DETERMINATION OF LONG-LIVED RADIONUCLIDES BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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1. Introduction

Long-lived radionuclides are present in the environment in a large extent from both natural and artificial sources. Members of the natural radioactive decay series include ^{232}Th, ^{235}U and ^{238}U, as well as their long-lived daughter nuclides (e.g. ^{226}Ra, ^{230}Th or ^{210}Pb), other primordial radionuclides, such as ^{40}K, ^{144}Nd or ^{187}Re in addition to some long-lived cosmogenic radionuclides, ^{10}Be or ^{14}C for instance, belong to this group. Their concentrations are regularly measured in environmental, biological and food samples for radiation protection purposes due to their radiotoxicity [1,2]. Moreover, their high variability in nature or different physical and chemical properties has been exploited in order to study biogeochemical processes (e.g. migration, oceanographic or sedimentation investigations) [3,4]. The radioactive characteristics of these nuclides and the variation of mother-to-progenies ratio as a function of time are used in dating measurements (e.g. ^{14}C or uranium-lead dating) and for the investigation of time dependant natural processes, such as migration or sedimentation studies [5-7].

Beside the natural radioisotopes, anthropogenic long-lived radionuclides, mainly the artificial transuranics (e.g. ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{241}Am) and the fission products (e.g. ^{99}Tc, ^{129}I and ^{135}Cs) constitute another component of radioactivity present in the environment. These radionuclides have been released into the environment as a consequence of nuclear power plant accidents, authorized discharges from reprocessing plants or atmospheric weapons tests [1,8]. Disposal of high-level wastes from nuclear power plants is also a potential source of actinide and fission product contamination in the future. The most hazardous radiotoxic actinide elements are plutonium and americium, as a consequence of their high formation yield, dose contribution and long half-lives, thus determination of their concentration is of high importance. Moreover, the isotopic composition of plutonium is also of great interest, since the isotope ratios can provide information on the possible origin of contamination or material. The ratios of the plutonium isotopes are characteristic of the source, which is of primary importance in environmental monitoring (to differentiate between nuclear weapon test or power plant accident), nuclear safeguards and nuclear forensic studies.

During the last two decades due to the rapid development of inorganic mass spectrometric instrumentation, inductively coupled plasma mass spectrometry (ICP-MS), especially instruments equipped with double focusing sector field analyzers (ICP-SFMS) have become a complementary and alternative tool to traditional radioanalytical methods (e.g. alpha spectrometry and liquid scintillation) for the analysis of long-lived radionuclides [9-11]. This technique has several favourable characteristics for the long-lived radionuclide determination, such as high sensitivity, good precision, very low detection limits or high sample throughput. Mass spectrometric methods are especially useful for the measurement of long-lived isotopes, whose determination by the use of the widely applied radioanalytical methods are hampered by the low specific activity of the analyte and the long counting time necessary for the analysis. However, in order to carry out reliable ICP-SFMS measurements, proper separation of the ultra-trace level radionuclide of interest is indispensable, and development of suitable sample preparation methods is still the most critical step of the analysis, which fundamentally determines the applicability and capabilities of this technique.

The aim of this work was to develop novel analytical methods for the measurement of long-lived radionuclides in various matrices by inductively coupled plasma sector-field mass spectrometry (ICP-SFMS). Approximately 60 radionuclides can be considered to be long-lived, however, only a relatively few of these radionuclides are significant in nuclear research and applications, radiation protection or for environmental investigations. The dissertation discusses two main fields of application of these long-lived radionuclides. The first topic focuses on the measurement of the most significant transuranics for environmental research and safeguards purposes: the plutonium isotopes and americium-241. Though several radioanalytical and mass spectrometric methods have been developed for such measurements, these methods, especially the sample preparations, are relatively tedious and labor-intensive. The analytical methods proposed significantly shorten analysis time and employ simple sample preparation prior to the measurement. The analytical procedures developed have been applied for assessment of origin and release date of plutonium dispersed in the environment by determination of the plutonium and americium isotopic composition. By the use of models developed, the origin and date of plutonium contamination can be estimated, which is of high importance in environmental monitoring and nuclear safeguards (for the control of the Nuclear Non-Proliferation Treaty). The second topic deals with the application of ICP-SFMS for nuclear forensic studies. Novel methods have been developed for the measurement of minor long-lived constituents (^{230}Th, ^{236}U, ^{239}Pu and ^{240}Pu) in uranium oxide matrix, which is the most important nuclear material. By the measurement of these nuclides, the production date (age) of the sample can be determined and the previous neutron irradiation (reprocessing) of the confiscated, illicit nuclear material can be revealed. As for these forensic investigations the preservation of sample, which serves as an evidence in the course of the legal procedure, is of high importance, quasi non-destructive laser ablation ICP-SFMS methods have been developed for the production date measurement and the detection of previous irradiation. These data obtained give information on the provenance of the nuclear material and help to trace back the possible route of the sample to its source, allowing the authorities to improve protection measures.

2. General Description of Long-lived Radionuclides

2.1. Definition and Occurrence of Long-lived Radionuclides

There is no exact definition of long-lived radionuclides. Those radionuclides (radioactive nuclides) are considered to be long-lived, which have half-lives sufficiently long so that it may pose long-term hazard or can raise difficulties in the radioanalytical measurements. As this term is frequently used in connection with two fields, namely in radioactive waste management (final disposal of waste and its long-term radiological effects, reprocessing and transmutation) and in analytical measurement techniques, the definitions used depend on the scope of investigation. According to the International Atomic Energy Agency (IAEA) definition for radioactive waste classification, long-lived radionuclides are those nuclides, which require long-term isolation from the biosphere due to their radiotoxicity and usually have half-lives greater than 30 years [12]. The definition of EURATOM (European Atomic Energy Community) for long-lived radionuclides is similar [13]. According to this recommendation, a radionuclide is considered to be long-lived, if the half-life is longer than that of ^{137}Cs or ^{90}Sr (approximately 30 years). These definitions are usually applied for waste disposal and referred to those radionuclides, which may pose hazard in the future in the long run.

In case of analytical chemistry (especially in radioanalytical methods) those radionuclides are considered to be long-lived, which have such long half-lives (thus such low specific activities) that their detection and measurement are hindered by the conventional radioanalytical methods due to the long counting time. As the detection capabilities of radioanalytical methods depend not only on the specific activity of the analyte, but also on several other parameters (e.g. decay mode, detected gamma or beta energy), this term is not as well-defined as for radioactive waste, and it ranges around 10^2-10^5 years.

More than 60 radionuclides up to curium can be considered to be long-lived on the basis of the IAEA definition. These radionuclides can be divided into two groups according to their origin. One of these groups is the naturally-formed long-lived radionuclides. Members of the decay series of primordial ^{232}Th, ^{235}U and ^{238}U, other primordial nuclides, such as ^{40}K, ^{144}Nd or ^{187}Re as well as some cosmogenic radionuclides (e.g. ^{10}Be or ^{14}C) belong to this group. These radionuclides have always been present in the earth's crust and within the tissues of living beings. Although the concentrations of these nuclides are relatively low in most natural substances, higher amounts can occur as a result of natural processes or human activities. A number of these radionuclides have high bioavailability; therefore, they also have high dose contribution. For instance, ^{40}K and ^{87}Rb are estimated to come out at approximately 15% of the annual effective dose in areas of normal background [1]. In case of mineral waters and uranium mine tailings, ^{226}Ra is of primary concern due to the high concentration and dose contribution.

Though transuranics are commonly understood to be anthropogenic, ^{239}Pu and ^{244}Pu isotopes are in fact natural radionuclides, though the naturally-formed Pu fraction presently is far less than that the man made component released into the environment during the 20th century [14]. After the discovery of nuclear fission, widespread use and application of nuclear techniques lead to the release of transuranics and fission products into the environment to a great extent. These isotopes have been released from several sources. Among these, the major source is the fallout from the atmospheric weapons test, which were conducted from 1945 and peaked in 1962 before the Partial Test Ban Treaty was signed. Accidents (e.g. Chernobyl or Khystym) and authorized release from reprocessing plants are also significant contributors to the actinide and fission products environmental inventories. Plutonium was also released during military accidents involving fractured nuclear weapons, or re-entry accidents of satellites containing ^{238}Pu as a power source (thermoelectric generators). Despite the commonly-used closed nuclear fuel cycle, long-term effects of disposed radioactive waste (e.g. release and migration from a waste repository), decommissioning of nuclear facilities or liberation from previous, inadequately disassembled nuclear devices (e.g. dumped submarines or reactors) are also possible sources of radionuclide contamination in the future. Characterization and continuous monitoring of key radionuclides at nuclear facilities (reactors and waste repositories) are vital, as the highest amount of artificial long-lived radionuclides derives from waste from operating nuclear reactors, presently kept in repositories, since the final treatment (e.g. by reprocessing or transmutation) or ultimate way of deposition of the spent fuel is not fully solved in the long run.

Long-lived radionuclides are widely used also for research and industrial purposes. Environmental research, such as geochronology (e.g. uranium-lead or rubidium-strontium dating), dosimetry, migration and sedimentation studies are the main fields of research involving natural radionuclides. Recently, their measurement is more extensively done in solid-state research and material control (e.g. production of high-purity metals, alloys, semiconductors and insulators for microelectronics). Determination of artificial long-lived radionuclides are mainly used in connection with the nuclear industry and radiation protection, as the main tasks are the characterization of nuclear waste with respect to its long-lived radionuclide content (e.g. Pu-isotopes, ^{237}Np, ^{241}Am, ^{99}Tc or ^{129}I), control of permissible releases from nuclear power plants or reprocessing facilities and environmental monitoring [11,15]. Recently, anthropogenic long-lived radionuclides have been used as tracers in biological, medical, geological research and analytical chemistry. For instance, deposited radionuclides from global fallout are increasingly used in oceanographic and sedimentation studies in order to calculate water fluxes of sea streams, measurement of erosion and sedimentation rates or to determine the exposure date of surfaces due to erosion or global warming [16-18]. Long-lived radionuclides are also widely used in analytical chemistry for isotope dilution measurements, for species-unspecific isotope dilution methods [19]. For instance, ^{129}I has been reported as an isotopic tracer for the determination of iodine concentration [20] or ^{229}Th, ^{233}U, ^{242}Pu for actinide measurements [10,11]. As the isotopic composition of long-lived radionuclides, especially for uranium and plutonium, is characteristic to its source and reflects the formation conditions or intended use, it can be exploited in nuclear safeguards and for the analysis of confiscated illicit materials (a field recently dubbed *nuclear forensics*). The measurement of such long-lived radionuclides allows the determination of several characteristics of the sample (e.g. origin and or production date). Therefore, those parameters help to identify the source or intended use of the nuclear material supporting authorities to detect and clear up clandestine activities (e.g. safeguards system of the Nuclear Non-Proliferation Treaty or smuggling of nuclear materials). The overview of the application fields of long-lived radionuclides is shown in **Fig. 1.**

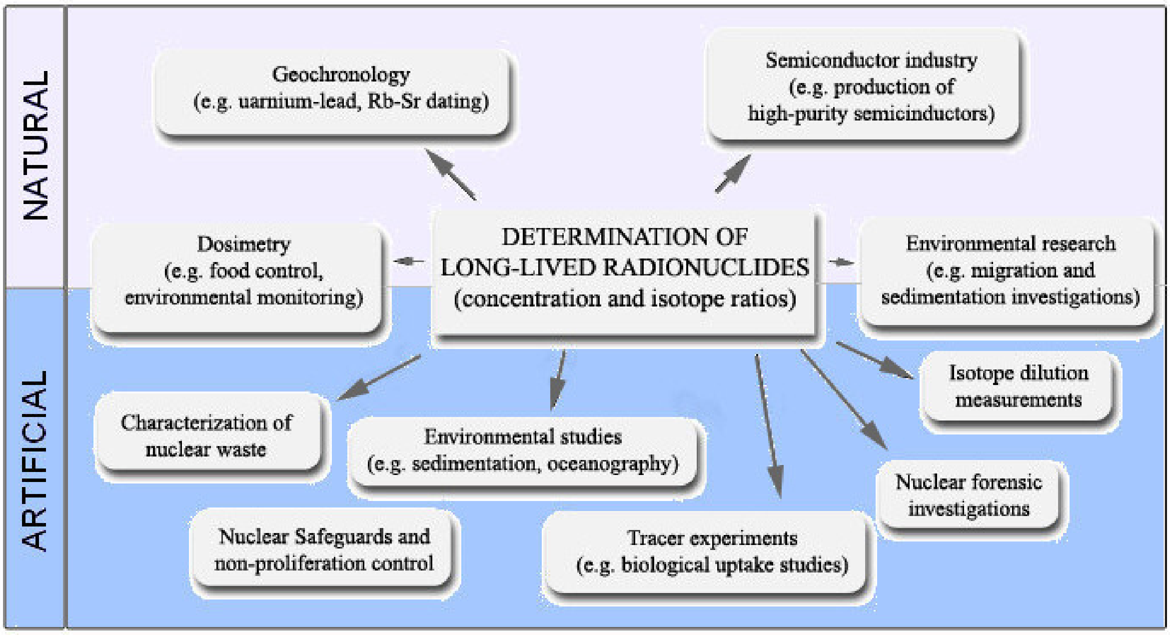


Fig. 1. Overview of the application fields of long-lived radionuclide measurements

2.2. General Properties of the Long-lived Radionuclides Studied

2.2.1. Description of Plutonium Isotopes

Plutonium has an atomic number of 94, is an actinide and the second element in the transuranics series. Essentially, all terrestrial plutonium is an artificial radionuclide, produced by neutron bombardment of ^{238}U followed by two sequential beta emissions, however, trace quantities of naturally-occurring plutonium can be found in the environment [14]. In nature, ^{239}Pu is continuously formed from ^{238}U by the capture of neutrons derived from spontaneous fission, resulting in an estimated concentration of 100 amol kg^{-1} in the earth's crust [14]. The present day abundance of ^{244}Pu ranges from 7×10^{-24} to 3×10^{-22} g kg^{-1} as a consequence of residual primordial ^{244}Pu, steady-state cosmic ray source bombardment or from a supernova explosion that occurred after the solar system was formed [14,21]. However, after the discovery of nuclear fission, widespread use and application of nuclear techniques led to the release of transuranics, especially plutonium, into the environment to a great extent. Plutonium has been released into the environment through several sources. Among these sources, the major source of plutonium in the environment is global fallout from the atmospheric weapons tests, which were conducted from 1945 and peaked in 1962 before the Partial Test Ban Treaty. The estimated release of ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu by the atmospheric testing of nuclear weapons is 0.33, 6.52, 4.35 and 142 PBq, respectively [1]. Accidents (e.g.

Chernobyl [22] or Khystym [23]) or authorized release from reprocessing plants (e.g. Sellafield reprocessing plant [24]) are also significant contributors to actinide emissions. Of the nuclear plant accidents, the Chernobyl accident resulted in an estimated release of ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu of 0.03, 0.03, 0.044 and 5.9 PBq, respectively [22]. Plutonium, especially ^{239}Pu has also been released into the environment during military accidents involving fractured nuclear weapons, such as in Thule in 1968 or in Palomares in 1966, although the release is negligible compared to weapons tests or nuclear accidents. However, these incidents posed an elevated local hazard. Re-entry accidents of satellites containing ^{238}Pu as a power source (thermoelectric generators), such as the SNAP-9A satellite in 1964, resulted in a several-fold increase in the global fallout of this isotope [25].

Plutonium has 18 isotopes with mass numbers ranging from 232 to 247, and all isotopes are radioactive. Some have long half-lives: the most important isotope, ^{239}Pu, has a half-life of 24110 years, but ^{242}Pu and ^{244}Pu, which are the commonly used isotopic tracers in analytical measurements, have much longer half-lives of 3.735×10^5 and 7.6×10^7 years, respectively. Other significant Pu isotopes, ^{238}Pu, ^{240}Pu, and ^{241}Pu have half-lives of 87.7, 6537 and 14.35 years, respectively. Four of these isotopes decay by alpha emission accompanied by weak gamma rays: ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu. In contrast, ^{241}Pu decays by beta emission with weak gamma rays, but its progeny, ^{241}Am, is an intense gamma emitter. ^{239}Pu and ^{241}Pu are fissile materials: they can be split by both fast and slow neutrons. ^{240}Pu and ^{242}Pu are fissionable, but have very small neutron fission cross-sections. ^{240}Pu partly decays by spontaneous fission, although a small amount of spontaneous fission occurs in most plutonium isotopes. The main characteristics of the most important plutonium isotopes are summarized in **Table 1.**

Table 1. The main characteristics of the most important plutonium isotopes

Isotope	Main decay mode	Half-life (years)	Main formation mechanism
^{238}Pu	Alpha	87.7	^{239}Pu(n,2n), ^{237}Np(n,γ), ^{242}Cm(alpha-decay)
^{239}Pu	Alpha	24110	^{238}U(n,γ), ^{240}Pu(n,2n)
^{240}Pu	Alpha	6537	^{239}Pu(n,γ), ^{242}Cm(alpha-decay)
^{241}Pu	Beta	14.35	^{240}Pu(n,γ)
^{242}Pu	Alpha	3.735×10^5	^{241}Pu(n,γ)
^{244}Pu	Alpha	7.6×10^7	Primordial (appr. 10 g)

The isotopic composition of plutonium is characteristic of its source and reflects the formation conditions or intended use. Thus, plutonium isotopic ratios are exquisite indicators of origin. The typical plutonium isotope ratios of various nuclear materials and sources are summarized in **Table 2.**

Table 2. The typical plutonium isotope ratios of various nuclear materials and sources

	^{238}Pu/^{239}Pu activity ratio	**^{240}Pu/^{239}Pu atom ratio**	**^{238}Pu/$^{239+240}$Pu activity ratio**	**^{241}Pu/^{239}Pu activity ratio**	**References**
Weapons-grade plutonium	0.017-0.52	0.036-0.062	0.015-0.42	5.8-13	[26,27]
Reactor-grade plutonium	> 0.5-1.3	> 0.33	> 2.1-2.9	> 130	[28-30]
Chernobyl accident	0.82-1.3	0.31-0.40	0.49-0.56	135-213	[22,28,30,31]
Fallout from weapon tests	0.042	0.182	0.025	2.7[a]	[1,32]
Fallout in the Northern Hemisphere (01.01.2000)		0.166-0.194		2.9	[32]
Fallout in the Southern Hemisphere (01.01.2000)		0.138-0.232		3.3	[32]

[a] Decay corrected to 1 July 2006.

The isotopic composition of reactor-grade plutonium varies significantly depending on burn-up and reactor design. Generally, plutonium deriving from reactor operation after a sufficiently long irradiation time and as a consequence of high neutron flux is characterized by relatively high ^{238}Pu content, high ^{240}Pu/^{239}Pu (up to 0.6 atom ratio depending on reactor type and burn-up) and ^{241}Pu/^{239}Pu ratios. Moreover, the presence of other transuranics (e.g. higher amount of ^{242}Pu, ^{244}Cm) is also characteristic of reactor origin due to the higher burn-up. The typical variation of plutonium isotopic composition as a function of fuel burn-up in a pressurized water reactor is shown in **Fig. 2.** [33]. However, actual activities vary besides burn-up as a function of reactor type, initial fuel enrichment, cooling time and several other parameters. Generally, plutonium derived from reactor operation after a sufficiently long irradiation time and as a consequence of high neutron flux, is characterized by relatively high ^{238}Pu content, high ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios. Large quantities of ^{239}Pu have been used as the fissile

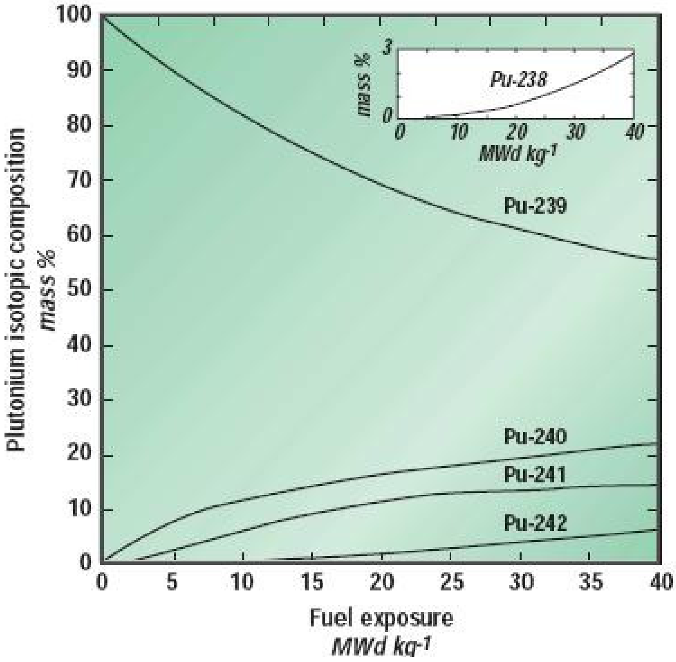


Fig. 2. Plutonium isotopic composition as a function of fuel exposure in a pressurized water reactor [33]

agent in nuclear weapons and as a reactor fuel when mixed with uranium (MOX fuel). It is also used to produce radioactive isotopes for research, including the study of breeder reactors. ^{238}Pu is used as a heat source to power instruments for space exploration (space probes such as Cassini) and implanted heart pacemakers.

Plutonium can form five oxidation states in solution, +3, +4, +5, +6 and +7 [34,35]. The first four are present in solution as Pu^{3+}, Pu^{4+}, PuO_2^{+}, PuO_2^{2+}. They coexist in dilute acid solutions and sometimes all four are present in substantial quantities. The equilibration problems of plutonium are among the most complex encountered in radiochemistry. Problems of disproportionation and auto-oxidation in freshly prepared solutions also complicate the chemistry of plutonium. The +7 state can form in alkaline solutions, and it has been suggested that the ion in solution is PuO_5^{3-}. Plutonium ions tend to hydrolyze and form complex ions in solution. The +4 ion can form long chain polymers that do not exhibit the usual chemical behaviour of the +4 oxidation state. Finally, the different oxidation states exhibit radically different chemical behaviour. As a result of these effects, it is possible to mix a plutonium sample with plutonium tracer, subject the mixture to a relatively severe chemical treatment using hot acids or similar reagents, and still selectively recover portions of either the tracer or the sample. This characteristic explains the challenge in achieving reproducible radiochemical results for plutonium. Numerous redox agents are available to oxidize and reduce any of the five states of plutonium to alternate oxidation states. For Pu reduction, N_2H_4, I^-, $NH_2OH.HCl$, SO_2, ascorbic acid or Fe(II) is generally used [34,35]. $NaNO_2$ is a widely used redox agent for the stabilization of Pu in the Pu(IV) state. To adjust Pu in the higher oxidation states, hot HNO_3, $S_2O_8^{2-}$ or AgO can be effectively used. Beside the several oxidation states, the affinity of plutonium for complexation to a highly variable degree also complicates its chemical behaviour. Plutonium ions tend to form complex ions in the following order:

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

Divalent anions tend to form stronger complexes with plutonium. Complexation is preferable through oxygen and fluorine rather than nitrogen, phosphorus or sulphur. Plutonium also forms complexes with ligands such as phosphate, acetate, and tri-n-butylphosphate (TBP). Strong chelate complexes form with EDTA, tartarate, citrate, 2-thenoyltrifluoroacetone (TTA), acetyl-acetone (acac), and cupferron. Plutonium(IV) forms a strong complex with fluoride (PuF^{3+}) that is used to solubilize plutonium oxides and keep it in the aqueous phase during extraction of other elements with organic solvents. The complex with nitrate, $Pu(NO_3)_6^{2-}$, allows the recovery of plutonium from nuclear fuels. Carbonate and acetate complexes prevent precipitation of plutonium from solution even at relatively high pH.

All isotopes and compounds of plutonium are toxic and radioactive. However, its toxicity highly depends on the isotope and way of exposure. Plutonium poses a health hazard only if it is taken into the body, because, with the exception of ^{241}Pu which decays via a low energy beta particle, all it's isotopes decay by emitting an alpha particle [1,36]. Minimal gamma radiation is associated with any of these radioactive decays. Inhaling airborne plutonium is the primary concern for all Pu isotopes, due to the potential for cancers resulting from the short ranged highly ionizing radiation characteristic of the element. The ingestion hazard associated with the common forms of plutonium is much lower than the inhalation hazard, because absorption into the body after ingestion is quite low. Most of plutonium that enters the bloodstream deposits about equally in the liver and the skeleton, where it remains for long period of time, with biological retention half-lives of about 20 and 50 years, respectively [36].

2.2.2. Description of Americium-241

Americium, with an atomic number of 95 is an actinide and the third element in the transuranics series. Twenty isotopes of americium including three metastable states are known: ^{232}Am through ^{248}Am. All isotopes are radioactive. Both ^{241}Am and ^{243}Am are alpha emitters and have the longest half-lives of 432.2 and 7370 years, respectively. Both ^{241}Am and ^{243}Am undergo spontaneous fission. ^{242m}Am has a half-life of 141 years, and the half-lives of the remaining isotopes are measured in hours, minutes, or seconds. ^{241}Am is the most common isotope of environmental concern, while ^{243}Am is widely used as isotopic tracer analytical purposes involving the determination of the element [34].

None of the isotopes of americium occur naturally. It is produced synthetically by neutron bombardment of ^{238}U or ^{239}Pu, followed by beta decay of the unstable intermediates. The most significant isotope, ^{241}Am has been released into the environment as a consequence of nuclear power plant accidents, (authorized) discharges from reprocessing plants [22,24] or atmospheric nuclear weapon tests [1]. In stored nuclear waste of spent fuels, ^{241}Am can be the major component of alpha activity present [37]. As ^{241}Am ($T_{1/2}$ = 432.2 years) is formed by the decay of ^{241}Pu ($T_{1/2}$ = 14.35 years), its concentration will increase in the environment in the future and it is estimated to reach its maximum activity in the middle of the 21st century. The estimated variation of transuranics released during the atmospheric weapons tests and the Chernobyl accident, as another significant source of fallout transuranics in Europe, are shown in **Fig. 3.** and **Fig. 4.**

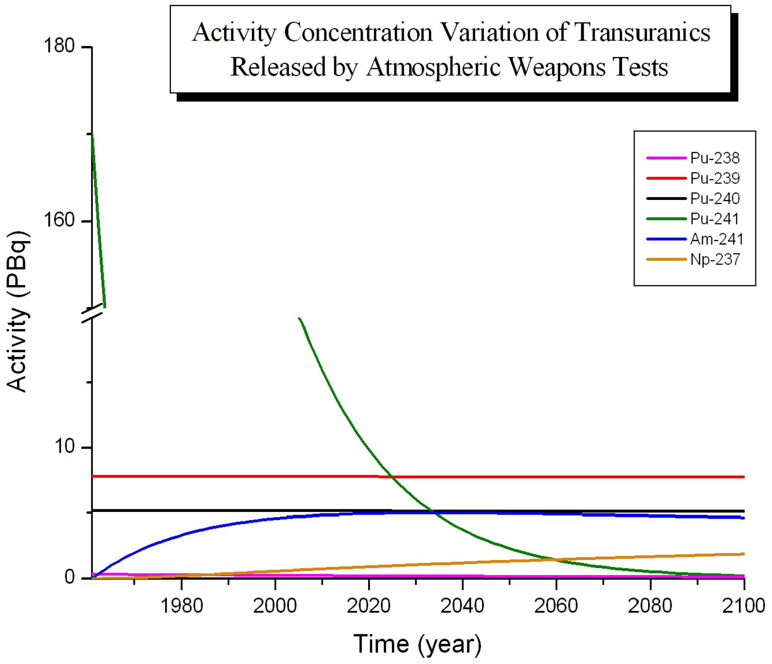


Fig. 3. Calculated variation of transuranics released by the atmospheric weapons tests. Note: transuranic inventories were taken from UNSCEAR report [1]. The total emission was normalized to 1961 (maximum yield of atmospheric weapon tests) as an initial formation time

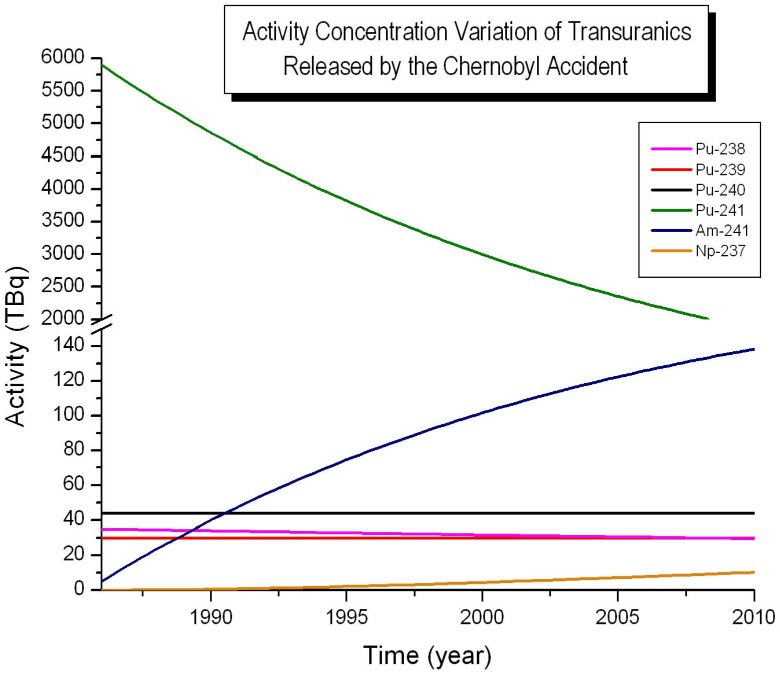


Fig. 4. Calculated variation of transuranics released during the Chernobyl accident. Note: inventories were taken from IAEA report [22]

Americium can exist in solution in the +3, +4, +5, and +6 oxidation states [34]. Simple aqueous ions of Am^{3+} (+3 oxidation state) and AmO_2^{+2} (+6 oxidation state) are stable in dilute acid, but Am^{3+} is the predominant oxidation state. The +3 oxidation state forms complexes in the following order of strength (in aqueous solution):

$$F^- > H_2PO_4^- > SCN^- > NO_3^- > Cl^-$$

Both americium +3 and +6 states form complexes with organic chelants. These are stable in aqueous and organic solvents. Americium(IV), however, can be easily reduced unless special oxidizing conditions are maintained. The actinide elements are known for their tendency to hydrolyze and, in many cases, form insoluble polymers. In the predominant +3 oxidation state in solution, americium, with its large radius, has the least tendency of the +3 actinides to hydrolyze, however, hydrolysis is expected to occur with some polymerization. Hydrolysis that does occur is complicated and depends on the nature of the cations present and may start at pH values as low as 0.5-1.0.

