. ^cAdded to the sample.

with the expected and certified values, in terms of concentration. As can be seen, there is a good agreement between the experimental and the expected values. The expected values have been calculated from the certified values after sample treatment.

Real sample

To verify the feasibility of the proposed analytical procedure for a real sample, lanthanides and actinides were determined in an irradiated nuclear fuel sample, which was dissolved in a hot cell following the standard procedure. Moreover, in order to control the accuracy of this analytical procedure based only on the use of a single column (CS5A), the sample was further analysed exploiting the two procedures previously developed for the lanthanide and actinide characterization.^{30,33}

Solutions containing natural lanthanides and ²⁴⁴Pu, ²³⁷Np, ²⁴³Am and ²⁴⁸Cm were added as spikes to the sample solution. The 250 μ l sample loop was used and three repeated measurements for each sample were performed. The results obtained, by applying the three different procedures for the same sample, along with the errors, are shown in Table 6. As can be seen, the concentration values obtained with the new analytical procedure are in agreement with those obtained with the other two procedures previously developed. The procedures are also comparable in terms of analytical precision.

The simultaneous separation of actinide and lanthanide elements was achieved using the analytical procedure proposed, employing 100 mM oxalic acid in 190 mM LiOH and 2 M HCl (see Table 4) and a Dionex CS5A mixed bed column. In all the samples, 0.2 M sodium nitrite was added and the

Table 6 Nuclear fuel characterization: lanthanide and actinide values (ng ml^{-1}) obtained with different procedures together with confidence intervals at 95% for $n = 3$

Isotope	Experimental value obtained according to ref. 30	Experimental value obtained according to ref. 33	Experimental value obtained according to the analytical procedure proposed
La-139	8.2 ± 0.3	—	8.5 ± 0.4
Ce-140	7.6 ± 0.4	—	7.3 ± 0.4
Pr-141	7.2 ± 0.4	—	7.4 ± 0.4
Sm-150	2.4 ± 0.2	—	2.5 ± 0.3
Eu-153	1.3 ± 0.1	—	1.3 ± 0.1
Nd-143	5.6 ± 0.3	—	5.5 ± 0.3
Nd-146	4.4 ± 0.2	—	4.4 ± 0.3
U-235	—	7.0 ± 0.4	7.1 ± 0.3
Np-237	—	0.64 ± 0.08	0.57 ± 0.09
Am-243	—	2.4 ± 0.2	2.5 ± 0.1
Pu-242	—	12.0 ± 0.6	12.7 ± 0.4
Cm-244	—	2.2 ± 0.2	2.4 ± 0.1

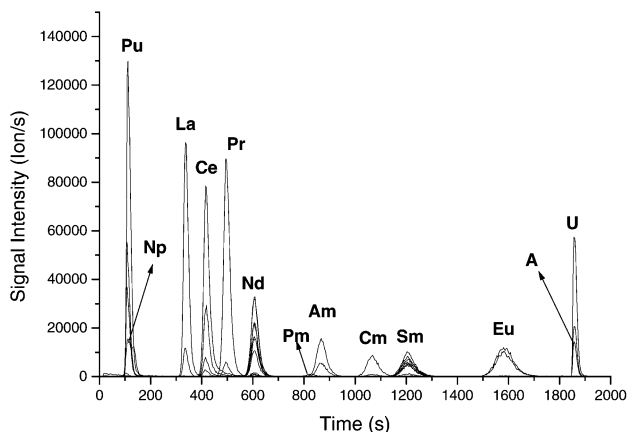


Fig. 2 Typical chromatogram obtained with a CS5A column and the proposed analytical procedure. The following isotopes (listed in decreasing signal intensity order) for each element were measured: Pu (240, 242, 244), Np (237), La (139, LaO⁺ 155), Ce (140, 142, CeO⁺ 156, 158), Pr (141, PrO⁺ 157), Nd (150, 144, 146, 142, 143, 145, 148), Pm (147), Am (243, 241), Cm (248, 244), Sm (152, 154, 147, 148, 150, 144), Eu (153, 151) and U (235, 233). See text for explanation of peak A.

chromatographic injection was made after 10 min of reaction. A typical chromatogram, scanning the mass range 139–160 and 230–250, is shown in Fig. 2. As can be seen, all the lanthanide and actinide isobaric interferences are resolved and all are eluted in 1900 s. The elution of lanthanide elements is performed under the same conditions as previously proposed.³⁰ Under these conditions, lanthanides elute in the order of increasing atomic number as anionic complexes. As can be seen in Fig. 2, the isobaric interferences present in the original sample between Ce and Nd, Nd and Sm, Pm and Sm, and Sm, Eu and Gd are well resolved. Moreover, no variation in the retention time of the lanthanides occurs. The presence of the oxide molecular ions for lanthanides was observed. These peaks would interfere in the determination of other heavier lanthanides (for example Gd). For purposes of comparison, Fig. 3 shows the chromatogram obtained for the same sample by the old procedure³⁰ over the mass range 139–160.

Np and Pu elute close to the solvent front (Fig. 2) and very far from U, which has its retention time after 1800 s, thus avoiding interference at mass 237 in samples with high uranium content (see peak A in Figs. 2 and 4). This is an advantage with respect to the previously developed procedure³³ for actinide separation. In fact, in that procedure, due to the small differences among their elution times (*ca.* 100 s), the maximum mass ratio of Np and Pu *versus* U needed to be 1 : 1 : 100.

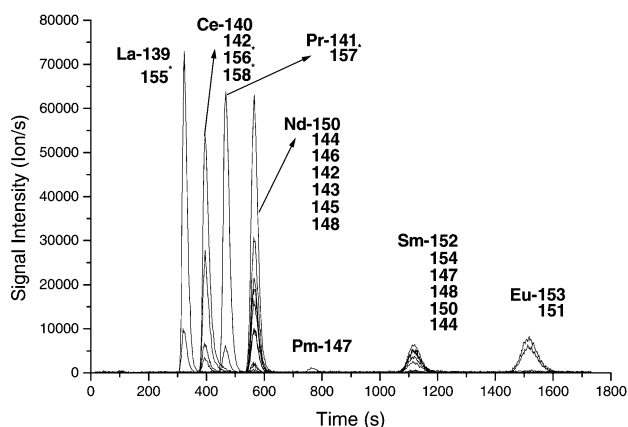


Fig. 3 Typical chromatogram obtained with a CS5A column according to ref. 30. The isotopes marked with (*) are relevant to the oxides of the element. The isotopes are listed in decreasing signal intensity order.

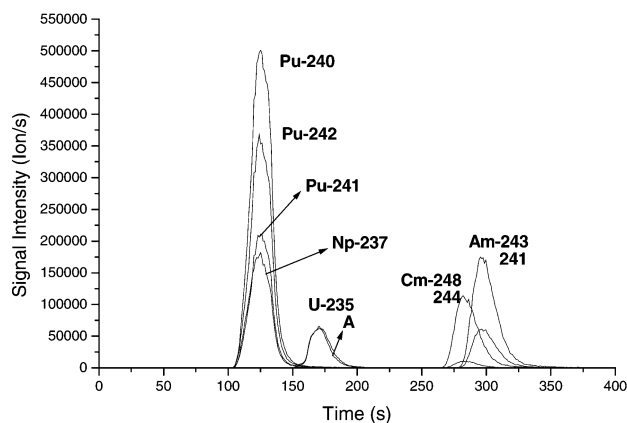


Fig. 4 Typical chromatogram obtained with a CS10 column according to ref. 33. The isotopes are listed in decreasing signal intensity order. See text for explanation of peak A.

For the same sample, the chromatographic separation of actinides was performed according to the method published by Barrero Moreno *et al.*³³ using 40 mM DAP (2,3-diaminopropionic acid) in 0.6 M HNO₃ and a Dionex CS10 cationic column. The sample was previously treated with 2.5 mg of silver oxide for 5 min to convert the plutonium in to Pu(vi). Due to the large amount of silver oxide added to the sample, a strong contamination to the system from silver occurs. This contamination has a considerable memory effect and can produce additional polyatomic interferences. Fig. 4 shows a typical chromatogram obtained scanning the mass range 230–250. At the time when this procedure was developed the interest was focused on Np–U–Pu separation, therefore no further investigations were made on Cm and Am separation. As can be seen, the chromatographic resolution between Am and Cm is not complete, but all isobaric interferences at masses 238 (U–Pu), 241 (Pu–Am) and 244 (Pu–Cm) and the interference of ²³⁸U on the ²³⁷Np (peak A Figs. 2 and 4) in samples with a high U concentration were resolved. As shown in Fig. 2, Am and Cm were completely separated, which was not the case in the old procedure.³³ This is exploited in our laboratory to isolate the Am fraction, which is then further analysed by α -spectrometry. This avoids the time-consuming radiochemical separation normally necessary for the isolation of Am from the matrix sample.

Conclusions

It has been demonstrated that IC-ID-ICP-MS can be exploited for the simultaneous determination of fission products (lanthanides) and actinides (Np, U, Pu, Am and Cm) using an anionic/cationic mixed bed exchange column. In comparison to the old procedures, the times of analysis and of sample handling are drastically reduced. The use of 0.2 M sodium nitrite permits the stabilisation of Np and Pu in the oxidation state iv to be completed after 10 min of reaction and avoids the contamination of the system from silver. Moreover, the advantages of the procedure are the large differences in the retention times of Np and Pu from U, and the possibility of resolving Am from Cm.

The method was applied to a spent fuel nuclear solution and the results obtained were in good agreement with those obtained using other separation procedures. The method could become that of choice for simultaneously obtaining the inventory of fission products and actinides. Improvements in the detection limits can be attained using an MCN nebulizer, as well as by adopting a preconcentration step. Investigations in this direction are in progress.

