University of Helsinki
Faculty of Science
Department of Chemistry
Laboratory of Radiochemistry
Finland

DEVELOPMENT AND COMPARISON OF ANALYTICAL METHODS FOR THE DETERMINATION OF URANIUM AND PLUTONIUM IN SPENT FUEL AND ENVIRONMENTAL SAMPLES

Dina Solatie

Academic Dissertation

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Author
Dina Solatie
Laboratory of Radiochemistry
Department of Chemistry
P.O. Box 55
FIN-00014 University of Helsinki

Supervised by:
Dr. Maria Betti
European Commission, Joint Research Centre
Institute for Transuranium Elements
P.O. Box 2340
D-76125 Karlsruhe

Reviewed by:
Dr. Christos Apostolidis
European Commission, Joint Research Centre
Institute for Transuranium Elements
P.O. Box 2340
D-76125 Karlsruhe

and

Prof. Timo Jaakkola
Laboratory of Radiochemistry
Department of Chemistry
P.O. Box 55
FIN-00014 University of Helsinki

Opponent:
Prof. Michel Genet
Radiochemistry Group
Institute of Nuclear Physics
University of Paris Sud
F-91405 Orsay

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Nothing in life is to be feared, it is only to be understood.

Marie Curie

ABSTRACT

Radionuclides represent a very important class of environmental contaminants. Therefore, it is necessary to have available accurate, reliable and precise analytical methods to determine their bulk concentrations as well as their isotopic composition. These procedures should also be as fast as possible in order to give results in emergency cases to take decision for radioprotection of the environment and human beings.

In this work, sample preparation methods for nuclear spent fuel and environmental samples have been developed and compared in terms of accuracy, precision and time response. Dissolution procedures as well as radiochemical separation based on anion-exchange and extraction chromatography have been investigated along with their applicability in different matrices. Attention has been given to uranium and plutonium. This because uranium, which is chemically toxic and may be enriched through food chain. Plutonium is an anthropogenic element with a high radiotoxicity and accumulates in bone and liver. Moreover, ^{241}Pu decays by β-particle emission to ^{241}Am, which is also a highly radiotoxic α-emitter with a half-life of 433 years.

Uranium and plutonium have been determined in environmental and spent fuel samples, and in aqueous leachate solutions from α-doped uranium oxide, by radiometric techniques (alpha- and gamma spectrometry and liquid scintillation counting). The results, whenever possible, were compared to those obtained by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) coupled on-line with ion chromatography (IC).

It was found out that the recoveries from the environmental samples are very much affected by matrix effects. This was not the case for the samples obtained from the spent fuel and aqueous leachate solutions. Separations based on the anion exchange, ion and extraction chromatography were demonstrated to be effective for attaining purified fractions of U and Pu before measurements. The minor isotopes ^{232}U and ^{236}Pu were also successfully analysed in spent fuels despite the large separation factors, which needed to be achieved. The comparison of radiometric and IC-ICP-MS confirmed that IC-ICP-MS is a powerful method for the detection of long-lived radionuclides. The

radiometric methods have a detection limit several orders of magnitude lower than IC-ICP-MS in the case of the shorter-lived nuclides.

Nuclear track methods have been exploited to locate and separate fuel particles in soil samples. The method has been applied to a soil sample stemming from a radioactively contaminated area after the Chernobyl accident. A comparison of α-track analysis with the total α-activity showed that about 90% of the α-activity was present as clearly detectable α-spots.

LIST OF PUBLICATIONS

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

I. D. Solatie, P. Carbol, M. Betti, F. Bocci, T. Hiernaut, V. V. Rondinella, J. Cobos, Ion Chromatography Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS) and radiometric techniques for the determination of actinides in aqueous leachate solutions from uranium oxide, Fresenius Journal of Analytical Chemistry (2000) 368:88-94.

II. D. Solatie, P. Carbol, P. Peerani, M. Betti, Investigation on separation/purification methodologies for the determination of ^{232}U and ^{236}Pu in solutions of spent nuclear fuels by α-spectrometry, Radiochimica Acta (2001) 89:551-556.

III. D. Solatie, E. Hrnecek, P. Carbol, T. Jaakkola, M. Betti, Sample preparation methods for the determination of plutonium and strontium in environmental samples by low level liquid scintillation counting and α-spectrometry, Radiochimica Acta, accepted.

IV. P. Carbol, D. Solatie, N. Erdmann, T. Nylén, M. Betti, Deposition and distribution of Chernobyl fallout fission products and actinides in a Russian soil profile, Journal of Environmental Radioactivity, submitted.

V. V. Rondinella, J. Cobos, Hj. Matzke, T. Wiss, P. Carbol, D. Solatie, Leaching behaviour and α-decay damage accumulation of UO_2 containing short-lived actinides, MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS, Scientific Basis for Nuclear Waste Management XXIV, in press.

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1. INTRODUCTION

Both natural and anthropogenic radionuclides occur in the environment. The major sources of natural radioactivity are the nuclides of very long half-lives, which have persisted since the formation of the earth, along with their shorter-lived daughter nuclides and nuclides produced by cosmic rays in the atmosphere at high altitude. Anthropogenic radionuclides can enter into the environment through a variety of different processes. The most relevant sources of artificial radioactivity are global fallout from atmospheric weapons tests, local fallout accidentally released from nuclear power plants and spent fuel reprocessing plants as well as short-lived nuclides from the production of radioisotopes for medical applications. The release of radionuclides from nuclear accidents and storage of nuclear wastes has also to be considered.

Nowadays, man-made radionuclides constitute an important class of environmental contaminants. Therefore, it is very important to have accurate, reliable and precise analytical methods available to measure their concentration and isotopic composition in different matrices. For example, from their isotopic composition it is possible to understand their source term and determine eventual clandestine nuclear activities [Donohue, 2002; Donohue and Ziesler, 1993]. From the knowledge of their concentration levels in spent fuels, the conditions for spent fuel waste repository, as well as leaching behaviour under specific environmental conditions can be investigated.

Plutonium is one of the major concerns of the artificial transuranium elements released into the environment. From an environmental point of view isotopes of importance are ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu. All of these decay by alpha particle emission, with the exception of ^{241}Pu, which decays by beta particle emission to ^{241}Am. The alpha emitting isotopes of plutonium have long half-lives, they accumulate in animals and man in bone and liver, and they are highly radiotoxic. However, the largest contribution to the total plutonium radioactivity in environmental samples is due to the beta emitting ^{241}Pu. Though its radiotoxicity is much lower than that of the α-emitting Pu isotopes, the decay product ^{241}Am is a highly radiotoxic alpha-emitting nuclide with a half-life of 433 years. It also has a long residence time in animals and humans, and it is much more mobile in the biosphere than Pu [Shelley et al., 2001; Iwasaki et al., 1998; Hakanen et al., 1984].

Uranium is a naturally occurring, ubiquitous, heavy metal present in all soils, rocks, seas, and in drinking water and food. However, it can enter the environment as a consequence of several technogenic processes [Valkovic, 2000]. ^{238}U has a long half-life ($4.5 \cdot 10^9$ year) and is chemically toxic.

Determination of plutonium and uranium in environmental samples by α-spectrometry requires several radiochemical procedures to separate these radionuclides from the matrix. The following steps must be performed: conversion of plutonium and uranium associated with the matrix into soluble form, radiochemical separation and preparation of the source for measurement. Many chemical separation techniques for U and Pu based on anion exchange chromatography, solvent extraction and extraction chromatography have been investigated in spent fuel and environmental samples in literature [Yamato, 1982; Horwitz et al., 1992].

The aim of this work has been to develop, improve and compare analytical methods for plutonium and uranium determination. Attention has been focused on sample preparation and separation procedures for samples stemming from different nuclear activities (nuclear spent fuel and aqueous leachate solutions) as well as environmental samples. After classical radiochemical separations, uranium and plutonium were mainly analysed by radiometric techniques. The results were compared to those obtained by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) on-line coupled with ion chromatography. The β-emitter ^{241}Pu was analysed by liquid scintillation counting (LSC). LSC was also applied for the determination of the oxidation state of plutonium in aqueous leachate solutions. ^{232}U and ^{236}Pu isotopes in spent nuclear fuel samples were analysed by α-spectrometry. Their determination is important for decision on the nuclear waste repository shielding after disposal of spent nuclear fuels. In fact, both radionuclides decay to ^{208}Tl whose β-decay to stable ^{208}Pb is accompanied by γ-radiation with an E_γ 2614 keV ($t_{1/2} \sim 3$ min). Therefore, the relatively high γ-energy emitted from ^{208}Tl requires a substantial radiological shielding to protect humans. An other reason for the analysis of these nuclides is that from the ratio of ^{236}Pu/^{232}U an approximate dating when the fuel irradiation ended can be calculated.

In addition to bulk analysis also some particle analysis were carried out. Autoradiographic methods were used to identify hot particles in a section of a soil profile sampled in a contaminated area around Chernobyl. By bulk analysis the total activity could be correlated to the total activity obtained from the hot particles detected.

2. ACTINIDES

The actinide series includes Ac, Th, Pa and U and the transuranium elements (Np, Pu, Am. Cm, Bk, Cf, Es, Fm, Md, No, Lr). Uranium and thorium, which were the first actinides known, occur naturally. All actinides are radioactive elements. In the actinide elements, the 5f electron shell is filled, analogous to the 4f shell of the lanthanides [Katz et al., 1986]. The chemical similarity between the actinide and lanthanide elements was recognised nearly 50 years ago. However, there exist differences in the oxidation states [Seaborg, 1993]. Actinides can exist in many different oxidation states, unlike the lanthanides. Their relevant oxidation states, half-lives and main alpha energies are given in Table 1. The most stable oxidation state in aqueous solutions (acid, non-complexing) is shown in bold, the most unstable (or those only found in the solid state) within parenthesis. The chemical properties are different for the different oxidation states, while in the same oxidation state the actinides closely resemble each other. The behaviour of actinides depends on the oxidation states, the chemical compound, complex formation capability, sorption and colloid formation ability [Silva and Nitsche, 1995].

Table 1. *The half-lives, main alpha energies and oxidation states of the relevant actinide isotopes.*

Nuclide	$t_{1/2}$ (a)	Main alpha energy (MeV)	Oxidation states [Katz et al., 1986]
U-232	69.85	5.3203	3 4 5 **6**
U-234	$2.45\cdot10^{5}$	4.7749	
U-235	$7.04\cdot10^{8}$	4.3960	
U-236	$2.34\cdot10^{7}$	4.4955	
U-238	$4.47\cdot10^{9}$	4.1985	
Pu-236	2.90	5.7677	3 **4** 5 6 (7)
Pu-238	87.76	5.4993	
Pu-239	$2.41\cdot10^{4}$	5.1562	
Pu-240	$6.57\cdot10^{3}$	5.1683	
Pu-242	$3.74\cdot10^{5}$	4.9005	
Am-241	433	5.4856	**3** 4 5 6
Am-243	7370	5.2757	
Cm-242	0.45	6.1129	**3** 4
Cm-243	30.02	5.7851	
Cm-244	18.11	5.8050	
Cm-245	$8.51\cdot10^{3}$	5.3620	
Cm-246	$4.73\cdot10^{3}$	5.3865	

2. 1 Chemical properties of plutonium

Plutonium (atomic number 94) belongs to the transuranic elements. Pu was discovered during fission investigations in 1940-1941 by G. T. Seaborg and collaborators. In practise, Pu is an artificial element, but it can be found in nature in very small amounts, formed by neutron reactions in uranium [Choppin et al., 2002]. Isotopes of plutonium from ^{232}Pu to ^{246}Pu are known. But only ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu are the most relevant from an environmental point of view.

The most important chemical properties of plutonium considering its environmental behaviour are its oxidation states, since solubility, hydrolysis, complexation, sorption and colloid formation reactions differ significantly from one oxidation state to another [Silva and Nitche, 1995]. Plutonium can exist in solution in four different oxidation states III, IV, V and VI, as Pu^{3+}, Pu^{4+}, PuO_2^+ and PuO_2^{2+} respectively. All four oxidation states undergo hydrolysis reactions in aquatic conditions. The tendency of plutonium ions to hydrolyse follows the order [Choppin et al., 2002]:

$Pu^{4+} > PuO_2^{2+} > Pu^{3+} > PuO_2^+$

Hydrolysis is a primary step to polynucleation and hence generation of colloids [Kim and Kanellakopulos, 1989]. The variation of the concentration of the free (non-hydrolysed) cations with pH is presented for the oxidation states of III to VI of Pu in Figure 1 [Choppin et al., 2002]. The curves, based on estimated values of the hydrolysis constants have sufficient accuracy to indicate the pH values at which hydrolysis becomes significant: e.g. ≤ 0 for Pu^{4+}, and 4-5 for PuO_2^{2+}, 6-8 for Pu^{3+}, and 9-10 for PuO_2^+. In addition, pH affects redox behaviour significantly. The lower oxidation states are generally stabilized by more acidic conditions and the higher oxidation states become more favored with increasing basicity. Such trends may be influenced by complexation or hydrolysis reactions, which can reverse the stability of different oxidation states.