Due to the high specific activity and dose contribution, measurement and monitoring of ^{241}Am concentration is of high importance [1,38]. Moreover, deposited ^{241}Am from the global fallout constitute unique tracer and is increasingly used in oceanographic and sedimentation studies [16]. Some industrial ionization sources also contain americium. Soft gamma emission from ^{241}Am (59.5 keV, 36% abundance) is used to measure the thickness of metal sheets and metal coatings, the degree of soil compaction, sediment concentration in streams and to induce X-ray fluorescence in chemical analysis. As an alpha emitter, it is mixed with beryllium to produce a neutron source for oil-well logging and to measure water content in soils and industrial process streams. The alpha source is also used to eliminate static electricity and applied as an ionization source in smoke detectors [36].

2.2.3. Minor Long-lived Radionuclide Components in Nuclear Materials

Nuclear samples (e.g. ore, intermediate products or fuel pellets) contain various types of trace-level impurities originating from the starting material, the chemicals added and as a result of contamination during the production process of the material (**Table 3.**). These impurities reflect the origin and history (e.g. production method or date) of the sample, thus they are important indicators for the identification and characterization of found or confiscated nuclear materials, such as uranium oxide or plutonium oxide matrices. These parameters give useful information on the production location and method of the material. Therefore, besides the production control of nuclear materials in fuel fabrication industry (e.g. fuel production, reprocessing facilities), such analyses are usually carried out in nuclear forensic investigations and form integral parts of combating nuclear smuggling and illicit trafficking [39].

Table 3. Trace-level impurities in nuclear materials, the analytical techniques used for their measurements and information retrievable

Impurity	Origin	Measurement methods	Information	References
Stable elements	Starting material, chemicals added, production method	ICP-OES, ICP-MS, GDMS	Production location, origin, production method	[39-42]
Decay products	Decay of base material	AS, GS, TIMS, ICP-MS, SIMS	Production date	[39,40,43,44]
Activation products	Irradiation	AS, SIMS, ICP-MS	Reprocessing, burn-up	[43,45]
Fission products	Irradiation	GS, ICP-OES	Reprocessing	[46]

Abbreviations: ICP-OES: inductively coupled plasma optical emission spectrometry; GDMS: glow discharge mass spectrometry; AS: alpha spectrometry; GS: gamma spectrometry; TIMS: thermal ionization mass spectrometry; SIMS: secondary ionization mass spectrometry

Stable elements, such as transition metals or rare-earth elements, are mainly introduced into the material from the original starting material (e.g. ore), the added chemicals used for the production and also as a result of contamination during the production route. Radionuclides, both minor short and long-lived nuclides (e.g. ^{236}U, plutonium or ^{241}Am) are introduced into the nuclear materials as major or trace components of the starting material, if previously irradiated uranium is used as the base material or if it is mixed with irradiated fuel in the course of reprocessing. Contamination during the fabrication process may be another source of radionuclides at trace-level. Fission and activation products in the nuclear material may also be present if the sample has been irradiated after the production (e.g. spent fuel samples). However, in irradiated nuclear materials, the amount of fission and activation products is usually higher than in those samples, which contain these radionuclides as impurities from the base material. Moreover, fission and activation product distribution within the nuclear material is different for irradiated samples and for reprocessed fuels. For instance, as burn-up of the nuclear fuel is higher at the rim, fission and activation product concentrations are usually higher at the superficies for cylindrical fuel pellets. The isotopic composition of activation and fission products varies significantly depending on burn-up and reactor design. However, the relative amount of high-mass plutonium isotopes increases with higher burn-up (**Fig. 2.**).

Progenies (decay products) of the nuclear materials are continuously growing-in within the nuclear material after the last chemical separation of the base material due to the decay of radioactive uranium or plutonium. The amounts of decay products are proportional to the amount of mother nuclide and the time elapsed since the last chemical separation, if the removal of the progenies was complete. **Fig. 5.** shows the concentration variation of main progenies for the most important nuclear radionuclides as a function of time.

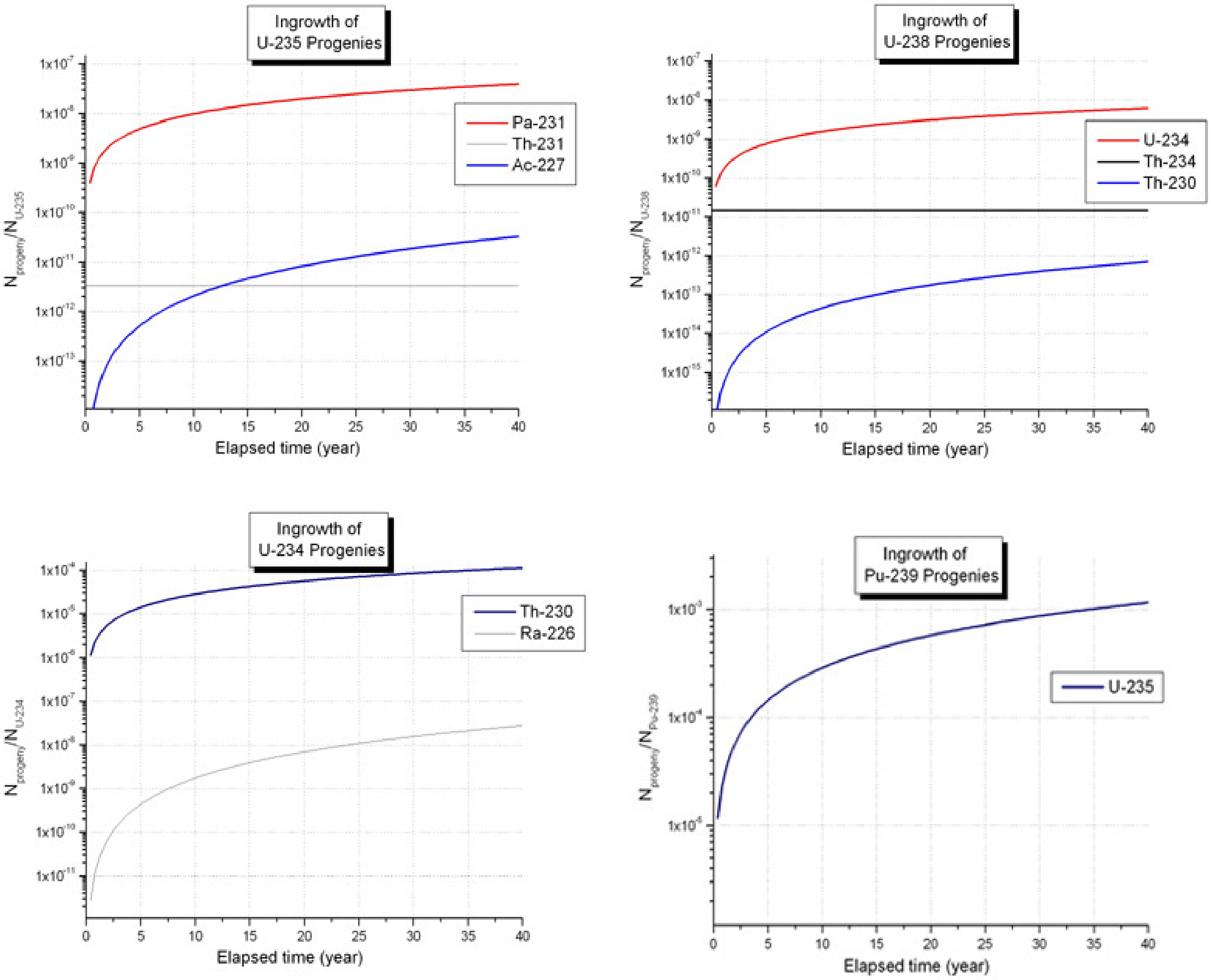


Fig. 5. The variation of main progeny-to-mother nuclide atom ratios for the most important nuclear radionuclides as a function of time

The measurement of progenies in nuclear materials is mainly used for nuclear forensic investigations, as their determination allows the calculation of production date (also called *age* of the material). The time elapsed since the last separation of the progenies can be calculated on the basis of the radionuclide mother-to-daughter ratio according to the equations of radioactive decays, assuming that the initial concentration of the daughter nuclide is zero after the last chemical separation (i.e. the separation was complete).

3. Recent Status of the Analytical Chemistry of the Investigated Radionuclides

3.1. Relationship between Radioanalytical Methods and Mass Spectrometry

Recently, due to the rapid development of commercially available mass spectrometers, especially ICP-MS instruments, mass spectrometry is increasingly used for long-lived radionuclide measurements. Some decades ago, the complicated instrumentation, difficult sample preparation and cumbrous operation of mass spectrometers (almost exclusively thermal ionization mass spectrometers, TIMS) precluded their widespread use for analytical measurements. For long-lived radionuclide analysis, mass spectrometry was used only in a few laboratories (especially for uranium and plutonium measurements), and radioanalytical methods (e.g. gamma or alpha spectrometry) were generally applied for this purpose. Nowadays, as commercially available mass spectrometers can routinely achieve very low detection limits (typically in the femtogram to picogram range), together with the significant improvement in the ease of use and maintenance, these instruments are more extensively employed for such measurements, which also led to the extension of investigated long-lived radionuclides.

Radioanalytical methods and mass spectrometric techniques use two different approaches for the radionuclide measurements. Radioanalytical methods are based on the detection of photons or particles formed during the decay of the analyte, thus the measured signal is proportional to the activity of the sample. Therefore, it is an indirect measurement of the radionuclide of interest. In contrast, mass spectrometry directly detects the isotope of interest before it decays, independently of the activity of the radionuclide investigated. Therefore, the signal measured by the mass spectrometric methods is proportional to the number of atoms or ions present in the sample. Thus, if the activity of a certain isotope in the sample is constant, the number of the radionuclide (atoms or ions) of interest is higher for the longer-lived isotope according to **Eq. 1.**,

$$N = \frac{A \cdot T_{1/2}}{\ln 2} \qquad \text{Eq. 1.}$$

where N is the number of atoms of radionuclide, A is the activity of the radionuclide in the sample and $T_{1/2}$ is the half-live of the isotope. Thus, the longer the half-life of the isotope, the easier it is to measure the radionuclide directly rather than by radioanalytical methods. For ICP-SFMS this fact can be easily demonstrated, if the absolute detection limit of a certain isotope, expressed in activity, is plotted as a function of the half-live (**Fig. 6.**). Typical detection limits of alpha spectrometry and liquid scintillation are also included in the diagram.

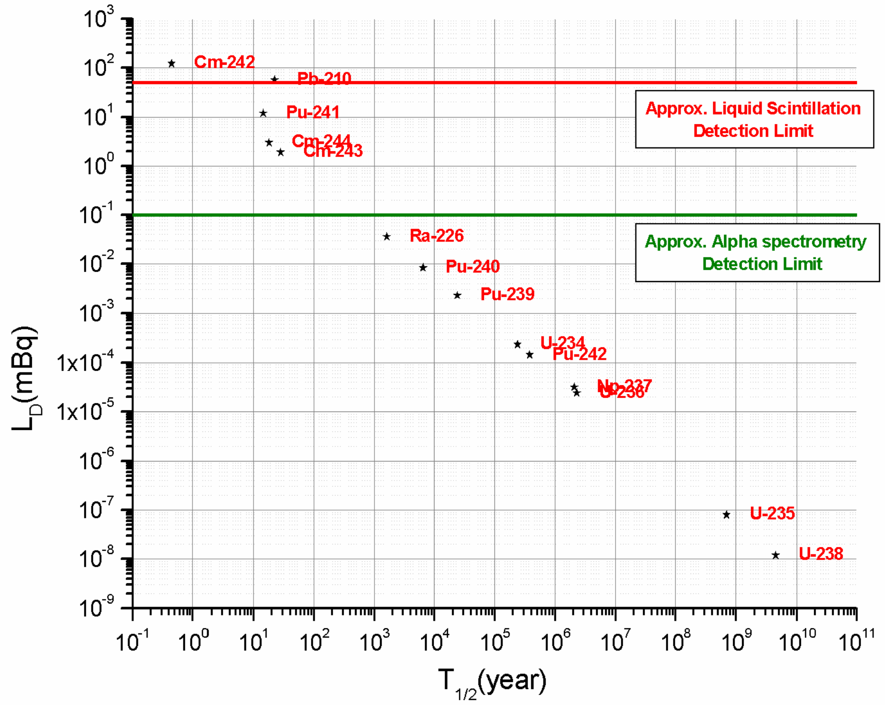


Fig. 6. Absolute detection limits of ICP-SFMS for some selected radionuclides as a function of their half-lives

However, this representation can be misleading, since the detection limits of mass spectrometric methods are not in related to the half-life (mass spectrometric methods detects isotopes directly, irrespectively of decay characteristics), this diagram clearly indicates that use of mass spectrometry is increasingly favourable for the longer-lived isotopes. Currently, the theoretical half-life minimum, when the detection capabilities of mass spectrometric techniques can be comparable to those of the radioanalytical methods, is approximately between 100 and 1000 years for ICP-SFMS. For radionuclides with half-lives longer than this range, the absolute detection limits of ICP-SFMS, expressed in activity, is better than that for the radioanalytical techniques. However, it has to be emphasized applicability and selection of the most sensitive technique for a certain radionuclide can also be affected by several other parameters (e.g. decay properties of the radionuclide, possible interferences or ionisation potential of the element).

3.2. Sample Preparation Methods of the Investigated Radionuclides

3.2.1. Sample Preparation Methods for Low-level Plutonium Determinations

As plutonium is present in most environmental samples at ultratrace-level (from fg g^{-1} to pg g^{-1} range, which is approximately equivalent to μBq g^{-1} – mBq g^{-1} range), sample preparation, which includes both pre-concentration and purification of the analyte, is of primary importance. As the detection limits of the non-destructive analytical techniques, such as gamma spectrometry, are far too high for most environmental plutonium measurements, destructive methods, such as alpha spectrometry, with selective chemical sample preparation are necessary for such measurements. Sample preparation, which is usually the most tedious and critical part of the destructive analysis, has to be properly planned and optimized depending on the data quality objectives and the measurement technique applied. In general, the requirements for the radioanalytical (e.g. alpha spectrometry or liquid scintillation counting) and mass spectrometric sample preparation methods are similar, and the procedures can be divided into four main, not necessarily consecutive parts: (1) general pre-treatment of the sample by drying, ashing, homogenization, filtering (in case of liquid samples), grinding or sieving, (2) the leaching, digestion or dissolution of the sample, (3) the pre-concentration of the analyte and (4) the final purification step (**Fig. 7.**). The sample pre-treatment methods are not different from those used in other analytical methods, though in some cases care has to be taken, if plutonium is present in hot particles (a small, highly radioactive object, with significant content of radionuclides) resulting in a highly inhomogeneous sample. In such cases, sub-sampling, processing higher sample amount or detection and verification the presence of the hot particle (e.g. by the measurement of ^{241}Am by gamma spectrometry) can be

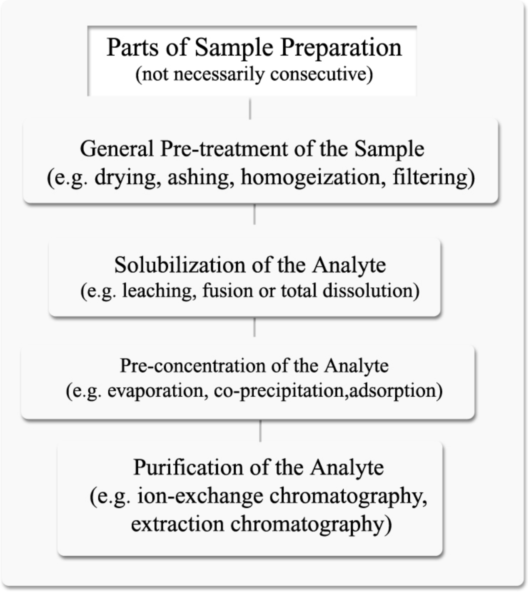


Fig. 7. Parts of sample preparation

effective in order to obtain a representative sample for measurement or for the proper interpretation of analysis results.

The aims of the second part of the sample preparation are to convert the analyte into liquid phase and to remove most of organics that may interfere during the following steps. These treatments are necessary for the solid phase samples (soil, sediment, air filters and biological matrices), while in case of liquid samples this step is usually carried out after the pre-concentration due to the very low concentration of plutonium. Care has to be taken to select a proper leaching or total dissolution procedure: incomplete dissolution of the analyte may result in negative error (low recovery). This is usually the case for samples containing refractory hot particles (e.g. originating from the close fallout of a weapon test or nuclear accidents), which require total dissolution with HF or alkali fusion. For example, Eriksson found that leaching with *aqua regia* is insufficient for the complete dissolution of plutonium from PuO_2 particles in contrast to HF/HNO_3 total dissolution or alkali fusion [47]. However, for most environmental samples containing global fallout or metabolized plutonium, relatively simple acid leaching (e.g. hot plate digestion using concentrated HNO_3) is sufficient. For instance, Nygren *et al.* found no significance difference between leaching with 8 M HNO_3 and lithium-borate fusion in case of soil and sediment samples [48]. Acid leaching has several advantages over total dissolution with HF or alkali fusion: it is not only much easier and faster, but also requires less hazardous chemicals and procedure. Moreover, higher sample amount can be processed. Use of closed vessel microwave systems can further decrease dissolution time and the amount of chemicals required; however, in such cases the sample amount is limited. Isotopic tracers, usually ^{236}Pu, ^{242}Pu or in some cases ^{244}Pu, are usually added to the sample in this phase, thus complete isotopic exchange between the tracer and the analyte has to be achieved during also the dissolution step.

With the exception of contaminated, highly active samples, when both sample amount and the quantity of chemicals added (e.g. acids, fusing agents) are low, pre-concentration of the analyte and removal of high amount of matrix components (e.g. acids used for the dissolution, alkali and alkali earth metal content of the sample, silicates) are necessary in order to avoid their negative effects on the subsequent liquid-liquid exchange (e.g. competitive reactions, precipitation) or chromatographic separations (e.g. competitive reactions, overloading or clogging of the column). The pre-concentration of the analyte can be achieved by filtration, centrifugation, evaporation of the sample (e.g. in case of the removal of excess acid), co-precipitation of plutonium or its adsorption on resin or cartridges. The pre-concentration step has to be in accordance with the forthcoming steps, thus its selection is highly dependant on the purification step. For example, extraction chromatographic separations (EXC) and on-line separation techniques coupled with ICP-MS measurements work well for low-volume load solutions with relatively low dissolved solid content compared to the anion exchange (A-IEX) or liquid-liquid extraction (LLE) separation due to the smaller particle size of the resin. Thus, decreasing of the total dissolved solid (TDS) content of the load solution for EXC and on-line separations by selective pre-concentration (i.e. co-precipitation or adsorption on specific resins) is necessary, while A-IEX and LLE separations can tolerate higher dissolved solid content, and in several cases simple evaporation and re-dissolution of the sample in the proper solvent is sufficient.

Maybe the most common and traditional methods for the pre-concentration and separation of radionuclides are precipitation and co-precipitation. Precipitation is used to isolate and collect a specific radionuclide from other foreign ions by forming an insoluble compound. Either the radionuclide is precipitated from solution itself, or the foreign ions are precipitated (scavenged), leaving the radionuclide in solution. In most radiochemical works, especially in case of environmental samples, radionuclides are usually present in solution at trace-level concentration, which means that its amount is so low that the radionuclide will not form an insoluble compound upon addition of even a high amount of counter-ion, because the product of the concentrations does not exceed the solubility product. The radionuclide can often be brought down selectively and quantitatively from a solution during the precipitation of an alternate insoluble compound (called *carrier*) by another process called *co-precipitation*. In these cases, the radionuclide is brought down from the solution by co-precipitation, associating it with an insoluble substance that precipitates from solution. As the term is used in radiochemistry, co-precipitation is the simultaneous precipitation of one compound that is normally soluble under the conditions of precipitation with one or more other compounds that form a precipitate under the same conditions. Co-precipitation is performed in a controlled process to associate the ion of interest selectively with a precipitate, while excluding the other foreign ions that would interfere with the analytical procedure. The three main mechanisms of co-precipitation are *inclusion* (uptake from solution of an ion similar in size and charge to the solid forming the precipitate in order to form a mixed crystal or solid solution), *surface adsorption* and *occlusion* (mechanical entrapment). Using a good precipitation technique minimizes the co-precipitation of impurities: the carrier should maximize the co-precipitation of the radionuclide of interest, while providing a well-formed solid that attracts a minimum of other foreign ions as impurities. In general, conditions that favour precipitation of a substance in macro amounts also favour the co-precipitation of the same material from tracer concentrations with a foreign substance. The radionuclide is efficiently carried by an ionic precipitate, if (1) the analyte ion is isomorphously incorporated into the precipitate, or (2) the analyte ion forms a slightly soluble or slightly dissociated compound with the oppositely charged lattice ion, or (3) if the precipitate has a large surface with charge opposite to that of the tracer ion (i.e. presence of excess of the oppositely charged lattice ion). For instance, radium is co-precipitated quantitatively with barium sulphate using excess sulphate in solution, because radium forms the least soluble sulphate of the other elements in the alkaline earth family (*Paneth-Fajans-Hahn* adsorption rule). Ferric hydroxide ($Fe(OH)_3$) is a very useful carrier for adsorbing cations, because it forms a very finely divided precipitate with a negative charge in excess hydroxide ion, and widely used for the co-precipitation of actinides from solutions.

In case of plutonium, another important parameter of co-precipitation is the oxidation state of the analyte. Differently charged plutonium ions co-precipitate completely distinctly, thus Pu oxidation state has to be properly controlled. For example, lanthanum fluoride, which is one of the most commonly used carrier to co-precipitate plutonium for the preparation of alpha spectrometric sources by micro co-precipitation, effectively co-precipitates Pu(III) and Pu(IV), leaving Pu(V) and Pu(VI) in solution [34]. Other important factors affecting co-precipitation are the reaction kinetics and the presence of competing agents (e.g. organic materials) in the sample. The effect of these parameters also has to be considered during method development.

For low-level plutonium determinations numerous sample separation methods applying co-precipitation as a pre-concentration step have been developed. Typical separation methods applying co-precipitation with carrier types and separation conditions for low-level plutonium measurements are presented in **Table 4.**

Table 4. Typical separation methods applying co-precipitation for low-level plutonium measurements

Sample type	Sample amount	Carrier	Conditions	Ref.
Bioassay samples (urine)	1500 mL	$BiPO_4$	Oxidation state: $NH_2OH.HCl$ pH = 1.5 Settling: overnight	[49]
Urine	1 L	$Ca_3(PO_4)_2$	pH = 2 Heating to 40 °C Settling: overnight	[35,50]
Seawater	950 mL	NdF_3	Oxidation state: Na_2SO_3/Fe^{2+} Settling: 30 min	[51]
Sediment	10 g	$La(OH)_3$	Oxidation state: $NH_2OH.HCl$ Heating to 100 °C, 1 hour Cooling: 2-3 hours	[52]
Seawater	200-400 L	MnO_2	pH = 7-8 Settling: overnight	[53]
Sediment	10-50 g	$Fe(OH)_3$	Oxidation state: $N_2H_4.H_2O/NaNO_2$ pH = 8-9	[53,54]

To conclude, co-precipitation is recently used mainly for such measurements, which require high pre-concentration of the analyte. Though some matrix components can be eliminated by co-precipitation, as its selectivity is limited, several further purification steps are required. Another disadvantage of co-precipitation is that for the high recovery it usually employs high amount of carrier, which has to be eliminated in the following steps. This disadvantage can be overcome by the use of adsorbents (selective or non-selective), which collect the analyte on the high surface. With this type of separation, higher sample amount can be processed and higher pre-concentration factor can be achieved without the need for processing of high amount of carrier thereafter. Adsorbents can be used either in batch mode or by filling it in a cartridge, and the analyte can be pre-concentrated by simply driving the liquid sample through the cartridge. For plutonium measurements from large volume water samples (mainly from seawater), manganese dioxide impregnated fibers filled in cartridges are used most frequently [55,56]. In these cases, the plutonium content of several hundreds liters of seawater can be relatively rapidly and quantitatively adsorbed on 10-50 g of resin, which has a MnO_2 content of approximately 2-10 g. Therefore, in the forthcoming separation steps much lower amount of MnO_2 has to be processed compared to co-precipitation simplifying the procedure and eliminating the problems associated with co-precipitation.

The final purification step of plutonium is possibly the most critical part of the sample preparation, which basically determines the accuracy and detection limit of the method, since most of interferences are eliminated in this step. Thus, the selectivity of the method for plutonium over the other elements or radionuclides that can cause interference during the measurement is one of the most important characteristics of this step. Several purification methods have been developed for low-level plutonium analysis. Anion exchange separations (A-IEX) have been used for decades for the separation of trace-level plutonium [35]. This separation schemes are based on the fact that Pu(IV) and Pu(VI) form anionic complexes at concentrated nitric or hydrochloric acids and so will absorb on anion exchange resins (**Chapter 2.2.1.**). After the oxidation state adjustment, the sample is loaded on the anion exchange column in a relatively concentrated HNO_3 medium (typically 8 M HNO_3). Thereafter, matrix ions (e.g. alkali and alkali earth metals) and possibly interfering elements and radionuclides (e.g. U, Th, Ra) are stripped by rinsing the column with 8 M HNO_3 and 9-12 M HCl. Plutonium elution from the resin is usually accomplished by the reduction of Pu to Pu(III), which has low affinity to the anion exchange resin. For the reduction, freshly prepared 0.1 M NH_4I/10 M HCl [54,57], $NH_2OH.HCl$/2 M HCl [58], 0.6% H_2O_2/1.2 M HCl [52] or 0.26 M HF/ 6 M HCl [59] have been used as eluent. The most typical resin used for plutonium separation is AG 1-X8, but other strong anion exchange resins, such as AG 1-X4 can also be used. The A-IEX separations for plutonium analysis have several advantages. The sample preparation can be carried out easily and at low cost using very simple equipment. However, for A-IEX separations relatively high amount of acid is consumed (one separation requires typically about 150 mL of 8 M HNO_3 and 120 mL 10 M HCl) and the separation procedure is rather slow. Moreover, though A-IEX separation works well for radioanalytical methods, for ICP-MS analysis repetition of the separation or further purification is necessary in order to completely remove the possible interferences, especially uranium. Due to the high amount of chemicals used, other stable contaminants, such as Pb, Bi or Hg, which can cause polyatomic interferences in the ICP-MS measurements, are also present in the final plutonium fraction in a large quantity. Therefore, in recent years, most laboratories replaced A-IEX methods with extraction chromatographic procedures.

Liquid-liquid extraction separation of plutonium, which is used in large-scale in reprocessing of spent fuels, has also been used long ago. Several extractants have been applied for plutonium analysis. Organo phosphorous compounds (e.g. tri-n-butylphosphate (TBP) [35], tri-n-octylphosphine oxide (TOPO) [35,60] or di(2-ethylhexyl)-phosphoric acid (HDEHP) [35,61,62] in various diluents (e.g. aliphatic kerosene or xylene)), thenoyl-trifluoroacetone (TTA) [56] in benzene or tri-n-octylamine in xylene [35,63] have been used as extracting solutions. The procedures used for plutonium separation by LLE are relatively simple: after the selective extraction in the organic phase, Pu is back extracted in the presence of a reducing agent, such as $NH_2OH.HNO_3$ or NH_4I. The advantages of LLE separations are that simple equipment is necessary and the analysis can be carried out at low cost. However, the tedious and labor-intensive procedures together with the necessity to use high amount of organic solvents hindered its widespread use for routine applications. Moreover, as high amount of chemicals are consumed and several extraction steps are necessary in order to obtain high recovery, the final fraction usually contains high amount of impurities, such as Pb or Hg, which are undesirable for ICP-MS analyses.