References

- 1 *Radioecology After Chernobyl*, ed. F. Waren and R.M. Harrison, John Wiley & Sons, New York, 1993.
- 2 V. Valković, *Radioactivity in the Environment*, Elsevier, Amsterdam, 2000.
- 3 M. Betti, *Microchem. J.*, 2000, **67**, 363–373.
- 4 R. L. Murray, *Understanding Radioactive Waste*, 4th edn., Battelle Press, 1994.
- 5 J. Hoefs, *Stable Isotopes Geochemistry*, Springer, Berlin, 1987.
- 6 M. Shima, *Geochim. Cosmochim. Acta*, 1986, **50**, 577–584.
- 7 G. Faure, *Principles of Isotope Geology*, Wiley, New York, 1986.
- 8 *Stable Isotopes in Human Nutrition*, ed. F. A. Mellon and B. Sandström, Academic Press, London, 1996.
- 9 L. Skipperud, D. Oughton and B. Salbu, *Sci. Total Environ.*, 2000, **257**, 81–93.
- 10 J. S. Crain, *At. Spectrosc. Perspectives*, 1996, **11**(2), 30–39.
- 11 J. S. Becker and H.-J. Dietze, *Adv. Mass Spectrom.*, 1998, **14**, 681–689.
- 12 C. K. Kim, R. Seki, S. Morita, S. Yamasaki, A. Tsumura, Y. Igarashi and M. Yamamoto, *J. Anal. At. Spectrom.*, 1991, **6**, 205–209.
- 13 D. Solatie, P. Carbol, M. Betti, F. Bocci, T. Hiernaut, V. V. Rondinella and J. Cobos, *Fresenius' J. Anal. Chem.*, 2000, **368**, 88–94.
- 14 J. S. Becker and H.-J. Dietze, in *The Encyclopedia of Analytical Chemistry*, ed. R. A. Meyers, John Wiley & Sons, 2000, pp. 12947–12961.
- 15 *Handbook of Inductively Coupled Plasma Mass Spectrometry*, ed. K. E. Jarvis, A. L. Gray and R. S. Houk, Blackie Academic and Professional, London, 1997.
- 16 *Inductively Coupled Plasma Mass Spectrometry*, ed. A. Montaser, Wiley-VCH, New York, 1998.
- 17 K. G. Heumann, *Int. J. Mass Spectrom. Ion Proc.*, 1992, **118**(119), 575–592.
- 18 J. I. Garcia Alonso, *Anal. Chim. Acta*, 1995, **312**, 57–78.
- 19 J. S. Becker, R. S. Soman, K. L. Sutton, J. A. Caruso and H.-J. Dietze, *J. Anal. At. Spectrom.*, 1999, **14**, 933–937.
- 20 L. Perna, M. Betti, J. M. Barrero Moreno and R. Fuoco, *J. Anal. At. Spectrom.*, 2001, **16**, 26–31.
- 21 M. Betti, *J. Chromatogr. A*, 1997, **789**, 369–379.
- 22 J. S. Becker, G. Küppers, F. Carsughi, W. Kerl, W. Schall, F. Ullmaier and H.-J. Dietze, *Ber. Forschungszentrums Jülich*, 1996, **3272**, 143.
- 23 W. Kerl, J. S. Becker, W. Dannecker and H.-J. Dietze, *Fresenius' J. Anal. Chem.*, 1998, **11**, 433–439.
- 24 J. B. Truscott, P. Jones, B. E. Fairman and E. H. Evans, *Anal. Chim. Acta*, 2001, **433**, 245–253.
- 25 J. B. Truscott, P. Jones, B. E. Fairman and E. H. Evans, *J. Chromatogr. A*, 2001, **928**, 91–98.
- 26 N. Demuth and K. G. Heumann, *Anal. Chem.*, 2001, **73**, 4020–4027.
- 27 J. R. Encimar, M. I. Monteverde Villar, V. Gotor Santamaria, I. J. Garcia Alonso and A. Sanz-Medel, *Anal. Chem.*, 2001, **73**, 3174–3180.
- 28 J. R. Encimar, P. R. Gonzales, I. G. Garcia Alonso and A. Sanz-Medel, *Anal. Chem.*, 2002, **74**, 270–281.
- 29 M. Betti, J. I. Garcia Alonso, Ph. Arbore, I. Sato and L. Koch, *Application of Plasma Source Mass Spectrometry*, ed. G. Holland and A. N. Eaton, Royal Society of Chemistry, Cambridge, 2nd edition, 1993, pp. 205–212.
- 30 J. I. Garcia Alonso, F. Sena, Ph. Arboré, M. Betti and L. Koch, *J. Anal. At. Spectrom.*, 1995, **10**, 381–393.
- 31 J. M. Barrero Moreno, J. I. Garcia Alonso, Ph. Arbore, G. Nicolaou and L. Koch, *J. Anal. At. Spectrom.*, 1996, **11**, 929.
- 32 M. Betti, L. Menichetti, J. M. Barrero Moreno and R. Fuoco, *Microchem. J.*, 2000, **67**, 285–290.
- 33 J. M. Barrero Moreno, M. Betti and J. I. Garcia Alonso, *J. Anal. At. Spectrom.*, 1997, **12**, 355–361.
- 34 J. M. Barrero Moreno, M. Betti and G. Nicolaou, *J. Anal. At. Spectrom.*, 1999, **14**, 875–879.
- 35 M. Betti and P. Papoff, *Crit. Rev. Anal. Chem.*, 1988, **19**, 271–322.
- 36 J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, Methuen, London, 1957.
- 37 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry—a Comprehensive Text*, Wiley, New York, London, 5th edn., 1988.
- 38 B. H. Jianyu, R. Odoj, T. Baosheng and E. Merz, *Radiochim. Acta*, 1998, **83**, 183–188.

Sample Cleanup by On-Line Chromatography for the Determination of Am in Sediments and Soils by α -Spectrometry

L. Perna,[†] J. Jernström,[†] L. Aldave de las Heras,[†] J. de Pablo,[‡] and M. Betti[†]

European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany, and Chemical Engineering Department, Universidad Politecnica de Catalunya, Av. Diagonal 647, 08028 Barcelona, Spain

A novel sample cleanup procedure for the Am determination in environmental samples by α -spectrometry is described. The method is based on the use of three analytical chromatographic columns. TEVA-Spec. from Eichrom has been packed in an analytical chromatographic column to carry out the lanthanide/actinide separation. A CS5A mixed-bed column from Dionex was used to separate Am from lanthanide impurities and other actinides. A TCC-II column from Dionex was used to connect the TEVA to the CS5A and act as a preconcentrator column for the trivalent ions. The behavior of the columns was studied by coupling the chromatograph to an ICPMS detector. A chromatographic fraction has been used for sample preparation for α -spectrometric determination of ^{241}Am . The analytical procedure has been validated with certified reference materials (sediment and soil) and was applied to sediment core samples from the Irish Sea and compared with the classical radiochemical separation of Am.

As a consequence of nuclear testing, reentry and disintegration of nuclear-powered satellites, nuclear reactor accidents, uranium mining, and nuclear weapons production, actinides have been introduced to different extents into the environment. Other further possible sources for their release to the environment might be disposal of high-level radioactive waste in mined repositories in geologic formations as well as the storage and disposal of uranium and plutonium from nuclear weapon.^{1,2} The mobilization of radionuclides in the environment has been studied for many years, with the prime objective of tracing the routes by which they accumulate in the food chain and become available for human consumption.^{3,4}

The main americium isotope of interest in environmental studies is ^{241}Am , which is a decay product of ^{241}Pu . Both nuclides

are released via atmospheric weapons testing and nuclear operations such as nuclear power production and spent fuel reprocessing (e.g., 6.4 TBq of ^{241}Am and 485 TBq of ^{241}Pu were discharged from BNFL Sellafield in 1982).^{5,6} ^{241}Am can be the major component for α -activity of wastes stemming from processing of high-burn-up fuels.⁷ The level of ^{241}Am in the environment will increase due to its incorporation from ^{241}Pu . For instance, the amount of ^{241}Am from the Chernobyl reactor has been calculated to increase to 33.6 times the initial activity until 2058.⁸ The measurement of ^{241}Am in environmental samples is of importance in monitoring its release (both controlled and accidental) and in assessing the environmental impact and radioecology of the nuclide.⁵ In addition, the measurement of ^{241}Am derived from fallout has found some application in the dating of lake sediments.⁹

It has been reported that for environmental samples containing less than 0.5 g of inorganic residue (water, air filters) TRU-Spec. resin can be used and no lanthanide separation is necessary for Am determination by α -spectrometry.¹⁰ However, the same authors assert that for samples containing high amounts of lanthanides ($\mu\text{g/g}$), as in soil and sediment samples, further Am/lanthanide separation is required.¹⁰

^{241}Am has a half-life of 432.2 years and can be measured both with α - and γ -spectroscopy. The determination of a high level of ^{241}Am is relatively straightforward using γ -spectrometry. For lower level analysis (fg/g or mBq/g) as well as for quality control purposes, where two independent methods are necessary to validate results, chemical separation and α -spectrometry are required. α -Spectrometry requires the preparation of chemically pure sources since even a small amount of other materials would attenuate the α -particle and degrade the α -energy spectrum. The chemical separation procedure must therefore be capable of isolating americium from all the other species present as major elements.⁵

* Corresponding author. Phone: +49 7247951491. Fax: +49 724795199651. E-mail: perna@itu.fzk.de.

[†] Institute for Transuranium Elements.

[‡] Universidad Politecnica de Catalunya.

(1) Silva, R. J.; Nitsche, H. *Radiochim. Acta* **1995**, *70/71*, 377–396.

(2) Warren, F.; Harrison, R. M. *Radioecology after Chernobyl*; John Wiley and Sons: New York, 1993; pp 33–53.

(3) Betti, M. *Microchem. J.* **2000**, *67*, 363–373.

(4) Valković, V. *Radioactivity in the Environment*; Elsevier: Amsterdam, 2000; pp 449–453.

(5) Warwick, P. E.; Croudace, I. W.; Carpenter, R. *Appl. Radiat. Isot.* **1996**, *47* (7), 627–642.

(6) Livens, F. R.; Singleton, D. L. *Analyst* **1989**, *114* (9), 1097–1101.

(7) Mathew, E.; Matkar, V. M.; Pillai, K. C. J. *Radioanal. Chem.* **1981**, *62* (1–2), 267–278.

(8) Pazukhin, E. M.; Drozd, I. P.; Tokarevskii, V. V. *Radiochemistry* **1994**, *36*, 590–595.

(9) Appleby, P. G.; Richardson, N.; Nolan, P. J. *Hydrobiologica* **1991**, *214*, 35–42.

(10) Goldstein, S. J.; Hensley, C. A.; Armenta, C. E.; Peters, R. J. *Anal. Chem.*, **1997**, *69*, 809–812.

Table 1. ICPMS Operating Conditions

ICP Ion Source	
rf power	1045 W
cooling Ar flow rate	15.0 l min ⁻¹
nebulizer Ar flow rate	0.98 l min ⁻¹
auxiliary Ar flow rate	0.9 l min ⁻¹
Lens Voltage	
Einzel lens E1	70
Bessel box B	76
photon stop S2	2
Bessel box P	45
Data Acquisition	
dwelt time	100 ms
replicate time	100 ms
scan mode	Peak hop
reading per replicate	1
sweeps per replicate	1

The chemical behavior of Am(III) is very similar to that of the trivalent lanthanides. This makes difficult its separation from these elements, particularly in environmental samples, due to the relatively high levels of trivalent lanthanides with respect to Am(III). Therefore, if the sample is not well purified, it can significantly interfere with the measurement of ²⁴¹Am by α -spectrometry.⁵

The standard method to determine Am in environmental samples based on α -spectrometry measurements is very time-consuming (2 days) due to the radiochemical separation from the other α -emitters necessary in order to avoid energy interference in its measurements.¹¹ In this paper, a new sample preparation procedure exploiting three on-line chromatographic columns to isolate a pure Am fraction is described. A TEVA column is employed for actinide/lanthanide separation, a TCC-2 column for the americium preconcentration, and a CS5A column for the final Am purification. The total time for the separation takes 1.5 h in comparison to the 2 days necessary for the anion exchange radioanalytical separation. The total recovery by the proposed procedure is ~85%. It can be applied for the Am determination by α -spectrometry as well as mass spectrometry.

EXPERIMENTAL SECTION

Instrumentations. A Sciex Elan 5000 inductively coupled plasma mass spectrometer (ICPMS) instrument (Perkin-Elmer Sciex, Thornhill, ON, Canada), modified to handle radioactive samples in a glovebox and coupled with a chromatographic system consisting of a GP 50 high-pressure chromatographic pump (Dionex, Sunnyvale, CA), was used. Details of the instrumentation setup have been previously published.^{12,13} Standard plasma and ions lens operating conditions are summarized in Table 1. The Dionex high-pressure pump was located outside the glovebox, and it was used connected on-line to an ICPMS to perform some preliminary studies with high-activity samples inside the glovebox,

(11) Hrncsek, E.; Irlweck, K. In *Determination of Am and Pu in Contaminated Soil Samples in Environmental Radiochemical Analysis*; Newton, G. W. A., Ed.; Royal Society of Chemistry: London, 1999; pp 73–80.

(12) Betti, M.; Garcia Alonso, J. I.; Arboré, Ph.; Sato, I.; Koch, L. In *Application of Plasma Source Mass Spectrometry*, 2nd ed.; Holland, G., Eaton, A. N., Eds.; Royal Society of Chemistry: Cambridge, 1993; pp 205–212.