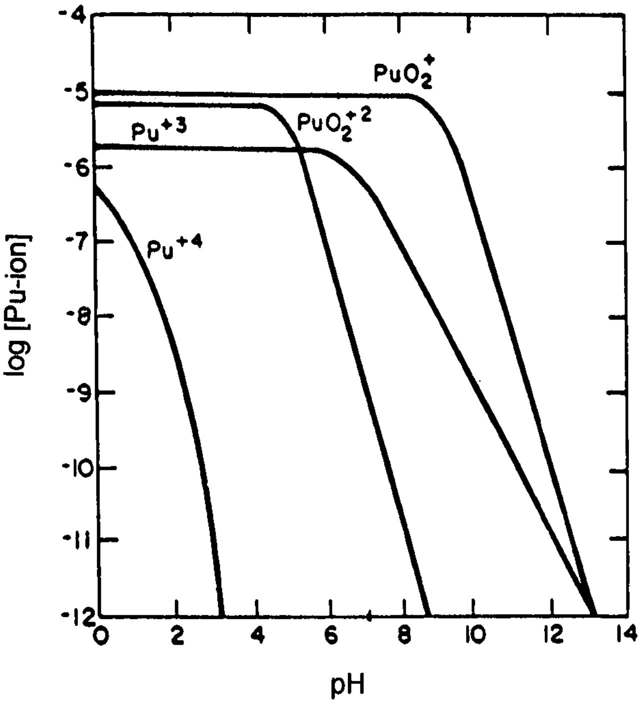


Figure 1. *Concentrations of free Pu ions at different oxidation states in solutions of different pH, showing the effect of hydrolysis [Choppin et al., 2002].*

2.2 Chemical properties of uranium

Uranium (atomic number 92) can be found in seawater and in most rocks, and is common in the earth's crust where its concentration is about 3-4 ppm. Natural uranium consists of three isotopes: ^{238}U (99.27% by mass), ^{235}U (0.72%) and ^{234}U (0.0054%), which emit alpha, beta and gamma radiation. 16 isotopes of uranium are known and all of them are radioactive.

Four well-defined oxidation states of uranium exist: III, IV, V and VI. In environment uranium exists primarily as UO_2^{2+}, under reduction conditions U^{4+} is also present. It has been shown that different oxidation states have different migration rates in the environment [Mitchell et al., 1995]. The migration rates depend on the solubility, sorption/desorption phenomena and interactions with inorganic anions and organic materials, all of which are greatly influenced by the oxidation state.

Uranium has achieved its significance in civil and military nuclear technology (nuclear power plants, nuclear weapons) because of its fissile isotope ^{235}U. Most reactors require uranium in which the ^{235}U content has been enriched from 0.72 to about 3-4%. The $^{234}U/^{238}U$ and $^{235}U/^{238}U$ activity and mass concentration ratios depend on the extent of the enrichment process and can be used for distinguishing the natural sources of U from the anthropogenic ones.

2.3 The sources of actinides in the environment

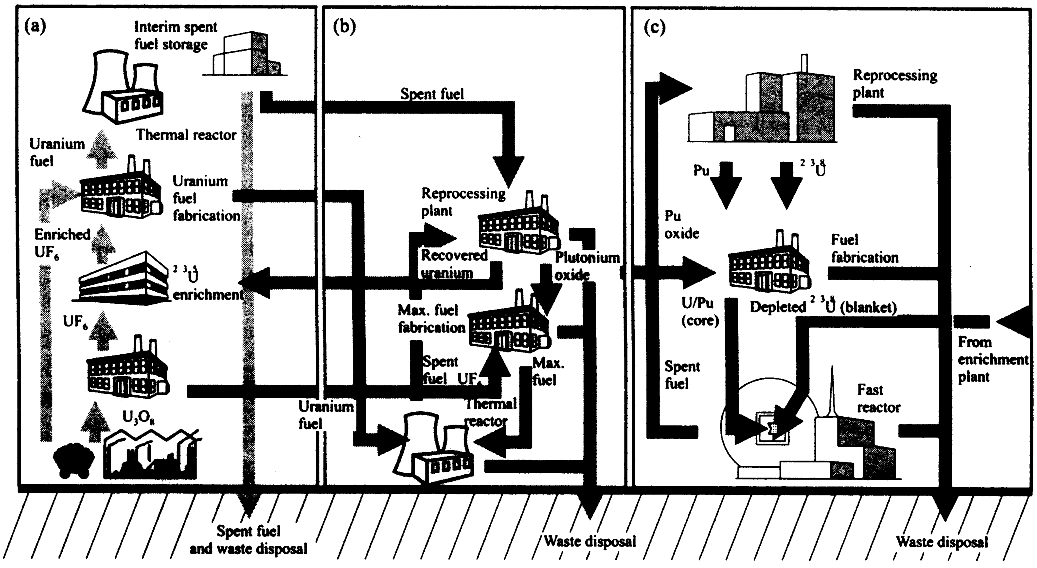
A variety of systems and processes may introduce radioactivity into the environment. The natural radionuclides, which are trapped in the earth's crust, can be released into the atmosphere by human technology. For instance, burning of fossil fuel is the most significant cause for the direct atmospheric release of pre-existing natural radioactivity (radionuclides from uranium and thorium series) [Betti, 2000]. Nuclear weapons fabrication and testing, nuclear fuel cycle processes (including uranium mining and milling, fuel fabrication and enrichment, reactor operation, storing of spent fuel and waste and reprocessing), radioisotope production and application, and nuclear accidents are typical sources of radioactivity releases [UNSCEAR, 2000]. In Table 2, the different sources of radioactivity releases into the environment are summarised.

Table 2. *The sources of radioactivity releases in the environment [UNSCEAR 2000; Salbu, 2001, Eisenbud, 1997].*

Source
Nuclear weapon tests Maralinga (Australia), 1953-1963 Marshall Islands, 1946-1958 Mururoa (French Polynesia), 1966-1996 Nevada test site (USA), 1952-1962 Semipalatinsk (Kazakhstan), 1949-1989 Novaya Zemlya (Russia), 1957-1980
Nuclear weapons fabrication
Nuclear fuel cycle Mining and milling Fuel enrichment Fabrication Reactor operation Spent fuel storages Reprocessing facilities Waste storage
Radioisotope production and uses
Accidents Windscale (UK), 1957 SNAP 9A (Mozambique), 1964 Palomares (Spain), 1966 Thule (Greenland), 1968 Rocky Flats Plant (USA), 1969 Cosmos 954 (Canada), 1978 Three Mile Island (USA), 1979 Chernobyl (Ukraine), 1986 Tokaimura (Japan), 1999

Atmospheric nuclear weapons testing – conducted from 1945 until 1980 - have introduced the majority of the deposited fractions of actinides onto earth's surface [Pentreath, 1995]. During a nuclear explosion a large amount of un-fissioned uranium and/or plutonium is dispersed, with a consequent release of radioactivity into the atmosphere. It has been estimated that about $1.1 \cdot 10^{16}$ Bq of ^{239,240}Pu have been globally released from atmospheric nuclear testing, mainly from explosions of megaton-range weapons that took place before 1963 [UNSCEAR, 2000]. The majority of Pu has been incorporated in sea-bottom sediments [Choppin and Wong, 1998].

Plutonium releases from the nuclear power fuel cycle have generally been much smaller and significant only at few locations (e.g. the Irish Sea near Sellafield/Windscale reprocessing plant). Due to the ending of atmospheric testing and the increasing use of nuclear power, however, the nuclear fuel cycle may be expected to become the predominant source for plutonium releases in the future. Typical reprocessing cycles are presented schematically in Figure 2. The main commercial reprocessing plants are located in the UK at Sellafield, in France at Cap de la Haque and in Japan at Tokai. There have been discharges to the sea and the atmosphere. For example the effluent from the reprocessing plant of Sellafield into the Irish Sea has been routinely monitored. The cumulative total discharge of $^{239,\ 240}$Pu have been $6.9 \cdot 10^{14}$ Bq [McCarthy and Nicholls, 1990].



Schematic presentations of (a) the once-through cycle (b) the thermal reactor cycle and (c) the fast reactor cycle. U_3O_8 = yellowcake, UF_6 = uranium hexafluoride, MOX = mixed oxide fuel (uranium/ plutonium) (after Semenov and Oi, 1993).

Figure 2. *Schematic presentations of nuclear fuel reprocessing [Semenov and Oi, 1993].*

Facilities for nuclear materials production and weapons fabrication exist in several locations in the United States, United Kingdom, France, China and Russia where contamination of the environment by radioactive materials has occurred [UNSCEAR, 2000]. For example a major fire occurred at the Rocky Flats Plant, in Colorado, USA in 1969 and the total amount of plutonium deposited on the site and its environs was $1.6 \cdot 10^{11}$ Bq [Eisenbud, 1997].

Other significant sources of actinides in the environment are accidents (Table 2). Especially the accident at the nuclear power plant at Chernobyl in the Soviet Union on 26th April 1986 was significant. The radionuclide releases from the damaged reactor occurred mainly over a 10-day period and about $2.6 \cdot 10^{13}$ Bq of ^{239}Pu have been estimated to be released into the environment [Eisenbud, 1997; Warner and Harrison, 1993]. An important world-wide atmospheric source of plutonium was the SNAP (System for Nuclear Auxiliary Power) device in an American satellite (SNAP 9A), which burned up some 46 km above the Mozambique channel shortly after take-off in April 1964. It contained plutonium metal, primarily as ^{238}Pu and about $6.3 \cdot 10^{14}$ Bq of

^{238}Pu have been estimated to be released into the environment [Salbu, 2001; Pentreath, 1995].

As for the fuel cycle, uranium mining and milling, fuel fabrication and enrichment are the main processes, which contribute to the increase in the amount of uranium and its daughters in the environment. In Figure 3 the uranium fuel cycle is represented. During the enrichment process of the uranium hexafluoride, depleted uranium (DU) is obtained as by-product. DU, due to its high density, which is about twice that of lead, and other physical properties, has been used in civil and military applications. For instance, it has been used as counterweights and ballast in aircrafts, 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 [Betti, 2002]. Two accidents which involved a crashing of aircrafts bearing DU as counterweights with consequent dispersion of uranium into the environment have been documented [Uijt de Haag et al., 2000].

DU 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 the dispersion of uranium into the environment as well as investigations of the radio and chemical toxicity of uranium have been carrying out by several instances [Sansone et al., 2001; Osan et al., 2001; WHO, 2001; UNEP, 2001].

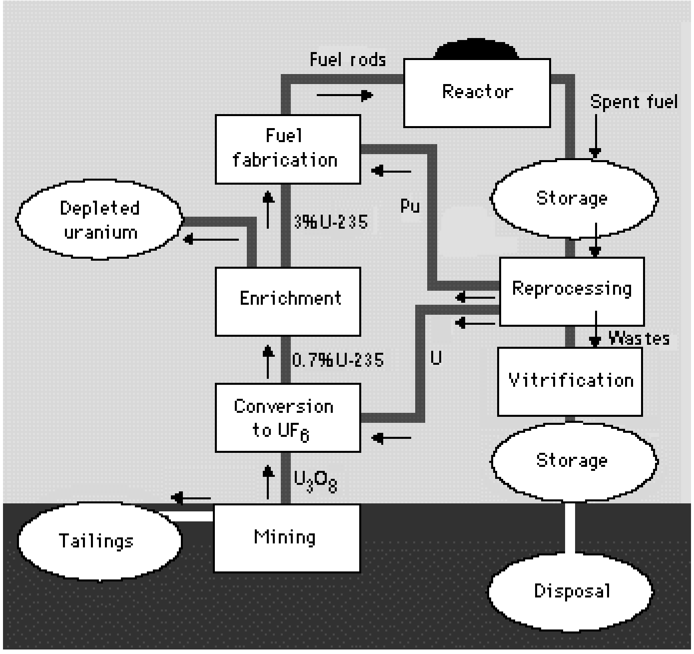


Figure 3. *The uranium fuel cycle.*

2.4 Behaviour of actinides in the environment

The distribution pattern of fallout depends on the weather conditions and the nature of the surface as well as the physico-chemical form of the radionuclide. This may vary depending on release and transport conditions in addition to the properties of the elements. A general distinction can be made between gases, aerosols and particulate material. Particles with higher activity concentration, known as hot particles, may result from atmospheric nuclear weapon tests or nuclear reactor accidents [Betti, 2000].

The actinides tend to attach to surfaces and accumulate in soils and sediments, which finally serve as storage reservoirs in the ecosystem. Subsequent movement is largely associated with geological processes such as erosion and sometimes leaching. Living organisms are exposed to the actinides mainly through surface contact, inhalation and ingestion. In aquatic systems, the actinides are easily adsorbed on the surfaces of plants and small animals such as zooplankton, and thus they then enter the food chain [Whicker and Schultz, 1982].

2.5 Actinides in spent fuel

Today 17% of the world's electrical energy is generated by nuclear power plants [UNSCEAR, 2000]. The nuclear reactor loaded with UO_2-fuel, enriched to 3-4 % in ^{235}U, consumes ^{235}U and produces energy, fission and activation products and actinides. Most of the longer-lived radionuclides generated by energy production exist in spent fuel storage ponds, reprocessing plants and high-level waste storage facilities. Normally, commercial power reactor fuel elements are removed from the reactor after four years, and kept in storage in pools, usually on-site, to let the short-lived activity decay. In some cases, after cooling the fuel elements are shipped to reprocessing plants for the extraction and separation of U and Pu. Fuel reprocessing is carried out to recover U and Pu from spent fuel for reuse in reactors. After extraction the remainder is called high-level waste, and would normally be sent to a waste tank facility for vitrification. Only about 5-10% of fuel is submitted to the reprocessing stage of the nuclear fuel cycle, because of a limited reprocessing capacity. The remaining fuel is kept in storage, usually near the reactor site.

The composition of spent fuel varies as a function of the type of fuel and reactor, neutron spectrum, flux, burn-up and the cooling time after removal from the reactor [Choppin et al., 2002]. Small amounts of ^{236}Pu and ^{232}U are also produced during the irradiation. The special interest in these two nuclides is that they decay, via a long decay chain, to ^{208}Tl. The β-decay of ^{208}Tl to stable ^{208}Pb is accompanied by γ-radiation with an E_γ 2614 keV ($t_{1/2} \sim 3$ min). The relatively high γ-energy emitted from ^{208}Tl requires a substantial radiological shielding to protect humans.