Over the last decade a novel separation method, extraction chromatography (EXC) has emerged the most favourable method for low-level radionuclide analyses, including the separation of plutonium. The technique itself became widely used in laboratories after the development and commercialization of relatively well-defined resins in the 1990s. The most frequently applied EXC resins are manufactured by Eichrom Inc. (Darien, Illinois, USA) and were developed by Horwitz and co-workers [64]. However, several research groups prepare their own resins for specific separation purposes or to decrease analysis costs. Frequently, EXC is described as a technique that combines the selectivity of liquid-liquid extraction (LLE) with the ease of operation of chromatographic methods. Extraction chromatographic separation is based on the distribution of the analyte ion between the liquid phase, which is usually an acidic solution, and the solid phase of the resin, which consists of a

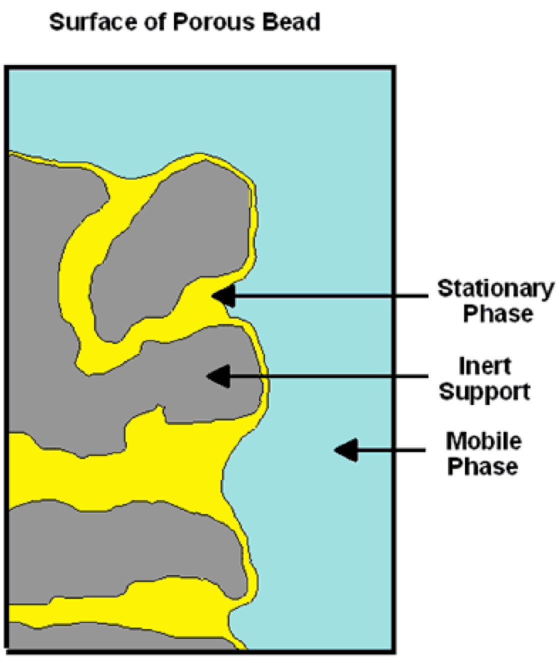


Fig. 8. Set-up of an extraction chromatographic resin particle [65]

liquid extractant immobilized on a porous, inert support resin bead (**Fig. 8.**) [65]. Different particle sizes of the resins, ranging from 20 μm to 150 μm have been studied and developed for various applications. Liquid materials, either single compounds or mixtures, are used as the extractants, and diluents can also be used to help solubilize the extractant and to increase the hydrophobicity. The selectivity of the resin, and by this means the possible applications, are determined by the type of the extractant. The most important resins, their main characteristics with the most frequently measured analytes are summarized in **Table 5.**

Table 5. The most important EXC resins, their main characteristics and applications

Resin name	Extractant	Diluent	Typical applications	Ref.
TEVA^{TM} Resin	Aliphatic quaternary amine	-	Pu, Tc, Np, Th, Am/lanthanide separations	[60,64]
TRU^{TM} Resin	Octylphenyl-N,N-di-isobutyl-carbamoyl methyl phosphine oxide	TBP	Pu, Am, Cm, Fe	[60,64]
UTEVA^{TM} Resin	Diamyl-amylphosphonate	-	U, Th, Pu, Np	[64]
Ln Resin^{TM}	di(2-ethylhexyl)-orthophosphoric acid	-	Lanthanides, Ra-228	[66,67]
Sr Resin^{TM}	4,4'(5')-di-t-butylcyclo-hexano-18-crown-6	1-octanol	Sr, Pb, Ra, Pu	[68-71]

Extraction chromatographic resins can be used either in batch mode or in column arrangement. The liquid phase (which is the mobile phase in case of column separations) is usually an acid solution, e.g., nitric or hydrochloric acid, although complexants, such as oxalic or hydrofluoric acids, are frequently used to enhance selectivity or for the stripping of strongly retained metal ions from the resin. Great advantage of extraction chromatography, beside the high affinity for the analytes of interest and selectivity, that the retention of the analyte can be altered by simply changing the liquid phase (e.g. using HNO_3 instead of HCl) or by the variation of acid concentration. This is especially useful for column separations, as different ions can be sequentially stripped from the column with different eluents. For example, the acid dependency curves of TEVA^{TM} resin for the actinides and technetium in nitric and hydrochloric acids are shown in **Fig. 9.** Tetravalent plutonium, neptunium and thorium show maximum uptake in the region of 2 to 4 M nitric acid. In this acid concentration range, hexavalent uranium and trivalent americium are not well retained, and as such, the resin can readily separate the tetravalents from the other actinides. Other common cations (e.g. Fe, Al, alkali and alkali earth metals) do not retain. These characteristics have been exploited for trace-level plutonium separations, which made TEVA^{TM} the most widely used extraction chromatographic resin for plutonium separations. Though the active component of TEVA^{TM} resin is identical to that of strong anion exchange resins, as the functional groups are in a liquid form rather than fixed to a polymer backbone (as with A-IEX resins), these groups have greater flexibility to coordinate around target anions. This means that the uptake of these ions is generally higher and often at lower acid concentrations. Another important advantage of TEVA^{TM} over most of the EXC resins (e.g. TRU^{TM} or UTEVA^{TM}) that U(VI), which is the main interference in plutonium measurements by ICP-MS, has significantly different affinity for the resin (about three orders of magnitude lower in HNO_3), thus better U/Pu separation can be achieved.

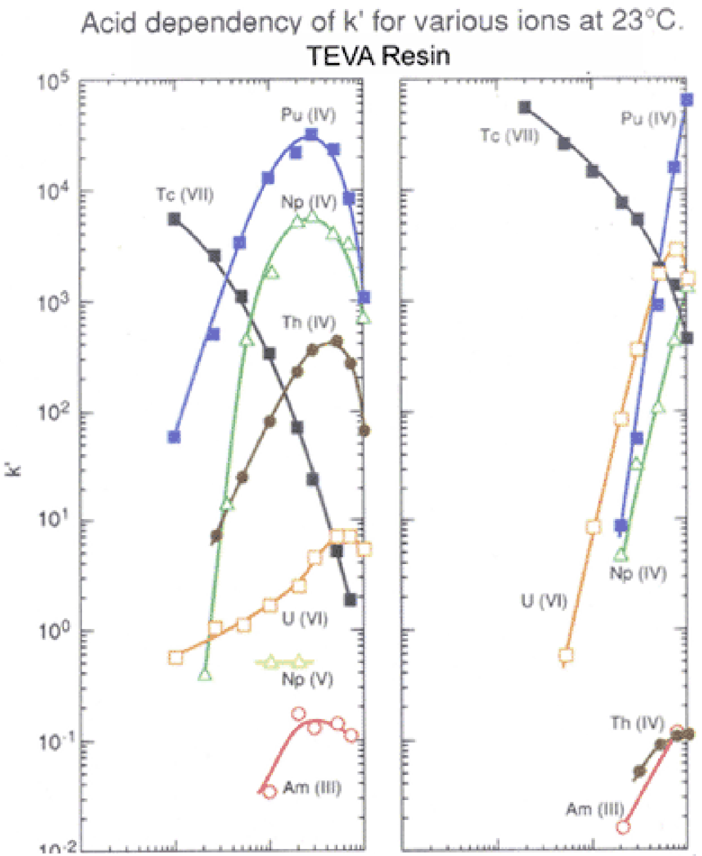


Fig. 9. Acid dependency curves of TEVA^{TM} for the actinides and technetium in nitric and hydrochloric acids [65]

For plutonium separations, several extraction chromatographic methods have been successfully applied. TEVA^{TM}, TRU^{TM}, Sr Resin^{TM} (previously marketed as Sr.Spec^{TM}) and UTEVA^{TM} resins have been reported for plutonium measurements in the literature. Various separation methods applying EXC for plutonium measurements with references are collected in **Table 6.**

Table 6. Typical separation methods applying extraction chromatography for low-level plutonium measurements

Sample type	EXC resin	Oxidation state adjustment	Separation scheme	Ref.
Nuclear waste solution	TEVA™	$NaNO_2$	Load: 3 M HNO_3 Wash: 3 M HNO_3, 4 M HCl Elution: 0.1 M $(NH_4)HC_2O_4$	[64]
Soil and sediment	TEVA™	$NaNO_2$ $(NH_2OH.HCl)$	Load: 2 M HNO_3 Wash: 2 M HNO_3, 9 M HCl Elution: 0.1 M H_2Q/9 M HCl	[72]
Soil and sediment	TEVA™, UTEVA™/TRU™	$NaNO_2$ Fe(II)/AA	Load: 3 M HNO_3 Wash: 3 M HNO_3, 9 M HCl Elution: 0.1% HEDPA	[48]
Sediment	TEVA™	$NaNO_2$	Load: 2 M HNO_3 Wash: 2 M HNO_3, 8 M HCl Elution: 0.05 M $(NH_4)_2C_2O_4$	[18]
Sediment	TEVA™	Fe(II)/$NaNO_2$	Load: 3 N HNO_3 Wash: 3 M HNO_3, 8-9 M HCl Elution: 0.02 N HNO_3/0.02 M HF	[52]
Urine	TEVA™	$NaNO_2$	Load: 3 M HNO_3 Wash: 3 M HNO_3 Elution: 0.05 N HNO_3/0.05 M HF	[73]
Soil and sediment	Sr.Spec™, TEVA™	$NaNO_2$	Load: 4 M HNO_3 Wash: 4 M HNO_3 Elution: 0.8 M HNO_3/2 M HCl	[74]
Sediment and seawater	TRU™	Fe(II)/$NaNO_2$	Load: 2.5 M HNO_3 Wash: 2.5 M HNO_3, 4 and 9 M HCl Elution: 0.1 M H_2Q/4 M HCl	[53]
Urine	UTEVA™/TRU™	Fe(II)/AA	Load: 3 M HNO_3 Wash: 3 M HNO_3, 2 M HNO_3/0.1M $NaNO_2$/4 M HCl Elution: 0.1 M $(NH_4)_2C_2O_4$	[75]
Soil and sediment	TEVA™	$NaNO_2$	Load: 3 M HNO_3 Wash: 2 M HNO_3 Elution: 0.02 N HNO_3/0.02 M HF	[60]

Abbreviations: H_2Q: hydroquinone, AA: ascorbic acid

Recently, extraction chromatography is more widely used for both radioanalytical and mass spectrometric plutonium analysis than A-IEX separation, due to the rapidity, better selectivity and lower chemical consumption. Another advantage of the lower chemical consumption in case of mass spectrometric methods is that the final fraction obtained contains much less stable element contaminants, such as Pb or Hg. However, there are several drawbacks of EXC. Firstly, it is still a relatively expensive technique compared to A-IEX in spite of the lower chemical consumption. Secondly, as the volume of the column is relatively low (typically 1-3 mL), the loading solution and the total dissolved solid (TDS) content should be as low as possible in order to avoid breakthrough of the analyte and low recoveries. That is why in case of complicated matrices (e.g. soil, sediment or samples with high TDS), another separation and/or pre-concentration of the analyte prior to the extraction chromatographic separations are required. In those methods, which apply EXC separation directly after leaching or total dissolution of the samples, the sample weight was lower than 3 grams in case of soil or sediment samples [18,53,60,74]. Otherwise, previous purification of the analyte by means of co-precipitation, LLE or A-IEX is necessary, which significantly increases analysis time. In such cases, though EXC significantly simplified the procedure, the time required for the sample preparation and the complexity of the analysis are determined not by the extraction chromatographic separation, but the preliminary steps.

The summary of the different purification steps applied for low-level plutonium analysis together with their advantages and disadvantages are summarized in **Table 7.**

Table 7. Overview of the different purification steps of low-level plutonium analysis

Chemical separation	Advantages	Disadvantages
Co-precipitation	▪ Can be highly selective and quantitative ▪ High pre-concentration is possible ▪ Can be easily carried out ▪ Cheap method	▪ Can be time consuming ▪ Further treatment (e.g. filtering) is required ▪ Selectivity poor in most cases ▪ Large amount of carrier might interfere in the next steps
Liquid-liquid extraction	▪ Can be highly selective and quantitative ▪ Robust ▪ Relatively cheap method ▪ Several parameters can be modified (e.g. by adding complexants)	▪ Can be time consuming ▪ Tedious ▪ Several repetitions are necessary to achieve high recovery ▪ Uses large amount of organic solvents
Anion exchange chromatography	▪ Can be highly selective and quantitative ▪ Ease of use ▪ Relatively robust ▪ Relatively cheap method ▪ Several parameters can be modified (e.g. by adding complexants)	▪ Can be time consuming ▪ Requires high amount of acids ▪ Tedious ▪ The final fraction usually contains high amount of stable contaminants (e.g. Pb)
Extraction chromatography	▪ Can be highly selective and quantitative ▪ Low chemical consumption ▪ Rapid and easy ▪ Pure Pu fraction can be obtained ▪ Several parameters can be modified (e.g. by adding complexants)	▪ Relatively expensive ▪ Robustness is limited ▪ Limited sample amount and samples with low TDS can be effectively used

To conclude, it can be stated that lots of methods have been described in the literature for the low-level plutonium separation from environmental matrices. As a matter of fact, each method has their advantages and drawbacks, thus selection of the most appropriate technique still depends on the data quality objectives and the possibilities of the analyst. In general, for complicated samples (e.g. soil and sediment samples) with truly low plutonium content, the sample preparation methods reported are still quite tedious and labor-intensive in spite of the implementation of extraction chromatography. For low-level plutonium samples, several purification steps are required to obtain pure Pu fraction. It also implies that method will be lengthy or tedious. Thus, the role of the preliminary pre-concentration steps is also as important as the final purification. Therefore, in order to develop a suitable, easy and simple method for plutonium analysis, not only the optimization of each step is necessary, but also these steps have to fit to one another.

3.2.2. Sample Preparation Methods for Low-level Americium-241 Measurements

^{241}Am can be detected and quantified either by destructive (e.g. alpha spectrometry) or non-destructive methods (e.g. gamma spectroscopy) in environmental samples. Therefore, the sample preparation method depends basically on the measurement mode. In case of gamma spectrometry this is significantly easier, as it is a non-destructive method, thus the measurement is carried out on the dried, homogenized sample without chemical treatment. In contrast, the sample preparation methods required for alpha spectrometric or mass spectrometric analysis are much more complicated, as pure americium fraction is necessary for the measurement. The chemical sample preparation procedure must therefore be capable of isolating americium from all other species present in macro quantities and from the trace-level interferences. It is also noteworthy that Cm isotopes can also be separated together with ^{241}Am, as their chemical properties are so similar that in most sample preparation schemes they behave in the same way. The methodologies used for americium sample preparation for destructive analyses (recently reviewed by Warwick *et al.* [76]) are similar to those of plutonium. The analyte is initially solubilized by a series of acid treatments (e.g. by HNO_3, HCl, HF mixtures depending on matrix) after the addition of ^{243}Am isotopic tracer. ^{241}Am is purified through co-precipitation (using iron hydroxide or calcium oxalate) or liquid-liquid extraction [76]. Thereafter, the final purification of the sample is achieved by a series of liquid-liquid extraction, anion exchange separation or extraction chromatographic steps. These procedures are usually more tedious than those of plutonium, as the analyte, Am(III) is relatively similar chemically to several matrix components, such as Fe(III), Bi(III) and the lanthanides, thus the removal of all these components requires several, well-designed steps.

For the rough removal of matrix components co-precipitation is the primary method. Ferric hydroxide [34,77], manganese dioxide [77], calcium oxalate [34,54,76,77] and lanthanum fluoride [34] are applied most frequently for this purpose. CaC_2O_4 has the advantage that the removal of the carrier is relatively simple, while Fe(III) and La(III) elimination can be cumbrous due to the similar chemical behaviour to Am(III). After the preliminary purification and pre-concentration of americium, the analyte is purified by liquid-liquid extraction, anion exchange chromatographic and extraction chromatographic steps. Usually several subsequent separations are necessary, as removal of (1) matrix components, (2) interfering radionuclides (e.g. ^{210}Po, ^{238}Pu) and (3) lanthanides that may cause broadening of the alpha peaks due to self-absorption is required to obtain accurate results. For liquid-liquid extraction, several organic extractants, such as TBP [34], TOPO [60], HDEHP [62,76,78] or DDCP (dibutyl-N,N-diethylcarbamoylphosphonate) [54,76] have been applied for the separation of americium. Cation exchange (C-IEX) separation is rarely used for americium separation as numerous other elements, especially lanthanides co-elute with Am, and for this reason C-IEX tends to be used more for pre-concentration than for its separation from the interfering elements [76]. As Am(III) forms stable anionic complexes (e.g. with SCN^-) in methanol-nitric acid system, A-IEX was found to be a successful final purification stage for ^{241}Am separation from lanthanides, and this system has been used in a number of separation schemes [54,76]. Various ratios of acid to alcohol have been applied for Am separation. For example, according to the standard method at IAEA Marine Environment Laboratory, Lee *et al.* used 1 M HNO_3/93% CH_3OH as a loading solution. Lighter lanthanides are removed by 0.1 M HCl/80% CH_3OH/0.5 M NH_4SCN, followed by the elution of ^{241}Am with 1.5 M HCl/86% CH_3OH [54]. It is noteworthy that for some environmental samples an apparent over 100% chemical recovery was found in case of alpha spectrometric measurements due to the interference of ^{210}Po (E_α = 5304 keV) on the ^{243}Am tracer peak (E_α = 5349 keV). Therefore, an additional ^{210}Po/Am separation step is necessary, e.g. by means of A-IEX separation in hydrochloric medium.

Similarly to plutonium, extraction chromatography offers a relatively easy and rapid option for americium separation substituting for LLE or A-IEX methods. Various procedures have been published for the isolation of americium using extraction chromatography despite that few resins (e.g. TRU^{TM} or DGA^{TM}) have significant affinity for Am(III) [76]. In most cases, TRU^{TM} resin was applied for americium separation, which has relatively high affinity to Am in the 1 to 4 M concentration range of HNO_3 [54,64,76]. In order to replace the standard Am/lanthanide separation in methanol/nitric acid medium, TEVA^{TM} resin was found to be an alternative, and the Am/Ln separation was accomplished using NH_4SCN/formic acid as a load solution [64].

Typical sample preparation methods for environmental, low-level americium-241 measurements with references are collected in **Table 8.**

Table 8. Typical sample preparation methods for environmental, low-level americium-241 measurements

Sample type	Pre-concentration	Purification	Ref.
Sediment, biota	CaC_2O_4	▪ TRU^{TM} for Am purification A-IEX separation (Am/Ln) using CH_3OH	[54]
Sediment	CaC_2O_4, $Fe(OH)_3$	▪ A-IEX for Pu separation ▪ A-IEX/C-IEX separation for the removal of main matrix components ▪ TRU^{TM} for Am purification ▪ Am/Ln separation by A-IEX in CH_3OH medium	[79]
Soil	LLE separation using TOPO	▪ TRU^{TM} for Am purification ▪ TEVA^{TM} for Am/Ln separation	[60]
Moss	Ashing	▪ EXC separation using self-prepared TNOA/Icorene resin ▪ EXC separation using self-prepared HDEHP/Icorene resin	[80]
Nuclear waste		▪ TRU^{TM} for Am purification	[81]
Lichen and peat samples	CaC_2O_4, $Fe(OH)_3$	▪ A-IEX for Pu separation ▪ TRU^{TM} for Am purification ▪ TEVA^{TM} for Am/Ln separation	[82]
Soil	LLE separation using TOPO	▪ TRU^{TM} for Am purification ▪ TEVA^{TM} for Am/Ln separation	[83]

Abbreviation: TNOA: tri-n-octylamine

To conclude, it can be stated that sample preparation methods for low-level ^{241}Am analysis are the most tedious and labor-intensive procedures routinely carried out in radioanalytical laboratories. Though the widespread use of EXC resins, especially

TRU^{TM}, significantly simplified these methods substituting for the LLE separations, because of the lack of an available EXC resin, which is selective for americium over the matrix components, actinides and lanthanides, several purification steps are required. Therefore, development of sample preparation methods for low-level ^{241}Am analysis is still a challenging field in analytical chemistry.

3.2.3. Sample Preparation Methods for the Measurement of Minor Long-lived Radionuclides from Nuclear Materials

In case of the determination of minor long-lived radionuclides (e.g. ^{236}U, Pu-isotopes or ^{241}Am) from nuclear materials (e.g. uranium or plutonium oxide, ore) the task is to detect and quantify the analyte in the presence of high amount of uranium or plutonium. The selection of the appropriate sample preparation methods applied for the determination of minor long-lived components from the nuclear materials usually depends mainly on analyte of interest and the measurement technique, since the matrices are relatively analogous. In the literature relatively few radioanalytical methods have been reported for such measurements, possibly due to the limited number of laboratories working in this field and the special conditions required for the handling of radioactive and nuclear materials. The sample preparation techniques used are similar to the previously described procedures, however, with the main difference that the matrix is relatively simple (high amount of uranium or plutonium), which has to be eliminated from the long-lived measurand. At first sight it seems to be an easier task than in case of, for example, environmental samples, when several matrices and interferences can occur. However, for the analysis of nuclear materials a very high decontamination factor (defined as the weight of the analyte of interest before the sample preparation in the sample and thereafter in the measured fraction) from uranium or plutonium, approximately 10^6 –10^{12}, has to be achieved so that the matrix can not interfere with the measurement. Moreover, care has to be taken to protect the laboratory and the instrument from contamination. In some cases it is either not necessary or possible to separate the analyte from the matrix chemically. For example, using a non-destructive technique (such as gamma spectrometry) for the measurement, or in those cases, when a minor isotope of the matrix should be measured (e.g. the measurement of ^{236}U in uranium materials), which can not be carried out without isotopic enrichment. In such cases, simple pre-treatment of the material (e.g. homogenization, drying or dissolution) can be sufficient as a sample preparation.

If the long-lived analyte of interest is present in the sample in trace-level, destructive sample preparation could be necessary to decrease background and improve detection limit. The main application fields of these analyses are the process control of trace constituents in the course of nuclear fuel production and for nuclear forensic investigations. The most frequently investigated sample types are ores, semi-finished products, uranium oxides, plutonium oxides, the mixture of UO_2 and PuO_2 (MOX), spent UO_2 fuel or found, confiscated illicit materials. As the matrix is more or less the similar in each case (solid uranium or plutonium containing matrix or liquid samples with excess U or Pu), the procedure has to be designed and optimized rather for the analyte. The sample preparation methods are similar to the above-mentioned low-level Pu and Am methods and can also be used for the determination of stable elements from nuclear materials. Several separation methods have been developed to separate and purify the analyte for measurements, such as co-precipitation with a suitable carrier, liquid-liquid extraction and ion exchange chromatography. For example, A-IEX separations have been applied for the separation of trace-level plutonium and ^{99}Tc from uranium oxide matrix [84], for the separation of ^{230}Th progeny from a highly-enriched uranium sample for age measurement [85] or for the separation of uranium from plutonium materials for the determination of production date [86]. However, as anion exchange separation generates relatively high amount of radioactive waste (e.g. eluents, wash solutions), extraction chromatographic separation tends to be favourable. EXC methods have been developed for the separation of Pu isotopes, ^{237}Np and ^{241}Am from depleted uranium ammunitions [45,87,88], for the separation of ^{230}Th or ^{231}Pa progenies from a highly-enriched uranium matrices for age measurement [89,90] or for the separation of uranium from solid plutonium materials for the determination of production date [86]. For instance, Morgenstern *et al.* developed a rapid, single-column extraction chromatographic method using UTEVA^{TM} resin for the separation of uranium, plutonium, neptunium and americium from nuclear materials [91], while Desideri *et al.* reported a sequential procedure, which is applicable for the simultaneous separation of Pu and ^{241}Am by self-prepared EXC resin from depleted uranium oxide materials [45]. Plutonium in nuclear materials could be used to assess the possible origin by Wallenius *et al.* on the basis of its isotopic composition [92]. As plutonium isotope ratios in spent nuclear fuel depend on the neutron energy spectrum and the irradiation time in the reactor, which is in turn, influenced by the reactor type and irradiation conditions, from the isotopic ratios the source and provenance can be traced back using reactor-production codes (e.g. ORIGEN2 or SCALE) [92].

To conclude, the sample preparation methods developed for the determination of minor long-lived components in nuclear materials are relatively easier compared to environmental analysis due to the rather simple, well-defined matrices. However, as very high decontamination factor has to be achieved in order to prepare a pure fraction for the measurement, several purification steps are necessary. Moreover, it is important to keep the amount of the reagents and chemicals used as low as possible, because they are converted into radioactive waste. Similarly, the sample amount submitted to analysis should also be minimized, which is even more essential in the case of nuclear forensic samples.

3.3. Radioanalytical Methods for the Determination of the Investigated Radionuclides

3.3.1. Determination of Trace-level Plutonium by Radioanalytical Methods

As plutonium is present in environmental samples in trace-level, determination of its concentration and isotopic composition requires highly sensitive techniques. The most widely used method for the determination of plutonium isotopes decaying by emitting an alpha particle (^{238}Pu, ^{239}Pu, ^{240}Pu and ^{242}Pu), is alpha spectrometry [93]. This technique requires the preparation of pure and thin sources for counting, as even small amounts of other materials would attenuate the alpha particles and degrade the alpha spectrum. Thus, the purified plutonium fraction prepared by the previously described sample preparation methods should be homogeneously dispersed on a flat holder before the alpha spectrometric measurement. Several alpha source preparation techniques have been described, such as direct evaporation [35], electrodeposition [35,94] or micro co-precipitation [95]. For routine applications in environmental analyses, the latter two methods are applied most frequently due to their rapidity and appropriate spectral resolution. Interfering radionuclides with similar alpha energies (e.g. ^{224}Ra, ^{228}Th and ^{241}Am for ^{238}Pu; ^{210}Po, ^{231}Pa and ^{243}Am for ^{239}Pu and ^{240}Pu) have to be separated in the course of sample preparation.

Various radiochemical tracers can be applied for the plutonium concentration measurement by isotope dilution in alpha spectrometry: ^{242}Pu is used most often, as its concentration in environmental samples is negligible and its maximal alpha energy (E_α

= 4902 keV) is lower than those of the measurand ^{238}Pu, ^{239}Pu and ^{240}Pu, thus the peak-tailing of the tracer does not affect the analyte peaks. However, for special applications, ^{236}Pu ($T_{1/2}$ = 2.86 years) or ^{244}Pu ($T_{1/2}$ = 7.6 × 10^7 years) can be used as isotopic tracers. The alpha spectrometric sources prepared are counted by a semiconductor alpha detector attached to an alpha spectrometer. The main types of semiconductor detectors are the silicon surface barrier (SSB) and passivated implanted planar silicon (PIPS) detectors. The counting time used for the analysis depends on the activity of the analyte (or tracer) and the precision required. Counting time is typically in the range of few hours to some weeks. The absolute detection limit of alpha spectrometry for the plutonium isotopes is approximately 0.02 – 0.1 mBq depending on counting time. A limitation of this technique is that usually only the sum of ^{239}Pu and ^{240}Pu activity can be determined due to similar alpha energies (5157 and 5168 keV, respectively), thus the ^{240}Pu/^{239}Pu isotope ratio, which could also be characteristic of the origin is mislaid. A typical plutonium alpha spectrum of an Irish Sea sediment sample is shown in **Fig. 10.**

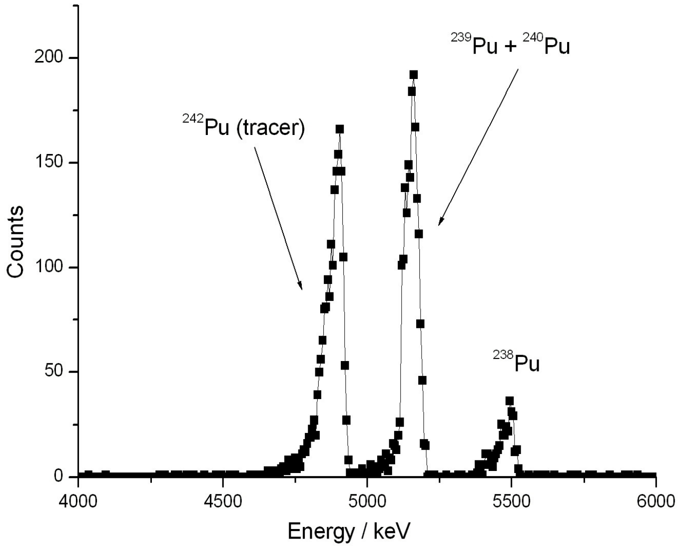


Fig. 10. A typical plutonium alpha spectrum of an Irish Sea sediment sample

The activity concentrations of the measurand plutonium isotopes are calculated according to the isotope dilution method.

The measurement of ^{241}Pu, which is a pure beta emitter with a maximum energy of 20.8 keV, is usually carried out by liquid scintillation counting (LSC). In this technique, the plutonium fraction obtained by the sample preparation or the alpha spectrometric source itself is directly placed in a vial (made of low-diffusion polyethylene or glass with low potassium content), mixed with the scintillation cocktail and counted in the LSC instrument. As the count rate measured by the LSC instrument is affected by a number of factors, such as the colour of the sample, chemical constituents and slight variations in the liquid scintillation cocktails, the activity concentration of ^{241}Pu can be obtained after calibration (i.e. using quench curves). The absolute detection limit of the method depends on several parameters (e.g. counting time, background, which highly depends on the instrument applied and measurement circumstances, scintillation cocktail type, etc.), but it ranges typically from 40 to 100 mBq. Another possibility for the determination of ^{241}Pu concentration is the measurement via its progeny, ^{241}Am [96]. After the separation of the pure plutonium fraction, the ^{241}Am is continuously formed by the decay of ^{241}Pu. Therefore, after a sufficiently long in-growth time, by the known elapsed time between the two chemical Am/Pu separations and the measured ^{241}Am concentration, the ^{241}Pu concentration can be calculated.