(13) Garcia Alonso, J. I.; Sena, F.; Arboré, Ph.; Betti, M.; Koch, L. *J. Anal. At. Spectrom.* **1995**, *10*, 381–393.

as well as to perform the environmental sample separations outside a glovebox. The same chromatographic system was used to prepare the pure Am fraction to be analyzed by α -spectrometry.

α -Measurements were performed with an OCTÈTE PC (EG&G Ortec) with Ultra ion-implanted silicon detectors with an active area of 450 mm². Calibration measurements were done with certified nuclide sources, energy calibrations with a mixed-nuclide source containing ²³⁷Np, ²⁴¹Am, and ²⁴⁴Cm (GM810, AEA Technology), and efficiency calibrations with a ²⁴¹Am source (GT223, AEA Technology). Measurements were evaluated using MAESTRO for Windows software (EG&G Ortec).

The pH was measured with a Orion 720A pH meter equipped with a Orion Ross 8102 combination electrode. The measuring procedure followed the instructions written in ASTM D 1293-95 standard. Calibration of the instrument was done with commercial calibration solutions.

A Wallac Quantulus 1220 counter (Wallac Oy, Finland) was used for liquid scintillation analysis. The counting efficiency for α -emitters was shown to be 100%.¹⁴

The γ -measurements were carried out using a HPGe detector with a relative efficiency of 52.5% and a fwhm of 1.80 keV at 1332 keV. The HPGe detector was coupled in anticoincidence with a solid scintillation detector (NaI(Tl)) to enhance low-level radioactivity measurements by reduction of Compton background.¹⁵

Reagents and Materials. IonPac CS5A analytical and guard mixed-bed columns and a TCC II trace cation concentrator column were obtained from Dionex (Sunnyvale, CA). The CS5A column is commercially available in the standard length of 250 mm and of 4-mm internal diameter. The TCC-II column has a length of 50 mm and of 4-mm internal diameter. TEVA resin was from Eichrom (Paris, France). Nitric, hydrochloric, and hydrofluoric acids were Suprapur grade from Merck (Darmstadt, Germany). Oxalic and formic acids, hydrogen peroxide, ammonium thiocyanate, and lithium hydroxide were from Merck. Buffer solutions of pH 4.01 and 7.01 were from Hanna Instruments (Villafraanca Padovana, Italy).

Natural element standards (U, La, Ce, Pr, Nd, Sm, Eu, Gd) were obtained from Spex (Grasbrunn, Germany) as 1000 μ g mL⁻¹ stock standard solutions. The solutions were diluted as necessary. Neodymium(III) oxide was from Merck. Certified enriched isotopes ²⁴³Am and ²⁴⁸Cm for mass spectrometric analysis were obtained from “D. I. Mendeleev” Institute for Metrology (St. Petersburg, Russia). Radioactive tracer solutions of ²⁴³Am and ²⁴³Cm were diluted from standard solutions from National Institute of Standards and Technology (NIST; Gaithersburg, MD). The activity of the diluted tracers was verified by liquid scintillation counting (LSC).

The certified material IAEA-135 was obtained from International Atomic Energy Agency (Vienna, Austria). SRM4353A was obtained from NIST.

All standard solutions, spikes, tracers, and samples were prepared by dilution by mass in polyethylene bottles appropriately cleaned for trace element determination.

Sample Preparation. Leaching. The transuranium elements were leached from the sample material using the following

(14) Hrncsek, E.; Aldave de las Heras, L.; Betti, M. *Radiochim. Acta* **2002**, *90*, 721–725.

(15) Peerani, P.; Carbol, P.; Hrncsek, E.; Betti, M. *Nucl. Instrum. Methods Phys. Res. A* **2002**, *482*, 42–50.

164 procedure. A known amount of dried sample (0.25–20 g) was put
 165 in a glass beaker, and a weighed amount of ^{243}Am (~ 0.2 –1 Bq)
 166 or ^{243}Cm (~ 0.2 –9 Bq) tracers was added. Sample was then
 167 leached on a hot plate for 4 h with 200 mL of 7.2 M HNO_3 . The
 168 solution was filtered with Schleicher & Schuell 589³ blue ribbon
 169 ashless filter paper.

170 **Calcium Oxalate Coprecipitation.** Coprecipitation with calcium
 171 oxalate is a convenient way of concentrating and purifying the
 172 analyte from the majority of leached matrix constituents. In the
 173 analysis of environmental samples, purification from abundant
 174 elements such as iron, aluminum, titanium, and some anions such
 175 as phosphate is essential.^{5,16} After leaching, the filtered solution
 176 was evaporated to dryness and the residue was dissolved in 100–
 177 200 mL of 1 M HNO_3 . An appropriate amount of oxalic acid (~ 1
 178 g/g of leached sample) and calcium chloride were added, and
 179 the pH of the solution was slowly increased to pH 2–3 with 25%
 180 NH_3 under vigorous magnetic stirring. Calcium chloride was
 181 added to ensure the presence of Ca^{2+} ions in the solution. After
 182 filtration (S & S 589³ filter paper), the filtrate was discharged.
 183 Three different treatments were performed with the precipitate
 184 in order to find a suitable method to dissolve the precipitate and
 185 collect Am.

186 (A) The filter with the precipitate was placed in a beaker and
 187 the precipitate was dissolved in 100 mL of 4 M HNO_3 . After
 188 washing, the filter was removed. After evaporating the sample to
 189 dryness, the residue was fumed several times with 65% HNO_3 and
 190 some drops of 30% H_2O_2 in order to decompose the oxalate.
 191 Finally, the residue was fumed with 0.1 M HCOOH several times.

192 (B) The filter was ashed in an oven for 10 h at 850 °C. The
 193 residue was dissolved in concentrated HNO_3 . After evaporation
 194 to dryness, the residue was fumed with 0.1 M HCOOH several
 195 times.

196 (C) The precipitate was collected from the filter and transferred
 197 in different microwave PTF vessels, 5 mL of 65% HNO_3 with 2
 198 mL of 30% H_2O_2 . After evaporation, the residue was fumed with
 199 0.1 M HCOOH several times.

200 Incomplete oxalate dissolution was achieved with methods A
 201 and C. Therefore, method B was chosen for the sample preparation
 202 during this investigation.

203 **Column Preparation.** The TEVA resin, which consists of
 204 particles with an external diameter of 80–160 μm , was packed in
 205 chromatographic analytical columns that were connected on-line
 206 to the chromatograph. For this purpose, columns of length of 250
 207 mm and of 4-mm internal diameter were used (column volume
 208 3.14 mL; ~ 1.2 g of resin). For every analysis, a new TEVA column
 209 was prepared. CS5A and TCC-II columns were washed with 2 M
 210 HNO_3 for 10 min and conditioned with 0.1 M oxalic acid in 0.19
 211 M LiOH for 20 min before every analysis.

212 **HPLC Sample Preparation.** After oxalate coprecipitation, the
 213 sample was fumed with 0.1 M HCOOH several times. The residue
 214 was dissolved in 8–10 mL of 2 M $\text{NH}_4\text{SCN}/0.1$ M HCOOH
 215 solution. The thiocyanate solution was added at least 10 min before
 216 the chromatographic separation in order to avoid the formation
 217 of a precipitate.

218 **Sample Cleanup Procedure.** A scheme of the column system
 219 developed for the Am isolation is given in Figure 1A. Every single
 220 chromatographic separation is discussed in detail in the Results

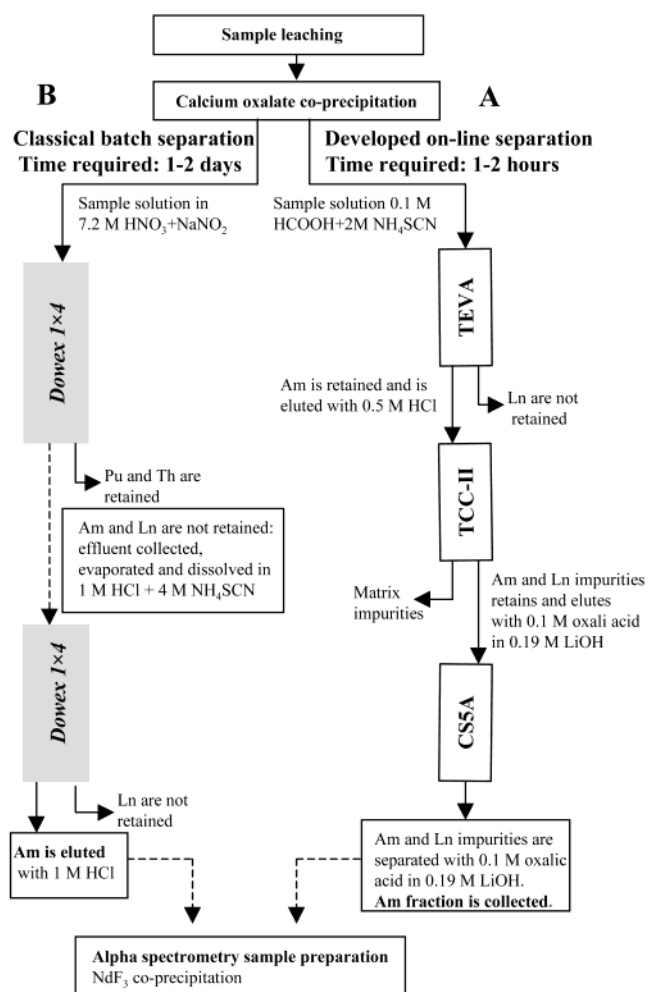


Figure 1. Scheme of the separation procedure of Am isolation by (A) the developed analytical procedure and (B) The classical radiochemical method.

and Discussion section. Here, the following experimental details
 are given.

Trivalent Actinide/Lanthanide Purification (TEVA Resin). At
 the beginning of the separation, the TEVA column was conditioned
 with 0.1 M HCOOH in 2 M NH_4SCN for 20 min with a flow rate
 of 0.5 mL/min. To load the 10-mL sample solution in the
 chromatographic column, the connector tube from the pump
 pistons was directly connected to the sample bottle. In this way,
 the chromatograph pumps the sample in the column instead of
 the eluent. The sample loading flow rate was always 0.5 mL/min.
 After the sample loading, the column was washed with 10 mL of
 0.1 M HCOOH in 2 M NH_4SCN and afterward with 10 mL of 0.1
 M HCOOH in 1 M NH_4SCN [flow rate 0.5 mL/min]. Am and Cm
 in thiocyanate/formic acid mixture are strongly sorbed in the
 TEVA whereas the lanthanides are washed out as thiocyanato
 complexes.¹⁷

Preconcentration (TCC-II). After the TEVA column is washed
 with 0.1 M HCOOH in 1 M NH_4SCN , it is connected on-line with
 TCC-II, opposite to the eluent flow. The trivalent cations are eluted
 from TEVA with 5 mL of 0.25 M HCl (flow rate 1 mL/min), and
 at the same time they are concentrated in the TCC-II.

(16) Yamato, A. *J. Radioanal. Chem.* **1982**, 75 (1–2), 265–273.

(17) Pimpl, M.; Higgy, R. H. *J. Radioanal. Nucl. Chem.* **2001**, 248 (3), 537–541.

242 *Final Separation (CS5A).* The TCC-II column was connected
243 on-line to the CS5A column. The residue traces of lanthanides
244 with Am and Cm were immediately eluted from the TCC-II using
245 0.1 M oxalic acid in 0.19 M LiOH as eluent. The elements were
246 separated in ~33 min in the CS5A column using the same eluent
247 (0.1 M oxalic acid in 0.19 M LiOH). The effluent from the CS5A
248 column was sequentially collected in four different 5-mL fractions.
249 Am and Cm were found in the second fraction, which was used
250 for α -spectrometry sample preparation by neodymium fluoride
251 microprecipitation.