Also curium and americium are produced in nuclear reactors. They are formed by multiple neutron capture and after formation they undergo radioactive decay to produce radioactive daughter species. The activity of Am increases with time after removal from the reactor due to radioactive decay of ^{241}Pu to ^{241}Am. For a period from 10 to 10^3-10^4 years, after discharge from the reactor, the environmental hazards will be dominant due to ^{241}Am; from 10^4-10^5 years the nuclides ^{239}Pu, ^{240}Pu and ^{243}Am will be the principal actinides present; and for the period after 10^6 years, ^{237}Np and ^{229}Th will be responsible for the greatest amount of radioactivity [Katz et al., 1986].

3. SAMPLE PREPARATION

Several steps must be performed before the α-spectrometric and LSC measurement of environmental samples: conversion of Pu and U associated with the matrix into acid soluble form, radiochemical separation, purification and source preparation for measurement. For spent nuclear fuel samples a chemical separation is also required before the instrumental measurement.

Environmental samples may be either totally dissolved using fusion or microwave digestion, or leached in strong mineral acids to get Pu and U into solution [Croudace et al., 1998; Toribio et al., 2001; Moreno et al., 1997; Kim et al., 2000]. Complete dissolution of soil and sediment samples usually requires the use of hydrofluoric acid, which is time-consuming and hazardous. Leaching allows large sample sizes to be processed but this method only dissolves the bio-available form of the Pu and U. For the determination of the total Pu and U content ashing, microwave digestion and fusion of the sample can be used since these treatments dissolve even the most insoluble PuO_2 formed at high temperatures. In the microwave digestion HF is used to destroy the silicate compounds in soil and sediment, and eliminate silica, which would interfere in the subsequent separation step. The problem is that HF is a strong complexing agent of tri- and tetravalent ions (including Pu) [Sill and Sill, 1995]. For example the use of HF for the dissolution of PuO_2 in soils can result in up to 50% of the Pu remaining with insoluble fluorides [Croudace et al., 1998]. Therefore fluorides should be dissolved in nitric acid media and complexed with boric acid after the microwave treatment [Montero Rubio et al., 2000].

After the samples are in solution a radiochemical separation of uranium and plutonium from each other and from other components and radionuclides in the sample, is required. Many techniques for the separation of Pu and U based on anion exchange chromatography [Yamato, 1982; Paatero and Jaakkola, 1994; Niese and Niese, 1985], solvent extraction [Ramebäck and Skalberg, 1998; Tomé et al., 2002] or extraction chromatography with TOPO (tri-n-octylphosphine oxide) [NAS-NS 3102, 1961; Parus and Raab, 1996; Delle Site et al., 1980] or with TOA (trioctylamine) [Bertaux et al., 1999], have been investigated. Especially, the application of extraction chromatography has been intensively exploited during the last decade, because of the availability of commercial extraction resins (Eichrom Industries, USA) [Horwitz et al., 1992; Croudace et al., 1998; Goldstein et al., 1997; Pilviö and Bickel, 1998; Dietz et al., 2001; Perna et al., 2001].

Generally the actinides of which most are α-decaying are analysed by α-spectrometry (after chemical separation). The detection limit of α-spectrometry is very low, but very thin deposited α-sources and chemically pure elements are needed to achieve high quality spectra. Sources for alpha spectrometric measurements are usually prepared by direct evaporation, vacuum sublimation [Lally and Glover, 1984], electrodeposition [Talvitie, 1972; Mitchell, 1960; Lee and Pimpl, 1999] or co-precipitation [Hindman, 1983]. Electrodeposition and co-precipitation are the most commonly used methods, since these techniques give high chemical recoveries and a very thin deposit, which is essential for a high resolution of the peak.

In this work two different dissolution methods, leaching and microwave assisted total dissolution, were applied for the determination of plutonium and uranium in environmental samples. After dissolution the chemical separations were made using extraction- and anion exchange chromatography. These chromatographic methods were developed and modified, for analysis of different sample matrices like aqueous leachate solutions, and spent fuel samples. For the source preparation for α-spectrometry electodeposition or co-precipitation were used. In addition to bulk analysis also some particle analysis were carried out. The locations of α-emitting particles in soil samples were obtained by α-track analysis. The radiometric methods were furthermore applied to the determination of oxidation states of Pu in aqueous leachate solutions from ^{238}Pu doped uranium dioxide. The methods used in this work are described below.

3.1 Pre-treatment of the samples

3.1.1 Spent fuel

The first sample came from a slice section from the fuel rod zone with an average burn-up of ~50 GWd/t IHM (initial heavy metal) and the second one from a low burn-up section having an average burn-up of ~30 GWd/t IHM. The fuel slices, including cladding, were dissolved in 6 M HNO_3 at 94 °C for 3 hours and the solutions then further diluted. All these operations were performed in a hot cell facility. About 300 mg of the diluted fuel solutions were taken from the hot cell and transferred into a glove-box. One aliquot of the sample was analysed directly and two were spiked with ^{232}U and ^{242}Pu [II].

3.1.2 Environmental samples

Two different dissolution methods, leaching and microwave assisted total digestion, were used for the determination of U and Pu in environmental samples as described in publications III, IV. The leaching method was chosen for the bio-available form of the Pu and U, which can be of harm to living organisms and the microwave digestion to obtain total dissolution of the sample. In addition the reference soil samples (NIST-4353) were digested by the microwave system. 1 g samples of the reference material were dried at a temperature of 550 °C. After cooling, the samples were transferred into the fluoroplastic ceramic vessels and three reagents were added: 4 ml of conc. HNO_3, 10 ml of conc. HCl and 6 ml of 48% HF and the digestion process was started. The maximum temperature used was 230 °C. After digestion, an evaporation step was carried out.

3.2 Chemical separation

3.2.1 Anion exchange chromatography

U and Pu were separated with Dowex 1 anion exchange resin [I-V]. This method was chosen, because it is fast and simple to be performed and gives pure chemical fractions.

The separation schemes are presented in publications I-III. The separation is based on the differences in exchange affinities of different anions in the anion exchanger.

The strongly basic anion exchanger Dowex 1 is constructed of polystyrene-divinylbenzene co-polymer and contains 7.5% divinylbenzene [Samuelson, 1952]. The functional group is trimethyl ammonium.

3.2.2 Extraction chromatography

Extraction chromatography is a combination of liquid/liquid extraction and the chromatographic technique. The mobile phase is an aqueous solution and the stationary phase is an organic solution loaded onto an inert support. Two extraction chromatography techniques were tested for uranium and plutonium separation in different matrices. An extraction chromatography by TOPO (tri-n-octylphosphine oxide) in cyclohexane loaded on silica gel was used for spent fuel samples [II] and UTEVA (Eichrom Industries, USA) extraction chromatography for environmental and spent fuel samples [II, IV]. These methods were chosen, since they are rapid, simple, produce less waste than anion exchange method, and give reproducible chemical recoveries and pure spectra.

UTEVA extraction chromatography

UTEVA resin, developed by Horwitz and co-workers, consists of a neutral organophosphorus diamyl amylphosphonate extractant sorbed on an inert polymeric support (Amberlite XAD-7) [Horwitz et al., 1992]. The chemical structure of diamyl amylphosphonate is shown in Figure 4.

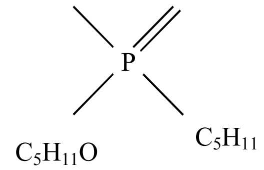


Figure 4. *Chemical structure of diamyl amylphosphonate.*

UTEVA resin absorbs U(VI) and tetravalent actinides from acidic nitrate solution, while the trivalent nuclides like Am(III) and Pu(III) are not retained. The uptake of the actinides increases with increasing nitric acid concentration as illustrated in Figure 5. It shows the capacity factor k' (the number of free column volumes to peak maximum) for the UTEVA resin for uranium and some other actinide ions as a function of nitric acid concentration [Horwitz et al., 1992]. It can be seen that the uptake is similar for each tetravalent actinide and U(VI), and that the sorbed uranium can be eluted from the resin with dilute nitric acid. Dilute HCl and dilute aqueous solution of ammonium oxalate may also be used for the elution of U [Horwitz et al., 1992; Apostolidis et al., 1998]. Most of the mono-, di-, and trivalent metal ions (e.g. Al, Ca and Fe) are not retained at 1-6 M nitric acid concentration [Horwitz et al., 1992].

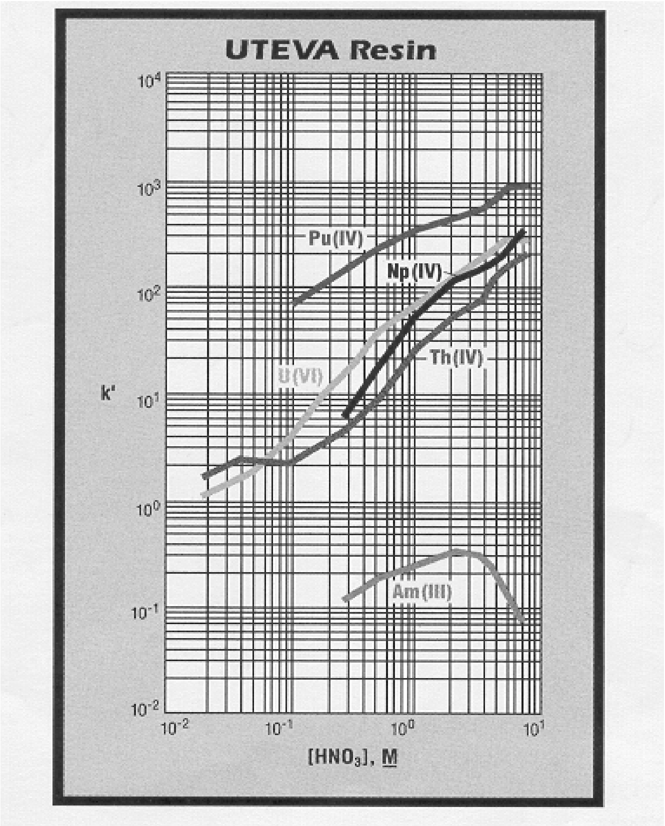


Figure 5. *Nitric acid dependency of k' (capacity factor) for actinide ions on 50-100 µm particle size UTEVA resin [Horwitz et al., 1992].*

In this study uranium was separated using a modified separation scheme previously described [Horwitz et al., 1992; Apostolidis et al., 1998]. The separation scheme is presented in publication II.

TOPO extraction chromatography

Extraction chromatography based on TOPO in cyclohexane supported on microporous polyethylene or silica gel can be used for the separation of plutonium/uranium in different matrices like spent fuel [Ziegler and Mayer, 1999] or environmental samples [Delle Site et al., 1980]. Silica-gel was chosen as support material because of its good capacity and suitable flow rate [Ziegler and Mayer, 1999].

Preparation of TOPO in cyclohexane loaded on silica gel resin

15.5 g of TOPO ($(C_8H_{17})_3PO$) was mixed with 156 g of cyclohexane. The mixture was stirred with magnetic stirrer for 1 hour. 25 g of the silica gel (63-200 μm) was washed with 100 ml of 3 M HNO_3 in a beaker. The acid was removed and Si-gel was washed 10 times with 500 ml of milliQ water. After washing the pH was 7. Si-gel was dried by heating at 100 °C for 12 hours after which it was mixed with TOPO/cyclohexane and the mixture was dried at room temperature over night.

The chemical separation of U and Pu from the fuel solution was carried out modifying the procedure described by Ziegler [Ziegler and Mayer, 1999]. The separation scheme is presented in publication II.

3.3 Preparation of sources for α-spectrometry

3.3.1 Electrodeposition

By electrodeposition the actinides are deposited on a cathode, which generally consists of platinum or stainless steel, during electrolysis of water. During this process H_2-gas from H_3O^+ is formed at the cathode. Consequently OH^--ions remain at the cathode in much higher concentrations than in other parts of the solution. If the pH in the initial solution is about 2, the high OH^--concentration at the cathode causes a precipitation of hydroxides, for example Pu^{4+} precipitates as $Pu(OH)_4$. The most applied methods for electrodeposition of actinides use electrolytes like NH_4Cl/HCl [Mitchell, 1960; Chu, 1971; McLendon, 1975; Irlweck, 1996], $(NH_4)_2SO_4/H_2SO_4$ [Talvitie, 1972; Kressin, 1977; Rodŕiguez et al., 2001], $(NH_4)_2C_2O_4/(NH_4)_2SO_4$ [Lee and Pimpl, 1999; Lee and Lee, 2000] or $(NH_4)_2C_2O_4/HCl$ [Puphal and Olsen, 1972]. Electrodeposition of actinides from organic solvents and other electrolyte solutions have also been investigated [Reformatskaya, 1971; Handley and Cooper, 1969; Hampson and Tennant, 1973; Hashimoto 1971; Levine and Lamanna, 1965].

In this work uranium and plutonium were electrodeposited from $(NH_4)_2C_2O_4/HCl$ according to a previously described method [Schüttelkopf, 1971]. This method is also described in publication I and it was chosen because it is fast and the chemical yields are close to 100%. After electrodeposition the cell, where electrodeposition was performed, was washed. A blank sample was prepared with the same method as the real sample and measured with α–spectrometer to control that no radioactivity was left in the electrodeposition cell.

3.3.2 Co-precipitation

There exist different techniques for co-precipitation of actinides for the source preparation of α-spectrometry. NdF_3, CeF_3 [Hindman, 1983; Rao and Cooper, 1995; Moreno et al., 1997, Hrnecek at al., 2002], $Ce(OH)_3$ [Sill and Williams, 1981], LaF_3 [Joshi, 1985], Be^{2+} and Al^{3+} [Lieberman and Moghissi, 1968] and $Fe(OH)_3$ [Lieberman and Moghissi, 1968; Lozano et al., 1997] have been used as carriers, producing high yields and sources of appropriate thickness. In this work plutonium was co-precipitated from 1 M HNO_3, with 40% HF as precipitant and Nd as the carrier [III]. This method was chosen because it is simple and fast to be performed, and less sensitive to trace of impurities when compared to the electrodeposition method. Before co-precipitation U(VI) must be reduced to U(IV) and plutonium converted to Pu(IV). This can be achieved by using $NaNO_2$ for Pu and $TiCl_3$ for U [Joshi, 1985].