Other radiochemical measurement techniques, such as fission track analysis (FTA) or photon electron rejecting alpha liquid scintillation (PERALS$^{®}$) are less frequently used for Pu determination. FTA technique, despite its excellent detection capability (absolute detection limit is in the µBq level) has not gained a widespread use due to the high analytical costs, the necessity to use a nuclear reactor and the low sample throughput. In spite of these drawbacks, some research groups developed FTA methods for low-level Pu analysis. For example, a research group in Brookhaven National Laboratory established an FTA method for ^{239}Pu measurement from urine sample with a detection limit of 3 µBq [97]. Beside these special applications, FTA is rather used as a routine technique for the investigation and localization of (also Pu containing) hot particles [98,99].

PERALS$^{®}$, which is the acronym of photon electron rejecting alpha liquid scintillation (registered by Ordela Inc.) is a relatively new method that combines a chemical separation by liquid-liquid extraction and the measurement of alpha activity in a water-immiscible scintillator [100]. This technique rejects up to 99.9% of beta-gamma background and was reported to lower the detection limit by a factor of 2-10 in comparison with the classical alpha spectrometry. On the other side, the poor energy resolution of 250-300 keV requires selective sample preparation [60,100]. For example, Ayranov *et al.* reported a method for plutonium measurement from soil matrix with an absolute detection limit of 28 mBq for $^{239+240}$Pu. However, as this technique is also based on the detection of alpha radiation similarly to alpha spectrometry, the ^{239}Pu and

^{240}Pu signals can not be resolved and are detected as a sum (i.e. $^{239+240}$Pu), thus the ^{240}Pu/^{239}Pu isotope ratio can not be obtained.

The main characteristics of various radiochemical measurement techniques for low-level plutonium measurement are summarized in **Table 9.**

Table 9. The main characteristics of radiochemical measurement techniques for low-level plutonium measurement

Measurement technique	Measurable plutonium isotopes	Advantages	Disadvantages
Alpha spectrometry	Isotopes with alpha decay, e.g. ^{238}Pu, ^{239}Pu, ^{240}Pu	▪ Routine method ▪ Cheap and simple instrumentation ▪ Sensitive	▪ ^{239}Pu+^{240}Pu peak can not be routinely resolved ▪ Resolution is sensitive to source preparation
Liquid scintillation counting	Isotopes with beta decay, e.g. ^{241}Pu	▪ Routine method ▪ Relatively cheap and simple instrumentation	▪ Sensitive to background ▪ Calibration can be problematic
PERALS®	Isotopes with alpha decay, e.g. ^{238}Pu, ^{239}Pu, ^{240}Pu	▪ Sensitive	▪ ^{239}Pu+^{240}Pu peak can not be routinely resolved ▪ Resolution is sensitive to source preparation ▪ Expensive instrumentation
Fission track analysis	Fissionable isotopes, e.g. ^{239}Pu	▪ Sensitive	▪ Expensive instrumentation ▪ Tedious sample preparation ▪ Need for a nuclear reactor

Radioanalytical methods are routinely used worldwide for environmental plutonium analysis due to their cheap instrumentation and ease of use. However, these techniques have several drawbacks. Firstly, as the half-lives of the most important plutonium isotopes, ^{239}Pu and ^{240}Pu are relatively long (24110 and 6537 years, respectively), these techniques are not sensitive enough for the measurement of very low activities. For instance, 10 µBq is equivalent to approximately 315 disintegrations per year, therefore either high pre-concentration of the sample or long counting time is necessary to obtain precise results. For most low-level plutonium determinations, the typical measurement time lasts from days to even several weeks. Secondly, the measurement of some important isotope ratios is not possible (e.g. ^{240}Pu/^{239}Pu by alpha spectrometry), and several different techniques are required for the measurement of each significant isotope ratio (^{238}Pu/^{239}Pu, ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) due to the different decay modes.

3.3.2. Determination of Americium-241 by Radioanalytical Methods

The measurement techniques used for ^{241}Am determination are similar to those for the measurement of plutonium isotopes decaying by emitting an alpha particle. However, in case of higher activity samples (in the Bq g^{-1} level) gamma spectrometry can also be applied by the measurement of low-energy gamma-emission of ^{241}Am decay (59.5 keV, 36% abundance) [101]. However, care must be taken to properly correct for the attenuation of gamma-photon in order to obtain accurate results. For low-level environmental samples the primary technique is alpha spectrometry using ^{243}Am as an isotopic tracer. Some groups found that for source preparation electrodeposition is favourable over micro co-precipitation due to the better spectral resolution [54]. Though the energy difference of 196 keV between ^{241}Am(analyte) and ^{243}Am(tracer) is not significantly different from that of the plutonium (the energy difference between ^{239}Pu(analyte) and ^{242}Pu(tracer) of 255 keV), as lanthanides can not be completely removed from the americium fraction, it results in the broadening of the alpha peaks. It is also noteworthy that generally curium can also be measured by alpha spectrometry simultaneously with ^{241}Am. A typical americium alpha spectrum of a Hungarian moss sample is shown in **Fig. 11.**

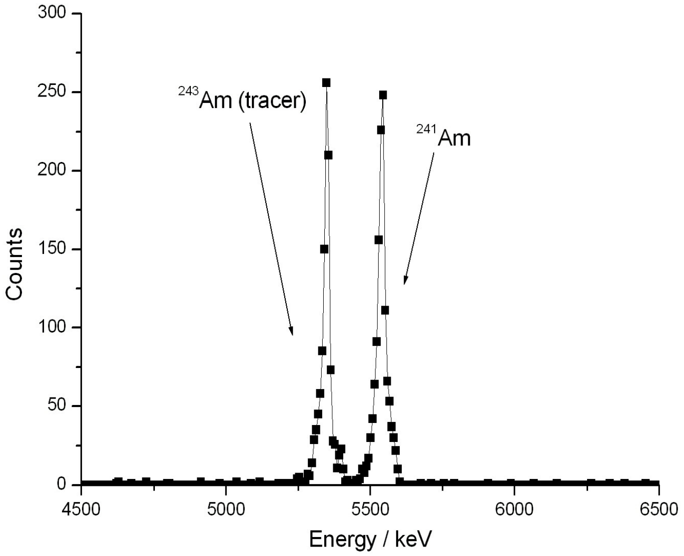


Fig. 11. A typical americium alpha spectrum of a Hungarian moss sample

PERALS® has also been applied for low-level ^{241}Am measurements with comparable detection limits to alpha spectrometry [60,102]. However, the need for a selective sample preparation and its worse resolution than alpha spectrometry encumber the widespread use for routine applications.

The disadvantages of ^{241}Am measurement by radioanalytical methods are similar to those of plutonium. Firstly, selective, tedious sample preparation is required to obtain accurate results. Moreover, for most environmental samples long counting time is necessary to decrease the detection limit, which reduces the sample throughput.

3.3.3. Radioanalytical Measurement of Minor Long-lived Radionuclides from Nuclear Materials

The radioanalytical measurement techniques used for the determination of minor long-lived radionuclides in nuclear materials (e.g. uranium or plutonium oxide materials) can be divided into two groups: non-destructive techniques, such as gamma spectrometry, and destructive methods, such as alpha spectrometry. In the literature relatively few radioanalytical techniques, especially destructive methods, have been applied for such measurements. The most frequently investigated long-lived radionuclides are the activation and fission products, which give information on previous irradiation conditions or reprocessing, and the progenies, which are used for the production date (*age*) determination of the nuclear material (**Table 3.**).

Out of the non-destructive methods, gamma spectrometry is the most commonly applied technique for the measurement of activation and fission products. However, in most cases gamma spectrometry is used only for the first screening and categorization of the nuclear material [103]. This allows the determination of the rough isotopic composition and hazardness of the material as well as possibly the intended use. Some long-lived radionuclides, such as ^{241}Am can also be measured in nuclear materials by high resolution gamma spectrometry (HRGS), however, the detection limit is inferior to that of the destructive methods due to the high background and the low-energy gamma-emission of ^{241}Am decay (59.5 keV). For example, Wallenius *et al.* used HRGS for the direct measurement of ^{241}Pu/^{241}Am ratio for age determination [86]. For more precise results and lower detection limits, use of the destructive radioanalytical techniques, such as alpha spectrometry is necessary. The instruments and measurement conditions are not different from those used for low-level environmental analysis (**Chapter 3.3.1.**). Alpha spectrometry has been used for the measurement of trace-level ^{236}U, plutonium and ^{241}Am from uranium oxide matrix (nuclear fuel or penetrator sample) [45,84,88], determination of ^{230}Th or ^{231}Pa progenies from a highly-enriched uranium sample for age measurement [40,85,90] or for the measurement of uranium fraction separated from plutonium materials for the determination of production date [86]. The alpha spectrometric methods developed are relatively simple and can be easily carried out. However, the detection capabilities of the technique highly depend on the sample preparation and the sample amount available. Moreover, as the measurement uncertainty is limited by the counting precision (typically 1 – 10% relative standard deviation) alpha spectrometry is less applicable to perform highly precise analysis, which is necessary, for example, for age determination. Though it is routinely used for production date measurement in nuclear forensic laboratories (e.g. in JRC Institute of Transuranium Elements), the age data obtained are less precise than those measured by the mass spectrometric techniques. For instance, according to Wallenius *et al.*, the combined uncertainty of production date results are with a factor of approximately 2 higher than that of TIMS [89], which can raise difficulties for provenance assignation of illicit materials. Other destructive radioanalytical methods, using such as proportional counter or LSC are rarely used. For instance, the concentration of ^{90}Sr is regularly measured in depleted uranium prior to final disposal at Savannah River Side by proportional counter after ion-exchange separation, while the concentration of ^{99}Tc is monitored by an LSC measurement following the EXC separation with TEVA^{TM} resin [84]. The measurement of ^{241}Pu, which is commonly done by LSC from environmental samples, in case of nuclear samples is usually carried out by mass spectrometric techniques or HRGS analysis via the ^{241}Am progeny [92,103] due to the better detection limits or easier sample preparation.

3.4. Mass Spectrometric Measurements of the Investigated Radionuclides

3.4.1. Determination of Trace-level Plutonium by Mass Spectrometry

During the last decade, the instrumental progress in mass spectrometry for the determination of long-lived radionuclides resulted in its expansive use in radioanalytical chemistry. Though the routine use of mass spectrometry in nuclear sciences is still relatively rare, the instrumental and methodological improvements as well as the wider accessibility to high sensitivity mass spectrometers made this technique a complementary technique to the conventionally applied radiometric methods for radionuclide measurements [104]. This is particularly true for the measurement of plutonium, which is the most frequently investigated anthropogenic radionuclide by mass spectrometric methods.

Several mass spectrometers with different ionization mode and analyzers have been applied for the measurement of plutonium. Traditionally, thermal ionization mass spectrometry (TIMS) was the primary tool for the concentration and isotopic composition measurement of long-lived radionuclides, including plutonium. In TIMS analysis, a small volume (down to 1 μl) of aqueous solution containing the analyte in the nanogram to microgram range is deposited on a cleaned filament surface (mostly high-purity Re), evaporated to dryness and ionized thermally thereafter by heating the filament. Due to the low initial energies (0.1 – 0.2 eV) of the ions formed on the hot thermal surface, mostly single magnetic sector-field mass spectrometers are used for ion separation. In TIMS, the limiting factors for the accuracy of measured isotopic ratios are mass discrimination of the instrument (also called mass bias, caused by the difference in ion transmission of the mass spectrometer depending on the mass-to-charge ratio) and the mass fractionation effects (arise during the evaporation of sample, when the measured isotope ratio changes with time). These effects can be corrected for by different internal calibration techniques or by using isotopic standard reference materials with well-known isotopic ratios. Thermal ionization mass spectrometry allows the determination of isotope ratios with a precision better than 0.01%, however, with a multiple ion collector system the most precise isotope ratios even down to 0.001% can be achieved. Thus, TIMS is mainly used for precise isotope ratio measurements, for instance, in the field of dating measurements (geochronology), food authentication or in nuclear sciences. Several TIMS methods have been developed for the determination of trace-level plutonium. For instance, Elliot *et al.* reported a procedure for the plutonium analysis of urine samples [49]. The absolute detection limit achieved was 0.53 fg. Kelley *et al.* used TIMS measurements for the calculation of global inventory of plutonium isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu) in the environment by the analysis of archived soil samples collected in the 1970s from 54 locations around the world [32]. By the accurate sample preparation and keeping the instrumental background near the detector noise level of 0.08 counts per second, an approximate detection limit of 10^4 atoms could be achieved [105]. Besides its excellent capabilities, TIMS has several disadvantages. Time consuming and tedious sample preparation is required to obtain a very pure, low-volume sample aliquot for the measurement, which has to be completely free from impurities. Moreover, TIMS lacks the multielemental capability (only one element can be measured at the same time) and is restricted to elements with ionization potential lower than 6 eV. Moreover, the use and maintenance of the instrument is complex and difficult. Therefore, in recent years this technique is being replaced by sensitive, multielemental ICP-MS techniques.

Glow discharge mass spectrometry (GDMS) was established as a powerful and efficient analytical method for the direct trace element and depth profile analysis of solids. In GDMS, an argon gas glow discharge at a pressure of 0.1 – 10 Torr is used as an ion source. The cathode surface consisting of the sample material is sputtered by Ar^+ ions, which are formed in low-pressure argon plasma and accelerated towards the cathode. Sputtered neutral particles of the sample are ionized in the glow discharge plasma (negative glow) by Penning and/or electron impact ionization and charge exchange processes. This instrument is mainly used for the determination of trace elements in electrically conducting materials with detection limits from the ng g^{-1} to µg g^{-1} concentration range. For the long-lived radionuclide analysis from environmental samples, Betti *et al.* reviewed the possibilities and limitations of GDMS for the determination of some radioisotopes (caesium, strontium, plutonium, uranium and thorium) in soil, sediment and vegetation samples. Detection limits were approximately in the pg g^{-1} level [106]. The same research group developed a GDMS method for the measurement of ^{237}Np concentration in highly contaminated Irish Sea sediment samples with direct current GDMS with a detection limit of 80 pg g^{-1}. The ^{237}Np concentrations in the sediment samples were in good agreement with the gamma spectrometry results. In spite of such possibilities, GDMS has not gained widespread use for low-level long-lived radionuclide measurements. Though GDMS is particularly suitable for the analysis of conductive, solid materials, the relatively high detection limits and the multitude interferences, which usually can not be separated before the measurements, encumber its use for low-level environmental plutonium analysis.

Resonance ionization mass spectrometry (RIMS) is a highly selective and sensitive mass spectrometric method for ultratrace-level and isotope analysis of long-lived radionuclides (^{41}Ca, ^{90}Sr, ^{99}Tc, ^{135}Cs, ^{210}Pb, ^{236}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{244}Pu) in environmental studies, cosmochemistry, dating investigations, nutrition and biomedical research [11,107-110]. In RIMS technique, the solid or liquid sample is initially vaporized and atomized (e.g. by thermal vaporization on a hot Re filament or by evaporation of the sample from a tantalum/titanium sandwich filament). The evaporated atoms are ionized using one, or in most cases, more dye lasers tuned precisely to the wavelength required for the excited states. The ions of interest are then separated and detected by a mass analyzer (e.g. by a time-of-flight analyzer) [11]. RIMS has been successfully applied in environmental studies at ultratrace-level with detection limits of approximately 10^6 atoms (0.4 fg for ^{239}Pu) with the isotope selectivity higher than 10^{10}. For instance, Erdmann *et al.* developed a RIMS method for the plutonium analysis of soil, sediment and urine samples with a detection limit of 10^6 – 10^7 atoms [108]. The excellent sensitivity and selectivity of RIMS instrumentation allowed the determination of the low-abundant plutonium isotopes, ^{238}Pu, ^{242}Pu and ^{244}Pu isotopes, which are difficult to measure by other mass spectrometric techniques [109]. In spite of the outstanding sensitivity, RIMS has not become a widely used technique due to the very expensive instrumentation and difficult operation.

The implementation of the first accelerator mass spectrometers (AMS) started approximately 25 years ago at nuclear physics laboratories. AMS is a highly selective and sensitive mass spectrometric technique. In AMS, the first ionization of the analyte is carried out by ion sputtering (e.g. using a Cs^+ primary ion source). The sputtered secondary negative ions are extracted into a two-stage mass filter. The mass-separated ions are then accelerated in a tandem accelerator with an accelerator potential of some MV and stripped in a gas target (or foil) stripper, where they loose electrons and gain high positive-charged states (e.g. $^{236}U^{5+}$) and thereafter are accelerated for the second time by the same potential. The stripping process has the advantage that it dissociates molecular ions, if enough electrons are stripped off. This effect results in the elimination of isobaric interferences. After the deceleration of ions and a final mass separation, the ions are detected. Today 63 accelerator mass spectrometers have been installed worldwide (including recycled tandem accelerator and new facility instruments), thus AMS has been emerged as a powerful routine method especially for ^{14}C dating [11]. With AMS, absolute detection limits of 10^6 atoms can be achieved. Furthermore, as the technique is capable to measure extremely low isotopic ratios (down to 10^{-15}) in very small samples, AMS is applied for the detection of extremely low concentrations of long-lived radionuclides mainly for research in geochronology and archaeology. Several plutonium analyses performed by AMS have also been reported [21,53,111-113]. For instance, McAninch *et al.* reported the measurement of plutonium concentration and isotopic composition in environmental samples with a detection limit of 2×10^7 atoms per sample (approximately 8 fg of ^{239}Pu). Among the mass spectrometric techniques, AMS is one of the possibility to find the traces of ^{244}Pu ($T_{1/2} = 7.6 \times 10^7$ years), as a live remnant of close-lying and relatively recent supernovae in geological records on the earth (see **Chapter 2.2.1.** or [21]).

Inductively coupled plasma mass spectrometry (ICP-MS) is at present the most frequently used inorganic mass spectrometric technique for concentration and isotope ratio measurements down to fg g^{-1} level. This powerful analytical technique is also increasingly used for the measurement of long-lived radionuclides, including plutonium. ICP-MS uses inductively coupled plasma as an ion source. The sample solution is introduced into the plasma by various sample introduction system (e.g. pneumatic nebulizer, ultrasonic nebulizer, electrothermal vaporization or laser ablation), where the sample decomposes into its atomic constituents in the (in most cases) argon plasma at a temperature of approximately 6000–8000 K and ionized at a high degree of ionization (ionization efficiency is higher than 90% for most chemical elements) with a low fraction of multiply charged ions. The positively charged ions are extracted from the plasma operating at atmospheric pressure into the high vacuum region of the mass spectrometer via an interface. Several types of analyzers can be used for the separation of the ions (e.g. quadrupol analyzers with or without a collision cell, time-of-flight or double-focusing sector field analyzers). Though ICP-MS instruments with quadrupol analyzers (ICP-QMS) are cheaper, more robust and easier to operate, for low-level plutonium measurements mainly ICP-SFMS instruments are used due to the better approximately with 1-3 orders of magnitude) detection limits. Moreover, such mass analyzers can achieve higher mass resolution (denoted as R, sometimes also $m/\Delta m$ notation is used. According to the most frequently applied definition, mass resolution is defined as the ratio of the mass of the isotope of interest divided by the full width at half maximum of the mass peak) compared to ICP-QMS instruments. Most commercially available ICP-SFMS instruments can operate with mass resolution up to 10000. Use of the higher mass resolution is very useful for the separation of the analyte peak from the spectral interferences; however, it also results in lower ion transmission, thus lower sensitivity. After the separation of the analyte ions according to their mass-to-charge ratios, the ions are detected and counted. Use of multiple detectors (so-called multi-collector ICP-SFMS instruments, MC-ICP-SFMS) improves the precision of the measurement (usually expressed in relative standard deviation, RSD), as it detects the isotopes of interest simultaneously and eliminates the fluctuations of the sample introduction and ion source [114]. The capabilities of the ICP-MS instruments are primarily determined by the analyzer and the detection system, since the ion source is the same. The typical figures of merit of different ICP-MS instruments for plutonium analysis are summarized in **Table 10.**

Table 10. The typical figures of merit of different ICP-MS instruments for plutonium analysis

Instrument	Typical detection limit	Precision (RSD%)	Ref.
ICP-MS with a quadrupol analyzer	0.01 – 0.6 pg	0.1 – 0.5%	[11,115-117]
ICP-MS with a quadrupol analyzer and collision cell	0.003 – 0.01 pg	0.07 – 0.1%	[11,117]
ICP-MS with a time-of-flight analyzer	0.1 – 1 pg	0.1 –1%	[11]
ICP-MS with a double-focusing sector field analyzer	0.02 – 1 fg	0.02 – 0.3%	[11,116,117]
MC-ICP-MS with a double-focusing sector field analyzer	0.6 – 0.2 fg	0.002 – 0.05%	[11]

The major problem in low-level plutonium analysis by ICP-MS is the appearance of isobaric interferences in the investigated *m/z* = 239 – 242 mass region. These isobaric interferences derive from polyatomic ions, which are generated in the plasma by the combination of the matrix elements in the sample (e.g. Bi, Pb, Pt, Hg, U), the elements of the solvent (e.g. H, O, N in case of nitric acid) and the elements of the plasma (e.g. Ar, C, O). These elements form polyatomic ions that appear in the mass spectrum causing elevated background and false results. For example, one of the main interferences of ^{239}Pu measurement is the occurrence of $^{238}U^{1}H^{+}$ ion at *m/z* = 239, however, due to the very low plutonium signal intensity, the presence of even relatively odd polyatomic ions can cause elevated background. For example, Wyse *et al.* showed the occurrence of $^{194}Pt^{14}N^{16}O_2^{+}$, $^{208}Pb^{16}O_2^{+}$ and $^{206}Pb^{35}Cl^{+}$ using medium mass resolution (R = 4000) in the investigated *m/z* = 239 – 242 region [118]. Nygren *et al.* verified the presence of lanthanide phosphate interferences during the analysis of plutonium from soil and sediment samples using ^{18}O enriched water [119]. Other research groups reported the occurrence of $^{238}U^{1}H^{+}$, $^{204}Pb^{35}Cl^{+}$, $^{204}Pb^{36}Ar^{+}$, $^{206}Pb^{36}Ar^{+}$ and $^{199}Hg^{40}Ar^{+}$ in the investigated *m/z* = 239 – 240 region [50,74,118,120,121]. The main isobaric interferences of the plutonium isotopes are collected in **Appendix A**. Several methods have been described in the literature to overcome these isobaric effects. In most cases, constituents of the interfering ions (such as U, Pb or Bi) are removed during the suitable chemical sample preparation steps. Therefore, especially in the case of low-level environmental samples, the most important and efficient way to obtain accurate results is the proper sample preparation and purification of the analyte. Chemical sample preparation can remove most of the elements, which can form polyatomic ions. However, the complete removal of several stable elements, such as Pb, Bi or Hg, is limited by the impurities of reagents and chemicals used for the sample preparation. These elements, even if they are present in the final fraction in the low ng g^{-1} level, can form hydride, oxide or argide molecular ions, which can cause elevated background comparable to the plutonium signal. In order to eliminate most hydride (e.g. $^{238}U^{1}H^{+}$, $^{238}U^{1}H_2^{+}$) and oxide (e.g. $^{206}Pb^{16}O_2^{+}$) interferences, special sample introduction devices have been developed for the removal of solvents and for the generation of dry aerosol. The principal of these instruments is the same: the wet aerosol produced by the conventional pneumatic or ultrasonic nebulizer is driven through a heated chamber, where the solvent evaporates. In the forthcoming step, the solvent vapour is removed either by condensation or by membrane desolvation. These instruments not only decrease the oxide and hydride background, but also have better transfer efficiency of the analyte, thus better sensitivity compared to the conventional nebulizers. Reduction of UH^{+} interference can also be accomplished in ICP-MS instruments equipped with a dynamic reaction cell using CO_2 as reaction gas [122]. An interesting possibility for the reduction of UH^{+}/U^{+} ratio is the use of D_2O as the solvent instead of H_2O proposed by Zoriy *et al.* [123]. However, in case of plutonium it also results in the increase of the background at $m/z = 240$ due to the formation of $^{238}U^{2}D^{+}$. Other groups proposed electrothermal vaporization (ETV) [17] or laser ablation (LA) [80,124] for the introduction of the plutonium fraction into the plasma in a dry aerosol form. In recent years, coupled techniques, such as on-line HPLC [125], on-line flow-injection [51,122] and sequential injection separations [126] have been implemented also for low-level plutonium analysis. These techniques have significantly shortened analysis time and reduced the sample amount used for the analysis, though they are less robust and more sensitive to the sample impurities than the conventionally used liquid sample introduction systems. As these sample introduction systems have relatively high detection limits (due to the limited sample volume) and produce less precise transient signals, they has not gained widespread use. Such recent instrumental improvements have contributed to the reduction of the potential polyatomic interferences. However, the complete removal of these interferences, especially if they are present in a large quantity, should be accomplished usually by the preliminary chemical sample preparation.

In those cases, when dissolution of the sample should be avoided (e.g. analysis of highly radioactive materials, confiscated samples, which are evidences in the course of forensic investigations), sample introduction by laser ablation can be the best choice. However, for low-level plutonium analysis from environmental matrices, the relatively high detection limit and the occurrence of polyatomic interferences, which can not be eliminated by the chemical sample preparation, encumber its use. For instance, Boulyga *et al.* studied the possibilities of laser ablation ICP-SFMS for the direct determination of plutonium from soil samples [124]. The achieved detection limit was in the pg g^{-1} level, which is suitable for the routine analysis of contaminated samples. Otherwise, for typical environmental samples, destructive sample preparation with pre-concentration and purification of plutonium is necessary.

For low-level plutonium analysis a number of ICP-MS methods using different instruments and sample introduction have been developed and published. A collection of these methods is presented in **Table 11.** The detection limits of the methods, which are usually given in concentration in the publications, have been converted to absolute detection limit for the easier and fair comparison.

To conclude, ICP-MS, especially instruments equipped with sector-field analyzers are used most often for the determination of low-level plutonium from environmental matrices. In most cases, single collector ICP-MS instruments are applied for such measurements, because besides the high cost of MC-ICP-SFMS instruments, the plutonium isotopic variations in nature are not so small that it would require the measurement of highly precise data. Different sample introduction devices, though they decrease the level of polyatomic interferences and enhance the sensitivity of the measurement, are only supplementary to the preliminary chemical sample preparation, which is the most effective way of interference reduction and LOD improvement. Therefore, in case of ultratrace-level plutonium analysis, the proper sample preparation prior to the mass spectrometric analysis is still the basis of the reliable and accurate analysis.

Table 11. Collection of ICP-MS methods developed for environmental plutonium determination

Sample type	Sample amount	Type of ICP-MS	Sample introduction	Absolute detection limit of	Ref.
Soil, moss,	1-100 g	ICP-SFMS	MCN-6000	4.2 fg	[127]
Groundwater	10 mL	ICP-SFMS	PFA-100	1.2 fg	[128]
Soil, sediment,	2-50 g	ICP-QMS	Meinhard	0.1 pg	[129]
Urine	1000 mL	ICP-SFMS	PFA-100, DIHEN	9 and 1.02 fg	[50]
Sediment	Not specified	ICP-SFMS	U-5000AT$^+$	50 fg	[130]
Biological	0.5 g	ICP-SFMS	U-6000AT$^+$/HPLC	10 fg	[131]
Sediment	10 g	ICP-SFMS	MCN-6000	0.5 fg	[132]
Soil, sediment	1 g	ICP-SFMS	MCN-6000	9.6 fg	[74]
Soil, peat	20-40 g	ICP-SFMS	U-5000AT$^+$	30 fg	[30]
Urine	10 g	ICP-SFMS	Aridus	47 fg	[133]
Biological	0.5 – 10 g	ICP-SFMS	On-line EXC	0.85 fg	[121]
Seawater	1000 mL	ICP-QMS	U-6000AT$^+$	5 fg	[51]
Seawater	100 L	MC-ICP-SFMS	Aridus	10 fg	[116]
Soil	1 g	ICP-SFMS	Aridus	130 fg	[88]
Soil, sediment	0.2 – 2 g	ICP-SFMS	Meinhard	5-15 fg	[48]

3.4.2. Determination of Americium-241 by Mass Spectrometry

In the literature very few papers deal with the analysis of ^{241}Am by mass spectrometric techniques due to its very short half life of 432.2 years. Though mass spectrometric methods work well for the longer-lived plutonium isotopes, in case of ^{241}Am the measured concentration results are usually below detection limit. For instance, Ayranov *et al*. developed a sequential method for environmental actinide analysis (for Pu-isotopes, ^{241}Am, Cm) by ICP-SFMS, PERALS® and alpha spectrometric detection [60]. Though ^{241}Am could be quantified by ICP-SFMS in the highly contaminated IAEA-135 (Irish Sea sediment) reference material (recommended ^{241}Am concentration is 2440 – 2560 fg g^{-1}), its measurement was not possible in the low-level IAEA-300 (Baltic Sea sediment) reference material (recommended ^{241}Am concentration is 9.5 – 12 fg g^{-1}), possibly due to $^{209}Bi^{32}S^{+}$ polyatomic interference at *m/z* = 241. Epov *et al.* developed an on-line flow injection (FI) pre-concentration matrix separation method using TRU^{TM} resin for the determination of ^{241}Am in human urine by ICP-MS with detection limit of 0.8 pg L^{-1} using a 10 mL sample volume [134]. A better detection limit, 0.046 pg L^{-1} was obtained, when the sample was digested and a two-step sample evaporation was applied prior to on-line pre-concentration. Though low detection limit could be achieved, the method is suitable only for simple matrices, such as urine. Moreover, as the pre-concentration factor is limited, only low sample amounts (up to 10 mL) can be processed, which also results in that the method is applicable for relatively high-level ^{241}Am measurements (e.g. for screening in emergency situation). The first method that aimed the determination of ^{241}Am from real-world samples was published by Agarande *et al.* [79]. They used the standard sample preparation method developed for alpha spectrometry. The method reported was found to be applicable for samples containing ^{241}Am as low as 1.6 pg kg^{-1}. Though the detection limit achieved is comparable to that of alpha spectrometry, high sample amount has to be processed (100 g of sample was used for low-level samples), the sample preparation lasts 15 days and the authors did not investigate the impact of different interferences on the measurements. Therefore, low-level ^{241}Am determinations by mass spectrometric techniques, in spite of their detection capabilities, presently are much less significant than the radioanalytical methods, especially alpha spectrometry.