252 **α -Spectrometry Determination.** Eluted fractions were evapo-
253 rated and fumed several times with 1 M HCl and some drops of
254 30% hydrogen peroxide. The sample was prepared for α -spectro-
255 metric measurement by precipitating Am with NdF₃.¹⁸ Nd³⁺ ions
256 were added to solution with concentrated HF. To determinate the
257 chemical yield of the step, ²⁴³Cm was added. The chemical yield
258 of NdF₃ microprecipitation was found to be between 85 and 90%.
259 After a minimum time of 30 min of cooling in ice, the sample
260 solution was filtered on a 0.1- μ m Supor polysulfone filter (Pall-
261 Gelman Science). Before filtration, the filter was coated with
262 NdF₃.¹⁹ Filters were mounted on brass holders and measured.
263 The efficiency of the α -detector depended on the measurement
264 distance between the sample and the detector. The most con-
265 taminated samples were measured at a distance of 15 mm with
266 an efficiency of 7.8%. In case of less contaminated samples, a
267 shorter distance (3 mm) was used and the efficiency was 33.2%.
268 The counting time varied between 80 000 and 200 000 s depending
269 on the sample activity. The uncertainties in α -spectrometry result
270 from tracer activity, peak area, and weighing. All errors are given
271 with 1 σ .

272 **Classical Radiochemical Separation for Am Determination**
273 **by α -Spectrometry.** There are several procedures in the literature
274 for determination of plutonium and americium. The ones reported
275 below are normally employed at ITU.¹¹ A scheme of the radio-
276 chemical separation is given in Figure 1B.

277 After leaching and oxalate coprecipitation, the residue was
278 dissolved in 7.2 M HNO₃ and heated with 0.5 g NaNO₂ to adjust
279 the oxidation state of Pu to Pu(IV). The cooled solution was
280 applied to an anion exchange batch column (Dowex 1 \times 2 resin,
281 preconditioned with 100 mL of 7.2 M HNO₃), and the column was
282 washed with 7.2 M HNO₃. The HNO₃ fraction was taken for Am
283 determination, while Th and Pu were retained onto the Dowex.
284 The evaporated HNO₃ fraction was fumed several times with 36%
285 HCl to remove traces of HNO₃ and dissolved in 2 mL of HCl and
286 20–40 mL of 4 M NH₄SCN. This solution was loaded to a
287 preconditioned anion exchange column (Dowex 1 \times 4, pre-
288 conditioned with 4 M NH₄SCN). The column was washed with 30
289 mL of 4 M NH₄SCN to remove Ca²⁺, followed by 5 mL of 1 M
290 HCl to remove most of the thiocyanates. Finally, Am was eluted
291 with 100 mL of 1 M HCl. The Am fraction was evaporated to
292 dryness, fumed several times with 65% HNO₃ and some drops of
293 H₂O₂ to remove residual sulfur, and then fumed with 36% HCl.
294 Sample for α -spectrometry was prepared by microprecipitation
295 with NdF₃, as described before (α -spectrometry determination).

(18) Hindman, F. D. *Anal. Chem.* **1983**, *55*, 2460–2461.

(19) Rao, R. R.; Cooper, E. L. *J. Radioanal. Nucl. Chem.* **1995**, *197* (1), 133–148.

RESULT AND DISCUSSION

Chromatographic Separations. *TEVA Column.* All the chro-
matographic separations have been studied, in synthetic solution,
with ICPMS coupled on-line to a GP50 Dionex chromatograph.

Because of their chemical similarity, lanthanides and trivalent actinides are frequently recovered together in chromatographic separations. However, macrolevels (mg/kg) of lanthanides interfere with the formation of the very thin sample layer required for α -spectrometry analysis of actinides. As a result, actinide determinations frequently require removal of lanthanides.²⁰ In the literature, several methods are described exploiting different stationary phases to achieve the lanthanide–actinide batch separations.^{11,17,20–22} Among those methods, the one using TEVA resin was chosen due to its simplicity to be packed in an analytical chromatographic column.²³ The active component of TEVA extraction resin is an aliphatic quaternary amine. As such, it has properties similar to those of typical strong base anion exchange resins. However, because the functional groups are in a liquid form, rather than fixed to a polymer backbone, as with anion exchange resin, these groups have a greater mobility to coordinate around target anions. This means that the uptake of these ions is generally higher, often at much lower acid concentration.

The Am and Cm fraction together with some lanthanide impurities and other actinides are eluted directly in the TCC-II column. Mono- and divalent ions are not retained in the present experimental condition.²⁰ An elution profile for ²⁴³Am and ²⁴⁸Cm obtained with ICPMS coupled on-line with a TEVA column is given in Figure 2.

As can be seen, Am, Cm, and lanthanides are quantitatively eluted with 0.25 HCl after 200 s. No further elution of Am and Cm was observed up to 2 M HCl on the column.

To evaluate the recovery of this separation, synthetic solutions containing ²³⁵U, ²³⁷Np, ²³⁸Pu, and ²⁴¹Am were loaded on TEVA resin. γ -Analysis and LSC analyses were performed before and after loading the sample and the elution steps as well as on the different elution fractions. It has been calculated that ~10% of Am is lost during the loading and the washing steps. Moreover, theoretic calculations on the sample solution has been done with the program Chess/Jchess ver. 3.0. The program calculates the species distribution at equilibrium in aqueous solution systems. For the sample solution, it has been calculated that the 86.5% of the americium is present as thiocyanate complexes and 13.5% as Am³⁺ (Table 2). This result is in agreement with those experiments described above.

To increase the Am recovery, a sample recycling was applied. A 10-mL sample of the solution coming out from the column during sample loading was collected and used for the first washing. This recycling was applied also to the solution coming out from this first washing. In this case, only half of the solution (5 mL) was used and diluted to 10 mL with 0.1 M formic acid. The recycling has a considerable effect on the procedure's chemical yield, which increases from 61% without recycling to 84% with recycling.

(20) Horwitz, E. P.; Dietz, M. L.; Chiarizia, R.; Diamond, H.; Maxwell, S. L.; Nelson, M. R. *Anal. Chim. Acta* **1995**, *310*, 63–78.

(21) Hill, C.; Madic, C.; Baron, P.; Ozawa, M.; Tanaka, Y. *J. Alloys Compd.* **1998**, *271–273*, 159–162.

(22) Modolo, G.; Odoj, R. *J. Alloys Compd.* **1998**, *271–273*, 248–251.

(23) Perna, L.; Betti, M.; Barrero Moreno, J. M.; Fuoco, R. *J. Anal. At. Spectrom.* **2001**, *16*, 26–31.

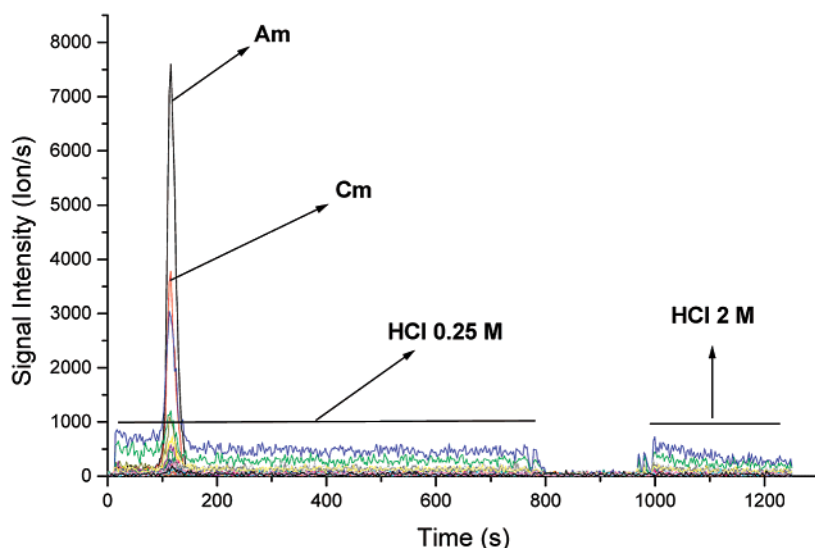


Figure 2. Am and Cm elution profile on TEVA column: eluent 0.25 M HCl and 2 M HCl and detector ICPMS. The other peaks eluting with Am and Cm correspond to some trace lanthanides still present.

Table 2. Species Distribution at the Equilibrium in the Sample Solution Calculated by the Program Chess/Jchess Version 3.0 (Am, 2×10^{-10} M, NH_4SCH 2 M, Formic Acid 0.1 M, pH 2.38)^a

	concentration (M)	species (%)
Am^{3+}	2.70×10^{-11}	13.5
AmSCN^{2+}	1.73×10^{-10}	86.5
AmOH^{2+}	5.51×10^{-16}	
$\text{Am}(\text{OH})_2^+$	1.04×10^{-21}	

^a $\text{Log } \beta_1^\circ (n = 1, 25^\circ \text{C}) = 1.300 \pm 0.3$ (NEA-OECD Database).²⁴

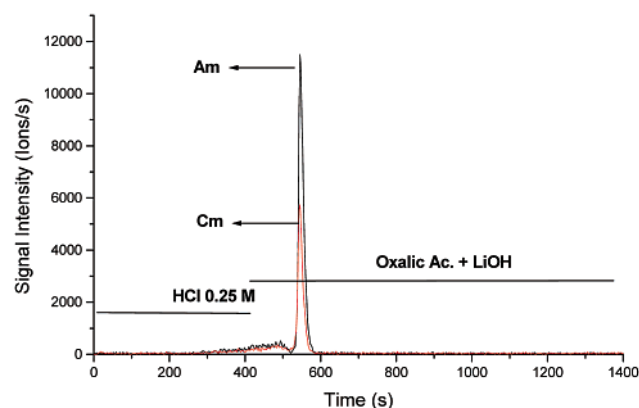


Figure 3. Am and Cm elution profile on TCC-II column with 0.25 M HCl and 0.1 M oxalic acid in 0.19 M LiOH.

349 *TCC-II Column.* The IonPac Trace Cation Concentrator Col-
 350 umn (TCC-II) is packed with a styrene/divinylbenzene copolymer
 351 that is surface sulfonated. The TCC-II column has already been
 352 used coupled with the CS5A to carry out lanthanide precon-
 353 centration and separation on-line to ICPMS.²⁵ The function of the TCC-
 354 II column is to strip the trivalent ions during TEVA elution. This
 355 process concentrates the desired analyte species onto the TCC-
 356 II. The trivalent actinides and the lanthanides can be easily eluted
 357 with 0.1 M oxalic acid in 0.19 M lithium hydroxide.

358 The flow direction during the concentration step should be
 359 opposite to the eluent flow. This configuration concentrates the
 360 cations in a compact band at the bottom of the TCC-II. When
 361 injected, all of the ions are rapidly eluted off the TCC-II and onto
 362 the guard and analytical columns. If the sample is loaded onto
 363 the TCC-II in the same flow direction as the eluent flow, the
 364 cations are concentrated at the head of the column rather than at
 365 the bottom. When injected, the cations begin the chromatographic
 366 separation on the concentrator before reaching the guard and
 367 analytical columns. Normally the function of the concentrator is

to strip the ions of interest from the sample matrix and not to act
 as an analytical column.²⁶ Figure 3 shows an Am and Cm elution
 profile on the TCC-II column. As soon as the eluent is switched to
 oxalic acid, the analytes and trace lanthanides are rapidly eluted.