Procedure

1. After anion exchange the plutonium sample was evaporated to dryness three times with conc. HNO_3 and dissolved in 4 ml of 1 M HNO_3.
2. A small amount of $NaNO_2$ was added to the sample. After addition of 50 µg of Nd-carrier (Nd_2O_3) and 0.6 ml of 40% HF the sample was shaken and allowed to stand in an ice bath for 30 min to permit the NdF_3 -precipitate to form.
3. A substrate solution was prepared by mixing 3.9 mg of Nd_2O_3 and 450 ml of 1 M HNO_3 and 48 ml of 40% HF. The substrate hinders the precipitate from penetrating the filter [Sill and Williams**,** 1981].
4. The filtering apparatus was attached to a vacuum system. A 0.1 µm membrane filter was mounted on a plastic support in an Erlenmeyer flask. First 5 ml of distilled water was filtrated through the filter, then 10 ml of the substrate solution and then the sample. After this the filter paper was washed two times with 5 ml of distilled water. Finally the filter was dried for 10 min under an infrared lamp and glued to the sample holder and the activity was measured.

3.4 α-track analysis

α-track analysis were used to locate the α-emitting particles in soil samples from the Gomel region, ca. 140 km north-east of the Chernobyl nuclear power plant [IV]. Polycarbonate or cellulose nitrate films can be used as detectors. They are sensitive to α-particles, which induce latent damages in the polymeric structure of the films when penetrating the film. These damages can be evidenced by etching the films with a base solution. A cellulose nitrate film (CN85, Kodak, France) was used in this study to detect α-radiation. This film has a good detection limit (10^{-6} Bq). The α-track films were exposed to the radiation for 46 days. In order to make the tracks visible in the microscope the film was etched with 6 M NaOH. The etched α-track film was systematically searched for α-tracks under an optical microscope. Hot particles were recognised by a star-shaped pattern of α-tracks [Boulyga et al., 1997; Povetko and Higley, 2001]. An α-active spot due to a hot particle was defined as a group of >10 tracks per 200 × 200 μm^2 area on the film. In addition, there were many single tracks observed on the film (not counted) that originates from natural background from radioactive decay of natural U and Th.

3.5 Speciation of Pu in aqueous leachate solutions from ^{238}Pu doped uranium dioxide

In this work speciation based on the oxidation states of Pu in aqueous leachate solutions of α-doped uranium dioxide was investigated as reported in publication V. In order to isolate and concentrate actinides in different oxidation states, techniques like co-precipitation, ion-exchange, micro- and ultrafiltration, liquid extraction, membrane extraction and chromatography can be exploited [Myasoedov and Novikov, 2001]. The method chosen in this work was co-precipitation procedure described by Lovett and Nelson [Lovett and Nelson, 1981]. It was chosen because it is simple and fast to be performed and the overall chemical recoveries are very good. This method is based on the principle that actinides in oxidation states (III) and (IV) can be removed from solution by the co-precipitation of rare earth fluoride.

An oxidant agent ($K_2Cr_2O_7$) was added to the aqueous leachate solution to prevent the reduction of Pu(VI) by any reducing agent (e.g. HF added to precipitate the rare earth fluoride). Dichromate oxidises also Pu(V) to Pu(VI) as well as Pu(III) to Pu(IV), but the oxidation of Pu(IV) to Pu(VI) is very slow (less than 1% per day) and can be ignored [Lovett and Nelson, 1981]. The reason for the slow oxidation of Pu(IV) is that oxidation state changes involving only electron transfer, e.g. from Pu^{3+}(III) to Pu^{4+}(IV) or PuO_2^{+}(V)$\leftrightharpoons$$PuO_2^{2+}$(IV), are faster and more facile than the changes which also involve the formation (or breakage) of the Pu-O bond [Lovett and Nelson, 1981; Choppin, 1999].

Procedure

The aqueous leachate solution was filtered through a 0.1 µm cellulose nitrate filter. The filter paper was dissolved in conc. HNO_3 and measured by LSC, like the filtrate. Thus the amount of Pu colloids could be calculated. Centrifuge ultrafiltration membrane was used to analyse colloids larger than 1.5 nm. It was assumed that no adsorption of Pu in the filtration system, filters and vessels occurs.

After this 0.05 ml of the filtrate was taken and 0.95 ml MQ-water and 0.1 ml of conc. HNO_3 was added. Then 0.06 ml of $K_2Cr_2O_7$ in 5 M H_2SO_4 was added and the sample was mixed well. Finally 0.1 ml of Nd_2O_3 in 8 M HNO_3 was added and the sample was allowed to stand for 30 min. After that 0.95 ml of 48% HF was added and the sample was let to stand for 15 min. The 0.1 µm cellulose nitrate filter was prepared by running 1 ml Nd-solution through it. The sample was filtered and the filtrate weighted. 0.50 µg of the filtrate was measured with LSC. The filter paper was transferred into a glass vial and 2 ml of conc. HNO_3 and 2 drops of conc. H_2O_2 were added. The sample was boiled gently until the filter paper was completely destroyed and the precipitate dissolved. The residue was diluted with 10 ml of MQ-water and a 0.1 ml aliquot was measured with LSC. The amounts of Pu in the filter paper (Pu(III+IV)) and in the filtrate (Pu(V+VI)) were calculated.

4. MEASUREMENT TECHNIQUES

The α-activities of samples in environmental surveys can be very low. Similarly, the activities of the uranium and plutonium isotopes, such as ^{236}Pu and ^{232}U in spent fuel solutions may be low. Measurement of low activity requires high detection efficiency, low background and a long measurement time. In some cases the time may exceed several days in order to minimise the influence of statistical errors. α-spectrometry allows for the lowest detection level for short-lived nuclides than any other radiation measurement technique the detection limit being as low as 100 µBq. This technique has been used in this work to measure the α-emitting isotopes of U and Pu. ^{241}Pu was analysed by LSC. The results are compared to those obtained by IC-ICP-MS.

4. 1. Radiometric techniques

Radiometric techniques (α- and γ-spectrometry and LSC) are normally used for the determination of short-lived radioisotopes. In α- and γ-spectroscopy semiconductor detectors have become dominant. Materials like silicon and germanium have resistivities between metals and insulators are normally employed. Silicon is predominantly used in the diode detectors primarily in charged particle spectroscopy, while germanium is more widely used in gamma-ray measurements. These detectors have a very good energy resolution, compact size, relatively fast timing characteristics, and an effective thickness that can be varied to match the requirements of the application.

Liquid scintillation counting is used for measurements mainly of β-emitters in liquid samples. The sample is directly dissolved in the liquid scintillation solution (scintillation cocktail) and the generated light output measured by photomultiplier tubes (PMT).

4.1.1 Alpha spectrometry

When a nuclear particle enters a detector it produces excitation and ionisation, both of which can be used for detection. In a detector the α-particles create electron-hole pairs, which are separated in the electric field and collected on their respective contacts. A charge-sensitive preamplifier finally generates a pulse with an 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 minimised.

The samples in this work were measured with an Octête PC (EG&G Ortec, USA) α-spectrometer equipment with ULTRA silicon detectors. These detectors can be cleaned easily, they have thin and rug front contact, good energy resolution, low electronic noise, high geometric efficiency and the surface is hard-wearing. The detection limits were in the range of mBq depending on counting time calculated according to Currie [Currie, 1968].

4.1.2 Gamma spectrometry

γ-spectrometry was used for the determination of ^{238}Pu activity in samples from the aqueous leachate solutions from uranium oxide [I]. 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 detector was connected to a DSPEC Spectrum Master (EG&G Ortec, USA). 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 background [Peerani et al., 2002].

4.1.3 Liquid scintillation counting

An ultra low level liquid scintillation counter Quantulus 1220 (Wallac Oy, Finland) was used for the determination of ^{241}Pu. 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 reduces the background to extremely low values. The electronic parts are cooled to reduce electronic noise. The system is also equipped with a pulse shape analyser (PSA), which allows discrimination between α and β pulses.

The counters have a low background and automated measurement is possible. One of the major limitations of scintillation counters is their relatively poor energy resolution for alphas compared to surface barrier detectors, even if the counter has α/β -discrimination [Schönhofer, 1995]. For example, ^{238}Pu and ^{239}Pu, whose α–energies differ by 344 keV, are easily separated by α-spectroscopy, but are not sufficiently resolved by LSC for quantitative work [Miglio, 1986]. Quenching is also always present in real samples and the degree of quenching can vary from one sample to another even within the same batch. Quenching causes a reduction in the number of photons reaching the photo cathode. It is shown as a shift of the energy spectrum towards lower energies, and as a reduction in the total number of counts. Therefore, a quench correction should be made for each sample. Quenching may be caused by chemical (impurity), colour or physical quenching. Chemical quenching occurs when electronegative elements (e.g. halogens), attract electrons to fill their outer shell. This destroys the higher energy excitation state of an electron, which than can not produce light in the scintillation vial. Colour quenching is absorption of light during the transmission of photons from scintillator to the photomultiplier tube. If the sample contains particles or precipitates, it can cause physical quenching [Mäkinen, 1995].

The degree of quenching is measured by the Spectral Quench Parameter of External standard method (SQP(E)), in which the channel number at the end point of the spectral distribution (external standard) indicates the degree of quenching [Mäkinen, 1995; Kaihola, 2000].

4.1.3.1 Calibration of the instrument

The counting efficiency for ^{241}Pu was determined by measuring a set of ^{3}H standard solution samples of known activity using external standardization. ^{3}H and ^{241}Pu have almost the equal maximum beta-energies, 18.6 keV and 20.8 keV, respectively, and thus the same beta-window could be used for the determination of the nuclides. The effect of quenching can be assumed to be equal for these low beta-energies. Therefore an acceptable efficiency calibration for ^{241}Pu can be obtained using ^{3}H standards. The PSA discrimination level used was 90. The quenching standards were made by mixing 2 ml (187 Bq) of the ^{3}H-standard solution in 0.1 M HCl and 18 ml of Optiphase Hisafe 3 scintillation cocktail. Different amounts of CCl_4 were then added to each standard sample. From the measured samples the quench curve could be determined. The calibration curve is shown in Figure 6. The counting efficiency for ^{241}Pu (channels 50-220) was 38-41% depending on the quenching. The background for the β-window was about 1.0 cpm. The counting efficiency for α-particles was 100%, which was verified by the ^{242}Pu standard solution. The background was counted for 600 min and gave a detection limit of 0.008 Bq for ^{241}Pu as calculated according to Currie, (Equation 1) [Currie, 1968].

$$DL = \frac{2.71 + 4.65\sqrt{cpm \cdot t}}{t \cdot 60 \cdot e \cdot 100} \qquad (1)$$

where

DL is the detection limit (Bq), cpm the net count rate for background, t the counting time (min) and e the counting efficiency (%).

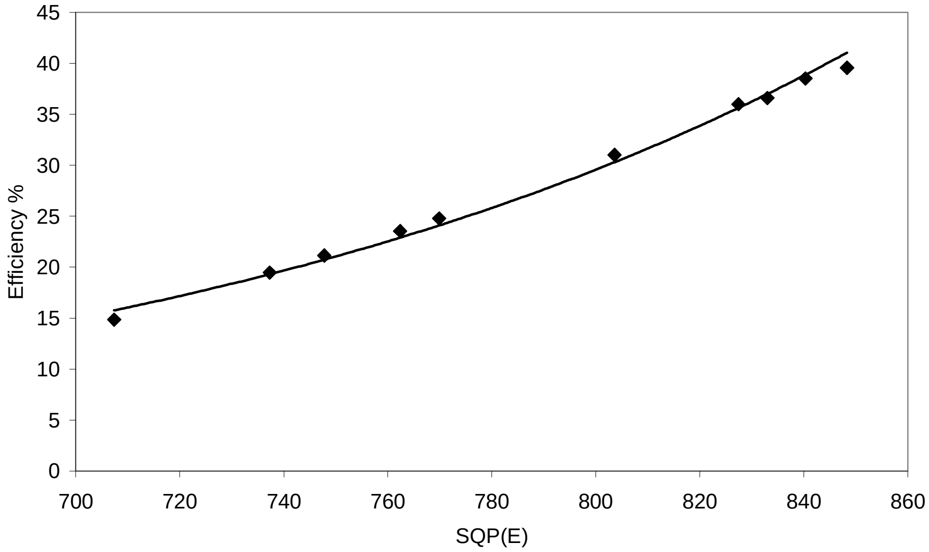


Figure 6. *The counting efficiency for ^{241}Pu as a function of SQP(E).*

4.2 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

ICP-MS is a powerful technique for trace metal analysis because of its high sensitivity. It has the capability to analyse a wide range of elements in a variety of sample matrices. As most elements can be measured simultaneously, the analyses are very rapid [Barrero Moreno et al., 1996; Becker and Dietze, 1998]. In this work an ion chromatography (IC) coupled to ICP-MS was used in order to perform U/Pu separation. In fact, IC-ICP-MS is a selective and sensitive method for the determination of a variety of anions and cations at trace and ultra trace levels [Betti, 1997].

An Elan 5000 (Perkin-Elmer SCIEX, Thornhill, Ontario, Canada) ICP-MS was used in this work. The instrument has been modified for installation into a glove box. It has a metallic structure with polycarbonate walls to protect the users from α- and β- radiation coming from the samples. Objects were introduced and the removed from the glove box in a plastic bag.

The ICP-MS was coupled with a chromatographic system. The eluent from the Dionex 4500I (Sunnyvale, CA, USA) gradient high-performance liquid chromatography (HPLC) pump passed inside the box through a Dionex CG guard column, which was used only as security column (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 sample injection prior the separation column, which was connected directly to the cross-flow nebulizer. A 250 µl sample loop was used for all the measurements. Helium gas was used for degassing the eluents and to activate the injection valve of the HPLC pump automatically. The waste from the spray chamber was pumped out with a two-way peristaltic pump and stored inside the glove box. A schematic diagram of the glove-box ICP-MS is presented in Figure 7.