3.4.3. Mass Spectrometric Measurement of Minor Long-lived Radionuclides from Nuclear Materials

Mass spectrometric methods have been used for the determination of minor long-lived radionuclides (e.g. ^{236}U, Pu-isotopes) from nuclear materials long ago. However, at an early stage, it was restricted only for determinations in the µg – mg concentration range due to the limitation in the detection capabilities of the instruments [35]. Afterwards, with the development in mass spectrometric instrumentation, the measurements have been extended also to the analysis of trace-level and ultratrace-level components.

Likewise the environmental analysis, formerly thermal ionization mass spectrometry (TIMS) was the primary mass spectrometric technique. In TIMS analysis, after the proper purification, the analyte (dissolved in a small volume (down to 1 µl) or collected on an organic resin bead) is deposited on a cleaned filament surface, and ionised by heating of the filament. Removal of matrix component and the preparation of a very pure analyte fraction therefore are required to avoid the reduction in ionization efficiency. However, if the analyte is one of the low-abundant isotopes of the matrix (e.g. determination of ^{236}U in uranium-based nuclear materials), chemical separation of the analyte is not possible, and the TIMS measurement can be carried out from a diluted aliquot of the sample [40]. In these cases, the biggest problem arises from the interference (overlapping) of the excess high-abundant uranium peaks (mainly $^{235}U^+$ and $^{238}U^+$) on the minor uranium isotopes. If the $^{236}U/^{235}U$ or $^{236}U/^{238}U$ ratios are lower than approximately 10^{-6}, the overlap of $^{235}U^+$ and $^{238}U^+$ signals at m/z = 236 hamstrings the ^{236}U determination [40]. These difficulties were also revealed in a recent inter-laboratory comparison campaign aiming to compare the capabilities of laboratories routinely carrying out uranium isotope ratio measurements [135]. In order to minimize the peak tailing contributions originating from ^{235}U and ^{238}U, Richter *et al.* reported a modified total evaporation technique TIMS method for the determination of the low-abundant isotopes, such as ^{234}U and ^{236}U [136]. If the analyte is a different element than those of the main matrix components and present in the nuclear material in trace-level, the removal of excess U or Pu is the best choice to obtain accurate results and improve the detection limit. In such cases, the successful analysis depends on the proper sample preparation similarly to the destructive radioanalytical methods (**Chapter 3.2.**). TIMS have been applied for the determination of several minor long-lived constituents from nuclear materials. For instance, Aggarwal *et al.* developed a method for the determination of plutonium from irradiated fuels, however, it is mainly applicable for the analysis of samples with relatively high plutonium concentration (above ng g^{-1}) [137]. At Savannah River Site, a routine TIMS method have been developed for the determination of plutonium concentrations and isotopic composition from depleted uranium samples [84]. The achieved detection limit is in the pg g^{-1} level using approximately 0.1 g of sample. Due to the excellent precision of TIMS measurements, the production date determination (age) of the nuclear material by the measurement of the mother-to-progenies ratios is favourable by TIMS. Several TIMS methods have been reported for the production date measurements. These methods with the most important characteristics are summarized in **Table 12.**

Table 12. TIMS methods for the production date determination of nuclear materials

Sample type	Isotope ratio used for age measurement	Sample amount	Enrichment	Ref.
Highly enriched uranium	$^{230}Th/^{234}U$	Few mg – g	$^{235}U > 50\%$	[89]
Low enriched uranium	$^{230}Th/^{234}U$	Approx. 0.5 g	$^{235}U = 2\%$	[40]
Natural uranium	$^{230}Th/^{234}U$	Approx. 100 µg	$^{235}U = 0.0056\%$	[85]
Plutonium samples	Various U/Pu ratios	Few mg – g	Reactor grade Pu	[86]

Though TIMS offers possibility for the very accurate and precise measurement of minor long-lived radionuclides, the time consuming and tedious sample preparation required hinder its widespread use. Another disadvantage of this technique is that relatively high amount of analyte (approximately in the nanogramm range) is required for the analysis. Moreover, the use and maintenance of the instrument is complex and difficult. Though it is still widely used, especially in those cases, when highly precise measurement is necessary (e.g. for production date measurements), in recent years this technique is being replaced by the sensitive, multielemental ICP-MS techniques similarly to the low-level plutonium analysis.

As glow discharge mass spectrometry is mainly suitable for the analysis of conducting materials, its use is rather limited for the analysis of the most important nuclear materials, uranium and plutonium oxides. However, Betti *et al.* used radio frequency GDMS for different applications to characterize radioactive waste materials in electrically conducting and non-conducting materials, e.g. for different types of nuclear fuels, alloys containing Pu and U, cladding materials, nuclear waste glasses [138]. The detection limits achieved (in the µg g^{-1} level) is suitable for the analysis of trace-level stable elements present in uranium oxide. However, it is still high for the ultratrace-level long-lived radionuclides, such as transuranics and progenies.

During the last decades ICP-MS became the primary technique for the determination of minor long-lived components from nuclear materials. It has been widely applied for the measurement of low-abundant isotopes of the matrix (e.g. ^{236}U or ^{241}Pu), fission products (e.g. caesium or lanthanides), transuranics as activation products (e.g. ^{239}Pu, ^{240}Pu and ^{237}Np) and progenies (e.g. ^{230}Th and ^{231}Pa). A summary of these methods is collected in **Table 13.**

Table 13. Summary of ICP-MS methods developed for the determination of long-lived radionuclides from nuclear materials

Sample type	Analyte	Instrumentation	Detection limit	Ref.
Depleted uranium penetrator	^{236}U and Pu	ICP-SFMS	1 × 10 µg g^{-1} (^{236}U) 1.1 ng g^{-1} (^{239}Pu)	[139]
UO_2 and MOX fuel	Pu and ^{237}Np	IC-ICP-QMS	0.006 – 0.026 ng mL^{-1}	[140]
UO_2 and MOX fuel	Ln and An	HPLC-ICP-QMS	pg mL^{-1}	[141]
UO_2 and MOX fuel	Pu	HPLC-MC-ICP-MS	fg g^{-1} – pg g^{-1}	[142]
HEU	^{230}Th and ^{231}Pa	MC-ICP-MS	pg g^{-1}	[89]

Abbreviations: IC-ICP-QMS: ion chromatography-inductively coupled plasma quadrupol mass spectrometry; HPLC-ICP-QMS: high-performance liquid chromatography-inductively coupled plasma quadrupol mass spectrometry

In several methods a chromatographic separation was coupled to the ICP-MS instrument, which allows decreasing the sample volume (10 – 500 µL) and enables an on-line sample preparation. Other advantages of these methods that usually much less (radioactive) waste is produced and the analyst is not exposed to radioactivity, due to the automatization of sample preparation and measurement. However, this technique has not gained widespread use because of the expensive instrumentation and relatively high detection limits (approximately 2 – 3 orders of magnitude higher than using the conventional sample introduction).

4. Experimental

4.1. Reagents and Materials

The ^{242}Pu (National Physical Laboratory, United Kingdom; NIST 4334F, USA) and ^{243}Am isotopic standards (National Physical Laboratory, United Kingdom; Amersham International, United Kingdom) were used to spike the samples. Multielement standard solution at a concentration of 1 ng g^{-1} purchased from Merck

(Darmstadt, Germany) was used for the optimization of the ICP-SFMS instrument. Natural uranium solution and U-500 isotopic standard (National Bureau of Standards, Washington D.C., USA) were used to correct for instrumental mass discrimination. The anion exchange resin (AG 1-X8, 100-200 mesh) and the TEVA^{TM} (100-150 µm particle size, active component: aliphatic quaternary amine), TRU^{TM} (100-150 µm particle size, active component: octylphenyl-N,N-di-isobutyl-carbamoyl methyl phosphine oxide dissolved in tri-n-butylphosphate) and UTEVA^{TM} (100-150 µm particle size, active component: diamyl amyl-phosphonate) extraction chromatographic resins were supplied by Eichrom Technologies Inc. (Darien, Illinois, USA). For the analysis, 1.8 mL of the resin was placed in plastic Bio-Rad holders (diameter: 8 mm) and plugged with wool on the top of the resin to avoid mixing. All reagents used were of analytical grade. Acids used in the final steps prior to ICP-MS analysis were Suprapur$^{®}$ grade (Merck, Darmstadt, Germany). For dilution, ultrapure water was used (Milli-Q System, Millipore, USA). The analysed certified reference materials, IAEA-308 (seaweed mixture), IAEA-384 (Fangataufa lagoon sediment), IAEA-385 (Irish Sea sediment) and IAEA-308 (Seaweed mixture) were supplied by the International Atomic Energy Agency.

4.2. Alpha Spectrometry

Alpha spectrometric sources were counted by a PIPS type Si alpha detector with a surface area of 450 mm^2 attached to an alpha spectrometer (Canberra Inc., USA). Counting time was typically 1–20 days, the detector background was less than 1 – 5 cps in the applied 3.5 – 9 MeV energy range. The efficiency of the detector was 0.32–0.41 depending on the geometry. The geometry (sample-to-detector distance) was optimized for each sample in order to have high efficiency and good spectral resolution. Alpha-sources for alpha spectrometric analysis were prepared by NdF_3 micro co-precipitation (plutonium analysis) or electrodeposition (plutonium and americium measurements).

4.3. Inductively Coupled Plasma Sector-field Mass Spectrometry

Mass spectrometric analyses were carried out with a double-focusing magnetic sector inductively coupled plasma mass spectrometer equipped with a single electron multiplier (ELEMENT or ELEMENT2, Thermo Electron Corp., Bremen, Germany). ELEMENT instrument was used for ^{241}Am measurement (**Chapter 5.3.**) and the analyses were carried out at IAEA Marine Environment Laboratory. ELEMENT2 is the newer version of the Thermo Electron Corp. with some improved features. No significant difference in the detection capabilities was found between the two instruments. The ELEMENT2 measurements were performed at the Institute of Isotopes of the Hungarian Academy of Sciences. The instrument was installed in 2005 in order to improve the Hungarian capabilities in the field of nuclear safeguards and nuclear forensics [143]. The sample introduction systems used for the measurements were selected depending on the data quality objectives. In case of plutonium and americium analysis, low-flow nebulizer (50 – 100 μl min^{-1}) operating in a self-aspirating mode attached to a desolvation unit was applied (Aridus or MCN-6000 from Cetac Technologies Inc., Omaha, USA) was used in order to decrease the level of hydride and oxide polyatomic interferences, as well as to enhance sensitivity. For the analysis of nuclear materials, a low-flow microconcentric nebulizer operated in a self-aspirating mode (flow rate was 100 μL min^{-1}) connected to a stable introduction system spray chamber (SIS, Elemental Scientific, Omaha, USA) was used in order to improve isotope ratio precision. In each case, diluted high-purity nitric acid was used as a rinse solution between the samples. Optimized instrumental settings and optimization aspects for each method can be found in the corresponding chapters and appendixes. Mass calibration of the instrument was verified every day before the measurements. Dead time correction of the detector was performed in each case, when the detector voltage had been changed. As the detector of the ELEMENT2 instruments is a dual-type detector (meaning that it can operate in analogue and counting mode), cross-calibration between the two modes were done daily prior to the measurement. Mass bias corrections were carried out using uranium standards with known isotope ratios every day before the measurements.

4.4. Sample Introduction by Laser Ablation

Laser ablation (LA) measurements of the samples were carried out using an UP-213 laser ablation system (New Wave, Freemont, USA) attached to the ELEMENT2 instrument. The ablated material is transported by argon as a carrier gas into the plasma. The schematic of the laser ablation unit is shown in **Fig. 12.** [144]. The UP-213 system applied has a Nd:YAG deep UV (213 nm) laser beam, which provides flat craters and high absorption for the analysis of also opaque and transparent materials. The deep UV 213 nm wavelength produces a finer particle distribution compared to higher wavelengths. This increases transport efficiency of the aerosol resulting in better sensitivities and minimize deposit formation.

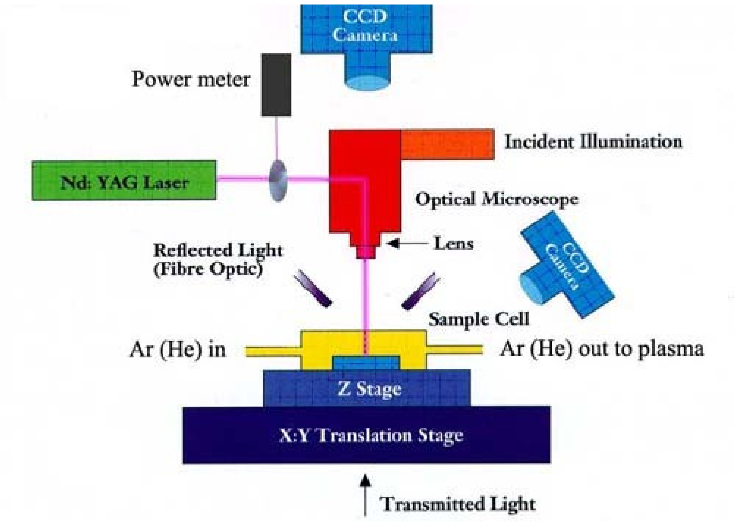


Fig. 12. The schematic of the laser ablation unit [144]

Optimization of the laser ablation was carried out with respect to maximum $^{238}U^+$ intensity besides good precision and minimum UO^+/U^+ ratio using a NIST 612 glass reference material (NIST, Gaithersburg, USA). Other optimized ICP-SFMS and laser ablation parameters can be found in the corresponding chapter and appendix.

5. Method Developments for the Analysis of Environmental Samples

5.1. Aims of the Method Developments

Though several sample preparation methods have been proposed in the literature for low-level actinide analysis, for difficult matrices they are tedious and labor-intensive (**Chapter 3.2.**). The use of extraction chromatography (EXC) highly simplified these procedures, but in these cases either low sample amount can be processed due to the limited capacity of the EXC column, or the pre-treatment of the sample is critical in order to remove those components, which may interfere with the EXC separation. Therefore, the aim was to develop simple and rapid procedures for the ICP-SFMS measurement of plutonium isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu) and ^{241}Am from environmental samples for environmental research, monitoring and safeguards purposes. The analysis should be easy, rapid (measurement data can be obtained within one day) and have sufficiently low detection limits for most environmental matrices (biota, soil, sediment). The method should be capable to measure those plutonium isotope ratios, which are necessary to assess the source of the transuranic contamination with acceptable uncertainties. As the radioanalytical measurement of low-level ^{241}Am from environmental matrices is cumbersome and time-consuming, the objective was to develop an ICP-SFMS method, which can be a comparable and competitive technique in the future. Most of the methods developed are also applicable for radioanalytical (e.g. alpha spectrometric and LSC) measurements.

5.2. ICP-SFMS Method Developed for Environmental Plutonium Analysis

5.2.1. Sample Preparation

In case of soil or sediment, the homogenized sample was weighted into a PFA microwave digestion vessel (0.5-3 g depending on the concentration level) and known amount of ^{242}Pu tracer (National Physical Laboratory, United Kingdom) was added to the samples by weight. In order to check the complete removal of ^{241}Am, known amount of ^{243}Am (National Physical Laboratory, United Kingdom) was added to the sample. Following the addition of 10 mL HNO_3, the sample was digested using a MARS5 microwave digestion system. The samples were heated up to 175 ^{o}C in 5.5 minutes and held at that temperature for 9.5 minutes. In case of biological samples and higher amount of soil or sediment samples (above approximately 3 grams, though it also depends on the organic content of the sample) in order to avoid overpressure in the closed microwave digestion system, conventional hot-plate (open vessel) digestion was used. The sample was placed in a glass beaker and was digested on a hotplate for at least 4 hours at 130 ^{o}C after addition of tracers and acid mixture. For the leaching, nitric acid (three times the volume of the sample) with 2 mL of H_2O_2 was used. After leaching, care was taken to reduce the HNO_3 volume to less than 8 mL by evaporation.

The sample was filtered gravimetrically through a double Whatman 2 type paper filter into a 50-mL polyethylene centrifuge tube. The PFA liner or the glass beaker was rinsed carefully, and the rinsing solution was added to the filtrate. The filtered sample was diluted to approximately 40 mL. To the sample 1 mL of 0.4 g mL^{-1} $Ca(NO_3)_2$ solution was added followed by the careful addition of 300 mg of $NH_2OH.HCl$. After complete dissolution, the centrifuge tube was placed in a 90 ^{o}C water bath for 10 minutes. During this step plutonium is reduced to Pu(III). After cooling 8 mL of concentrated HF was added carefully to the sample and was mixed thoroughly. After 15 minutes the precipitate was centrifuged and the supernatant was discarded. The precipitate was rinsed with 10 mL 10% HF solution. The final precipitate was dissolved in 15 mL 3 M HNO_3 and 500 mg of H_3BO_3 by placing it in a hot water bath and by vigorous shaking. In case of some samples with higher alkaline earth content, addition of further 100-600 mg of boric acid was necessary. 0.5 mL of 25 w/w% $NaNO_2$-solution was added to the sample, which stabilizes Pu in the Pu(IV) state within 10 minutes.

The plutonium was purified by extraction chromatography using TEVA^{TM} resin. The proposed method is less prone to matrix effects in contrast to other separation procedures applying TEVA^{TM} due to the effective separation of the interfering components (e.g. phosphate, sulphate) in the pre-concentration step. After conditioning of the resin with 10 mL of 3 M HNO_3, the sample was loaded on the column. After loading, the tube and the column were rinsed twice with 2.5 mL of 3 M HNO_3. The retained U and Th were eluted with 20 mL of 3 M HNO_3 and 15 mL 6 M HCl, respectively. Finally, plutonium was eluted by 20 mL of 0.1 M HNO_3/0.1 M HF and collected in a PFA beaker. The solution was repeatedly evaporated to almost dryness (3 times) with successive addition of 2 mL of ultrapure HNO_3 to remove HF and organic content. The residue was dissolved in dilute ultrapure nitric acid (1.6 mL) with gentle heating of the PFA beaker on a hotplate, and the sample was divided into a 0.5 mL part for ICP-SFMS analysis and a 1.1 mL part for alpha spectrometric measurement. The schematic diagram of the sample preparation is shown in **Fig. 13.**

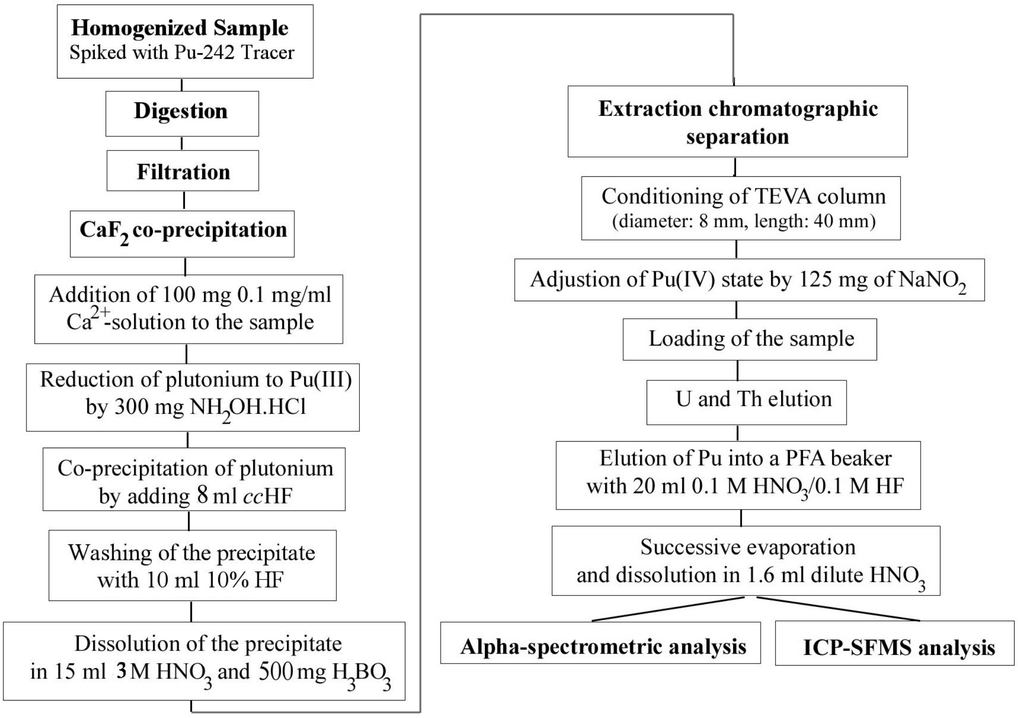


Fig. 13. Schematic of the sample preparation developed for environmental plutonium analysis

5.2.2. Analysis by ICP-SFMS and Alpha Spectrometry

Plutonium isotope ratios and concentrations were determined using a double-focusing magnetic sector inductively coupled plasma mass spectrometer equipped with a single electron multiplier (ELEMENT2, Thermo Electron Corp., Bremen, Germany). All measurements were carried out in low resolution mode ($m/\Delta m$ = 300) using a low-flow T1-H nebulizer in self aspirating mode (flow rate approximately 60 µL min^{-1}) in combination with a desolvation unit (Aridus, CETAC Technologies Inc., Omaha, USA) that removes most of the solvent, thus significantly decreasing hydride and oxide interferences. Optimized operating parameters and data acquisition parameters are summarized in **Appendix B**. Prior to the analysis of samples, the instrument was tuned using a 1 ng mL^{-1} uranium standard solution. Sensitivity was about 2 x 10^6 cps ppb^{-1} for ^{238}U. Concentrations of plutonium isotopes were calculated as a function of $^{239}Pu/^{242}Pu$, $^{240}Pu/^{242}Pu$ and $^{241}Pu/^{242}Pu$ atom ratios according to the isotope dilution method. All raw data were corrected for instrumental mass bias using linear correction. Alpha sources for alpha spectrometric analysis were prepared by NdF_3 micro co-precipitation. Alpha spectrometric sources were counted by a PIPS type Si alpha detector with a surface area of 450 mm^2 attached to an alpha spectrometer (Canberra Inc., USA). The overall uncertainty was calculated with error propagation rules taking into account the uncertainty of the weight measurements, tracer concentration and the measured intensities.

5.2.3. Removal of Interferences and Matrix Components

In case of environmental samples, especially for sediment and soil samples, the effective removal of the matrix components that could interfere with the extraction chromatographic separation and may result in increased background is of high importance (see **Chapter 3.4.1.** and [60,64]). The main advantage of the above-described CaF_2 pre-concentration step in contrast to the commonly applied alkali (e.g. $Fe(OH)_3$, $Ca_3(PO_4)_2$) co-precipitations is that it is carried out in acidic medium leaving the main matrix components (e.g. alkali metals and most transition metals) and possible interferences of extraction chromatography (e.g. phosphate, sulphate) or ICP-SFMS analysis (e.g. uranium) in the liquid phase. Those co-precipitation separations, which are carried out in alkali medium, can be regarded as a pre-concentration rather than a separation, since most matrix components (e.g. transition metals, such as Fe and Mn, or other metals, such as Si and Al) also precipitate or co-precipitate. That is why a selective co-precipitation was sought, which works also in acidic medium. During the method development, several co-precipitation agents, Ca-oxalate, LaF_3 and CaF_2, were tested, which can be used in acidic medium for plutonium analysis according to the literature [34,35]. In order to check the applicability and selectivity of these carriers, test samples spiked with known amount of ^{232}Th (stable), U (natural), ^{242}Pu and ^{243}Am standards were prepared. The standards added were approximately 250 pg (^{242}Pu), 25 pg (^{243}Am) and 500 ng (Th and U). The test samples were 1 M HNO_3 solution; the sample volume was 100 mL in case of Ca-oxalate and 30 mL for LaF_3 and CaF_2. After addition of the tracers, the oxidation state was adjusted and the analytes investigated were co-precipitated upon addition of the components of the carrier. Following thorough mixing and settling, the concentrations of the elements investigated in the supernatant were determined by ICP-SFMS using external calibration with rhodium internal standard. In case of the Ca-oxalate supernatant, the sample aliquot was diluted approximately 50-fold, in case of the HF containing samples, 0.1% H_3BO_3 solution was added to the sample aliquot. The exact experimental conditions of these preliminary investigations with the results obtained are summarized in **Table 14.**

Table 14. Experimental conditions of the preliminary investigations for the selection of the proper carrier

Carrier	Reagents added	Redox conditions	Amounts in the supernatant (%)			
			Th	U	Pu	Am
CaC_2O_4	Standards, 100 mg Ca^{2+}	▪ 620 mg of $NH_2OH.HCl$ ▪ Placing in a 90 °C water bath, for appr. 10 min ▪ Cooling to 30 °C ▪ Addition of 7 g of $(COOH)_2.2H_2O$ ▪ pH adjustment to 1.6-1.9 with *cc*NH_3-solution ▪ Settling: 2 hours	< 5%	104 ± 9	< 4%	< 3%
CaF_2	Standards, 100 mg Ca^{2+}	▪ 3 mL of 0.1 mg mL^{-1} $NH_2OH.HCl$ ▪ Placing in a 90 °C water bath, for appr. 10 min ▪ Cooling to 30 °C ▪ Addition of 5 mL *cc*HF ▪ Settling: 1 hours ▪ Centrifugation	< 6%	86 ± 6	< 2%	< 5%
LaF_3	Standards, 50 mg La^{3+}	▪ 3 mL of 0.1 mg mL^{-1} $NH_2OH.HCl$ ▪ Placing in a 90 °C water bath, for appr. 10 min ▪ Cooling to 30 °C ▪ Addition of 5 mL *cc*HF ▪ Settling: 1 hours ▪ Centrifugation	< 3%	96 ± 5	< 4%	< 3%

Each carrier tested behaved similarly under the experimental conditions: all co-precipitate Th, Pu and Am, while leaving most of U in solution. CaF_2 turned out to be the optimal agent because of its simplicity (it is not necessary to destroy the oxalate content in the forthcoming steps), rapid co-precipitation kinetics and low cost. CaF_2 has the advantage over LaF_3 (or other lanthanide fluoride) that if the method is to be extended to Am measurement, it is not necessary to carry out tedious Am/Ln separation due to the excess amount of carrier. The idea was to couple this selective co-precipitation as a pre-concentration step with extraction chromatography, which further purifies the analyte. The selective pre-concentration step overcomes the problem of the overloading the extraction chromatographic column and higher sample amount can be processed without impairing the chemical recovery. The application of extraction chromatographic separation further purifies the plutonium fraction removing the leftover Th, U and other components (e.g. Pb, Bi) that could possibly form molecular interference (e.g. $^{238}U^{1}H^{+}$, $^{207}Pb^{16}O_2^{+}$, $^{204}Pb^{36}Ar^{+}$ or $^{209}Bi^{32}S^{+}$) in mass spectrometric analysis (**Chapter 3.4.1.** and **Appendix A**). The complete removal of ^{241}Am in the course of the sample preparation, which could impair the measurement of the isobaric ^{241}Pu, was checked by the addition of ^{243}Am tracer to the sample. The U and Th content in the samples investigated were determined in an independent analysis. The decontamination factors (the ratio of the weight of the element of interest in the sample and the final Pu fraction) were above 10^5 for U, Th and ^{243}Am. Thus, the effect of ^{241}Am on the ^{241}Pu signal was negligible. In order to check the complete removal of molecular interferences, a "blank" soil sample, free from artificial radionuclides taken from a cave at a depth of 80 meters was also analysed together with the samples. The measured signals at m/z = 239, 240, 241 and 242 agreed with the method blank within the measurement uncertainty. The possible hydride and oxide interferences (e.g. $^{238}U^{1}H^{+}$ or $^{207}Pb^{16}O_2^{+}$) were further reduced using Aridus desolvation sample introduction system (UH^{+}/U^{+} ratio was less than 5×10^{-6}). Mathematical correction of hydride interference was not necessary.

5.2.4. Figures of Merit and Validation of the Method

The limits of detection (LOD) of the ICP-SFMS analysis and alpha spectrometry are calculated for 1-gram of sample for easier comparison (**Table 15.**). Calculation of LOD of ICP-SFMS was based on three times the standard deviation of the method blank, in case of alpha spectrometry Currie-method [145] was applied for a counting time of 14 days.