CS5A Column. The analytical chromatographic column CS5A
 (Dionex) is a mixed-bed anionic/cationic column. The column
 resin has a 55% cross-linked, microporous, hydrophobic resin core
 that has been agglomerated with two layers of permeable latex
 particles. The latex particles carry the actual cation and anion
 exchange functionality. The first layer is a fully sulfonated latex
 for cation exchange. The second layer is a fully aminated layer
 for anion exchange.²⁷ In our laboratory, the CS5A column has been
 used for the inventory of fission products^{13,28,29} and actinides³⁰ in
 spent nuclear fuel solutions as well as in environmental samples.
 The separation obtained for the final sample purification from
 lanthanides is shown in Figure 4.

(24) Silva, R. J.; Bidoglio, G.; Rand, M. H.; Robouch, P. B.; Wanner, H.; Piugdomenech, I. *Chemical thermodynamics Vol. 2. Chemical thermodynamics of Americium*; North-Holland, Elsevier Science Publishers B. V.: Amsterdam, The Netherlands, 1995; 166–170.

(25) Perna, L.; De Pablo, J.; Betti, M. Lanthanides preconcentration and separation by TCC-II and CS5A columns coupled on-line to ICP-MS. Poster presented at 2002 Winter conference on Plasma Spectrochemistry, Scottsdale, AZ, 6–12 January 2002.

(26) Dionex document 034466. *IonPac TCC-II Trace Cation Concentrator Column*, 1998; p 4.

(27) Dionex document 031188. *IonPac CS5A Analytical Column*, 1999; p 4.

(28) Barrero Moreno, J. M.; Garcia Alonso, J. I.; Arboré, Ph.; Nicolaou, G.; Koch, L. *J. Anal. At. Spectrom.* **1996**, *11*, 929–935.

(29) Barrero Moreno, J. M.; Betti, M.; Nicolaou, G. *J. Anal. At. Spectrom.* **1999**, *14*, 875–879.

(30) Perna, L.; Bocci, F.; Aldave de las Heras, L.; De Pablo, J.; Betti, M. *J. Anal. At. Spectrom.* **2002**, *17*, 1166–1171.

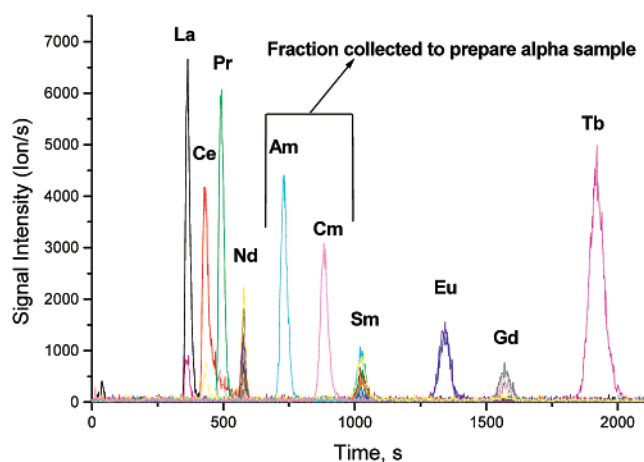


Figure 4. Lanthanides with Am and Cm elution profile obtained using CS5A column coupled on-line to an ICPMS.

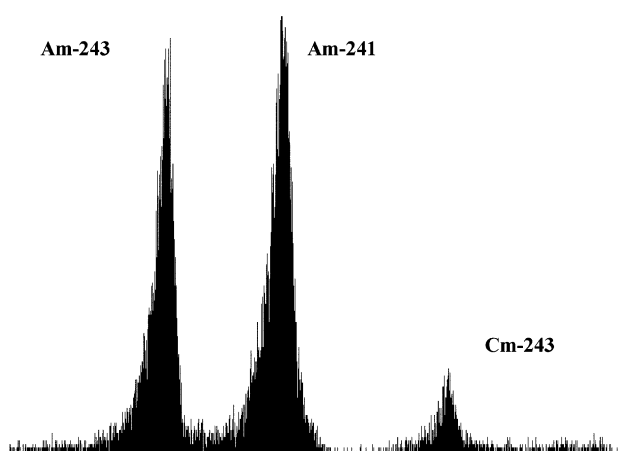


Figure 5. α -Spectrum of the IAEA 135 sediment sample after treatment with the developed procedure.

Table 3. Experimental and Expected Values, Together with the Chemical Yields, for ^{241}Am Determination by the Proposed Analytical Procedure

sample	^{241}Am (Bq/kg)		chemical yield (%)
	experimental	information	
IAEA 135 (sediment)	337 ± 18	318 ± 6.4	90.6
NIST 4353A (soil)	1.3 ± 0.1	1.25 ± 0.09	86.3

384 **Validation of the Analytical Procedure.** To validate the
 385 analytical procedure, certified sediment and soil samples were
 386 analyzed. IAEA-135 sediment sample was collected in 1991 at
 387 Cordon Green, Lune Estuary, U.K. This area is influenced by the
 388 radioactive discharges from the nuclear reprocessing plant of
 389 Sellafield. SRM 4353 (NIST) is a soil collected in 1980 from Rocky
 390 Flats, CO.

391 In Table 3 are reported the obtained ^{241}Am activity values for
 392 both certified samples together with the chemical yields of the
 393 analytical procedure. As can be seen, the developed analytical
 394 method is efficient for both kinds of samples. The fwhm of the
 395 ^{241}Am peak was in most cases below 30 keV, which is similar to
 396 the fwhm values obtained with anion exchange. In Figure 5, the
 397 α -spectrum of the IAEA-135 sediment sample obtained after
 398 treatment with the analytical procedure developed is shown.

Table 4. ^{241}Am Activities in Chosen Samples Determined by the Proposed Analytical Method and Compared with Values Determined with γ -Spectroscopy^a

sample	^{241}Am (Bq/g)	
	experimental	γ -spectroscopy
blank	<MDA ^b	-
sediment core		
2–4 cm	2.9 ± 0.1	2.8 ± 0.1
6–8 cm	3.4 ± 0.1	3.2 ± 0.1
18–20 cm	13.2 ± 0.4	12.6 ± 0.4

^a The samples originate from Irish Sea sediment. Reference date is December 2002. ^b MDA (80000 s) 0.45 mBq (calculated according to Currie³²).

Table 5. ^{241}Am Activities in Chosen Samples Determined by the Proposed Analytical Method and Compared with Values Determined with Classical Radiochemical Procedure^a

sample	^{241}Am (Bq/g)	
	proposed procedure	Dowex
sediment sample		
0–2 cm	3.7 ± 0.1	3.7 ± 0.1
12–14 cm	6.1 ± 0.1	5.9 ± 0.2

^a The samples originate from Irish Sea sediment. Reference date is December 2002.

Real Samples. To verify the feasibility of the proposed
 analytical procedure for environmental samples, sediments from
 the Irish Sea have been analyzed. The samples were collected in
 1993 in the Irish Sea (54.294° N, 3.338° W) by the German Federal
 Maritime and Hydrographic Agency (Hamburg, Germany) and
 consisted of 2-cm layers of a sediment core (48 cm high). The
 core was characterized by high ^{241}Am content (between 2.8 and
 17.9 Bq/g). ^{241}Am activity was previously analyzed by γ -spectrom-
 etry,³¹ and these results were used in choosing the proper sample
 size for the α -analysis as well as comparing with the results
 obtained. The obtained results, together with the γ -values, are
 reported in Table 4. As can be seen, they are in very good
 agreement. To determine the memory effect of the procedure,
 one blank sample was analyzed and found to contain less than
 the minimum detectable activity (MDA) of ^{241}Am (Table 4). The
 procedure has also been tested without performing the oxalate
 coprecipitation. The chemical yields for environmental samples,
 however, did not exceed 5%. This demonstrates the necessity of
 purifying the sample solution before on-line separation.

Comparison with the Classical Radiochemical Procedure.
 A comparison between the developed procedure and the classical
 radiochemical separation method has been performed, and the
 results are given in Table 5. As can be seen, the results are in
 agreement. The chemical yield of the developed method is
 comparable (70–90%) to those obtained with the classical proce-
 dure, but the analysis time is remarkably reduced by 1–2 days.
 A separation method with anion exchange resins requires large
 volumes of rather concentrated acids, and this increases the waste

(31) Hrnccek, E. EC-JRC-ITU Technical Note 2001/20, 2001; pp 28–38.
 (32) Currie, L. A. *Anal. Chem.* **1968**, *40*, 586–593.

427	management costs. With the new procedure, a reduction in acid	sediment reference material as well as to sediment samples from	440
428	volume and concentration is achieved.	the Irish Sea.	441
429	CONCLUSIONS	ACKNOWLEDGMENT	442
430	It has been demonstrated that HPLC can be exploited for	The authors thank Dr. E. Hrnccek and Dr. C. Apostolidis for	443
431	α -spectrometry sample preparation for Am determination. In	the useful discussions. The authors also thank Dr. H. Nies from	444
432	comparison with the batch separation procedures in the proposed	the Bundesamt für Seeschifffahrt und Hydrographie, Hamburg,	445
433	analytical method, the analysis times and sample handling are	Germany, for the courtesy of providing the Irish Sea sediment	446
434	drastically reduced. The chemical yields are competitive with those	samples.	447
435	obtained with traditional methods. Moreover, cross-contamination		
436	of the samples can be avoided with respect to the batch separation		
437	procedure. An advantage is that in case of large amount of samples	Received for review January 31, 2003. Accepted March 27,	448
438	the system can be automated. Further investigation on this subject	2003.	449
439	is ongoing. The method was successfully applied to soil and	AC034093P	450

CHARACTERISATION OF A RADIOACTIVELY CONTAMINATED MARINE SEDIMENT CORE BY RADIOMETRIC AND MASS SPECTROMETRIC TECHNIQUES.

L. Perna^a, J. Jernström^a, L. Aldave de las Heras^a, E. Hrncsek^b, J. de Pablo^c and M. Betti^{a*}

^aEuropean Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125, Karlsruhe, Germany

^bARC Seibersdorf research GmbH, A-2444 Seibersdorf, Austria.

^c Universidad Politecnica de Catalunya, Chemical Engineering Department, Av. Diagonal 647, 08028 Barcelona, Spain.

* Corresponding author: fax +497247951186, e-mail: betti@itu.fzk.de

ABSTRACT

A radioactively contaminated marine sediment core has been characterized by radiometric and mass spectrometric techniques as for ²³⁷Np, ²⁴¹Am, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu, ¹³⁷Cs and ¹⁵⁴Eu.

The data obtained with independent methods in the framework of a QA/QC program as compared with the source term discharges as well as with those reported in literature resulted to be in good agreement.

INTRODUCTION

Radioactivity may be introduced in the environment through a variety of systems and processes^{1,2}. A general distinction can be made between gases, aerosol and particulate material. Particles with higher activity concentration, known as “hot particles”, may result from atmospheric nuclear weapon tests or nuclear reactor accidents as well as from discharge effluents^{1,3-5}. This activity is diluted as material is transferred to soil and water directly or via vegetation and movement through other biota. Therefore, for monitoring radioactivity in the environment it is necessary to analyze bulk samples from all biosphere compartments as well as single microparticles.

During the 5th Framework Program (FP5) of the European Commission, at the Institute for Transuranium Element (ITU) a reference laboratory for the measurement of radioactivity in the environment (MaRE lab) has been set up. MaRE Lab provides scientific and technical support to the policy of the General Directorate Transport and Energy (Radiation Protection Unit H4) of the European Commission, both for the implementation of the requirements on environmental radioactivity surveillance (Art. 35-36 of the Euratom Treaty)⁶ and in the framework of the OSPAR⁷ (Oslo-Paris, Convention) strategy on the management of radioactive substances for the protection of marine environment of the North-East Atlantic.