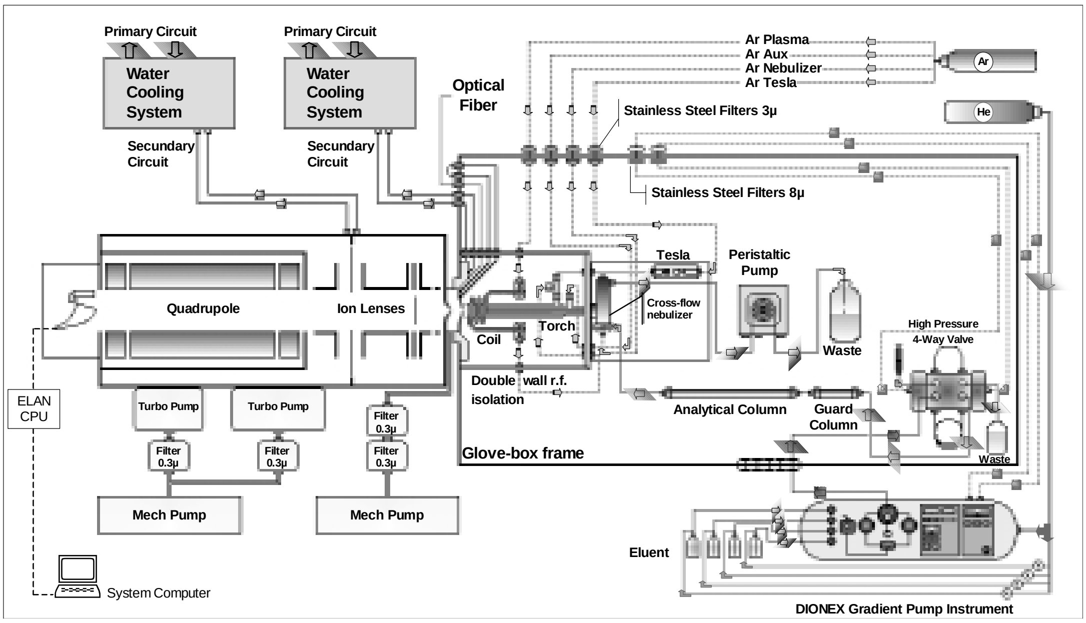


Figure 7. *A schematic diagram of the glove-box ICP-MS [I].*

Vaporisation, atomisation and ionisation of the dissolved solid part of the sample take place in the plasma at 7000 K. A fraction of the ionic species produced is introduced, through an interface, in the spectrometer where the ion beam is collimated. The collimator has a central disc, which reduces the amount of emerging photons from the plasma, which upon reaching the detection system, produce a large noise. The ions are analysed by a quadrupole mass spectrometer and detected with an electromultiplier. The glove-box ICP-MS system is shown in Figure 8.

The separation of the actinides was performed in order to eliminate isobaric interference at masses 238 (U-Pu) and 241 (Pu, Am) by IC. The separation was carried out by using 1 M HNO_3 eluent and a Dionex column (CS10) [Betti, 1997]. The samples were treated with solid Ag(II) oxide in order to oxidise all plutonium valencies to Pu(VI). Chromatographic elution was performed at an eluent flow-rate of 1 ml/min. An external calibration was made by using multiple standards of ^{232}Th, ^{238}U, ^{239}Pu, ^{243}Am and ^{248}Cm in the range of 0.5-60 ng/ml.

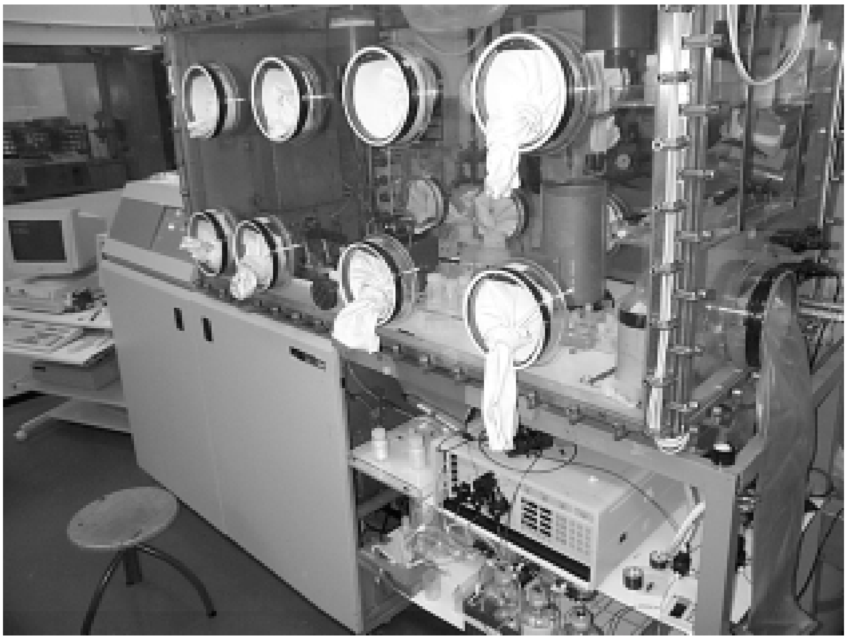


Figure 8. *A glove box ICP-MS system installed in the hot laboratory. The HPLC pump can be seen under the glove-box.*

5. RESULTS AND DISCUSSION

5.1 Plutonium

5.1.1 Sample dissolution

Two different methods were used for the treatment of environmental samples for the determination of plutonium [III, IV]. The leaching method was chosen for the bio-available form of the plutonium, which can be of harm to living organisms and the microwave digestion to obtain total dissolution of the sample. The advantages of using microwave digestion compared to leaching are a shorter digestion time and use of lesser amounts of acids per sample. The main limitation on microwave digestion is that only a small sample size can be treated (up to 2 g). Both methods proved to be suitable for the recovery of technogenic Pu from environmental samples as can be seen in analysis of certified reference material [III].

5.1.2 Determination of plutonium by α-spectrometry

Both electrodeposition and co-precipitation were used for the preparation of α-sources. Considerations on the resolution obtained by using the different source preparation methods can be drawn from α-spectra of plutonium obtained for the IAEA-135 sediment sample, shown in Figure 9. The sample was divided into two equal parts after anion exchange. One part was electrodeposited and the other co-precipitated.

The broken line corresponds to co-precipitated sample, the black line to electro-deposited sample. As can be seen, the resolution in the co-precipitated sample (FWHM 58 keV, for ^{242}Pu) was slightly higher than in the electrodeposited (FWHM 54 keV, for ^{242}Pu). The co-precipitation method is simpler, less costly, faster to be performed and less sensitive to trace of impurities when compared to the electrodeposition method. The chemical recoveries in both methods were generally between 90-100 %.

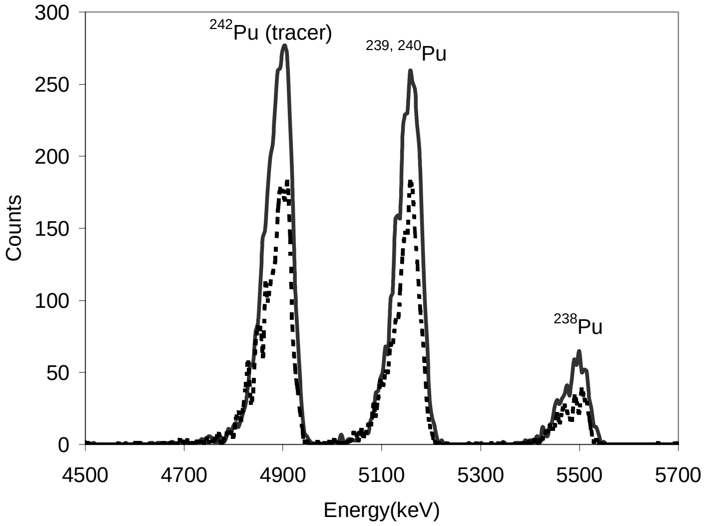


Figure 9. *Plutonium spectra of the IAEA-135 sediment sample measured by α-spectrometry. The black line corresponds to the electrodeposited sample and the broken line to the co-precipitated sample.*

Problems in α-spectrometry are that ^{238}Pu and ^{228}Th have very similar alpha energies (5.50 and 5.42 MeV, respectively). Thorium has a tendency to tail in the ion-exchange separation procedures used for the separation of plutonium in environmental samples and, if the separation is not carefully carried out, the ^{228}Th may be seen as a shoulder on the ^{238}Pu peak. ^{241}Am (E_α 5.49 MeV) and ^{224}Ra (E_α 5.69, 5.45 MeV) also have energies very close to that of ^{238}Pu. Therefore, a chemical separation is needed prior to measurement. A separation method based on the use of a Dowex anion exchanger proved to be effective in the attainment of purified fractions of Pu in environmental samples prior to measurement (α-spectrometry and LSC measurements) [III, IV].

The minor isotope ^{236}Pu was determined by α-spectrometry in the spent nuclear fuel solutions [II]. The presence of ^{243}Cm with (E_α 5.79 MeV) and ^{244}Cm (E_α 5.81 MeV) interfered with the determination of ^{236}Pu (E_α 5.77 MeV), therefore an additional purification was needed. A separation/purification based on the use of TOPO, and Dowex anion exchange were effective for attaining purified fractions of Pu before α-spectrometry measurements. The anion exchange method was faster to be performed than the TOPO method, and it was found out that the efficiency of TOPO adsorbed on silica gel for the separation Pu strongly depends on the stability of the adsorbed chromatographic phase. In the case that the chromatographic phase was not too stable, after the initial separation on TOPO, a subsequent purification of Pu fractions was necessary.

The ratio of α-activities of ^{238}Pu to ^{236}Pu was about 10^4. To obtain adequate counting statistics for the ^{236}Pu peak counting time of several days were needed even though the sources were relatively active.

Also for the samples from aqueous leachate solutions the α-spectrum showed substantial tailing due to the high activity from decay of ^{238}Pu. The ^{238}Pu-tail stretched down to the energy region of ^{242}Pu (E_α 4.90 MeV). The spectrum was investigated to find the ^{242}Pu-peak but the low activity of ^{242}Pu in the sample, in combination with the small amount of sample (0.01 g) and the long half-live ($t_{1/2}$ $3.869\cdot10^5$ years) made it impossible to observe ^{242}Pu. In increase in the amount of sample made the tailing worse. All the other Pu isotopes were successfully determined.

5.1.3 Determination of ^{241}Pu by liquid scintillation counting

The β-emitter ^{241}Pu was analysed in all type of samples by LSC (I-IV). Liquid scintillation counting (LSC) with α/β -discrimination has many advantages when measuring low-energy beta particles or alpha particles compared to most other detectors. LSC has a high counting efficiency: which for ^{241}Pu is ~40% and for α-emitters is ~100%. Another important advantage is the homogeneous distribution of the sample in the scintillation cocktail, which prevents self-absorption.

Comparison of the results of the LSC and mass spectrometry analysis of fuel samples showed a good agreement for ^{241}Pu [I, II].

5.1.4 Chemical recoveries

When new separation methods are developed it is important to obtain a high chemical recoveries and pure chemical fractions. The pure fractions are most important achievement especially in a case of active samples. A summary of the chemical recoveries obtained with both anion exchange [I-V] and the extraction chromatographic method with TOPO [II] is presented in Figure 10. The chemical recoveries for the soil, grass and sheep feaces samples were lower than those of the sea water, aqueous leachate and spent fuel samples. This is a consequence of the matrix effects. The determination of trace radioisotopes in environmental samples (like soil, sediment, vegetation) requires leaching or dissolution of a large amount of sample, which introduces high concentrations of other elements into the system. Therefore the chemical recoveries may vary considerably, because of the matrix effects provoked by the interfering ions of the major elements [Kim et al., 2000; Toribio et al., 2001]. In the spent fuel samples the chemical recoveries, by extraction chromatography method (TOPO) and anion exchange, were in the same range of 80-90 % [II]. The chemical recovery for the sample from aqueous leachate solution from uranium oxide using anion exchange was 80% [I].

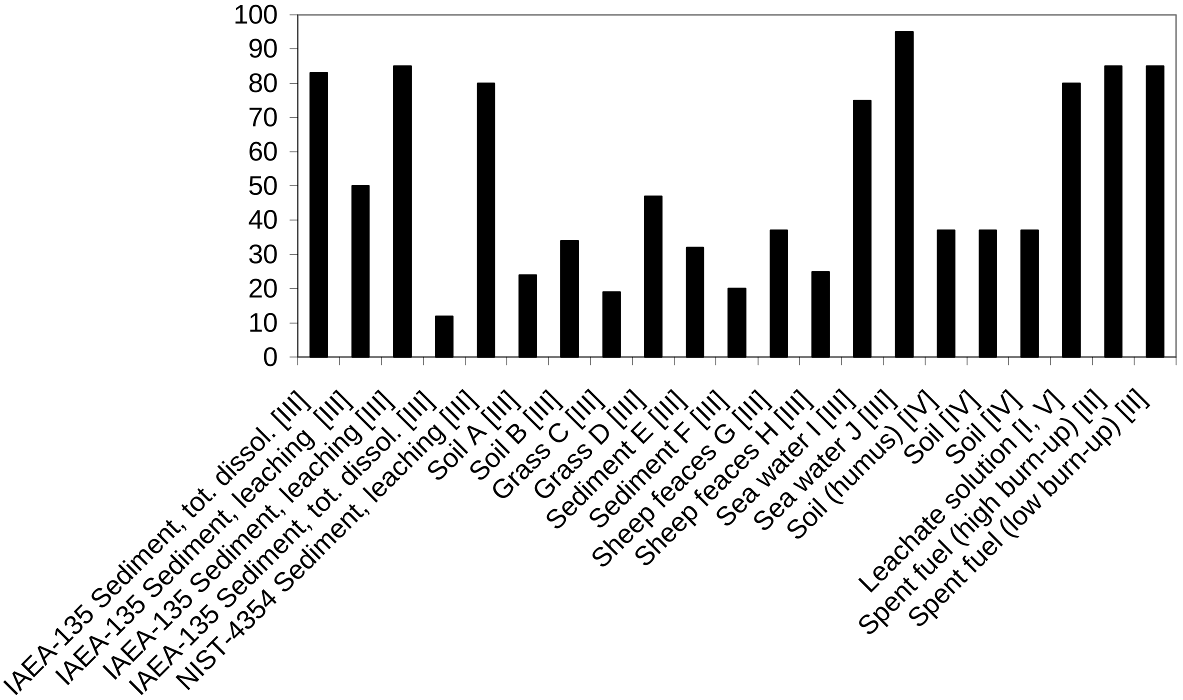


Figure 10. *Chemical recoveries (%) of the analysed plutonium samples.*

5.1.5 Comparison of the methods

The results obtained for Pu isotopes in the environmental reference material were all in good agreement with those expected, independently of the sample preparation methods [III]. Also the results of the Pu isotopes in spent fuel and aqueous leachate samples analysed by α-spectrometry (LSC for ^{241}Pu) and mass spectrometry were compared, and showed a good agreement [I, II].