Table 15. Limits of detection calculated for 1-gram of sample. In case of $^{239+240}$Pu analysis by alpha spectrometry the detection limit is ^{240}Pu/^{239}Pu isotope ratio dependant, if it is expressed in mass

Isotope	Technique	LOD in fg	LOD in mBq
^{238}Pu	Alpha spectrometry	0.032	0.02
^{239}Pu	ICP-SFMS	9.0	0.021
^{240}Pu	ICP-SFMS	1.7	0.014
^{241}Pu	ICP-SFMS	3.1	11.9
$^{239+240}$Pu	Alpha spectrometry	N/A	0.02

Using higher sample amount (i.e. higher pre-concentration) or in case of alpha spectrometry longer measurement time, the LODs of the method can be improved. The LODs of ICP-SFMS and alpha spectrometry are comparable, though other aspects (analysis time, determination of ^{238}Pu and ^{241}Pu concentration or ^{240}Pu/^{239}Pu ratio) may affect choosing the appropriate measurement technique. However, if the comprehensive characterization of the sample is necessary, use of both radioanalytical techniques and mass spectrometric analysis is required [104]. The sample preparation developed can also be used for the analysis of ^{241}Pu by radioanalytical methods, for example, by the direct LSC analysis of a sample aliquot or by the measurement of alpha spectrometric source. The analysis of ^{238}Pu by ICP-SFMS is precluded by the presence of even a small amount of ^{238}U in the Pu-fraction, which makes ^{238}Pu determination unreliable by mass spectrometric methods. Since the ^{238}Pu activity concentration (usually 0.01-1 Bq kg^{-1} (0.016-1.6 fg g^{-1}) in environmental samples) is much lower, than the typical ^{238}U content of the final solution

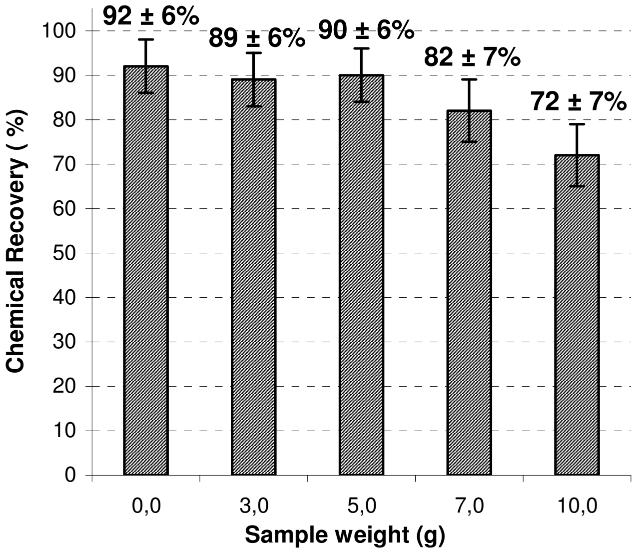


Fig. 14. Recovery study of the sample preparation by analyzing increasing amount of IAEA-385 sea sediment sample

(approximately 10-500 pg), deriving mainly from reagent and instrumental background, the ^{238}Pu measurement results by ICP-SFMS are highly unreliable. The ^{238}Pu and ^{238}U peaks can not even be separated by means of higher instrumental mass resolution, because the required mass resolution, R = 192000, is higher than the maximum resolution of today's commercially available ICP-MS instruments. The precision of the isotope ratios by ICP-SFMS varied between 5-15% and 23-47% (at 95% confidence level) in case of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios, respectively, depending on plutonium concentration. This precision can be improved using higher sample amount or without dividing the sample for alpha spectrometric analysis. The recovery of the sample preparation, calculated as the ratio of ^{242}Pu tracer content before and after the procedure, ranged between 72% and 92%. The robustness of sample preparation was tested by the analysis of increasing amount of IAEA-385 (Irish Sea sediment) sample. The recovery results are shown in **Fig. 14.** The high yields indicate the robustness and reliability of the method. The sample preparation for one batch of samples can be carried out within one day, which is particularly useful for environmental monitoring purposes.

In order to validate the sample preparation method, three international reference materials, IAEA-308 (Seaweed Mixture), IAEA-384 (Fangataufa Lagoon Sediment) and IAEA-385 (Irish Sea Sediment) were analysed. The determined activity concentrations of ^{239}Pu, ^{240}Pu and ^{241}Pu obtained by ICP-SFMS together with ^{238}Pu and $^{239+240}$Pu results measured by alpha spectrometry are presented in **Table 16.** The information or recommended values are also indicated in the table.

Table 16. Activity concentration (Bq kg^{-1}) of plutonium isotopes in the analysed reference materials (number of replicates: 3). All data are presented at 95% confidence level (k = 2). The results are decay corrected to 01.06.2006. ^{a}: Information value

		IAEA-308	**IAEA-384**	**IAEA-385**
Recovery (%)		90 ± 4	85 ± 4	89 ± 5
ICP-SFMS Results (Bg kg^{-1})	**^{239}Pu**	0.314 ± 0.034	97.2 ± 8.2	1.75 ± 0.07
	^{240}Pu	0.206 ± 0.018	17.2 ± 2.2	1.14 ± 0.04
	^{241}Pu	1.1 ± 1.0	47 ± 11	17.1 ± 4.8
	$^{239+240}$Pu	0.520 ± 0.038	114.4 ± 8.5	2.89 ± 0.08
Alpha spectrometry Results (Bg kg^{-1})	**^{238}Pu**	0.023 ± 0.006	40.6 ± 3.6	0.57 ± 0.08
	$^{239+240}$Pu	0.52 ± 0.04	112.2 ± 5.5	3.03 ± 0.24
Recommended Values (Bg kg^{-1})	**^{238}Pu**	0.014-0.020	38.1-40.1	0.45-0.50
	$^{239+240}$Pu	0.46-0.52	105-110	2.81-3.14
	^{241}Pu	N/A	30-116^{a}	15.0-19.8^{a}

The measured results are in good agreement with the recommended or information values [146-148]. However, ^{241}Pu results can have relatively high uncertainty, if signal intensity is low. Though only leaching with nitric acid (using microwave digestion or hot-plate digestion) was used for the analysis of the samples, which is partially suitable for the complete dissolution of the possibly occurring refractory hot particles, significant difference between the recommended values and replicate results was not observed. It is also noteworthy that ^{237}Np could also be identified in the mass spectra at *m/z* = 237 in case of IAEA-384 and IAEA-385 samples. As neptunium behaves similarly to plutonium in the above described separation scheme (Np(IV) co-precipitates with CaF_2 in reductive medium and has high affinity to TEVA^{TM} resin (**Fig. 9.**)), it indicates that the method can be extended to neptunium analysis, though its quantification is hindered by the lack of a suitable and widely available Np tracer.

5.2.5. Novelty and Significance of the Method Developed

A novel rapid and simple procedure has been developed for the determination of plutonium (concentration and isotope ratios) from various environmental matrices (biota, soil and sediment) by ICP-SFMS and alpha spectrometry. The proposed method effectively eliminates the possible polyatomic interferences of the mass spectrometric analysis and also removes interfering radionuclides that may disturb the alpha spectrometric measurement. For ^{239}Pu, ^{240}Pu and ^{241}Pu limits of detection of 9.0 fg g^{-1} (0.021 mBq), 1.7 fg g^{-1} (0.014 mBq) and 3.1 fg g^{-1} (11.9 mBq) were achieved by ICP-SFMS, respectively, and 0.02 mBq by alpha spectrometry, which is sufficiently low for most environmental applications and comparable to other methods described in the literature (**Table 11.**). The proposed sample preparation method is significantly faster and easier to carry out than the other procedures described in the literature. Using ICP-SFMS detection, plutonium concentration and isotopic composition can be obtained within one day, which is highly advantageous for nuclear preparedness or if numerous samples have to be processed. The method was validated by the analysis of certified reference materials and the measured plutonium concentrations agreed well with the recommended or information values. The high recovery of the sample preparation indicates the robustness of the method, which is substantial in the case of sediment or soil samples, and provides opportunity for higher pre-concentration of the analyte and, by this means, for the further improvement of the detection limit.

5.3. Method Developed for Environmental ^{241}Am Analysis by ICP-SFMS

5.3.1. Sample Preparation

After the addition of ^{243}Am tracer (Amersham International, UK) to the homogenized sample (0.5-10 g depending on activity level), digestion and leaching were carried out on a hotplate using twice the volume of concentrated HNO_3 with some drops of H_2O_2. The sample was heated for at least 3 hours. After cooling to room temperature, the sample was filtered gravimetrically through a Whatman 2 type paper filter into a 50-mL polyethylene centrifuge tube. The residue was rinsed carefully with dilute nitric acid and the rinsing solution was added to the filtrate. The filtered sample was diluted to approximately 35 mL.

To the sample 1 mL of 0.4 g mL^{-1} $Ca(NO_3)_2$ solution was added. After complete dissolution, 7 mL of concentrated HF was added carefully to the sample and mixed thoroughly. In contrast to the plutonium method, reduction of the sample is not necessary at this stage. After 15 minutes, the sample was centrifuged, the supernatant was discarded. The precipitate was rinsed with 5 mL 4% HF solution, the washing solution was discarded. The final precipitate was dissolved in 15 mL 3 M HNO_3 containing 500 mg of H_3BO_3. To the solution, 1.5 mL of freshly prepared 0.6 M ferrous-sulphamate solution and 200 mg of ascorbic acid were added to reduce traces of Fe(III), which may interfere with the uptake of Am on TRU^{TM} resin [64]. This pre-concentration in acidic media effectively removes the major matrix cations (e.g. alkali metals and transition metals) and main anions (phosphate and sulphate) that may interfere with the TRU^{TM} extraction chromatographic separation, similarly to the plutonium determination described previously. Most of uranium is also separated from the analyte in this step. After conditioning of the TRU^{TM} resin with 10 mL of 3 M HNO_3, the sample was loaded on the column. Flow rate was approximately 1 mL min^{-1}. The column was rinsed with 8 mL of 3 M HNO_3, 1 mL of 3 M HNO_3/0.1 M $NaNO_2$ and 10 mL of 3 M HNO_3, successively. This combination of eluents is used for the on-column oxidation of remaining Pu to Pu(IV), which strongly retains on the column, thus it allows a complete separation from the analyte in the following step. Americium was eluted from the column using 2 mL of concentrated HCl and 20 mL of 4 M HCl into a PFA beaker. The eluate was evaporated to almost dryness followed by successive addition of 2 mL HNO_3 and drops of H_2O_2 to destroy organic resin residual and to remove HCl that may cause chloride interferences. Finally, the residue was dissolved in three times 300 µL of 2% nitric acid while heating slightly. The schematic diagram of sample separation is shown in **Fig. 15.** In order to validate the ICP-SFMS measurements, the ^{241}Am concentrations in the samples were determined also by alpha spectrometry. The alpha spectrometric procedure is the standard methods used at IAEA Marine Environment Laboratory and described in details elsewhere [54]. In short, after the addition of ^{243}Am tracer and proper dissolution (digestion and leaching with HNO_3/H_2O_2 mixture) thorium and plutonium were removed by anion exchange chromatography. The ^{241}Am in the effluent and wash solutions was pre-concentrated by calcium oxalate co-precipitation. After ashing the precipitate, americium was separated from the interfering polonium by means of anion exchange chromatography in concentrated hydrochloric medium. The leftover matrix components (alkali earth metals, some transition metals) were removed by extraction chromatography using TRU^{TM} resin or liquid-liquid extraction with DDCP. Finally, lanthanides that may result in the deterioration of alpha spectrum due to self-absorption were separated by anion exchange chromatography applying methanol/hydrochloric acid mixture as a mobile phase. Sources for alpha spectrometry were prepared by electrodeposition in order to achieve better resolution (**Chapter 3.3.2.**). The chemical recovery ranged between 41 and 70%. The sample preparation for alpha spectrometry usually lasts 5-6 days.

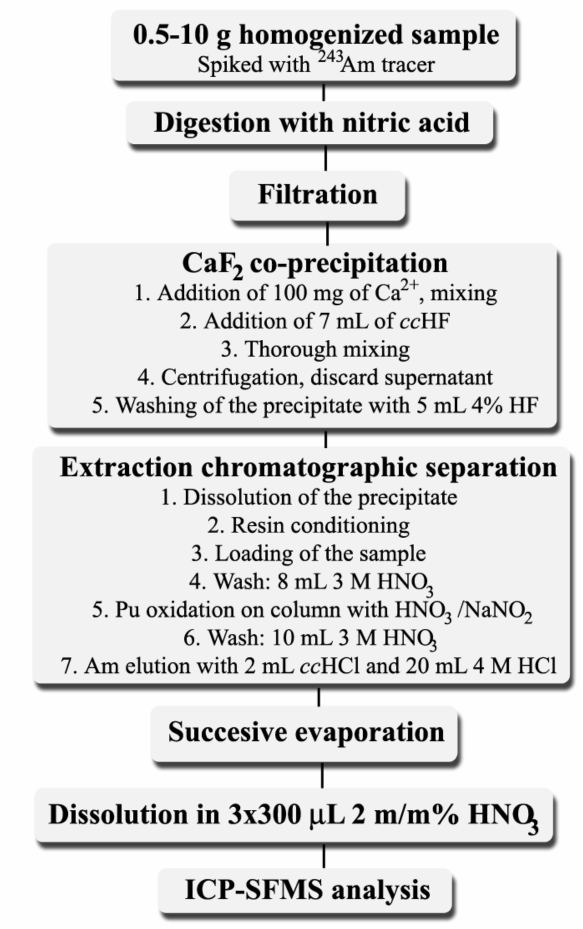


Fig. 15. Schematic diagram of ^{241}Am sample preparation for ICP-SFMS analysis

5.3.2. Analysis by ICP-SFMS and Alpha Spectrometry

The mass spectrometric analysis was carried out using a double-focusing magnetic sector inductively coupled plasma mass spectrometer equipped with a single electron multiplier (ELEMENT, Thermo Electron Corp., Bremen, Germany). All measurements were carried out in low resolution mode (*R* = 300) using a low-flow microconcentric nebulizer operated in a self-aspirating mode (flow rate was 60 µL min^{-1}) in combination with a desolvation unit (MCN-6000, CETAC Technologies Inc., Omaha, NE, USA). Optimized operating parameters are summarized in **Appendix C**. Prior to analysis of samples, the instrument was tuned using a 1 ng g^{-1} multielement solution (Merck, Darmstadt, Germany). The optimization was carried out with respect to maximum uranium sensitivity and low UO$^+$/U$^+$ ratio. Sensitivity was approximately 1.2 × 10^6 cps for 1 ng g^{-1} ^{238}U, UH$^+$/U$^+$ and UO$^+$/U$^+$ ratios were less than 6.6 × 10^{-6} and 3 × 10^{-4}, respectively. Sources for alpha spectrometry were prepared by electrodeposition [94]. Alpha sources were counted by a PIPS type Si alpha detector with a surface area of 450 mm^2 attached to an alpha spectrometer (Canberra Inc., USA).

5.3.3. Removal of Interferences and Matrix Components

In case of ultra-trace level ^{241}Am analysis by ICP-SFMS the complete removal of possible isobaric (e.g. ^{241}Pu from ^{241}Am) and polyatomic (e.g. $^{209}Bi^{16}O_2^+$ or $^{206}Pb^{35}Cl^+$ at *m/z* = 241) interferences is of vital importance in order to obtain accurate results (**Chapter 3.4.**). The main possible spectral interferences that can arise during americium analysis by ICP-SFMS together with required mass resolution and their relative abundances are summarized in **Table 17.**

Table 17. Potential ICP-MS spectral interferences of ^{241}Am determination with required mass resolution and relative abundances

Isotope		**Required mass resolution**	**Relative abundance (%)**
^{241}Am (analyte) (*m/z* = 241)	$^{241}Pu^+$	10786988	-
	$^{209}Bi^{32}S^+$	2310	95
	$^{209}Bi^{16}O_2^+$	2783	99.6
	$^{206}Pb^{35}Cl^+$	2124	18.3
	$^{205}Tl^{36}Ar^+$	2099	0.24
	$^{204}Pb^{37}Cl^+$	2045	0.34
	$^{207}Pb^{34}S^+$	2132	0.93
	$^{201}Hg^{40}Ar^+$	1942	13.1
^{243}Am (tracer) (*m/z* = 243)	$^{208}Pb^{35}Cl^+$	2097	39.7
	$^{207}Pb^{36}Ar^+$	2061	0.075
	$^{206}Pb^{37}Cl^+$	2009	5.8
	$^{209}Bi^{34}S^+$	2149	75.8
	$^{203}Tl^{40}Ar^+$	1919	29.4

As higher resolution (e.g. R = 4000) results in lower sensitivity, the interferences were eliminated by chemical separation instead of using higher instrumental mass resolution. The application of CaF_2 as a selective co-precipitating agent effectively removes the major matrix constituents and those components that interfere with the TRU™ extraction chromatographic separation (e.g. alkali metals, most transition metals together with Fe(III), sulphate and phosphate) similarly to the method developed for Pu analysis (**Chapter 5.2.3.**). The separation of these interferences is more important for TRU™ procedures, as for ^{241}Am separation this resin is less robust to several matrix components than TEVA™ [64]. However, another cleaning step is necessary to obtain a pure americium fraction for analysis, and to completely remove the relatively high amount of naturally occurring Bi, Pb, Hg and Tl as well as the anthropogenic ^{241}Pu from the final fraction that may result in elevated background and incorrect result. In order to test the complete removal of these interferences, a test solution containing known amounts of Bi, Pb, Hg and Tl in the 1 – 10 µg g^{-1} concentration range was processed. The decontamination factors (defined as the weight of the analyte of interest before the sample preparation in the sample and thereafter in the measured fraction) were higher than 18000, 12000, 8000 and 24000 for Bi, Pb, Hg and Tl, respectively. The elimination of ^{241}Pu was verified by the addition and measurement of ^{242}Pu isotopic tracer (NIST 4334F, USA) at m/z = 242. The decontamination factor of plutonium was higher than 25000. The separation of Pb(II), Tl(I) and Hg(II) was accomplished by the extraction chromatographic step as TRU™ has low distribution coefficient for these ions [64]. Though Bi(III) and Pu(III) have similar distribution coefficients to that of Am(III), Bi(III) forms highly stable complex with ascorbic acid impeding its retention on the resin, while plutonium, oxidised to Pu(IV) on-column by the addition of 3 M HNO_3/0.1 M $NaNO_2$ during rinsing, has extremely high affinity to TRU™ resin strongly retaining Pu(IV) through the Am elution step [64] . The concentration of Pb, Bi, Hg, Tl and U in the final fractions of each sample was less than 4 ng g^{-1}, 0.05 ng g^{-1}, 0.08 ng g^{-1}, 0.05 ng g^{-1}, 0.2 ng g^{-1}, respectively, which is comparable to that of the method blank with background intensities at m/z = 241 and m/z = 243 of less than 0.2 cps. As the ^{241}Pu concentration in most environmental samples is below 100 fg g^{-1}, the decontamination factor of 25000 is high enough to eliminate the isobaric ^{241}Pu interference. Since the hydride formation rate using desolvation sample introduction system is approximately 10^{-5}-10^{-6}, hydride interferences (e.g. $^{240}Pu^{1}H^{+}$ at m/z = 241) do not cause elevated background. Thus, the final fraction obtained after extraction chromatography separation is free of potentially interfering elements that enables to achieve low background and accurate results.

5.3.4. Figures of Merit and Validation of the Method

The detection limit of ^{241}Am analysis by ICP-SFMS (on the basis of three times the standard deviation of method blank) calculated for 1-gram of sample without pre-concentration for easier comparison is 0.86 fg g^{-1} (0.11 mBq g^{-1}), which is comparable to that of alpha spectrometry (typically 0.1 mBq, depending on chemical recovery and counting time). Using higher pre-concentration factor the detection limit can be further improved. The precision of Am isotope ratio measurements, which is the most significant parameter for the assessment of total uncertainty ranged between 8-40% at 95% confidence level (k = 2) depending on activity level. The chemical recovery of sample preparation calculated using ^{243}Am tracer was between 72 and 94%, which is better than that of alpha spectrometry, possibly due to the fewer sample preparation steps. The entire analysis (both sample preparation and ICP-SFMS measurement) can be accomplished within one day, thus significantly faster than alpha spectrometry. The main characteristics of ICP-SFMS analysis in comparison with alpha spectrometry are summarized in **Table 18.**

Table 18. Main characteristics of alpha spectrometric and ICP-SFMS analysis for ^{241}Am determination

	Alpha spectrometry	**ICP-SFMS**
Absolute detection limit	0.79 fg (0.1 mBq)	0.86 fg (0.11 mBq)
Precision (*k* = 2)	5-35%	8-40%
Sample preparation duration	5-6 days	1 day
Measurement time	3-10 days	2 hours
Chemical recovery	41-70%	72-94%

Different types of low-level environmental reference materials were measured to validate the procedure. The results of IAEA-384 (Fangataufa lagoon sediment), IAEA-385 (Irish Sea sediment) and IAEA-308 (mixed seaweed from the Mediterranean Sea) obtained by both ICP-SFMS and alpha spectrometry together with reference or recommended values [146-148] are shown in **Table 19.**

Table 19. ^{241}Am analysis results and reference values of the investigated reference materials. All data are presented at 95% confidence level (k =2). Number of replicates: n = 2. Reference date: 1 May, 2006.

	Alpha spectrometry	**ICP-SFMS**	**Reference value**
IAEA-384 Fangataufa lagoon sediment	56 ± 5 fg g^{-1} (7.1 ± 0.6 mBq g^{-1})	55.7 ± 7.5 fg g^{-1} (7.07 ± 0.95 mBq g^{-1})	58-65 fg g^{-1} (7.4-8.3 mBq g^{-1})
IAEA-385 Irish Sea sediment	28 ± 4 fg g^{-1} (3.6 ± 0.5 mBq g^{-1})	33.5 ± 3.9 fg g^{-1} (4.25 ± 0.50 mBq g^{-1})	31-35 fg g^{-1} (3.9-4.4 mBq g^{-1})
IAEA-308 Mixed seaweed	1.7 ± 0.4 fg g^{-1} (0.22 ± 0.05 mBq g^{-1})	1.94 ± 0.64 fg g^{-1} (0.246 ± 0.081 mBq g^{-1})	1.3-2.0 fg g^{-1} (0.16-0.25 mBq g^{-1})

In case of IAEA-384 and IAEA-385, the reference values were corrected by both the decay of ^{241}Am and the in-growth from ^{241}Pu (correction factors are 1.10 and 1.08, respectively). As reference or information value for ^{241}Pu concentration is not available in for IAEA-308, only uncorrected ^{241}Am activity concentration is presented, which is estimated to be 5-10% lower than the corrected value as a consequence of ^{241}Am in-growth [149]. The measured ICP-SFMS results are in good agreement with the reference values and those obtained by alpha spectrometry.

5.3.5. Novelty and Significance of the Method Developed

An improved and novel analytical method has been developed for ^{241}Am analysis by ICP-SFMS. The sample preparation method proposed is significantly easier and less labor-intensive than those required for the radioanalytical techniques. The entire analysis (both sample preparation and ICP-SFMS measurement) can be accomplished within one day, thus much faster than gamma or alpha spectrometry. The procedure involves a selective CaF_2 pre-concentration, which can be suitably combined with the following extraction chromatographic separation using TRU^{TM} resin. The achieved absolute detection limit of 0.86 fg (0.11 mBq) is comparable to that of alpha spectrometry (0.1 mBq) and suitable for low-level environmental measurements. Analysis of different kinds of environmental standard reference materials (IAEA-384 – Fangataufa lagoon sediment, IAEA-385 – Irish Sea sediment and IAEA-308 – Mixed seaweed from the Mediterranean Sea) and alpha spectrometry were used to validate the procedure. The results obtained are in good agreement with reference values and those measured by alpha spectrometry. As the proposed method offers a rapid and less labor-intensive possibility for low-level ^{241}Am determination than the traditionally applied radioanalytical techniques, it can be a competitive alternative for environmental ^{241}Am analysis.

5.4. Sequential Method for the Simultaneous Determination of Plutonium and ^{241}Am by ICP-MS and Alpha Spectrometry

5.4.1. Sample Preparation

The dissolution and CaF_2 pre-concentration of this method is similar to the previously described procedures. After weighing the homogenized sample (0.5-3 g depending on activity level) into a PFA microwave digestion vessel, ^{242}Pu (NIST 4334F, USA) and ^{243}Am (Amersham International, UK) tracers were added to the sample. Following the addition of 10 mL concentrated HNO_3, the sample was digested employing a MARS5 microwave digestion system using temperature control. The sample was heated up to 175 ^{o}C in 5.5 minutes and held at that temperature for 9.5 minutes. After cooling to room temperature the sample was filtered gravimetrically through a Whatman 2 type paper filter into a 50-mL polyethylene centrifuge tube. The soil residue and the PFA liner were rinsed carefully, the rinsing solution was added to the filtrate. The sample was diluted to approximately 35 mL.

To the filtered sample 1 ml of 0.4 g mL^{-1} $Ca(NO_3)_2$ solution was added. After mixing, 300 mg of $NH_2OH.HCl$ was added carefully to the sample. After complete dissolution, the tube was placed in a 90 ^{o}C water bath for 10 minutes. Plutonium is reduced to Pu(III) in this step leaving Am in Am(III) state. After cooling down to room temperature, 5 mL of concentrated HF was added carefully to the sample and mixed thoroughly. After 15 minutes the sample was centrifuged and the supernatant was discarded. The precipitate was rinsed with 10 mL 5% HF solution. The final precipitate was dissolved in 15 mL 4 M HNO_3 and 500 mg of H_3BO_3. To the solution, 2 mL of freshly prepared 0.6 M ferrous-sulphamate solution and 200 mg of ascorbic acid were added to reduce traces of Fe(III) which may interfere with the uptake of Am on TRU^{TM} resin [64]. The pre-concentration in acidic media effectively removes the major matrix cations (e.g. alkali metals and transition metals) and main anions (phosphate and sulphate) that may interfere with the extraction chromatographic separation. Most of uranium is also separated from the analytes in this step.