Among the radiometric and mass spectrometric methods in use at MaRE laboratory, γ -spectrometry can be used for fast screening of the sediment samples for Am and fission products. Alpha spectrometry is exploited for the determination of the activity of americium and plutonium isotopes. Mass spectrometric methods are used for long-lived radionuclides determination as well as to confirm radionuclides concentrations for QA/QC purpose. For instance, ^{237}Np has been measured by glow discharge mass spectrometry (GDMS)⁸. High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) has been used for the determination of ^{239}Pu and ^{240}Pu isotopes that cannot be determined individually by alpha spectrometry⁹. Secondary ion mass spectrometry (SIMS) is exploited for the characterisation of the “hot particles” detected in the samples by autoradiography¹⁰.

For over four decades radioactive waste discharges in the north-eastern Irish Sea have been dominated by those from the nuclear facilities sited at Sellafield. Many studies have been performed in order to understand the behaviour of radionuclides and their fate in the marine ecosystems^{4,11,12}. The purpose of this paper is not to provide an assessment of the dispersion of the radionuclides but to illustrate how independent analytical techniques are exploited in order to

detect radioactive contamination. An attempt has been made, however, in comparing the results obtained with those reported in the main literature sources. Due to the large amount of data and studies this comparison might not be exhaustive but sufficient to explain the findings here reported.

EXPERIMENTAL

α -measurements were performed with an OCTÊTE™ PC (EG&G Ortec) with ULTRA ion-implanted silicon detectors with an active area of 450 mm². Energy was calibrated with a mixed nuclide source containing ²³⁷Np, ²⁴¹Am and ²⁴⁴Cm (GM810, AEA Technology). For efficiency calibrations an ²⁴¹Am source (GT223, AEA Technology) was used. Am and Pu activities in the samples have been determined according to the procedures previously published^{13,14}.

γ -analysis were performed with a γ -spectrometer system designed for low level applications¹⁵. Energy, FWHM and efficiency calibrations of the HPGe detector were performed using a certified γ -source containing a mixture of radionuclides (GL571, AEA Technology QSA GmbH).

An ultra low level liquid scintillation (LSC) counter Quantulus 1220 (Wallac Oy, Finland) equipped with a pulse shape analyser (PSA), which allows discrimination between α and β pulses, was used for the determination of ²⁴¹Pu after radiochemical separation¹⁴.

A Finnigan MAT Element 2 high-resolution ICP mass spectrometer, modified to handle radioactive samples in a glow-box, was used for ²³⁹Pu and ²⁴⁰Pu determination⁹.

A CAMECA IMS 6f secondary ion double-focusing mass spectrometer (SIMS) was employed. The instrument was also equipped with a spatially resolved pulse-counting resistive anode encoder (RAE) used for mapping the entire sample surface¹⁶.

A VG9000 GD-MS instrument (Winsford, UK) previously described¹⁷ consisting of a dc glow discharge ion source coupled to a double-focusing mass spectrometer of reverse (Nier-Johnson) geometry. Ion detection is accomplished by a dual detection system consisting of a Faraday cup for measurement of a large ion current (typically $> 10^{-13}$ A) and a transverse mounted Daly detector for the measurement of small ion currents. Standards and samples were prepared according to a previously published procedure⁸.

RESULTS AND DISCUSSION

The initial dispersion of radionuclides discharged to the marine environment is influenced by a numbers of factors including the chemical form of the radionuclides in the effluent, local hydrographic conditions, the composition of the bottom sediments and the variation of the discharged rate¹⁸. Actinides released in particulate or hydrolyzed form are quickly removed from the water column by direct precipitation or scavenging by suspended particulate matter. The tendency of actinide radionuclides to adsorb onto particles and become associated with deposited sediments strongly influences their present distribution and is probably the most relevant feature controlling their long-term fate^{18,19}.

Low-level liquid radioactive waste has been discharged under authorization from BNFL Sellafield to the Irish Sea since 1952²⁰. Discharge rates were at a maximum in the 1970s but, since then, releases of transuranium radionuclides have been reduced by approximately two orders of magnitude in comparison with the peak discharges²¹.

Americium profile

It has been estimated that nearly all of the ²⁴¹Am discharged has been rapidly incorporated into a narrow belt of fine grained sediments lying off the Cumbrian coastline²². It has been also

reported that americium discharge from Sellafield as being totally in the form of reduced and highly particle-reactive Am(III)¹⁸.

The ²⁴¹Am activity in the core was measured with two independent techniques, alpha and gamma spectrometry (Table 1). The ²⁴¹Am concentration profile in function of core depth is presented in Figure 1. As can be seen the results are in fair agreement, only small discrepancies between the values exist. This can result from the non-homogeneity of the samples due to the fact that ²⁴¹Am can be agglomerated in particles. On the basis of the activity profile, the layer corresponding to the depth 26-28 cm, where the highest activity was detected, was investigated for radioactive particles by autoradiography. A big hot spot was detected after 2 weeks of exposition time (Figure 2a). The presence of isotopes at mass 241 was revealed by SIMS (Figure 2b). Since no signals were obtained at masses 239 and 240, corresponding to plutonium isotopes, the inclusion at mass 241 could be attributed to ²⁴¹Am. This indicates that americium is agglomerating in particles and explains the non-homogeneity of the samples. It has to be pointed out that, prior to the introduction of modern effluent treatment plant, the actinides were dominantly associated with the particulate phase of waste²³ and “hot particles” occurred in sediments of this area. Also agglomerates of smaller particles, bonded by organic matter and coated with iron and manganese oxides have been detected²⁴. A recent investigation of the particles found in the present study, performed by X-ray microanalytical methods based on synchrotron radiation techniques²⁵ has also shown a strong association of these particles with manganese and iron.

The mean value of the ²⁴¹Am/²³⁹⁽⁴⁰⁾Pu ratio (Table 2) was found to be 1.6 and it was in agreement with that reported by Beks²⁶ and confirmed Sellafield discharges as source term²⁶.

Plutonium profile

The discharge of $^{239(40)}\text{Pu}$ to the marine environment from Sellafield was 5.92TBq up to the end of 1992, representing 45% of the estimated inventory of $^{239(40)}\text{Pu}$ in the North Atlantic due to the global fallout²⁷. Approximately all of the plutonium released is in the almost insoluble IV oxidation state¹⁸. The remaining was either dissolved (predominantly in the more soluble V oxidation state^{11,28}) or associated with suspended particulate material (almost entirely in the IV oxidation state²⁹), with some inter-conversion occurring between each species. This fraction has been transported out of the Irish Sea^{21,23}. This dual mechanism for dispersion of plutonium affects ^{241}Am distributions, since decay of Sellafield ^{241}Pu provides an *in situ* source of ^{241}Am in the environment³⁰.

^{238}Pu , $^{239(40)}\text{Pu}$ activities were determined by alpha spectrometry. ICP-MS was employed for the measurement of ^{239}Pu and ^{240}Pu ; LSC was used for ^{241}Pu determination. The plutonium activity profile in function of core depth is presented in Table 1 and Figure 3. This profile shows similarity with the americium one, both presenting an increase of activity after 10-12 cm layer. Generally, the activity of $^{239(40)}\text{Pu}$ is low in the upper and deeper sections, but increases rapidly in the middle of the profile. The ^{238}Pu activity profile, decay corrected to 1993, had a similar trend. Plutonium isotope ratios have been also measured in the sediment core, and can be related to the history of reprocessing operations at the Sellafield site³¹. The decay corrected $^{238}\text{Pu}/^{239(40)}\text{Pu}$ activity ratios profile are given in Table 2. The results for all sections core are higher than 0.06, which is characteristic of plutonium released from Sellafield rather than nuclear weapons fallout³¹. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios show a similar pattern to the $^{238}\text{Pu}/^{239(40)}\text{Pu}$ activity ratios for the 6 uppermost core sections and as can be seen in Table 3 varied between 0.22-0.24⁹. This is in general agreement with other published results^{11,12}. Such

changes in the $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios should relate to change in the type of fuels reprocessed at Sellafield site¹¹. The earliest Sellafield releases were related to UK weapons program and were characterized by low burn-up times and therefore very low $^{238}\text{Pu}/^{239(40)}\text{Pu}$ activity and very low $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios (0.03 and 0.06 respectively). In contrast, the power reactor fuels, which gave rise to the large majority of the effluents after the late 60s, had a higher burn-up reflected in higher $^{238}\text{Pu}/^{239(40)}\text{Pu}$ activity ratios (up to 0.38) and higher $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios (as high as 0.25). None of the plutonium found at depth in this profile has the isotopic composition expected from the earliest discharge (Table 2). This implies that, limited redistribution of plutonium in the core has occurred. It has been calculated that a remobilization of 1% of plutonium from a section in the core with a $^{238}\text{Pu}/^{239(40)}\text{Pu}$ activity ratio of 0.31 and a $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.21, to a section of the core with a $^{238}\text{Pu}/^{239(40)}\text{Pu}$ activity ratio of 0.06 and a $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.07, gives a final $^{238}\text{Pu}/^{239(40)}\text{Pu}$ activity ratio of 0.19 and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.14¹². These values are consistent with those here reported.

$^{238}\text{Pu}/^{239(40)}\text{Pu}$ activity ratios in the uppermost section of the core (see Table 2) reflects the presence of a mixed sediment within the core being the expected ratios from Sellafield discharges 0.33 ± 0.03 ²⁹. In conclusion, it can be summarized that the presence of higher ratio material in the sections of the core correspond to more recent years, and an increase at depth suggests remobilization of a small fraction of younger material to depth in the core.

$^{241}\text{Pu}/^{239(40)}\text{Pu}$ ratios (Table 2) varied between 9 and 20. These values correspond to those of Sellafield discharges³² and are of the same order of those reported by other authors¹⁸.

Neptunium profile

Research on neptunium in the environment, and in general in the Irish Sea, are sparse^{33,34}. From the investigations carried out it clearly results that neptunium contamination is widespread

throughout the Irish Sea and suggests that although neptunium is more mobile in the environment than other transuranics it is generally less bioavailable³⁴. The consequence of its long half-life ($t_{1/2} = 2.1 \times 10^6$ years) and the comparative mobility of neptunium in the environment is such that ^{237}Np will, however, be the most hazardous material in high-level waste in geological repositories from $1 \cdot 10^4$ to $3 \cdot 10^7$ years after disposal³³. Therefore, research on environmental neptunium from low-level waste disposal in the Irish Sea may give important information for future waste management programs.

In the Irish Sea, neptunium may be present from different source terms³⁴. At the Sellafield site ^{237}Np arises mainly from the reprocessing of Uranium from fission reactors. Data on discharges are available from 1978. These values range from approximately 0.03-0.4 TBq per annum during the 1990s with no constant trend³⁴. A total discharges activity of 6-8 TBq until 1989 has been estimated from consideration of a sediment core³⁵.

^{237}Np content in the sediment core was analyzed by measuring the 312.17 keV gamma line of ^{233}Pa , which can be assumed to be in equilibrium (Table 1). The reliability of the gamma analysis was confirmed by results obtained with a direct current glow discharge mass spectrometry (d.c. GD-MS)⁸. As can be seen in Table 4, the results obtained with the two independent techniques are in very good agreement. Dc-GD-MS allows fast determination of ^{237}Np directly on solid samples and gives advantages respect to γ -spectrometry, where it needs to be evaluated on the basis of ^{233}Pa .