The detection limits for the Pu isotopes obtained by the different analytical techniques are reported in Table 3. It is evident that α-spectrometry is most appropriate for the analysis of Pu isotopes, because of the low detection limits (0.1-0.2 mBq). The detection limit for ^{238}Pu by γ-spectrometry was as high as 46 Bq, because the γ-ray branching ratio for ^{238}Pu is in the order of 10^{-4}-10^{-5}. The detection limit obtained by ICP-MS was determined by measuring the blank repeatedly. Assuming that the detection limit is three times the standard deviation of the measured signal of the blank, it was possible to calculate the detection limit that in these experimental conditions typically was typically $3.0\cdot10^{-2}$ ng/ml for the actinides. The detection limits achieved with IC-ICP-MS are higher than those attained when the sample is directly injected into the ICP-MS. This discrepancy may be explained by the inherent inability of the pneumatic nebulizer used in the ICP system to reach equilibrium with the rapidly changing concentration of the analyte, which is eluted from the ion chromatograph in a very small volume, since such nebulizers typically have large internal volumes [Garcia Alonso et al., 1995]. It should be noted that the mass spectrometry detector of the ICP-MS used in this work was quadrupole, with the recently developed high resolution magnetic sector ICP-MS, improvement in the detection limit can be attained [Becker and Dietze, 2000].

Table 3. *Half-lives, specific activities and the detection limits (DL) of the plutonium isotopes analysed by α- and γ-spectrometry, LSC and IC-ICP-MS. The detection limits for IC-ICP-MS are based on 1 ml solution injected.*

Nuclide	$t_{1/2}$ (years)	Specific activity (Bq/g)	Method	DL (Bq)	Counting time (h)
^{236}Pu	2.90	$1.93\cdot10^{13}$	IC-ICP-MS	599	-
			α-spectrometry	0.0001	83.3
^{238}Pu	87.7	$6.34\cdot10^{11}$	IC-ICP-MS	19	-
			α-spectrometry	0.0002	50
			LSC	0.001	1
			γ-spectrometry	46Bq	14
^{239}Pu	$2.41\cdot10^{4}$	$2.29\cdot10^{9}$	IC-ICP-MS	0.07	-
^{240}Pu	$6.57\cdot10^{3}$	$8.40\cdot10^{9}$	IC-ICP-MS	0.26	-
			α-spectrometry	0.0002*	50
^{241}Pu	14.41	$3.81\cdot10^{12}$	IC-ICP-MS	118	-
			LSC	0.008	1
^{242}Pu	$3.74\cdot10^{5}$	$1.46\cdot10^{8}$	IC-ICP-MS	0.0045	-
			α-spectrometry	0.0002	50

*^{239}Pu and ^{240}Pu

The determination of the ^{239}Pu/^{240}Pu ratio was not possible by α-spectrometry, because of the overlapping of the ^{239}Pu and ^{240}Pu peaks in the spectrum. Instead the determination of ^{239}Pu and ^{240}Pu could be made by IC-ICP-MS with high accuracy [I].

The isobaric interference of ^{241}Pu and ^{241}Am was resolved by ion chromatography on-line before the ICP-MS [I]. However, the detection limit for ^{241}Pu is much lower in LSC than IC-ICP-MS. The ^{241}Pu LSC spectrum is characteristic and can only be influenced by the presence of low β-energy emitters such as ^{3}H. Furthermore, the LSC analysis of ^{241}Pu is accurate, fast and easy.

The determination of ^{236}Pu in spent nuclear fuel was only possible by α-spectrometry because of its high specific activity [II].

5.1.6 Use of isotopic ratios

Isotopic activity ratios can be used for the identification of the source term of the observed contamination. The ^{238}Pu/$^{239, 240}$Pu ratios are 0.25, 0.026, 0.47 and 0.014 in the releases from nuclear reprocessing facilities, atmospheric weapon tests, the Chernobyl accident and in weapon-grade plutonium, respectively [Holm et al. 1992]. The ratio of ^{241}Pu/$^{239, 240}$Pu in the global fallout due to the atmospheric nuclear weapon tests was about 15 in the beginning of the 1960's [Hakanen et al., 1984; Taylor et al., 2000]. In the Chernobyl fallout the ratio of ^{241}Pu/$^{239, 240}$Pu, in 1996, was 50 [Paatero and Jaakkola, 1994].

The determined and some literature ^{238}Pu/^{239,240}Pu and ^{241}Pu/^{239,240}Pu activity ratios in environmental samples from different origins are compared in Table 4. The ratio of ^{238}Pu/$^{239, 240}$Pu ranged between 0.15-0.67 and the ratios of ^{241}Pu/$^{239, 240}$Pu between 1-8 in the samples collected near to a nuclear facility and analysed in this work. These ratios indicate that Pu mainly originates from sources like nuclear industries rather than atmospheric nuclear tests and Chernobyl accident [III].

The ^{238}Pu/^{239,240}Pu activity ratio was 0.28 and that of ^{241}Pu/^{239,240}Pu 71 in the soil sample collected near Chernobyl (in 1996). Therefore, from the ratios determined for plutonium in the soil samples it can be concluded that Pu mainly originates from Chernobyl nuclear power plant accident [IV].

Table 4. *The ^{238}Pu/^{239,240}Pu and ^{241}Pu/^{239,240}Pu activity ratios in environmental samples from different origins.*

DESCRIPTION OF SAMPLE SITE	SAMPLE	^{238}Pu/^{239,240}Pu	^{241}Pu/^{239,240}Pu	Ref.
Very close of nuclear facility (1996)	Soil	0.15±0.02	2.1±0.1	[III]
Very close of nuclear facility (1996)	Grass	0.43±0.08	7.9±0.7	[III]
Very close of nuclear facility (1996)	Sheep feaces	0.66±0.12	2.8±0.4	[III]
Close in of nuclear facility (1996)	Sediment	0.33±0.03	2.6±0.3	[III]
Background of nuclear facility (1996)	Soil	0.23±0.05	1.0±0.1	[III]
Background of nuclear facility (1996)	Sediment	0.16±0.05	5.7±0.6	[III]
Sellafield (1996)	IAEA-135 sediment	0.19±0.02	9.9±0.8	[III]
Rocky Flats, Colorado	NIST-4354 sediment	0.054±0.016	n.a.*	[III]
Russia , 140 km from Chernobyl (1996)	Soil	0.28±0.15	71± 16	[IV]
Irish Sea (1989)	Sea water	0.21-0.22	18.4-21.3	[Mitchell et al., 1995]
Northern England (1979)	Sheep feaces	0.10-0.16	n.a.*	[Eakins et al., 1984]
Austria (28.4-9.5.1986)	Surface air	0.33-0.76	31.6-74.6	[Irlweck and Wicke, 1998]
Finland (1960-1971)	Lichen	0.02-0.09	7.2-16.4	[Hakanen et al., 1984]
Palomares (1966)	Soil	0.023±0.003	5.7±1.5, 8.4±0.8	[Irlweck and Hrnecek, 1999]

*n.a. = not analysed

5.1.7 Speciation of Pu in aqueous leachate solutions from ^{238}Pu doped uranium dioxide

Understanding the behaviour of plutonium released in geologic formations associated with nuclear waste repositories requires knowledge of prevailing oxidation state(s) as each has a different chemistry [Kobashi and Choppin, 1988]. Two samples from the aqueous leachate solutions from ^{238}Pu doped uranium dioxide were subject to speciation by the co-precipitation method [3.5]. The results (Table 5) indicate that a small amount (<5%) of colloids is present, and that Pu is predominantly in the oxidation states (V) and (VI). LSC with α/β -discrimination was found to be a fast and accurate technique for the measurements of the leachate samples because ^{238}Pu is responsible for the most of the activity.

Table 5. *Speciation of plutonium in the aqueous leachate solutions from ^{238}Pu doped UO_2.*

	Sample 1	Sample 2
Colloids, real (%)	1.6	1.6
Pu(III,IV) (%)	20.6	27.7
Pu(V,VI) (%)	77.6	69.3
Recovery (%):	99.8	98.6

5.2 Uranium

Determination of anthropogenic uranium in environmental samples is demanding due to the high background concentration of natural uranium. The amount of deposited uranium can be less than that occurring naturally in the soils.

Uranium was also determined in reference materials IAEA-135 (sediment) and NIST-4353 (soil) and these results are presented in Table 6. The α-sources were prepared by electrodeposition. It was found that the microwave assisted total dissolution was necessary to obtain a good accuracy and recovery in the analysis of the certified environmental reference samples. Leaching only dissolves the bio-available form of the

U (see Table 6). In the case of soil and sediment samples, the chemical recoveries for uranium were low <40%. This may be explained by the possible interference of the Al cation in electrodeposition [Rodŕiguez et al., 2001]. A similar effect has also been described when ions such as Ca^{2+}, Fe^{3+}, Bi^{3+} and La^{3+}, are present, even at low concentrations, in the electrolytic solution [Zarki et al., 2001]. Instead of electrodeposition co-precipitation could be used because it is less sensitive to trace of impurities [III].

Table 6. *Uranium activities (Bq/kg dry wt.) in reference materials. The total errors are given for 1σ uncertainty.*

Reference sample	^{234}U (Bq/kg)	^{238}U (Bq/kg)	^{234}U (Bq/kg) Recommended value	^{238}U (Bq/kg) Recommended value
NIST-4353 Soil leaching	15.6±1.8	16.0±1.9	39.1±1.4 (value for total dissolved sample)	38.9±2 (value for total dissolved sample)
NIST-4353 Soil total dissolution	37.0±3.2	36.4±3.3	39.1±1.4	38.9±2
NIST-4353 Soil total dissolution	35.7±2.6	36.4±2.6	39.1±1.4	38.9±2
NIST-4353 Soil total dissolution	31.4±4.4	38.4±4.9	39.1±1.4	38.9±2
IAEA-135 Sediment leaching	9.6±1.5	8.6±1.3	14 (11.7-18.5)*	13 (11.3-18.1)*

* Information value only

Three different separation methods were used to separate uranium in spent nuclear fuel samples and in samples from aqueous leachate solutions from uranium oxide: anion exchange [I, V] and extraction chromatography with TOPO and UTEVA [II].

After the initial separation of U with TOPO extraction chromatography, a subsequent purification of the U-fraction was necessary because of the large amount of Pu-activity ($^{238,\,239,\,240}$Pu) in the fuel samples. In fact, the dominating Pu-activity caused a tail in the α-spectrum, which made it impossible to evaluate the ^{232}U and ^{234}U-activities without further purification. Additionally, the repeated separations avoided the spectral interference between ^{243}Am (E_α 5.28 MeV) and ^{232}U (E_α 5.32 MeV). The presence of Pu (as ^{241}Pu) in the U-fraction was controlled with LSC, and the purification steps were repeated until the ^{241}Pu amount was below the detection limit of the LSC measurement.

Tailing caused also problems in the samples of aqueous leachate solutions from uranium oxide. In order to determine ^{234}U by α-spectrometry a chemical separation of U and Pu was necessary because of a substantial tailing of the ^{238}Pu-peak (E_α 5.50 MeV) into the ^{234}U-peak region (E_α 4.78 MeV) and the relatively low activity of ^{234}U compared to ^{238}Pu in the sample. Even after the separation of ^{238}Pu, the determination of ^{234}U by α-spectrometry still had a significant uncertainty because of the low number of counts. It was not possible to determine ^{238}U by the radiometric methods due to the low specific activity. The separation factor of Pu in the uranium fraction was calculated to be $4 \cdot 10^4$.

5.2.1 Comparison of the methods

The mean values of the chemical recoveries, after separation and electrodeposition, are presented in Figure 11. Anion exchange was the first separation method used but the recovery was found to be low. Therefore separation methods based on UTEVA or TOPO extraction chromatography were chosen for other samples.

The results of the uranium isotopes analysed by α-spectrometry and mass spectrometry showed a good agreement independently of the sample preparation methods [I, II].

The detection limits obtained by the different analytical techniques for the U isotopes are reported in Table 7. Comparison of the values confirmed that ICP-MS is a powerful method for the detection of long-lived radionuclides. The radiometric methods have a lower detection limit than IC-ICP-MS in the case of the short-lived radioisotopes. On the other hand, the required sample preparation and the duration of the analysis are more time-consuming than in ICP-MS.