The developed separation method is a modified procedure proposed by Horwitz *et al.* [64] and Thakkar [75]. This method is less prone to matrix effects due to the effective separation of the interfering components in the CaF_2 pre-concentration step. Although the procedure is applicable for the separation of U, Th/Np, Pu and Am/Cm, the aim was to optimise the method for the anthropogenic Am and Pu analysis, which are the most important radionuclides for environmental monitoring and safeguards purposes. Moreover, for U and Th analysis lower sample amount would be sufficient due to their higher concentration level. The UTEVA^{TM} and TRU^{TM} columns were placed in tandem, i.e., the eluate passing through the UTEVA^{TM} resin enters directly into the TRU^{TM} column. By this arrangement, the upper UTEVA^{TM} column retains U and Th, the lower TRU^{TM} column collects the analytes (Pu(III) and Am(III)), while the matrix components (e.g. alkali and alkali earth metals or Fe(II)) are not extracted by either resin and removed from the column by the load and washing steps. After conditioning of the columns with 10 mL of 4 M HNO_3, the sample was loaded on the columns. After rinsing the columns twice with 4 mL of 4 M HNO_3, the columns were separated, and only the TRU^{TM} column was used for the further steps. The Pu on the resin was oxidized to Pu(IV) by addition of 5 mL 4 M HNO_3/0.1 M $NaNO_2$. First americium was eluted from the column using 3 mL of 9 M HCl and 20 mL of 4 M HCl into a PFA beaker. The eluate was evaporated three times with successive addition of HNO_3 to remove HCl, and the residue was dissolved in dilute nitric acid (1.6 mL) after slight heating. Traces of Th (1-5%) that may pass through the UTEVA^{TM} resin were removed by adding 20 mL 0.3 M HF/4 M HCl to the TRU^{TM} column. Finally, plutonium was eluted by 10 mL of 0.1 M ammonium-bioxalate solution. The solution was repeatedly evaporated to near dryness (3 times) with successive addition of concentrated HNO_3 and H_2O_2 to remove organic residue and to eliminate the HCl content in the sample that may cause chloride molecular interferences at the ICP-SFMS analysis (**Appendix A**). The residue was dissolved in dilute nitric acid (1.6 mL) after heating slightly. The Am and Pu fractions obtained were divided into a 0.5 mL aliquot for ICP-SFMS analysis and a 1.1 mL aliquot for alpha spectrometric measurement. The schematic diagram of the sequential separation is shown in **Fig. 16.**

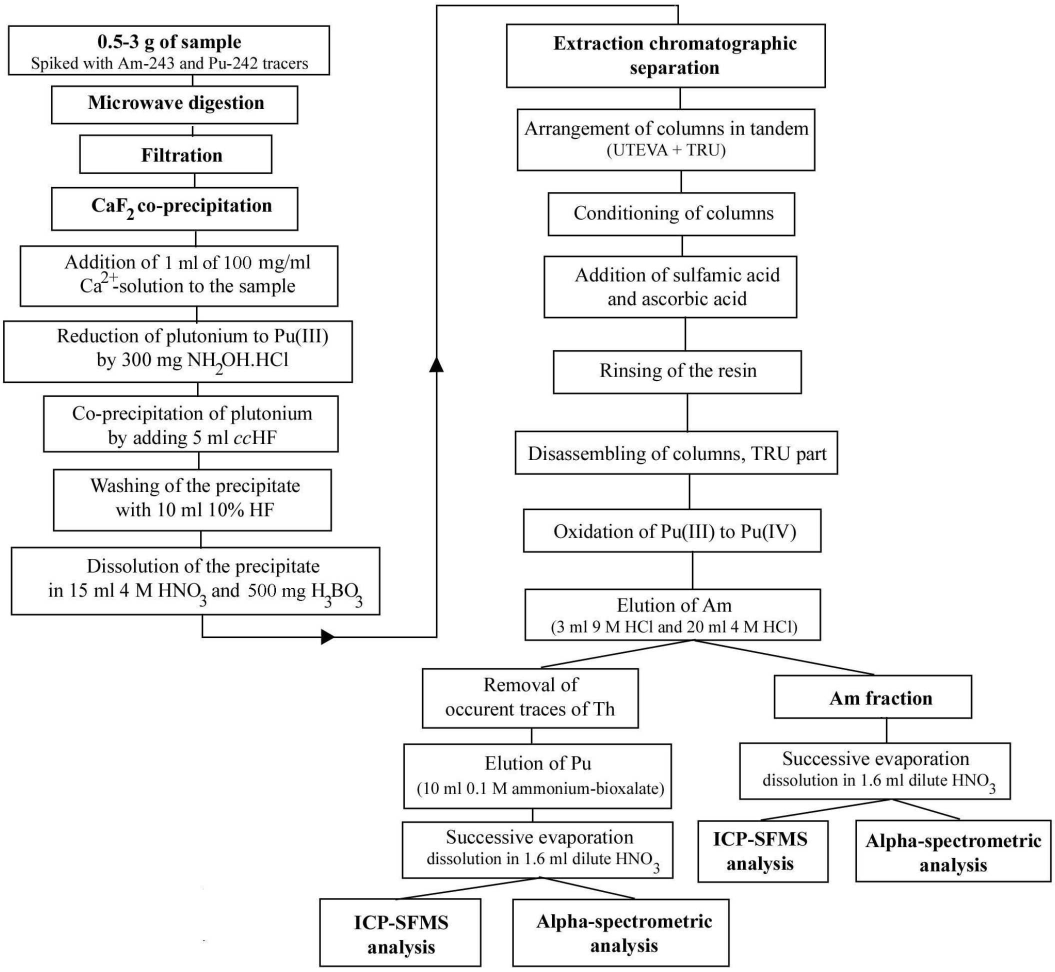


Fig. 16. Schematic diagram of the sample preparation of the sequential method

5.4.2. Analysis by ICP-SFMS and Alpha Spectrometry

The mass spectrometric analyses of americium and plutonium were carried out using a double-focusing magnetic sector inductively coupled plasma mass spectrometer equipped with a single electron multiplier (ELEMENT2, Thermo Electron Corp., Bremen, Germany). All measurements were carried out in low resolution mode ($R = 300$) using a low-flow T1-H nebulizer operated in a self-aspirating mode (flow rate was 60 µL min^{-1}) in combination with a desolvation unit (Aridus, CETAC Technologies Inc., Omaha, NE, USA). Optimized operating parameters are summarized in **Appendix D**. Prior to the analysis, the instrument was tuned using a 1 ng g^{-1} uranium standard solution. Sensitivity was about 2×10^6 cps for 1 ng g^{-1} ^{238}U. Alpha sources were counted by a PIPS type Si alpha detector with a surface area of 450 mm^2 attached to an alpha spectrometer (Canberra Inc., USA). Concentrations of isotopes of interest were calculated as a function of $^{239}Pu/^{242}Pu$, $^{240}Pu/^{242}Pu$, $^{241}Pu/^{242}Pu$ and $^{241}Am/^{243}Am$ ratios according to the isotope dilution method. All raw data were corrected taking into account instrumental mass bias using linear correction [150]. Sources for alpha spectrometric analysis were prepared by NdF_3 micro co-precipitation (plutonium) [95] and electrodeposition (plutonium and americium) [94]. The overall uncertainty was calculated with error propagation rules taking into account the uncertainty of the weight measurements, tracer concentrations and the measured intensities.

5.4.3. Removal of Interferences and Matrix Components

The main advantage of the above-described pre-concentration step is that it is carried out in acidic media leaving the major matrix components (e.g. alkali metals and most transition metals) and possible interferences of extraction chromatographic separation (e.g. phosphate, sulphate) and mass spectrometric analysis (e.g. most of uranium) in the liquid phase (**Chapter 5.2.3.**). The pre-concentration step involving CaF_2 has a great advantage that it can be used in combination with the different resins (i.e. UTEVA^{TM} and TRU^{TM}), though these resins require different conditions for the ideal separation. The removal of iron, which may supersede Pu(III) and Am(III) and cause low recoveries, as a stable fluoride-complex assures the proper conditions for the TRU^{TM} separation [64]. In this scheme, UTEVA^{TM}, in fact, serves only as a clean-up from U and Th. The selective pre-concentration step also overcomes the problem of overloading of the extraction chromatographic column. The application of the extraction chromatographic separation further purifies the americium and plutonium fractions removing the leftover Th, U and other components (e.g. Pb, Bi, Hg) that could possibly form molecular interference (e.g., $^{238}U^{1}H^{+}$, $^{207}Pb^{16}O_2^{+}$, $^{204}Pb^{36}Ar^{+}$, $^{209}Bi^{31}P^{+}$ or $^{200}Hg^{40}Ar^{+}$) during the ICP-SFMS measurement (see **Chapter 3.4.**). The major interfering nuclides in the alpha spectrometric analysis (e.g. ^{210}Po, ^{228}Th) are separated from the analytes and cross contamination between the Pu and Am fractions is also avoided by the on-column oxidation of Pu(III) to Pu(IV), which highly retains on TRU^{TM} with significant difference in the distribution coefficient with Am(III). The decontamination factors (the ratio of weight of the element of interest in the sample and the final Am and Pu fractions) are presented in **Table 20.**

Table 20. Decontamination factors (DF) of the actinides in Am and Pu fractions

Fraction	DF_{Th}	DF_U	DF_{Pu}	DF_{Am}
Am	1×10^6	5×10^5	$> 10^3$	-
Pu	1×10^4	1.5×10^4	-	$> 10^3$

The U and Th contents of the sample were determined in an independent analysis. In order to check the complete removal of molecular interferences, a "blank" soil sample, free from artificial radionuclides taken from a cave at a depth of 80 meter was also analysed together with the samples. The measured signals at *m/z* = 239, 240, 241, 242 and 243 were negligible and agreed with the procedural blank within the measurement uncertainty. The level of possible hydride and oxide interferences (e.g. $^{238}U^1H^+$ or $^{207}Pb^{16}O_2^+$) were further reduced by using Aridus desolvation sample introduction system (UH^+/U^+ ratio was less than 5×10^{-6}), thus mathematical correction of hydride interference at *m/z* = 239 was not necessary.

5.4.4. Figures of Merit and Validation of the Method

The limits of detection (LOD) of the ICP-SFMS analysis and alpha spectrometry are calculated for a 1-gram sample for easier comparison (**Table 21.**). Using higher sample amounts (i.e. higher pre-concentration) or longer measurement time (in case of alpha spectrometry) the LODs can be further improved. Calculation of the LOD of ICP-SFMS was based on three times the standard deviation of the method blank, in the case of alpha spectrometry the Currie-method [145] was applied. The LODs expressed in activity concentration of the two different methods depend on the half-lives of the isotopes of interest. The longer the half-life of the isotope (the lower its specific activity), the lower the LOD of ICP-SFMS analysis, while on the contrary alpha spectrometry provides higher sensitivities for the short-lived nuclides having higher specific activity. For instance, the lowest LOD in activity was achieved for ^{239}Pu, as this is the longest-lived and the LODs are similar for each radionuclide. For the determination of activity concentration of ^{241}Pu radioanalytical methods, for example liquid scintillation can be applied to validate the ICP-SFMS results. The recovery of the sample preparation calculated as the ratio of ^{243}Am and ^{242}Pu tracer amount before and after the procedure was between 81-94%. This high yield indicates the robustness of the method. The ^{241}Am results measured by ICP-SFMS are comparable to those of alpha spectrometry indicating that ^{241}Am analysis by ICP-SFMS with the sequential method can be applicable for the analysis of environmental samples even with low ^{241}Am content (approximately 1 Bq kg^{-1}). Though the LODs of the sequential method are inferior to those of the methods optimized for either Pu or ^{241}Am (**Chapter 5.2.** and **Chapter 5.3.**), the sequential analysis can be performed much faster and less sample amount is required, as the analytes are determined from one sample simultaneously. Moreover, the LODs can be further improved, if dividing of the final fraction is not necessary.

Table 21. Limits of detection of the sequential method calculated for 1-gram of sample. ^{a} ^{240}Pu/^{239}Pu ratio dependant

Isotope	Technique	LOD in fg	LOD in mBq
^{238}Pu	Alpha spectrometry	0.2	0.1
^{239}Pu	ICP-SFMS	15	0.034
^{240}Pu	ICP-SFMS	9.2	0.077
$^{239+240}$Pu	Alpha spectrometry	-^{a}	0.1
^{241}Pu	ICP-SFMS	14	54
^{241}Am	ICP-SFMS	23	2.9
^{241}Am	Alpha spectrometry	0.8	0.1

In order to validate the procedure, two international reference materials, IAEA-384 (Fangataufa Lagoon sediment) [147] and IAEA-385 (Irish Sea sediment) [148] were analysed by the method developed. The determined activity concentrations of ^{239}Pu, ^{240}Pu and ^{241}Am obtained by ICP-SFMS as well as ^{238}Pu, $^{239+240}$Pu and ^{241}Am results by alpha spectrometry are presented in **Table 22.** and **Table 23.** The recommended or information values are also indicated in the tables. For the decay correction of ^{241}Am both the decay of ^{241}Am and the in-growth from ^{241}Pu using the information values of ^{241}Pu were taken into consideration.

Table 22. Activity concentrations of ^{241}Am and plutonium isotopes in IAEA-384 reference material in Bq kg^{-1}. All data are presented at 95% confidence level. Number of replicates: n = 3. Reference date: 20 January, 2006. ^{a}: Information value

	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Am	$^{239+240}$Pu
ICP-SFMS	-	95.6 ± 4.8	18.7 ± 1.5	7.5 ± 2.8	-
Alpha spectrometry	35.0 ± 3.0	-	-	7.1 ± 0.6	102 ± 11
Recommended value [147]	38.1-40.1	85-109^{a}	14.0-19.2^{a}	7.4-8.3	105-110

Table 23. Activity concentration of ^{241}Am and plutonium isotopes in IAEA-385 reference material in Bq kg^{-1}. All data are presented at 95% confidence level. Number of replicates: n = 3. Reference date: 20 January, 2006. ^{a}: Information value

	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Am	$^{239+240}$Pu
ICP-SFMS	-	1.63 ± 0.12	1.12 ± 0.18	3.7 ± 0.8	-
Alpha spectrometry	0.51 ± 0.07	-	-	3.6 ± 0.5	3.01 ± 0.35
Recommended value [148]	0.45-0.50	1.30-2.07^{a}	0.97-1.32^{a}	3.9-4.4	2.81-3.14

The measured results agree well with the recommended or information values. The analysis of ^{238}Pu by ICP-SFMS is precluded by the presence of even a small amount of ^{238}U in the Pu-fraction, which makes ^{238}Pu determination difficult by the mass spectrometric methods. In the Pu-fractions, ^{241}Pu was also detected at m/z = 241 above the detection limit, though it could not be quantified due to the low signal intensity. If higher pre-concentration is used or only ICP-SFMS analysis is done without dividing the sample, the analysis of ^{241}Pu can also be possible.

5.4.5. Novelty and Significance of the Method Developed

An improved and novel sequential sample preparation method has been developed for the simultaneous determination of the most important plutonium isotopes and ^{241}Am by ICP-SFMS spectrometry and alpha spectrometry. The method allows a simple and rapid measurement possibility for the plutonium and americium measurements from environmental matrices. Using the method developed, the determination of Pu and ^{241}Am from environmental matrices can be carried out easier and less tediously than by the traditionally applied radioanalytical and mass spectrometric methods. The procedure involves a selective CaF_2 pre-concentration followed by an extraction chromatographic separation using UTEVA^{TM} and TRU^{TM} resins. The achieved detection limits of 1-10 fg g^{-1} is suitable for low-level environmental analysis. Analysis of different kinds of environmental standard reference materials (IAEA-384 – Fangataufa lagoon sediment, IAEA-385 – Irish Sea sediment) and alpha spectrometry were used to validate the procedure. The results obtained are in good agreement with the reference values and those measured by alpha spectrometry. The method is particularly useful, if rapid measurement is required, limited sample amount is available, or if it is important that plutonium and americium concentrations should be measured from the same sample, such as for origin assessment investigations.

6. Origin Assessment of Environmental Transuranics by Isotopic Composition

6.1. Objectives and Methodologies Used for Origin Assessment

The aim of this study was to evaluate the applicability of ICP-SFMS and alpha spectrometry for the characterization and origin assessment of environmental plutonium contamination. By the measurement of plutonium and americium isotopic composition (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{241}Am) using the analytical methods described in the previous chapters, we can obtain information not only on the concentration and hazard, but also on the possible origin of the environmental actinides, which is a basic parameter in safeguards and environmental monitoring. As plutonium isotope ratios reflect the formation conditions (**Chapter 2.2.1.**), it can be exploited for the identification of the release source. However, as the dispersion in the environment is highly inhomogeneous, and in most cases several sources with highly variable isotopic pattern can contribute to the plutonium content, it is a difficult task to interpret the isotope ratios of real environmental samples. Thus, for environmental monitoring and safeguards purposes, measurement of as many isotope ratios as possible is required by radioanalytical methods (e.g. alpha spectrometry or liquid scintillation) together with the use of high sensitivity mass spectrometric techniques. Moreover, application of models is necessary for the reliable interpretation of isotope ratios and qualitative data treatment.

Contribution calculations of a certain contamination source by its isotopic composition have already been applied by some research groups. For instance, Kelley *et al.* applied ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu ratios to recognize non-fallout isotopic components and to calculate the troposheric and stratospheric debris contributions [32]. For the calculation of SNAP-9A (^{238}Pu-powered) satellite accident contribution to the global fallout plutonium, Hardy *et al.* used ^{238}Pu/$^{239+240}$Pu ratio. Ketterer *et al.* could calculate the contribution of Chernobyl accident to the total deposited plutonium in Poland using the ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios. These studies and calculations were applied in those cases, when the contaminating source was known. However, to give a prediction on the possible origin is more complicated. Moreover, as plutonium isotopic composition depends on the formation and irradiation conditions, different plutonium isotopic ratio can be characteristic and can be a better indicator for a certain contamination. Therefore, a certain plutonium isotope ratio can be more suitable and sensitive to a specific release. The previous studies were based on the measurement of one or two isotope ratios, therefore, these models are applicable for only two emission sources, and, more importantly, are not capable to detect (identify) the presence of another (third) contamination source. The previous studies do not investigate the minimal detectable contribution of a certain contamination. This value derive from the mathematical calculation of the origin calculation, and similar to the generally-used detection limit. As all data (isotope ratios measured or taken from the literature) used for the calculation have uncertainty, the contribution of a contamination source obtained also possesses error, which results in a statistically insignificant range. This uncertainty can be very high in several cases, for example, for low-level environmental samples or due to the highly discrepant literature values. Therefore, for the correct interpretation of origin assessment, these calculations have to be performed.

In this study higher and less contaminated environmental samples of several different locations were analysed and data obtained were used to assess the origin and release date of their plutonium content. Mixing models, similar to those developed earlier, were used to calculate the contribution of each source. The applicability and limitations of different plutonium isotope ratios (^{238}Pu/^{239}Pu, ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu) obtained by the different techniques (i.e. alpha spectrometry and ICP-SFMS) were investigated. In order to estimate the date of irradiation (or release date of the transuranics), which is an essential information in safeguards to distinguish previous contamination (e.g. Chernobyl) from a recent release, a feasibility study of the ^{241}Am/^{241}Pu isotope ratio for this purpose was carried out.

6.2. Samples Investigated for Origin Assessment

In order to evaluate the methods developed for origin assessment, several types of samples (soil, sediment and moss) from different locations, containing plutonium from different origins have been investigated. As the source of plutonium in several samples was known (almost for certain), these data served as reference values besides the literature values for origin assessment. In most cases commercially available reference materials supplied by the International Atomic Energy Agency were used due to their well-documented sampling conditions and wide variety of sampling sites. Furthermore, bioindicators, especially moss samples were measured. These samples were taken from higher-contaminated (collected by the Hungarian Nuclear Society in Chernobyl and Pripjaty in 2005) and less-contaminated (Hungary and south France) sites. The sample types, sampling locations and dates are summarized in **Table 24.** The sampling locations are shown in **Fig. 17.**

Table 24. The sample types investigated with locations and dates of sampling

Sample name	Sample type	Sampling location	Sampling date
AUSSED	Sediment	Neusiedlersee, 80 km southeast of Vienna, Austria	1986
AUSSOIL	Soil	Ebensee, Upper Austria	1983
BALTSED	Sediment	Baltic Sea	October 1986
CHERMOSS	Moss	Red Forest, Chernobyl Exclusion Zone, Ukraine	2005
ENEWSED	Sediment	Enewetak, Central Pacific Ocean	1990
HUNBIOTA	Biota (mixed weed and grass)	Central Hungary	May 1986
HUNMOSS	Moss	Gerecse Mountains, Hungary	2004
HUNMOSS2	Moss	Gerecse Mountains, Hungary	2004
IRSED	Sediment	Irish Sea	1995
IRSED2	Sediment	Lune Estuary, Irish Sea	1991
MEDWEED	Seaweed	Shore of Principality of Monaco	October 1986
MONMOSS1	Moss	La Turbie, Monaco	2006
MONMOSS2	Moss	Tete de Chien, Monaco	2006
PRIPMOSS	Moss	Pripjaty, Chernobyl Exclusion Zone, Ukraine	2005
FANSED	Sediment	Fangataufa, French Polynesia	1996
RUSSOIL	Soil	Novozybkov, Brjansk, Russia	1990

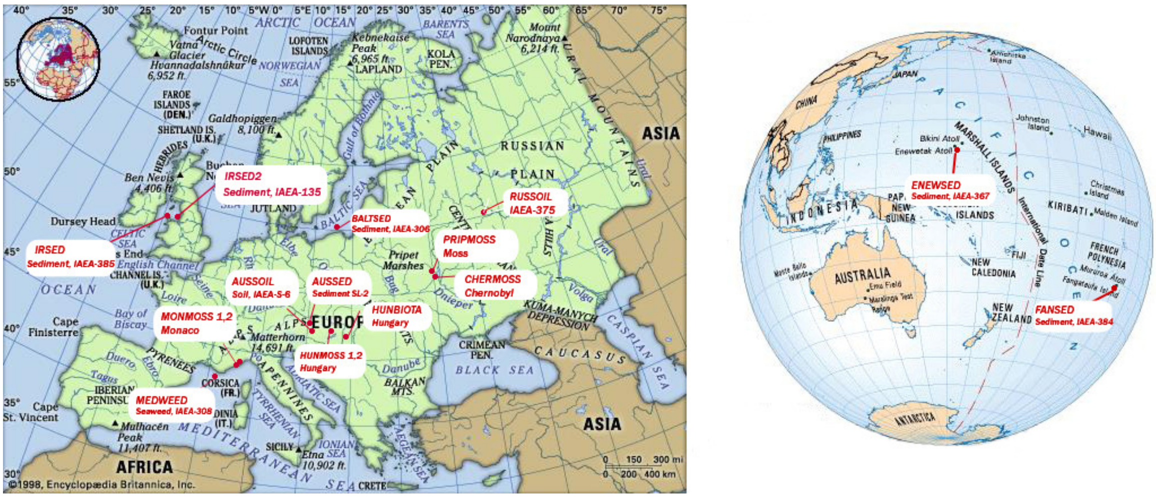


Fig. 17. Sampling locations of the samples investigated

6.3. Isotope ratios of the Investigated Samples

The measured activity ratios and atom ratios are shown in **Fig. 18.** The average fallout values of ^{238}Pu/^{239}Pu activity ratio (0.042 ± 0.015) and ^{240}Pu/^{239}Pu (0.018 ±

0.014) atom ratios in the Northern Hemisphere are also indicated (**Table 2.**). All ratios in **Fig. 18.** are decay corrected to 01.06.2006.

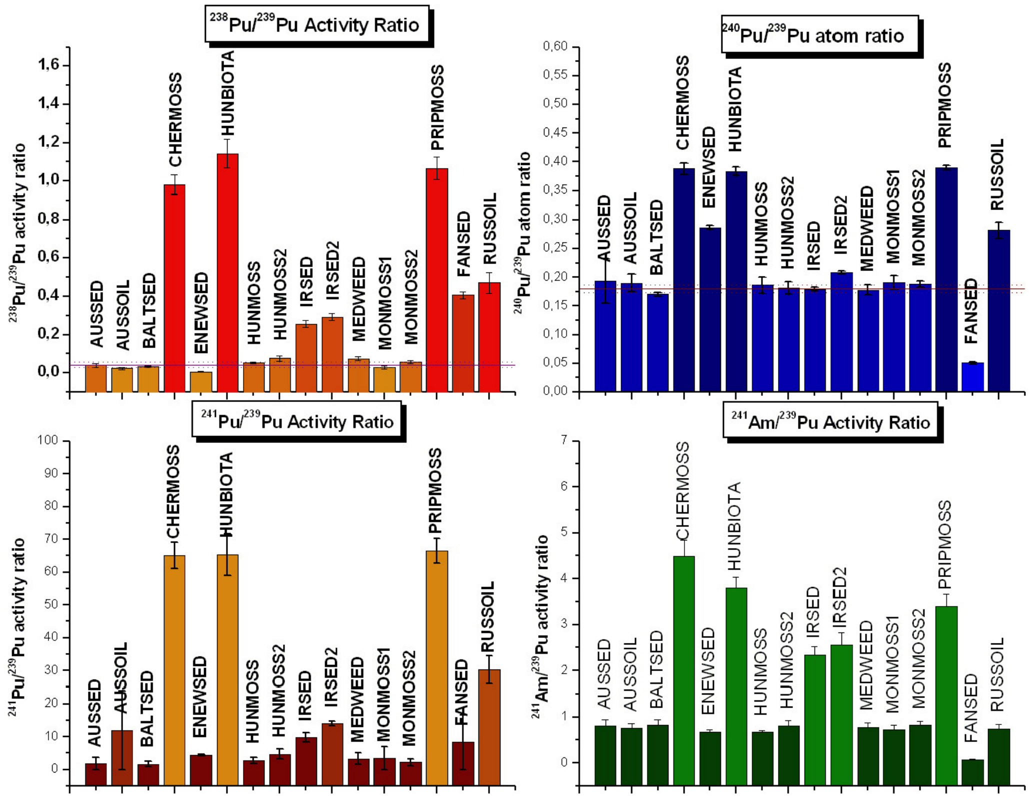


Fig. 18. The measured activity ratios and atom ratios in the samples investigated

According to the Pu isotope ratios, most low-level European environmental samples (AUSSED, AUSSOIL, BALTSED, HUNMOSS, HUNMOSS2, MEDWEED, MONMOSS1 and MONMOSS2) are mainly contaminated with plutonium from the global fallout of previous weapons tests, as all isotope ratios agree with the typical fallout values within the uncertainty indicated. It is important to note that each isotope ratios is in accordance with the global fallout values, thus it is unexpected that other sources highly contribute to their plutonium content. However, proper statistical evaluation of the data has to be performed in order to express quantitatively the contributions of each source, as small contribution of other sources may be "masked" and undetectable by the measurement uncertainty. Samples collected near the Chernobyl power plant (CHERMOSS and PRIPMOSS) contain dominantly reactor-grade plutonium with high burn-up (**Table 2.** and **Fig. 2.**). Similarly, biota (mixed weed and grass) sample collected in Hungary right after the Chernobyl accident has an indistinguishable isotopic pattern to that of the Chernobyl samples. The occurrence of different plutonium isotope ratios is the result of the inhomogeneous distribution of Chernobyl fallout deposition in Hungary, though to a lower extent than those of reported for Finland [151] or Poland [30]. The Chernobyl origin is also supported by the identical $^{243+244}$Cm/^{241}Am activity ratios measured by alpha spectrometry in the americium fraction, which was found to be 0.029 ± 0.005, 0.025 ± 0.009 and 0.021 ± 0.009 for the CHERMOSS, PRIPMOSS and HUNBIOTA samples, respectively. For the Irish Sea sediments (IRSED and IRSED2) the elevated level of higher mass plutonium isotopes possibly derives from contamination from Sellafield reprocessing plant [152]. It is important to note that contribution from reactor-grade plutonium was undetectable in IRSED sediment sample only using the ^{240}Pu/^{239}Pu atom ratio, as the measured value (0.179 ± 0.003) agreed within measurement uncertainty with the global fallout value of the Northern Hemisphere (0.180 ± 0.014) [32]. Thus, for reliable interpretation of isotope ratios, measurement of further plutonium isotopes, ^{238}Pu and ^{241}Pu was necessary. Samples taken from previous weapons tests site, ENEWSED and FANSED have completely different isotopic pattern. FANSED sample deriving from Fangataufa lagoon (French Polynesia) contains weapons-grade plutonium (^{239}Pu abundance is above 95%), which is typical in ^{239}Pu-enriched nuclear weapons (Pu-bomb) [27,153]. In case of Enewetak sample, the very low ^{238}Pu/^{239}Pu activity ratio and relatively high ^{240}Pu/^{239}Pu ratio are similar to those found after the Chinese fusion device test (H-bomb) in 1976 in Lop Nor by De Geer [154]. The elevated level of high-mass Pu isotopes can be explained by the multiple captures of neutrons in the natural uranium blanket in the extremely high neutron fluencies [154]. Thus, it is assumed that ENEWSED sample also contains transuranics of H-bomb origin. As the plutonium isotopic composition of the Russian soil sample (Novozybkov, Brjansk) differs from global fallout values, it is assumed to be contaminated by the Chernobyl accident. For the calculations of quantitative Chernobyl contribution fallout to the total transuranic content, application of mixing models is required.

6.4. Mixing Models for Source Contribution Calculations

It can be concluded from the isotopic patterns that different plutonium isotope ratios vary distinctly and their sensitivity to indicate contribution from other sources is different. Thus, it is an important parameter to assess which plutonium isotope ratio is a sensitive indicator for distinguishing various sources. In most cases the most frequent task is to differentiate between global fallout and reactor-grade plutonium in environmental samples for environmental monitoring and safeguards to monitor and evaluate possible accidents or (non-reported) radionuclide releases. For the calculation of the contributions of different sources having different isotopic composition, mixing models can be used [30,32], which allows the quantitative calculation of the contributing sources. The principal of this model is similar to isotope dilution. In most cases, use of two-component models is sufficient, when it is assumed that plutonium contains two distinct components with known isotope composition, for example A and B. The contribution of component A ($X\%$) to the total plutonium content can be calculated as follows:

$$X\% = \frac{R_M - R_B}{R_A - R_B} \cdot 100 \qquad \text{Eq. 2.}$$

where R_M, R_A and R_B are the isotope ratios of the sample, component A and component B, respectively. For more components the mixing model can be extended. As **Eq. 2.** contains the isotope ratios of the contributing Pu sources, the isotope ratios and their uncertainty used for contribution calculation have fundamental role, which have not been investigated in the previous works. The isotope ratios and their error define the minimum contribution of each component that can be determined at a certain statistical level. It is highly important in those cases, when the isotopic composition of the components have relatively high uncertainty, as it will result in high uncertainty in the contribution calculation as well. This holds for the inhomogeneous samples of close fallout of nuclear weapons tests or for Chernobyl accident, due to the presence of hot particles and fuel materials with completely different formation path and isotopic composition. Similarly, if the measurement uncertainty is high, it will cause the deterioration of contribution precision. As plutonium isotopic composition depends on the formation conditions, the sensitivity and applicability of a certain isotope ratio for the detection and calculation of a specific source contribution depends on the isotope ratio of the source. For example, for the assessment of ^{238}Pu-powered generator accidents to the total plutonium, only ^{238}Pu/^{239}Pu is suitable, as the other isotopes (e.g. ^{239}Pu, ^{240}Pu or ^{241}Pu) are not significant. In order to determine and compare the sensitivities of the different isotope ratios, the model was applied using two components, global fallout and Chernobyl, as the main contributors of plutonium contamination in Europe. Applying the two-component model (**Eq. 2.**), the contribution of the different sources for the analysed samples and the detectable minimum contribution of Chernobyl-derived plutonium can be calculated. The minimum detectable Chernobyl-derived plutonium contribution to global fallout was calculated at 99% confidence level (k = 3) in order to minimize acceptance error (also called *type II* or *error of the second type*). It means that the false detection (alarm) of Chernobyl-components should be as low as reasonable possible. The results obtained and the characteristics of the different isotope ratios used for origin calculations are summarized in **Table 25.**

Table 25. Characteristics of the different isotope ratios used for origin calculations

Isotope ratio	Minimum Chernobyl contribution detectable (3s)	Advantages	Disadvantages
^{238}Pu/^{239}Pu	2% contribution	Sensitive indicator	Alpha spectrometric analysis required
^{240}Pu/^{239}Pu	6% contribution	Rapid	Less sensitive
^{241}Pu/^{239}Pu	1% contribution	Sensitive indicator, rapid	Decay dependant, LOD critical

For the calculations, plutonium activity ratios and atom ratios of the global fallout reported by Kelley *et al.* [32] and UNSCEAR report values [1] have been applied (**Table 2.**); for the Chernobyl-derived components, plutonium isotope ratios summarized by the IAEA [22] and UNSCEAR [28] have been employed, which are the most comprehensive data collection available. By the results it can be established that ^{238}Pu/^{239}Pu and ^{241}Pu/^{239}Pu activity ratios are more sensitive indicator for distinguishing global fallout from reactor-grade (Chernobyl) plutonium than ^{240}Pu/^{239}Pu ratios. This derives from the fact that ^{238}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios vary over a wider range. However, ^{238}Pu/^{239}Pu was found to be the best indicator, as it is not prone to the decay of the shorter-lived ^{241}Pu isotope ($T_{1/2}$ = 14.35 years) and more data is available in the literature for Chernobyl ^{238}Pu/^{239}Pu value, which further improves the contribution calculation uncertainty in case of samples with low Chernobyl contribution. Moreover, as ^{240}Pu/^{239}Pu atom ratio differs only by a factor of two for global fallout and reactor-grade plutonium isotope ratios (approximately 0.18 and 0.4, respectively), small changes in the ratios are masked by the relatively high uncertainty of global fallout values and reactor-grade isotope ratios or the low ICP-SFMS measurement precision (between 0.4-40% in case of low-level plutonium analysis). However, it is important to note that the main uncertainty of contribution calculations derives from the uncertainty of the isotope ratios of contributing sources and not the measurement uncertainty. Thus, using mass spectrometers with single collectors can be effectively used for origin assessment and more precise data, which can be obtained by TIMS or MC-ICP-SFMS do not improve significantly the precision of the contribution calculation. Other parameters, such as measurement time may be also an important factor for selecting the appropriate technique. Use of mass spectrometry, especially ICP-SFMS has the advantage of rapid analysis and high sample throughput. Thus, in emergency situation this technique can give most information on the plutonium contamination within the shortest time. Though, for the comprehensive characterization of the samples application of both radioanalytical and mass spectrometric techniques is desirable, and ICP-SFMS and alpha spectrometry were found to be a good choice to measure all important isotope ratios (^{238}Pu/^{239}Pu, ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) with suitable precision.