In Figure 4, the ^{237}Np activity profile in function of the core depth is reported. The profile does not match with discharge data available from Sellafield^{12,36}, and is impossible to explain in terms of simple accumulation of contaminated sediment. However, the profile found is similar to those reported by other authors^{12,35}. The neptunium activity is enhanced in the upper layer of the

core corresponding to the young sediment, which implies that an upwards movement of neptunium is occurring. The net upwards flow of water provides a possible mechanisms whereby Np could be carried upwards in the solution phase, through the sediment core.

Neptunium can exist in environment in oxidation states (IV) and (V)³⁷. Although the neptunium is presumably discharged as Np(IV)³⁴, inorganic speciation modeling has confirmed that the dominant oxidation state for neptunium in saline environment is Np(V)¹². As consequence only a minor fraction is incorporated into the sediment as Np(IV), unlike the mobile Np(V) remains in the aqueous phase. This has been also confirmed from laboratory experiments^{38,39}.

Evidence for oxidation state changes or other remobilization processes from surface and core sediment is varied. No clear changes in the $^{237}\text{Np}/^{239(40)}\text{Pu}$ ratio with distance away from Sellafield was noted⁴⁰. Values of $^{237}\text{Np}/^{239(40)}\text{Pu}$ ratio varying from 0.19% to 0.41% for surface sediment samples unaffected by Springfields discharges have been reported. Other authors have found for Shetland and Norwegian coastal waters that the $^{237}\text{Np}/^{239(40)}\text{Pu}$ ratio increased in the aqueous phase with the distance from the source³⁴. This apparent conflict may reflect changes in Pu speciation with distance or simply the complicating effects of sediment mixing during transport prior to deposition making surface sediments an unreliable medium to study this effect⁴⁰. In cores, no apparent movement of ^{237}Np relative to Pu producing visual changes from the discharge pattern were noted by Kuwabara *et al*³⁵, whereas Morris and Livens³⁶ observed an apparent upward movement of Np relative to Pu. The same findings than Morris and Livens³⁶ were observed in the present investigation. In fact, the $^{237}\text{Np}/^{239}\text{Pu}$ ratio, was found to be between 0.04 and 0.09 in the first five layers of the sediment core (0-10 cm). ^{237}Np derived from Sellafield discharges has thus accumulated in areas of fine-grained sediment such as estuaries

and offshore mud patches but is likely to be more available for remobilisation than other actinides due to its lower K_d value³⁴.

Fission product profiles

Published data and radioactive decay and ingrowth calculations indicate that by the 90s the discharge had generated environmental inventories of about 3×10^4 TBq of ^{137}Cs ²⁹. Most of the radiocaesium remains in solution in seawater and is transported out of the Irish Sea in a year or less^{29, 41}, but about 10% is taken up by Irish Sea sediments. As for ^{154}Eu no data have been found in literature. Europium is generally one of the more immobile radioactive metals in the environment. It preferentially adheres fairly tightly to soil, and the concentration associated with soil particles is estimated to be about 240 times higher than in interstitial waters⁴². Therefore, more studies should be performed on its behavior in marine environment.

The activity profiles of cesium and europium are reported in Figure 5. They are similar to those of plutonium and americium, in the sediment core, with a pronounced sub-surface maximum and shapes bearing a qualitative resemblance to the Sellafield discharge patterns^{12, 29, 43}. However, the cesium peak is apparently broader than that of Pu or Am, and also broader than expected from Sellafield discharges. This “broadening”, however, is not likely to be an effect of mixing as $^{239(40)}\text{Pu}$, ^{238}Pu and ^{241}Am show peaks which can clearly be discriminated. There appears to be “excess” ^{137}Cs both in the younger, upper sections of the core, perhaps more significantly, at depth in the core. The enhancement in ^{137}Cs activity in the uppermost sections of the profile is consistent with the sediment transport model of Mackenzie *et al*²⁹. However, the enhanced ^{137}Cs activity observed at depth in the core cannot be explained by this model and probably reflects downwards, post-depositional migration of ^{137}Cs in the sediment core⁴⁴. The half-life corrected

cesium concentration in the surface layer of the core was compared to the Marina II study^{32, 45} and found to be in agreement.

CONCLUSIONS

The combined exploitation of radiometric and mass spectrometric techniques allows to perform a complete characterization of sediment samples as for radionuclides in the two different phases. Correlation between measurements of radionuclides in bulk and in particles can be performed in order to highlight their behavior in marine ecosystems. Thus information on the radionuclides activities and ratios can reveal their source term. For an effective QA/QC program is a benefit to have independent techniques to confirm the reliability of the results as for routine measurement as well as for research studies.

REFERENCES

1. V. VALKOVIĆ, Radioactivity in the Environment, ELSEVIER SCIENCE B. V. (2000).
2. M. BETTI, Microchemical Journal, 67 (2000) 363.
3. F. WARNER & R. M. HARRISON, Radioecology after Chernobyl, J. WILEY & SONS (1993).
4. P. GUÉGUÉNIAT, P. GERMAIN, H. MÉTIVIER, Radionuclides in the Oceans Input and Inventories, Les éditions de physique (1996) 155.
5. L. ALDAVE DE LAS HERAS, G. TAMBORINI, E. HRNECEK & M. BETTI, Radioprotection, 37 (C1) (2002) 993.
6. European Commission, Euratom Treaty, Rome 27 – 3 – 1957.
7. OSPAR Commission, www.ospar.org
8. L. ALDAVE DE LAS HERAS, E. HRNECEK, O. BILDSTEIN & M. BETTI, J. Anal. At. Spectrom., 17 (2002) 1011.
9. E. HRNECEK, L. ALDAVE DE LAS HERAS & M. BETTI, Radiochim. Acta, 90 (2002) 721.
10. P. CARBOL, D. SOLATIE, N. ERDMANN, T. NYLÉN & M. BETTI, J. of Environ. Radioactivity, in press (2003).
11. P. J. KERSHAW, D. S. WOODHEAD, M. B. LOVETT & K. S. LEONARD, Appl. Radiat. Isot., 11 (1995) 1121.
12. K. MORRIS, J. C. BUTTERWORTH & F. R. LIVENS, Estuarine, Coastal and Shelf Science, 51 (2000) 613.
13. L. PERNA, J. JERNSTRÖM, L. ALDAVE DE LAS HERAS, J. DE PABLO & M. BETTI, Anal. Chem., accepted (2003).
14. E. HRNECEK & K. IRLWECK, Contaminated Soil Samples in Environmental Radiochemical Analysis; Ed. Newton G. W. A., RS•C (1999), 73.
15. P. PEERANI, P. CARBOL, E. HRNECEK & BETTI M., Nucl. Instr. Meth. in Phys. Res. A, 482 (2002) 42.
16. M. BETTI, G. TAMBORINI & L. KOCH, Anal. Chem., 71 (1999) 2616.
17. M. BETTI, G. RASMUNSEN, T. HIERNAUT, L. KOCH, D. P. M. MILTON, R.C. HUTTON, J. Anal. At. Spectrom., 9 (1994) 385.
18. P.I. MITCHELL, J. VIVES I BATTLE, L. LEÓN VINTRÓ & C. A. MCMAHON, Science of the Total Environment, 44 (1999) 223.

19. K. S. LEONARD, D. MCCUBBIN, P. BLOWERES & B. R. TAYLOR, *Science of the Total Environment*, 44 (1999) 109.
20. J. GRAY, S. R. JONES & A. D. SMITH, *J. Radiol. Protect.*, 15(2) (1995) 99.
21. P. MACDONALD, J. VIVES I BATTLE, A. BOUSHER, A. WHITTALL & N. CHAMBERS, *Science of the Total Environment*, 44 (1999) 129.
22. P. E. WARWICK, I. W. CROUDACE & R. CARPENTER, *Appl. Radiat. Isot.*, 47(7) (1996) 627.
23. R. J. PENTREATH, B. R. HARVEY & M. B. LOVETT, *Radioactive Waste Management*, IAEA, Vienna, 5 (1984) 315.
24. E. I. HAMILTON, *Marine Pollution Bulletin*, 20 (1989) 603,
25. S. TÖRÖK, J. OSÁN, L. VINCZE, S. KURUNCZI, B. ALFÖLDY; M. BETTI, C. A. PÉREZ and G. FALKENBERG, Identification of hot particles in the environment using single particle X-ray emission and absorption analysis, *Annual Report HASYLAB* (2002).
26. J. P. BECKS, *Continental Shelf Research*, 20 (2000) 1941.
27. UNSCEAR, *Ionizing Radiation: Sources and Biological*, United Nation, New York, (1982).
28. D. BOUST, P. I. MITCHELL, K. GARCIA, O. CONDREN, L. LEÓN VINTRÓ & G. LECLERC, *Radiochimica Acta*, 74 (1996) 203.
29. A. B. MACKENZIE, R. D. SCOTT, R. L. ALLAN, Y. A. BEN SHABAN, G. T. COOK & I. D. PULFORDD, *J. of Environ. Radioactivity*, 23 (1994) 39.
30. G. P. DAY & J. E. CROSS, *Nature*, 292 (1981) 43.
31. P. J. KERSHAW, D. S. WOODHEAD, S. J. MALCOLM, D. J. ALLINGTON & M. B. LOVETT, *J. of Environm. Radioactivity* 12 (1990) 201.
32. D. JACKSON, B. LAMBERS & JGRAY, *J. Radiol. Prot.*, 20 (2000) 139.
33. R. C. THOMPSON, *Radiation Research*, 90 (1982) 1.
34. D. J. ASSINDER, *J. of Environm. Radioactivity*, 44 (1999) 335.
35. J. KUWABARA, M. YAMAMOTO, D. J. ASSINDER, K. KOMURA & K. UENO, *Radiochimica Acta* 73 (1996) 73.
36. K. MORRIS & F. R. LIVENS, *Radiochimica Acta*, 74 (1996) 195.
37. A. S. HURSTHOUSE, M. S. BAXTER, F. R. LIVENS & H. J. DUNCAN, *J. of Environm. Radioactivity*, 14 (1991) 147.
38. D. MACCUBBIN & K. S. LEONARD, *Marine Chemistry*, 56 (1997) 107.
39. E. W. BONDIETTI & C. W. FRANCIS, *Science*, 203 (1979) 1337.
40. D. J. ASSINDER, M. YAMAMOTO, C. K. KIM, R. SEKI, Y. TAKAKU, Y. YAMAUCHI, K. KOMURA, K. UENO & G. S. BOURNE, *J. of Environm. Radioactivity*, 14 (1991) 135.
41. M. S. BAXTER, I. G. MCKINLEY, A. B. MACKENZIE & W. JACK, *Marine Pollution Bulletin*, 12 (1979) 116.
42. Human Health Fact Sheet, www.ead.anl.gov/pub/doc/europium.pdf, ANL (2001).
43. P. J. KERSHAW, D. S. WOODHEAD, S. J. MALCOLM, D. J. ALLINGTON & M. B. LOVETT, *J. of Environm. Radioactivity*, 12 (1990) 201.
44. J. J. ZWOLSMAN, G. W. BERGER & G. T. M. VAN ECK, *Marine Chemistry*, 44 (1993) 73.
45. MARINA II, <http://europa.eu.int/comm/environment/radprot> European Commission (2002).

Table 1. Results (Bq/g) obtained measuring the core sediment samples from Irish Sea by alpha, gamma spectroscopy and LSC.