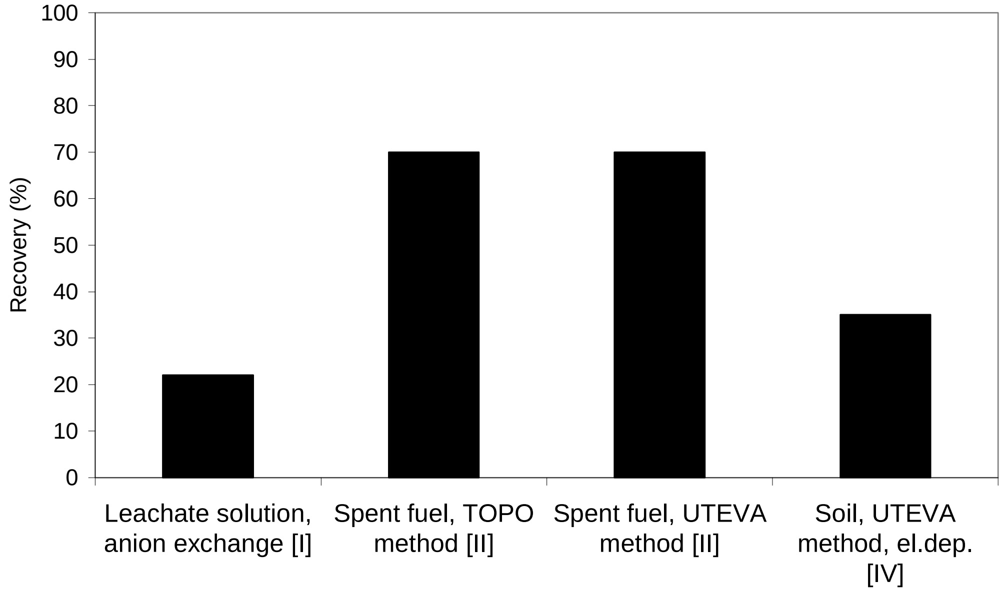


Figure 11. *The mean values of the chemical recoveries in the analysed uranium samples.*

Table 7. *Half-lives, the specific activities and the detection limits (DL) of the uranium isotopes analysed by α- and γ-spectrometry, LSC and IC-ICP-MS. The detection limits for IC-ICP-MS are based on 1 ml solution injected.*

Radionuclide	$t_{1/2}$ (years)	Specific activity (Bq/g)	Analysis method	DL (Bq)	Counting time (h)
^{232}U	69.85	$8.17 \cdot 10^{11}$	IC-ICPMS α-spectrometry	24.5 0.0001	- 83.3
^{234}U	$2.45 \cdot 10^{5}$	$2.30 \cdot 10^{8}$	IC-ICPMS α-spectrometry	0.007 0.0001	- 83.3
^{235}U	$7.04 \cdot 10^{8}$	$8.00 \cdot 10^{4}$	IC-ICPMS α-spectrometry	$2.3 \cdot 10^{-6}$ 0.0001	- 83.3
^{236}U	$2.34 \cdot 10^{7}$	$2.39 \cdot 10^{6}$	IC-ICPMS α-spectrometry	$7.2 \cdot 10^{-5}$ 0.0001	- 83.3
^{238}U	$4.47 \cdot 10^{9}$	$1.24 \cdot 10^{4}$	IC-ICPMS α-spectrometry	$3.7 \cdot 10^{-7}$ 0.0001	- 83.3

5.3 α-track analysis

The physical location of radioactive contaminants in soils is an important factor in understanding the contaminant migration mechanisms. The common assumption that radionuclides are homogeneously distributed either uniformly or with some exponential depth profile under the ground surface, is generally taken. Moreover, the analysis of homogenised samples is generally performed. However, soil consists of different size clay, sand, rock, etc., particles bonded together by organic and inorganic materials. The soil pores provide networks for vertical and horizontal transport of water, gases, dissolved nutrients etc. In order to determine the physical location of contaminants in soil thin sections of soil, which preserve the undisturbed characteristics of the original soil, need to be examined.

Solid state nuclear track detectors have been exploited in several applications, like for instance, measurements of radon, heavy ions, fission fragments, cosmic rays, underground contaminated sites, hot spots and for investigation of transuranic material accumulation [Espinosa and Silva, 2001; Oufni and Misdaq, 2001].

In this work autoradiography methods were used in order to identify “hot particles” in sections of a depth soil profile from a contaminated area around Chernobyl (IV). The distribution of Pu isotopes was investigated in layers of humus and soil along a depth profile down to 4 cm by bulk analysis and the total activity was correlated to the total activity obtained from hot particles detected. The particles were categorised according to the number of tracks developed. In Figure 12 the image of one of the hottest particles detected is shown. Here, it can be seen that the particles broke up into several fragments probably during the fixation process of the soil to the films. Assuming a detection probability of alpha particles in the detector of 100% and a geometric detection efficiency of 40%, the alpha activity in this particles, developing about 600 tracks, was calculated to be 0.48 mBq.

From a comparison of alpha autoradiography results with the total alpha activity from the bulk analysis it could be concluded that about 90% of the alpha activity is present in the particulate forms.

In order to distinguish which alpha emitter had provoked this damage in the detector, a further characterisation of the particles by SIMS (Secondary Ion Mass Spectrometry) would be necessary. Moreover, further analysis of the isotopic composition of the radionuclides in the particles could give information on its source term. These investigations were out of the scope of this work.

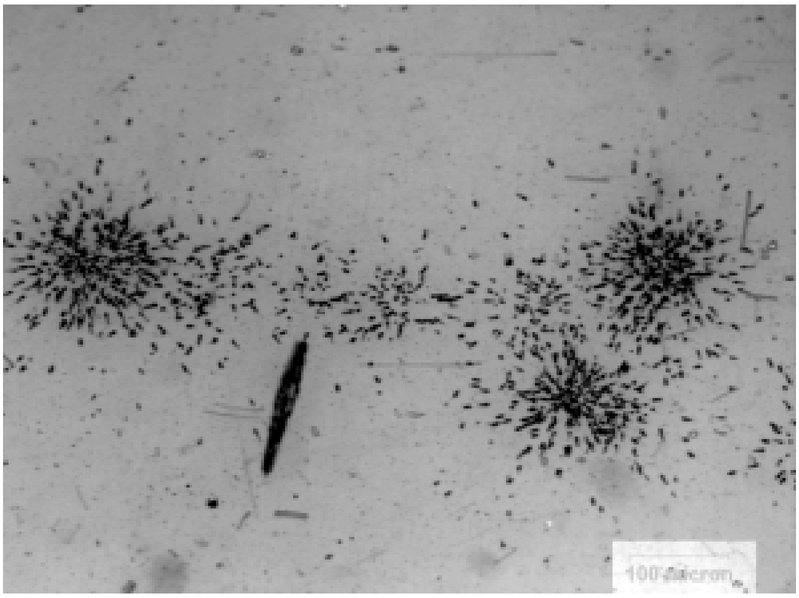


Figure 12. *α-tracks of a hot spot from the analysis of the humus layer.*

6. CONCLUSIONS

Leaching is an adequate sample pre-treatment for determination of the bio-available form of plutonium in environmental samples. On the other hand, determination of uranium in environmental sample requires the total dissolution method of which microwave digestion of the sample under pressure is effective and safe. The drawback is that only a small sample size can be dissolved and the overall chemical recovery may be low due to matrix effects.

Uranium and plutonium were separated in samples of high and low activity by different chromatography techniques. Separations based on the use of TOPO, Dowex anion exchanger and UTEVA resins were demonstrated to be effective for attaining purified fractions of U and Pu before measurements by α-spectrometry or LSC. The analytical results were in good agreement with certified values, and those obtained from mass spectrometry analysis. The developed methods could therefore be used with confidence. The minor isotopes ^{232}U and ^{236}Pu were also successfully analysed in spent fuels despite the large separation factors needed. By radiometric techniques it was possible to measure samples containing very low activity. The detection limits were in the range of mBq.

Choice of the analytical method for the determination of actinides has to be made considering several parameters: the detection limit of each isotope, the sample preparation procedure in terms of duration and complexity, counting time and interferences. The comparison of radiometric and ICP-MS techniques confirmed that IC-ICP-MS is a powerful method for the detection of long-lived radionuclides. In the case of short-lived radioisotopes the radiometric methods had a detection limit several orders of magnitude lower than IC-ICP-MS. In fact, the determination of ^{236}Pu and ^{232}U in spent fuel was only possible by α-spectrometry because of these nuclides short half-lives.

From the radioactivity ratios of ^{241}Pu to $^{239, 240}$Pu and ^{238}Pu to $^{239, 240}$Pu, it is possible to estimate the source of release of plutonium found in environmental samples as indicated for atmospheric weapons test, Chernobyl fallout and nuclear industry in the present studies.

Nuclear track methods, particularly α-tracks can be exploited to locate hot particles in soil samples. From a comparison of the results of the α-track analysis with the total alpha activity determined by bulk analysis, in a soil profile from a contaminated area around Chernobyl, it could be concluded that about 90% of the alpha activity was present in particulate form.

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8. REFERENCES

Apostolidis, C., Molinet, R., Richir, P., Ougier, M., Mayer, K., 1998. Development and validation of a simple, rapid and robust method for the chemical separation of uranium and plutonium, *Radiochim. Acta*, **83***,* 21-25.

Barrero Moreno J. M., Garcia Alonso J. I., Arbore P., Nicolaou G., Koch L., 1996. Characterization of spent nuclear fuels by Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry, *J. Anal. Atom. Spectrom.*, **11**, 929-935.

Becker J. S., Dietze H-J., 1998. Inorganic trace analysis by mass spectrometry, *Spectrochim. Acta B*, 1475-1506.

Bertaux M., Hanssens A., Madic C., 1999. Alpha spectrometric determination of trace level of $^{239\text{-}240}$Pu and ^{238}Pu in uranium compounds and solutions, *Radiochim. Acta,* **84**, 11-19.

Betti M., 2002. Civil use of depleted uranium, *J. Env. Radioactivity*, in press.

Betti M., 2000. Environmental monitoring of radioisotopes by mass spectrometry and radiochemical methods in urban areas, *Microchem J.*, **67**, 363-373.

Betti M., 1997. Use of ion chromatography for the determination of fission products and actinides in nuclear applications, *J. Chromatogr A.*, **789**, 369-379.

Boulyga, S. F., Erdmann, N., Funk, H., Kievets, M. K., Lomonosova, E. M., Mansel, A., Trautmann, N., Yaroshevich, O. I., Zhuk, I. V., 1997. Determination of isotopic composition of plutonium in hot particles of the Chernobyl area. *Radiation Measurements,* **28**, 349-352.

Choppin G., Rydberg J., Liljenzin J. O., 2002. *Radiochemistry and Nuclear Chemistry*, Butterworth-Heinemann Ltd, Oxford.

Choppin G. R., 1999. Utility of oxidation state analogs in the study of plutonium behaviour, *Radiochim. Acta*, **85**, 89-95.

Choppin G. R., Wong P., 1998. The chemistry of actinide behaviour in marine systems, *Aquat. Geochem.*, **4**, 77-101.

Chu N. Y., 1971. Plutonium determination in soil by leaching and ion-exchange separation, *Anal. Chem.*, **43**, 449-452.

Croudace I., Warwick P., Taylor R., Dee S., 1998. Rapid procedure for plutonium and uranium determination in soils using a borate fusion followed by ion-exchange and extraction chromatography, *Anal. Chim. Acta*, **371**, 217-225.

Currie, L. A., 1968. Limits for qualitative detection and quantitative determination. *Anal. Chem.*, **40**, 586-593.

Delle Site A., Marchionni V., Testa C., 1980. Radiochemical determination of plutonium in marine samples by extraction chromatography, *Anal. Chim. Acta*, **117**, 217-224.

Dietz M. L., Horwitz E. P., Sajdak L. R., Chiarizia R., 2001. An improved extraction chromatographic resin for the separation of uranium from acidic nitrate media, *Talanta*, **54**, 1173-1184.

Donohue D., 2002. Strengthened nuclear safeguards, *Anal. Chem.*, **74**(1), 28A-35A.

Donohue D., Ziesler R., 1993. Analytical chemistry in the aftermath of the Gulf War. *Anal. Chem.*, **65**(7), 359A-360A, 364A-368A.

Eakins J. D., Lally A. E., Cambray D., Kilworth D., Morrison R. T., Pratley F., 1984. Plutonium in sheep faeses as an indicator of deposition on vegetation, *J. Environ. Radioactivity*, **1**, 87-105.

Eisenbud M., 1997. *Environmental Radioactivity, From Natural, Industrial and Military Sources*, edition 3, Academic Press, Inc., New York.

Espinosa G., Silva R. J., 2001. Mapping of transuranic elements in soil by nuclear track methodology, *J. Radioanal. Nucl. Chem.*, **248**(3), 579-582.

Garcia Alonso J. I., Sena F., Arboré Ph., Betti M., Koch L., 1995. Determination of fission products and actinides in spent nuclear fuels by isotope dilution ion chromatography inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* **10**, 381-393.

Goldstein S. J., Rodriquez J. M., Lujan N., 1997. Measurement and application of uranium isotopes for human and environmental monitoring, *Health Phys.* **72**(1), 10-18.

Hakanen M., Jaakkola, T., Korpela H., 1984. Simultaneous determination of ^{241}Pu, ^{238}Pu and ^{239,240}Pu in low activity environmental samples. *Nucl. Instrum. Meth. Phys. Res. A*, **223**, 382-385.

Hampson B. L., Tennant D., 1973. Simultaneous determination of actinide nuclides in environmental materials by solvent extraction and alpha spectrometry, *Analyst*, **98**, 873-885.

Handley T. H., Cooper J. H., 1969. Quantitative electrodeposition of actinides from dimethylsulfoxide, *Anal. Chem.*, **41**(2), 381-383.

Hashimoto T., 1971. Electrodeposition of americium and observation of the surface by means of alpha particle on a cellulose nitrate film, *J. Radioanal. Chem.* **9**, 251-258.

Hindman F. D., 1983. Neodymium fluoride mounting for α spectrometric determination of uranium, plutonium and americium, *Anal. Chem.*, **55**, 2460-2461.

Holm E., Rioseco J., Pettersson H., 1992. Fallout of transuranium elements following the Chernobyl accident, *J. Radioanal. Nucl. Chem.* **156**, 183-200.

Horwitz, E., Dietz, M., Chiarizia, R., Diamond, H., 1992. Separation and preconcentration of uranium from acidic media by extraction chromatography, *Anal. Chim. Acta*, **266**, 25-37.

Hrnecek E., Aldave de las Heras L., Betti M., 2002. Application of microprecipitation on membrane filters for alpha spectrometry, liquid scintillation counting and mass spectrometric determination of plutonium isotopes, *Radiochim. Acta*, in press.

Irlweck K., Hrnecek E., 1999. ^{241}Am concentration and ^{241}Pu/$^{239(240)}$Pu ratios in soils contaminated by weapons-grade plutonium, *J. Radioanal. Nucl. Chem.*, **242**(3), 595-599.

Irlweck K., Wicke J., 1998. Isotopic composition of plutonium immission in Austria after the Chernobyl accident, *J. Radioanal. Nucl. Chem.*, **227** (1-2), 133-136.

Irlweck K., 1996. Effects of Fe(III) ions on the electrodeposition of trace amounts of plutonium and americium, *J. Radioanal. Nucl. Chem. Let.*, **214**(5), 429-437.

Iwasaki T., Fujiwara D., Hirakawa N., 1998. Time-integrated radiotoxicity index for study of transmutation of long-lived radionuclides. *Progress in Nuclear Energy*, **32**/3-4, 449.

Joshi S. R., 1985. Lanthanium fluoride coprecipitation technique for the preparation of actinides for alpha particle spectrometry, *J. Radioanal. Nucl. Chem.*, **90**, 409-414.

Kaihola L., 2000. Radionuclide identification in liquid scintillation alpha-spectroscopy, *J. Radioanal. Nucl. Chem.*, **243**(2), 313-317.

Katz J.J., Seaborg G.T., Morss L. R. 1986. *The Chemistry of the Actinide Elements*, Vol **1** and **2**, Second edition, Chapman & Hall, New York.

Kim G., Burnett W. C., Horwitz E. P., 2000. Efficient preconcentration and separation of actinide elements from large soil and sediment samples. *Anal. Chem.*, **72**, 4882-4887.

Kim J. I., Kanellakopulos B., 1989. Solubility products of plutonium(IV)oxide and hydroxide, *Radiochim. Acta*, **48**, 145-150.

Kobashi A., Choppin G. R., 1988. A study of techniques for separating plutonium in different oxidation states, *Radiochim. Acta*, **43**, 211-215.

Kressin I. K., 1977. Electrodeposition of plutonium and americium for high resolution a-spectrometry, *Anal. Chem.*, **49**, 842-845.

Lally A. E., Glover K. M., 1984, Source preparation in alpha spectrometry, *Nucl. Instrum. Meth. Phys. Res.,* **223**, 259-265.

Lee M. H., Lee C. W., 2000. Preparation of alpha emitting nuclides by electrodeposition, *Nucl. Instrum. Meth. Phys. Res. A.*, **447**, 593-600.

Lee M. H., Pimpl M., 1999. Development of a new electrodeposition method for Pu-determination in environmental samples, *Appl. Radiat. Isot.*, **50**, 851-857.

Levine H., Lamanna A., 1965. Radiochemical determination of plutonium-239 in low-level environmental samples by electrodeposition, *Health Phys.*, **11**, 117-125.

Lieberman R., Moghissi A. A., 1968. Coprecipitation technique for alpha spectroscopic determination of uranium, thorium and plutonium, *Health Phys.*, **15**, 359-362.

Lovett M.B., Nelson D.M., 1981. Determination of some oxidation states of plutonium in sea water and associated particulate matter. *Proc. Technical Committee Meeting of IAEA and CEC*, IAEA, Vienna, 27-35.

Lozano J. C., Fernandez F., Gomez J. M. G., 1997. Preparation of alpha-spectrometric sources by coprecipitation with $Fe(OH)_3$: Application to actinides, *Appl. Radiat. Isot.*, **48**(3), 383-389.

McCarthy W., Nicholls T. M., 1990. Mass spectrometric analysis of plutonium in soils near Sellafield, *J. Environ. Radioact.*, **12**, 1-12.

McLendon H. R., 1975. Soil monitoring for plutonium at the Savannah river plant, *Health Phys.*, **28**, 347-354.

Miglio J., 1986. Simultaneous determination of americium and plutonium by liquid scintillation counting using a two-phase cocktail, *Anal. Chem.*, **58**, 3215-3218.

Mitchell P. I, Batlle J. V, Downes A. B., Condren O. M., León Vintró L., Sánchez-Cabeza J. A., 1995. Recent observations on the physico-chemical speciation of plutonium in the Irish Sea and western Mediterranean, *Appl. Radiat. Isot.*, **46**(11), 1175-1190.

Mitchell R. F., 1960. Electrodeposition of actinide elements at tracer concentrations, *Anal Chem.*, **32**, 326-328.

Moberg L., Persson B. Å., 1996. Tio år efter kärnkraftolyckan i Tjernobyl, Radiologiska konsekvenser och svensk beredskap mot framtida olyckor, Statens strålskyddinstitut, Sweden.

Montero Rubio M. P., Sanchez Martin A., Vazquez Crespo M. T., Murillo Gascon J. L., 2000. Analysis of plutonium in soil samples, *Appl. Radiat. Isot.*, **53**, 259-264.

Moreno J., Vajda N., Danesi P. R., Larosa J. J., Zeiller E., Sinojmeri M., 1997. Combined procedure for the determination of ^{90}Sr, ^{241}Am and Pu radionuclides in soil samples, *J. Radioanal. Nucl. Chem.* **226**(1-2), 279-284.

Myasoedov B. F., Novikov A. P., 2001. Radiochemical procedures for speciation of actinides in the environment. Methodology and data obtained in contaminated regions of Russia by radionuclides, Evaluation of Speciation Technology, Workshop proceedings Tokai-mura, Ibaraki, Japan 26-28 October
1999, 27-39.

Mäkinen P., 1995. Handbook of liquid scintillation counting, B. Sc. Thesis. Turku Institute of Technology.

NAS-NS 3102, National academy of Science, National Research Council, 1961. Separation by solvent extraction with tri-n-octylphosphine oxide, Oak Ridge, Tennessee.

Niese U., Niese S., 1985. Determination of actinide nuclides in water samples from the primary circuit of a research reactor, *J. Radioanal. Nucl. Chem. Articl.*, **91**(1), 17-24.

Osan J., Torök S., Kurunczi S., Betti M., Bocci F., Bildstein O., Falkenberg G., 2001. Study of the oxidation state of depleted uranium particles in soil using micro-XANES, Annual report, Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen-Synchroton (DESY).

Oufni L., Misdaq M. A., 2001. Radon emanation in a limestone cave using CR-39 and LR-115 solid state nuclear track detectors, *J. Radioanal. Nucl. Chem.*, **250**(2), 309-313.

Paatero J., Jaakkola T., 1994. Determination of the Pu-241 deposition in Finland after the Chernobyl accident. *Radiochim. Acta*, **64**, 139-144.

Parus J. L., Raab W., 1996. Determination of plutonium in nuclear materials with the combination of alpha and gamma spectrometry, *Nucl. Instrum. Meth. Phys. Res. A.*, **369**, 588-592.

Peerani, P., Carbol, P., Hrnecek, E., Betti, M., 2002. Assessment of a compton-event suppression gamma spectrometer for the detection of fission products at trace levels, *Nucl. Instrum. Meth. Phys. Res. A.*, **482**, 42-50.

Pentreath R. J., 1995. The analysis of Pu in environmental samples: A brief historical perspective, *Appl. Radiat. Isot.*, **46**(11), 1279-1285.

Perna L., Betti M., Barrero Moreno J. M., Fuoco R., 2001. Investigation on the use of UTEVA as a stationary phase for chromatographic separation of actinides on-line to inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, **16**, 26-31.

Pilviö R., Bickel M., 1998. Separation of actinides from a bone ash matrix with extraction chromatography, *Journal of Alloys and Compounds*, **271-273**, 49-53.

Povetko O. G., Higley K. A., 2001. Application of autoradiographic methods for contaminant distribution studies in soils, *J. Radioanal. Nucl. Chem.*, **248**(3), 561-564.

Puphal K. W., Olsen D. R., 1972. Electrodeposition of alpha-emitting nuclides from a mixed oxalate-chloride electrolyte, *Anal. Chem.*, **44**(2), 284-289.

Ramebäck H., Skalberg M., 1998. Separation of neptunium, plutonium, americium and curium from uranium with di-(2-ethylhexyl)-phosphoric acid (HDEHP) for radiometric and ICP-MS analysis, *J. Radioanal. Nucl. Chem.*, **235**(1-2), 229-233.

Rao R. R., Cooper E. L., 1995. Separation of low levels of actinides by selective oxidation/reduction and co-precipitation with neodymium fluoride, *J. Radioanal. Nucl. Chem.,* **197**(1), 133-148.

Reformatskaya A. I., 1971. The application of layers of Th, U, Np and Pu on instrument parts by the method of electrolytic deposition, *Radiokhimiya,* **13**, 84-87.

Rodŕiguez B. P., Vera Tomé F., Lozano J. C., 2001. Concerning the low uranium and thoroim yields in the electrodeposition process of soil and sediment analyses, *Appl. Radiat. Isot.*, **54**, 29-33.

Salbu B., 2001. Actinides associated with particles, *Plutonium in the Environment*, A Kudo ed, Elsevier, Amsterdam.

Samuelson O., 1952. *Ion Exchanger in Analytical Chemistry*, John Wiley & Sons, Inc., New York.

Sansone U., Danesi P. R., Barbizzi S., Belli M., Camptell M., Gaudino S., Jia G., Ocone R., Pati A., Rosamilia S., Stellato L., 2001. Radioecological survey at selected sites hit by depleted uranium ammunitions during the 1999 Kosovo conflict, *Sci. Total Environm.*, **281**, 23-35.

Schönhofer F., 1995. Liquid scintillation spectrometry in environmental measurements, *Sci. Total Environm.*, **173/174**, 29-40.

Schüttelkopf, H., 1971. Determination of plutonium in environmental surveillance samples, International Atomic Energy Agency, Wien, STI/PUB-289, CONF-710705, 183-197.

Seaborg G. T., 1993. Overview of the actinide and lanthanide (the f) elements, *Radiochim. Acta*, **61**, 115-122.

Semenov B. A., Oi N., 1993. Nuclear fuel cycles: adjusting to new realities. IAEA Bulletin, 3, 2.

Shelley A., Akie H., Takano H., Sekimoto H., 2001. Radiotoxicity hazard of inert matrix fuels after burning minor actinides in light water reactors. *Progress in Nuclear Energy*, **38**/3-4, 434.

Sill C. W., Sill D. S., 1995. Sample dissolution, *Radioact. Radiochem.*, **6**, 8-14.

Sill C. W., Williams R. L., 1981. Preparation of actinides for alpha spectrometry without electrodeposition, *Anal. Chem.*, **53**, 412-415.

Silva R. J., Nitsche H., 1995, Actinide environmental chemistry, *Radiochim. Acta*, **70/71**, 377-396.

Talvitie N. A. 1972. Electrodeposition of actinides for alpha spectrometry determination, *Anal. Chem.*, **44**, 280-283.

Taylor R. N., Warneke T., Milto J. A., Croudace I. W., Warwick, Ph. E., Nesbit, R. W., 2000. Plutonium isotope ratio analysis at femtogram to nanogram levels by multicollector ICP-MS. *J. Anal. At. Spectrom.* **16**, 279-284.

Tomé F. V., Blanco Rodŕiguez M. P., Lozano J. C. 2002. Study of the representativity of uranium and thorium assays in soil and sediment samples by alpha spectrometry, *Appl. Radiat. Isot.* **56**, 393-398.

Toribio, M., García, J. F., Rauret, G., Pilviö, R., Bickel, M., 2001. Plutonium determination in mineral soils and sediments by a procedure involving microwave digestion and extraction chromatography. *Anal. Chim. Acta*, **447**, 179-189.

Uijt de Haag, P. A., Smetsers R. C., Witlox H. W., Krus H. W., Eisenga A. H., 2000. Evaluating the risk from DU after the Boeing 747-568F crash in Amsterdam. *J. Hazard. Mater.*, **76**, 39-58.

UNEP, 2001. Depleted Uranium in Kosovo, post-conflict Environmental Assessment.

UNSCEAR. 2000. United Nations scientific Committee on the Effects of Atomic Radiation. *Sources and Effects of Ionizing Radiation*, Report, Annex C, United Nations, New York.

Valkovic V., 2000. *Radioactivity in the Environment*, Elsevier, Amsterdam.

Warner F., Harrison R. M., 1993. *Radioecology after Chernobyl, Biogeochemical Pathways of Artificial Radionuclides*, SCOPE 50, John Wiley & Sons, New York.
Whicker W. F., Schultz V., 1982. *Radioecology: Nuclear Energy and the Environment*, Vol 1, CRC Press, Inc. Boca Raton, Florida, USA.

WHO, Depleted Uranium, Fact Sheets N° 257, April 2001.

Yamato A., 1982. An anion exchange method for the determination of ^{241}Am and plutonium in environmental and biological samples, *J. Radioanal. Chem.*, **75**, 265-273.

Zarki R., Elyahyaoui A., Chiadli A., 2001. Preparation of α-sources of U(VI) and Th(IV) by the electrodeposition technique in the presence of Ca^{2+} and some trivalent metals, *Appl. Radiat. Isot.*, **55**, 167-174.

Ziegler, H., Mayer, K., 1999. Development of an optimised method for faster and more reliable automated U/Pu/Np separations, *Radiochim. Acta*, **86**, 123-128.