Sediment core, cm	²⁴¹ Am (α)	²⁴¹ Am (γ)	²³⁷ Np (γ)	²³⁸ Pu (α)*	²³⁹⁽⁴⁰⁾ Pu (α)	²⁴¹ Pu (β)*	¹³⁷ Cs (γ)	¹⁵⁴ Eu (γ)*
0-2	3.70±0.10	3.22±0.09	0.084±0.006	0.55±0.02	2.24±0.06	36.68±1.46	1.07±0.03	0.065±0.007
2-4	2.93±0.06	2.78±0.08	0.088±0.006	0.41±0.01	1.78±0.03	30.42±1.02	1.03±0.03	0.062±0.011
4-6	2.80±0.06	3.31±0.09	0.077±0.007	0.45±0.01	1.85±0.03	35.81±1.16	1.49±0.04	0.068±0.012
6-8	3.44±0.07	3.19±0.09	0.077±0.006	0.45±0.01	1.91±0.03	29.11±1.75	1.42±0.04	0.070±0.008
8-10	2.11±0.06	3.81±0.10	0.093±0.007	0.57±0.02	2.47±0.08	38.28±1.60	1.97±0.06	0.073±0.007
10-12	4.95±0.12	4.12±0.11	0.068±0.006	0.75±0.02	3.11±0.09	48.33±1.89	2.90±0.08	0.101±0.009
12-14	6.12±0.13	6.43±0.17	0.064±0.007	0.90±0.03	4.11±0.10	55.78±2.79	3.88±0.11	0.115±0.008
14-16	10.34±0.28	9.77±0.26	0.062±0.007	1.72±0.06	8.15±0.18	117.77±5.89	6.03±0.17	0.196±0.013
16-18	11.11±0.23	12.41±0.33	0.066±0.008	1.83±0.06	8.98±0.20	126.98±6.35	6.91±0.20	0.312±0.017
18-20	12.52±0.26	12.55±0.33	0.081±0.008	2.00±0.07	9.15±0.21	134.58±6.73	7.44±0.21	0.317±0.012
20-22	11.41±0.24	11.56±0.30	0.051±0.007	1.86±0.07	9.15±0.21	89.16±4.46	6.83±0.20	0.200±0.009
22-24	12.88±0.28	14.63±0.38	0.044±0.006	1.81±0.06	8.41±0.19	120.16±6.01	7.55±0.22	0.208±0.012
24-26	17.78±0.37	16.36±0.43	0.041±0.006	1.80±0.05	8.68±0.16	96.65±4.83	6.81±0.20	0.196±0.010
26-28	19.06±0.40	17.92±0.47	0.033±0.006	1.71±0.06	8.63±0.17	98.16±4.91	6.69±0.19	0.212±0.011
28-30	13.85±0.28	13.32±0.35	0.035±0.007	n.a.	n.a.	n.a.	6.05±0.17	0.163±0.009
30-32	9.49±0.19	9.34±0.25	0.018±0.004	n.a.	n.a.	n.a.	5.17±0.15	0.113±0.008
32-34	8.38±0.17	9.21±0.24	0.024±0.007	n.a.	n.a.	n.a.	5.44±0.16	0.124±0.009
34-36	10.41±0.16	9.87±0.26	0.020±0.005	n.a.	n.a.	n.a.	5.88±0.17	0.135±0.008
36-38	7.62±0.15	7.80±0.21	0.019±0.005	n.a.	n.a.	n.a.	5.66±0.16	0.111±0.010
38-40	10.70±0.11	11.20±0.29	<0.014	n.a.	n.a.	n.a.	6.02±0.17	0.140±0.009
40-42	8.34±0.18	9.75±0.26	0.024±0.005	n.a.	n.a.	n.a.	5.65±0.16	0.165±0.010
42-44	7.95±0.19	8.17±0.22	0.018±0.005	1.53±0.02	8.51±0.09	81.79±4.09	5.37±0.15	0.104±0.005
44-46	8.79±0.21	8.10±0.21	0.017±0.004	1.12±0.02	6.32±0.09	76.73±3.84	4.71±0.14	0.132±0.008
46-48	6.40±0.16	6.55±0.17	<0.014	0.82±0.02	4.39±0.07	54.80±2.74	4.82±0.14	0.125±0.009

- Decay corrected to 01 Dec. 1993
- n.a.: not analyzed

Table 2. Plutonium isotope ratios.

Sample	$^{241}\text{Am}/^{239(40)}\text{Pu}$	$^{241}\text{Pu}/^{239(40)}\text{Pu}$	$^{238}\text{Pu}/^{239(40)}\text{Pu}$
Sediment core, 0-2 cm	1.82±0.07	16.38±0.79	0.23±0.01
Sediment core, 2-4 cm	1.58±0.04	17.09±0.64	0.22±0.01
Sediment core, 4-6 cm	1.65±0.04	19.36±0.70	0.23±0.01
Sediment core, 6-8 cm	1.80±0.05	15.24±0.95	0.22±0.01
Sediment core, 8-10 cm	1.61±0.07	15.50±0.82	0.23±0.01
Sediment core, 10-12 cm	2.10±0.08	15.54±0.76	0.22±0.01
Sediment core, 12-14 cm	1.49±0.05	13.57±0.75	0.20±0.01
Sediment core, 14-16 cm	1.27±0.04	14.45±0.79	0.20±0.01
Sediment core, 16-18 cm	1.24±0.04	14.14±0.77	0.19±0.01
Sediment core, 18-20 cm	1.47±0.05	14.71±0.81	0.20±0.01
Sediment core, 20-22 cm	1.47±0.05	9.74±0.54	0.22±0.01
Sediment core, 22-24 cm	1.53±0.05	14.29±0.78	0.20±0.01
Sediment core, 24-26 cm	2.05±0.06	11.13±0.59	0.19±0.01
Sediment core, 26-28 cm	2.21±0.06	11.37±0.61	0.18±0.01
Sediment core, 42-44 cm	0.93±0.02	9.61±0.49	0.17±0.01
Sediment core, 44-46 cm	1.39±0.04	12.14±0.63	0.17±0.01
Sediment core, 46-48 cm	1.46±0.04	12.48±0.65	0.17±0.01

Table 3. Analysis results of sediment samples from the Irish Sea.

Sample	Activity ratio		Atom ratio
	$^{238}\text{Pu}/^{239(40)}\text{Pu}$	$^{241}\text{Pu}/^{239(40)}\text{Pu}$	$^{240}\text{Pu}/^{239}\text{Pu}$
0 – 2 cm	0.231 ± 0.007	11.2 ± 0.6	0.233 ± 0.005
2 – 4 cm	0.220 ± 0.005	11.8 ± 0.4	0.229 ± 0.005
4 – 6 cm	0.228 ± 0.005	13.3 ± 0.5	0.231 ± 0.005
6 – 8 cm	0.220 ± 0.004	10.5 ± 0.6	0.225 ± 0.005
8 – 10 cm	0.220 ± 0.008	10.6 ± 0.6	0.234 ± 0.005
10 – 12 cm	0.229 ± 0.006	10.7 ± 0.5	0.238 ± 0.005

Reference date is 07 09 2001 for ^{241}Pu .**Table 4.** Quantitative results of ^{237}Np in the several Irish Sea sediments determined by GDMS and γ -spectrometry⁸.

Sediment layer	GDMS		γ -spectrometry	
	ng g ⁻¹	mBq g ⁻¹	ng g ⁻¹	mBq g ⁻¹
18-20 cm	3.29 ± 0.31	86 ± 8	3.11 ± 0.31	81 ± 8
20-22 cm	1.96 ± 0.29	51 ± 7	1.96 ± 0.27	51 ± 7
22-24 cm	1.79 ± 0.29	47 ± 7	1.69 ± 0.23	44 ± 6

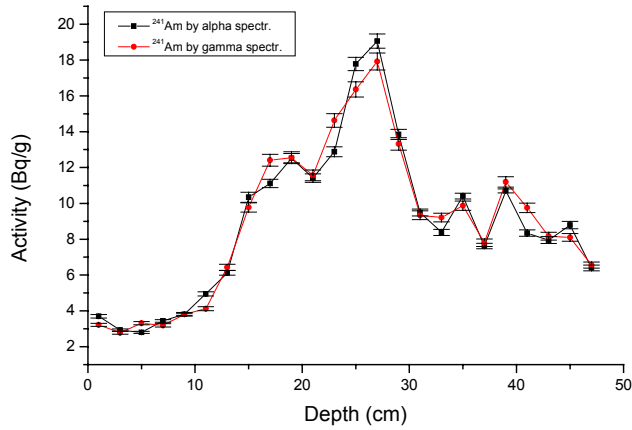


Figure 1. ^{241}Am activity profile in function of depth for a sediment core from Irish Sea obtained with alpha and gamma spectrometry.



Figure 2. A. Autoradiography of the Am particle found in the layer 26-28 cm. B. SIMS image of the particle.

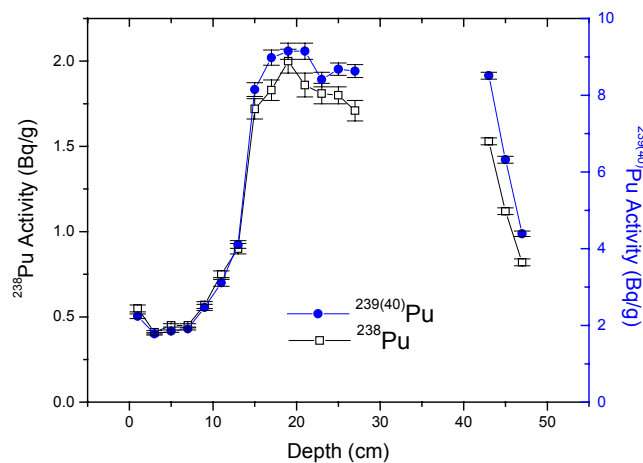


Figure 3. $^{239(40)}\text{Pu}$ and ^{238}Pu activity profiles in function of depth for a sediment core from Irish Sea obtained by alpha spectrometry.

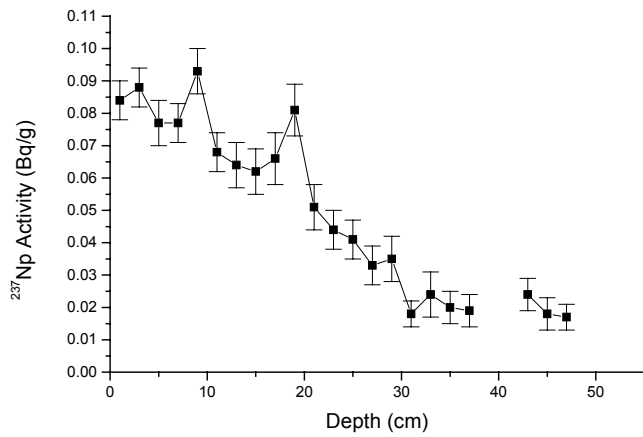


Figure 4. ²³⁷Np activity profile in function of depth for a sediment core from Irish Sea obtained by gamma spectrometry.

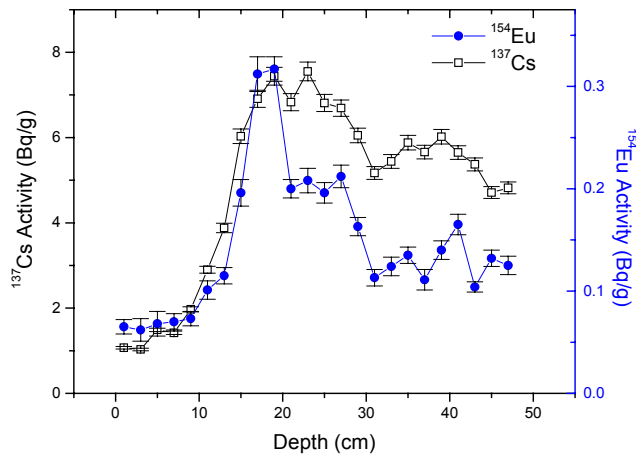


Figure 5. ¹³⁷Cs and ¹⁵⁴Eu activity profiles in function of depth for a sediment core from Irish Sea obtained by gamma spectrometry.