This two-component model was applied for the analysed European samples, in which the presence of two plutonium sources, global fallout and Chernobyl, are expected from the isotope ratios. The contribution of global fallout and Chernobyl to the total plutonium content in the samples is shown in **Table 26.**

Table 26. The contribution of global fallout and Chernobyl to the plutonium content in the investigated samples

Sample name	Calculated contribution from global fallout of weapons tests	Chernobyl contribution
AUSSED	> 98%	< 2%
AUSSOIL	> 98%	< 2%
BALTSED	> 98%	< 2%
CHERMOSS	< 5%	> 95%
HUNBIOTA	< 5%	> 95%
HUNMOSS	> 98%	< 2%
HUNMOSS2	> 98%	< 2%
MEDWEED	> 98%	< 2%
MONMOSS1	> 98%	< 2%
MONMOSS2	> 98%	< 2%
PRIPMOSS	< 5%	> 95%
RUSSOIL	56 ± 5%	44 ± 4%

In most European environmental samples taken far from Chernobyl, plutonium derives significantly (more than 98%) from the global fallout of the 1950s and 1960s. However, in order to decrease the minimum detectable reactor-grade plutonium contribution, knowledge and survey on the present level of environmental plutonium (deposited previously as a consequence of the global fallout and Chernobyl accident) is necessary, as this has significant uncertainty in the mixing model calculations. By this, a smaller reactor-grade plutonium (from Chernobyl or other releases) contribution could be detected, which is essential for environmental monitoring, safeguards purposes and nuclear preparedness. In the case of Irish Sea samples, IRSED and IRSED2, applying that Sellafield release had a ^{238}Pu/($^{239+240}$Pu) ratio of 0.1-0.3 depending on the date of release [22], the contribution of Sellafield to the total plutonium is between 42% and 86%. The highest uncertainty in this calculation is the initial isotope ratio of Sellafield release, which varies with a factor of approximately two depending on the plant operation profile, thus sample inhomogeneity and literature data make the calculation unreliable. In the case of RUSSOIL and HUNBIOTA samples, when it is assumed by the isotope ratios that plutonium derives from the Chernobyl accident, results with lower uncertainty can be obtained. For the RUSSOIL and HUNBIOTA samples the calculated Chernobyl-contribution values are 44 ± 4% and above 95%, respectively. It is important to emphasize that these origin assessments are verified by all isotope ratios. Thus, the source identification (both the type and number of contributing sources) can be carried out with higher reliability than the assumptions used in the literature, which apply one or two isotope ratio for this purpose.

6.5. Estimation of Release Date by ^{241}Am/^{241}Pu Isotope Ratio

^{241}Pu is the shortest lived radionuclide among the main plutonium isotopes. It decays to ^{241}Am with a half-life of 14.35 years, which also decays to the long-lived ^{237}Np isotope with a half-life of 432.2 years. Although ^{241}Am is not produced directly in nuclear explosions, it is present in the environment due to the decay of ^{241}Pu, and its amount continuously increases as ^{241}Pu decays. ^{241}Am concentration will increase in the future in the environment and it is estimated to reach its maximum activity in the middle of the 21st century (**Fig. 3.**). Other sources of ^{241}Am are accidents and authorized release from reprocessing plants (**Chapter 2.2.2.**).

The time dependency of the ^{241}Am concentration can be exploited for the assessment of release date assessment (i.e. date of formation), which is a very important parameter to distinguish a recent contamination or accidental release from previous emissions, such as Chernobyl. This parameter helps to control nuclear facilities for safeguards purposes and supports nuclear safety.

Age and formation measurement on the basis of ^{241}Am/^{241}Pu ratio have been successfully utilized in nuclear forensics, where the age of plutonium containing sample is a key parameter for deducing the history of the nuclear material [86]. In case of environmental samples, however, it is more complicated to directly adapt the method, as following the release it must be ensured or controlled that there is no chemical fractionation between the ^{241}Pu mother and ^{241}Am daughter nuclide. In case of seawater samples, this condition does not hold entirely true, due to the enhanced scavenging of americium in the water column by settling particles [155]. However, as the behaviour of plutonium and americium in soil is similar with comparable migration rates [156,157], by careful sampling and using wider sampling depth, the effect of fractionation and slightly different mobilities of Pu and Am on the measurement results can be avoided. For example, Bossew *et al.* investigated the vertical distribution of actinides in soil of a grassland site in the Chernobyl exclusion zone [158]. The migration rates of plutonium and americium were similar in different core samples (the migration rates of ^{241}Am and $^{239+240}$Pu were 0.151 – 0.197 and 0.165 – 0.216 cm per year, respectively); however, the ^{241}Am migration velocities were slightly (approximately 10%) higher in each case. Mboulou *et al.* studied the migration behaviour of transuranics in agricultural soil samples contaminated by the Chernobyl accident [159]. The vertical migration profiles of Pu and ^{241}Am in the soil samples taken eight years after the accident were identical. Similarly, bioindicators, such as moss or lichens, where correlation was found between the different transuranic radionuclide concentrations, indicates the possible applicability for release date estimation. For instance, Testa *et al.* investigated the vertical profiles of Italian mosses and lichens [160]. According to their results, the Pu and Am vertical distributions are very similar in very old *Sphagnum* mosses containing transuranics of weapons test origin. The authors concluded that these mosses retain plutonium and americium and that these elements are not mobile along the plant. Peats act as efficient filters in trapping airborne radioactive contaminants as well as natural reservoirs from which these radionuclides are released and can be recommended as very good biological indicators of Pu and Am. Paatero *et al.* found that the transfer of americium and curium from the lichen to the underlying litter and soil layer can occur slightly faster than that of plutonium [151]. Thus, for my study soil samples with properly thick sampling depths and moss samples seemed to the possible options according to the literature data.

Assuming no chemical fractionation takes place between plutonium and americium, applying the decay laws one can calculate the elapsed time after formation of ^{241}Pu as a function of ^{241}Am/^{241}Pu activity ratio. The elapsed time between the formation of ^{241}Pu and date of measurement can be calculated as follows:

$$t = \frac{1}{\lambda_1 - \lambda_2} \ln\left(\frac{R \cdot (\lambda_2 - \lambda_1) - \lambda_2}{R_0 \cdot (\lambda_2 - \lambda_1) - \lambda_2}\right) \qquad \text{Eq. 3.}$$

where λ_1 and λ_2 are decay constants of ^{241}Pu and ^{241}Am, respectively, and R_0 and R are the ^{241}Am/^{241}Pu activity ratios at the time of formation and measurement, respectively. In case of nuclear weapon tests, R_0 is zero, as ^{241}Am is not formed directly at explosion. Using this equation, the date of ^{241}Pu formation (which is usually equal to the release date) can be calculated. The estimated release dates of Pu in some investigated samples are summarized in **Table 27.**

Table 27. The estimated release dates of plutonium in some investigated samples

Sample	**Calculated age**	**Estimated contamination date**
CHERMOSS	23 ± 2	1983 ± 2
PRIPMOSS	19 ± 2	1987 ± 2
HUNBIOTA	21 ± 2	1985 ± 2
HUNMOSS	47 ± 3	1959 ± 3
MEDWEED	43 ± 3	1963 ± 3
IRSED	45 ± 3	1961 ± 3
FANSED	36 ± 3	1970 ± 3

The release dates of plutonium low-level European samples agree with the peaking of the atmospheric weapon tests, while release dates of samples collected in Chernobyl verify their origin. In case of HUNBIOTA sample, the calculated age confirms its Chernobyl origin, which is very important to demonstrate and verify that plutonium does not derive from any recent contamination. For the Fangataufa sample, the estimated contamination date of 1970 ± 3 year agrees with the maximum of French test activities at the Pacific [1]. In case of multiple sources (e.g. RUSSOIL or IRSED samples), the calculated contamination date is the weighted mean of the release date of the constituents. Thus, this contamination date assessment usually works well for single component sources. Another problem for the release date assessment calculation that it requires the precise measurement of the low-abundant ^{241}Pu and ^{241}Am. Therefore, in order to obtain results with small uncertainty, in most cases higher sample amount (i.e. higher degree of pre-concentration) is necessary.

7. Long-lived Radionuclide Analysis for Nuclear Forensic Studies

7.1. Aims of the Method Developments

Minor long-lived radionuclide content of the nuclear materials gives fundamental pieces of information on the origin and history of the sample for nuclear forensic studies (**Table 3.**). For instance, it allows the determination of the production date (*age*) of the material. Furthermore, by the measurement of the activation and fission products, information can be obtained on the history of the material. For example, ^{236}U and Pu-isotopes, which are formed by the neutron capture of uranium, are very good indicators of a previous irradiation of uranium, so they give information on the provenance and history (type of starting material, e.g. reprocessed spent fuel, irradiation conditions, reactor type) of the nuclear material. In this dissertation, the aim was to develop analytical methods for the production date measurement and for the detection of previous irradiation (reprocessing) of the most important nuclear materials, uranium-based matrices by ICP-SFMS methods. The methods developed give basic information on the nuclear material, which can be used for nuclear forensic purposes and help authorities to reveal the origin of the nuclear material. The aim was to shorten analysis time required for the investigation in order to give information to the authorities on the provenance of the material, so that they could take the necessary steps as soon as possible. Another important purpose was to decrease sample amount required for the investigation, as these materials serve as evidences during the legal procedure, thus the sample amount consumed for the analysis should be minimized. Furthermore, as the radioanalytical methods (including the most commonly applied alpha spectrometry) have limited measurement precision resulting in relatively high uncertainty, typically in the range of 1-15% relative standard deviation, it is important to improve precision in case of age measurements compared to previous methods published in the literature (**Chapter 3.3.3.** and **Chapter 3.4.3.**). By this, a better tool is obtained for nuclear forensics, which helps authorities to constrict the possible provenance of the illicit nuclear materials.

7.2. Methodology Used for the Production Date Determination of Nuclear Materials

For the detection of the previous neutron irradiation the methodology is quite simple: if the sample contains ^{236}U or plutonium isotopes, it is for certain that the material itself has been previously irradiated or mixed with irradiated uranium. If the material was irradiated, for example, the ^{236}U/^{235}U and ^{239}Pu/^{238}U ratios can be used to deduce the irradiation conditions. The measurement of activation products can be feasible, as it is more difficult to completely separate e.g. plutonium from uranium due to the similar chemical behaviour. Thus, they are present in reprocessed nuclear materials in higher amount compared to, for example, fission products. Moreover, as several uranium and plutonium isotopes are formed by the neutron irradiation (e.g. ^{232}U, ^{236}U, ^{239}Pu, ^{240}Pu or ^{241}Pu), the isotopic composition can be used to identify the irradiation conditions, such as reactor type and irradiation circumstances. Thus, in order to find out if the uranium in the samples was irradiated (or mixed with irradiated uranium) the best option is to measure ^{236}U and plutonium isotopes.

However, for production date measurement, the selection of the optimal radionuclides is less straightforward. There are several mother-to-progeny ratios, which can be used for production date measurements (**Fig. 5.**). However, only a few of them can be applied effectively, as the measurement capabilities depend on several parameters, such as the amount of progeny to be measured, the analytical technique, the amount of mother nuclide or the elapsed time. In most cases, the determination of the progeny is the critical task, as its concentration is far below than that of the mother nuclide. This is less problematic for old or higher-enriched materials, as these samples contain progenies in higher concentration.

There are some conditions, under which highly accurate and precise age data can be obtained for nuclear materials: the half-life of the progeny should be longer than 1 – 10 years (in order to avoid secular equilibrium). For the radioanalytical techniques it is advantageous, if the half-life is not so long in contrast to mass spectrometry, as it entails higher specific activity. For all age measurements, it is a crucial parameter to know the initial concentration of the progenies. Most nuclear end-products (e.g. pellets, fuel materials) meet these requirements, as the impurity levels are very strictly controlled. In order to have high amount of well-measurable decay product of the base uranium material, it is important that the progeny of interest has to be among the first members of the decay series and its mother nuclides should not have very long half-life. For example, for uranium-based materials, ^{210}Pb is not suitable for age determination, as its in-growth is impeded (virtually stopped) by the preceding long-lived ^{230}Th and ^{226}Ra nuclides (**Fig. 5.**). Therefore, taking all these conditions into consideration, for uranium-based materials the best possibilities are ^{230}Th, ^{226}Ra and ^{231}Pa. The first two are the decay products of ^{234}U, the latter is the progeny of ^{235}U. Out of these three options, ^{230}Th was found to be the best possibility. ^{226}Ra amount is very low even after a long time (**Fig. 5.**) due to the slow in-growth of its ^{230}Th mother nuclide and the accurate measurement of ^{231}Pa is cumbrous, as suitable, long-lived isotopic tracer is not available.

Production date determination by ^{230}Th/^{234}U ratio is based on the decay of the relatively long-lived ^{234}U ($T_{1/2}$ = 245250 ± 490 years, [161]) to ^{230}Th ($T_{1/2}$ = 75690 ± 230 years, [161]) and the disequilibrium between these two radionuclides. After the last chemical separation of ^{234}U in the course of the preparation of the nuclear material, the concentration of ^{230}Th daughter nuclide is continuously increasing in the uranium oxide material (**Fig. 19.**). The theoretical ^{230}Th amount formed by the decay can be calculated by the use of equations of the radioactive decays assuming that the initial concentration of the daughter nuclide is zero after the last chemical separation (i.e. the separation was complete) and utilizing the approximation that ^{234}U amount in the sample is constant over the investigated time scale. These assumptions are usually valid for nuclear fuel samples. The variation of ^{230}Th/^{234}U atom ratio as a function of time can be calculated as follows:

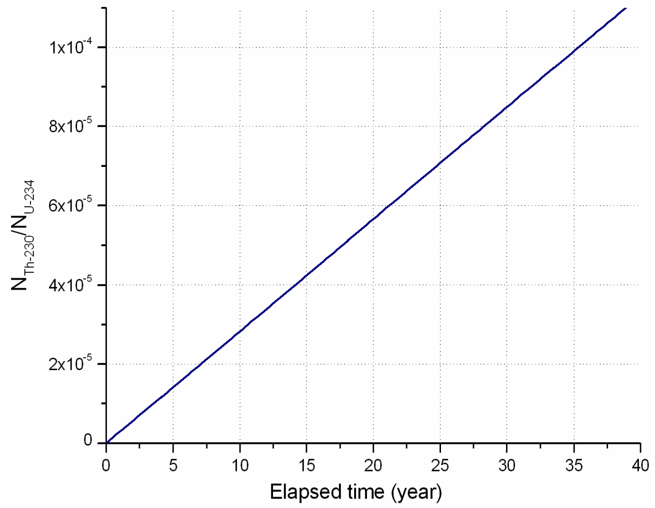


Fig. 19. Variation of the ^{230}Th/^{234}U atom ratio in uranium-oxide as a function of time

$$\frac{N_{Th-230}}{N_{U-234}} = \frac{\lambda_{U-234}}{\lambda_{Th-230} - \lambda_{U-234}} (1 - e^{(\lambda_{U-234} - \lambda_{Th-230})t}) \qquad \text{Eq. 4.}$$

where N_{Th-230}/N_{U-234} is the atom ratio in the sample, λ_{Th-230} and λ_{U-234} are the decay constants of ^{230}Th and ^{234}U, respectively, and t is the elapsed time since the last separation of the radionuclides (age of the material). If the atom ratio of ^{230}Th and ^{234}U is experimentally determined, the elapsed time and the production date can be calculated as follows:

$$t = \frac{1}{\lambda_{U-234} - \lambda_{Th-230}} \ln(1 - \frac{N_{Th-230}}{N_{U-234}} \cdot \frac{\lambda_{Th-230} - \lambda_{U-234}}{\lambda_{U-234}}) \qquad \text{Eq. 5.}$$

For the accurate and highly precise ^{230}Th measurement, use of a proper Th-tracer is indispensable. For this purpose, ^{228}Th, ^{229}Th and ^{232}Th are the possible options. For mass spectrometric measurements the disadvantage of ^{228}Th (the commonly used isotopic tracer for thorium measurements by alpha spectrometry) is its short half-life ($T_{1/2}$ = 1.91 years), thus relatively high activity should be used for the analysis. ^{232}Th (the main naturally-occurring Th-isotope) could be a feasible possibility for isotope dilution measurements, which was demonstrated by Wallenius *et al.* performing TIMS analyses [89]. As the level of thorium in nuclear end-products is strictly controlled and its concentration is very low, use of ^{232}Th as isotopic tracer is a possible option. However, it has several drawbacks. Firstly, for nuclear materials it has to be verified that either its concentration is negligible compared to the isotopic tracer added or it has to be very accurately determined for the proper isotope dilution calculation. It can be performed by parallel measurements (with and without tracer), which implies that the sample available has to be split into two measurements (lower pre-concentration is possible). Secondly, as it is a naturally-occurring isotope, the chemicals added and sample preparation environment can highly contribute to the blank value, which results in higher uncertainty in the final result. Finally, natural thorium standard also contains ^{230}Th in a small amount, which also contributes to higher background and worsens precision. Thus, for the production date measurement I found ^{229}Th the best option, which has sufficiently long half-life, not present in most nuclear materials (with the exception of ^{233}U-based nuclear materials) and does not occur naturally. Though ^{229}Th is also available commercially, its concentration uncertainty is too high for most age determinations. Thus, to obtain more precise age data, its concentration has to be re-measured by reverse isotope dilution with ^{232}Th, which is accessible with much more precise concentration.

7.3. Destructive Analysis of Long-lived Radionuclides from Uranium Oxide

7.3.1. Reagents and Materials

The ^{233}U (New Brunswick Laboratory, USA) isotopic standard was used to spike the samples for ^{234}U measurements and was also employed to obtain (“milk”) the ^{229}Th tracer for the ^{230}Th analysis. For the reverse isotope dilution measurement of the prepared ^{229}Th tracer, natural Th-solution (Sigma-Aldric Inc., USA) was applied. Multielement standard solution at a concentration of 1 ng g^{-1} purchased from Merck (Darmstadt, Germany) was used for the optimization of the ICP-SFMS instrument. Natural uranium solution was used to correct for instrumental mass discrimination. The UTEVA™ (100-150 µm particle size, active component: diamyl amyl-phosphonate) and TEVA™ (100-150 µm particle size, active component: aliphatic quaternary amine) extraction chromatographic resins were supplied by Eichrom Technologies Inc. (Darien, Illinois, USA). For the analysis, 1.8 mL of the resin was placed in plastic Bio-Rad holders (diameter: 8 mm). All reagents used were of analytical grade. Acids used in the final steps prior to ICP-MS analysis were Suprapur® grade (Merck, Darmstadt, Germany). For dilution, ultrapure water was used (Milli-Q System, Millipore, USA). All sample preparation and measurement procedures were carried out under clean room conditions (Class 100 000).

7.3.2. Investigated Nuclear Samples

Three uranium oxide pellets or materials confiscated in Hungary were analysed in this study. The samples have different ^{235}U enrichment: HU-DEP is a depleted uranium pellet (^{235}U/^{238}U isotope ratio is 0.00258 ± 0.00004), HU-NAT is a natural uranium containing material, presumably a nuclear by-product (^{235}U/^{238}U isotope ratio is 0.00713 ± 0.00014), while HU-LEU is a low-enriched uranium pellet (^{235}U/^{238}U isotope ratio is 0.0255 ± 0013). For the laser ablation investigation, uranium oxide standard (referred to as UOX-STD henceforth) was prepared from natural uranyl acetate (Lachema Ltd., Czechoslovakia). In order to validate the methods, highly-enriched uranium oxide powder from a Round Robin interlaboratory exercise (RR-HEU) organized by the Nuclear Smuggling International Technical Working Group (ITWG) was used. For the destructive analyses, the known amounts of the uranium oxide materials were dissolved in 6 M ultrapure nitric acid while heating slightly in a water bath.

7.3.3. Preparation of ^{229}Th Tracer

The ^{229}Th tracer used for the ^{230}Th determination was prepared by separating ("milking") the ^{229}Th from a 18-year-old ^{233}U standard solution (New Brunswick Laboratory, USA). Approximately 1 g of 479 µg g^{-1} ^{233}U-solution was evaporated to approximately 200 µL and diluted to 20 mL with 8 M HNO_3/0.4 M $Fe(NO_3)_3$. After thorough mixing, the Th-content of the sample was separated from uranium by extraction chromatography using UTEVA™ resin. For the column preparation, 1.8 ml of UTEVA™ resin was placed in a plastic Bio-Rad holder (diameter: 8 mm). After conditioning of the resin with 10 mL of 8 M HNO_3/0.4 M $Fe(NO_3)_3$, the sample was loaded on the column. Flow rate was approximately 1 mL min^{-1}. After rinsing the column with 10 mL of 8 M HNO_3/0.4 M $Fe(NO_3)_3$ and 5 ml of 8 M HNO_3, thorium was stripped from the column using 4 mL of 9 M HCl and 15 mL of 4 M HCl. In order to further purify the sample, the extraction chromatographic separation was repeated after evaporating the thorium fraction. The Th-fraction obtained after the second purification was evaporated to dryness and dissolved in approximately 15 mL of 1 M HNO_3 (stock solution). The working solution used for the isotope dilution analyses was prepared by gravimetric dilution (approximately 200-fold) of this stock solution. The ^{229}Th concentration in the working solution obtained was determined by reverse isotope dilution ICP-SFMS measurement applying certified natural Th-solution. The ^{229}Th concentration in the tracer working solution was 22.50 ± 0.18 pg g^{-1}, the ^{230}Th/^{229}Th and ^{232}Th/^{229}Th isotope ratios were $(7.5 \pm 0.1) \times 10^{-3}$ and 0.50 ± 0.03, respectively (reference date: 07.02.2007). The ^{233}U concentration in the tracer was 0.89 ± 0.03 ng g^{-1}, thus adequately pure for the ^{230}Th measurements.

7.3.4. Sample Preparation for ^{234}U and ^{236}U Determination

Approximately 100 μg aliquot of the dissolved uranium oxide sample was used for the analysis. The sample was diluted twice successively with 2% utrapure nitric acid solution. Each dilution was approximately 200-fold. The ^{234}U and ^{236}U concentrations following the second dilution were determined by isotope dilution ICP-SFMS measurement using ^{233}U standard. All dilutions were carried out gravimetrically.

7.3.5. Sample Preparation for ^{230}Th and Pu Determination

The sample preparation method developed is based on the procedure optimized for environmental plutonium measurements (**Chapter 5.2.**). Approximately 100 μg aliquot of the dissolved uranium oxide sample was placed in a polyethylene Eppendorf tube. The sample was spiked with approximately 1 pg of ^{229}Th and 20 pg of ^{242}Pu tracers gravimetrically. 1 mL of 3 M HNO_3 was added to the sample to adjust the HNO_3 concentration to approximately 3 M, which is the optimum for the TEVA™ separations (**Fig. 9.**). Care has to be taken that uranium concentration in the load solution is lower than 20 mg mL^{-1}, as it may result in lower recoveries. After thorough mixing, the Th and Pu content of the sample was separated from uranium by extraction chromatography using TEVA^{TM} resin (column volume 1.8 mL, diameter: 8 mm). After conditioning of the resin with 15 mL of 3 M HNO_3, the sample was loaded on the column. Flow rate was approximately 1 mL min^{-1}. After rinsing the Eppendorf tube twice with 1 mL of 3 M HNO_3 and adding the rinsing solution to the column, the uranium was stripped from the column with 15 mL of 3 M HNO_3. Finally, the thorium and plutonium fractions were eluted together using 20 mL of 9 M HCl, 2.5 mL of 4 M HCl and 20 mL 0.1 M HNO_3/0.1 M HF into a PFA beaker. The time of separation was registered, as production date is calculated from the elapsed time up to this point. In order to further purify the sample, the extraction chromatographic separation was repeated. The eluate was evaporated to almost dryness followed by successive addition of 2 mL concentrated HNO_3 to destroy organic resin residual and to remove remains of HCl that may preclude thorium retention on the resin. The residue was dissolved in 2 mL 3 M HNO_3 while slight heating. After cooling to room temperature, the extraction chromatographic separation with TEVA^{TM} resin was repeated, but in this second separation the Th fraction (elution by 20 mL of 9 M HCl and 2.5 mL of 4 M HCl) and the Pu fraction (elution by 20 mL 0.1 M HNO_3/0.1 M HF) were collected separately. The fractions obtained were evaporated to almost dryness followed by successive addition of 2 mL concentrated HNO_3 to destroy any organic resin residual. Finally, the residue was dissolved in three times 300 μL of 2% nitric acid while heating slightly. The schematic diagram of the sample separation for ^{234}U – ^{236}U and ^{230}Th – Pu determination is shown in **Fig. 20.**

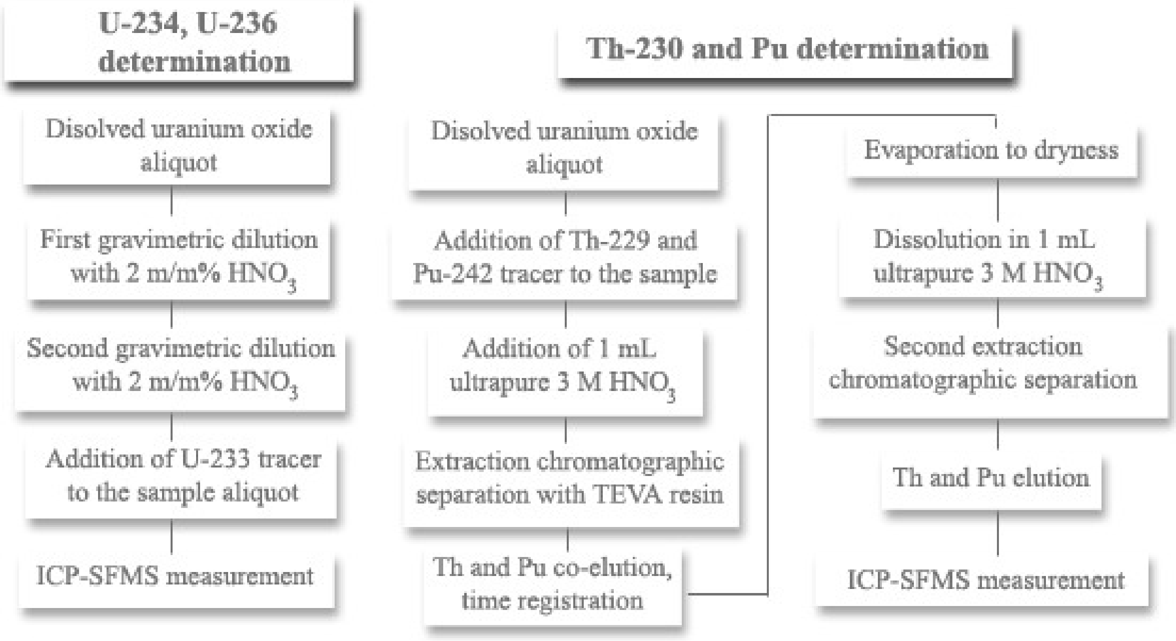


Fig. 20. Schematic of sample preparation for simultaneous Th and Pu determination from uranium oxide

7.3.6. Analysis by ICP-SFMS

The mass spectrometric analysis was carried out using a double-focusing magnetic sector inductively coupled plasma mass spectrometer equipped with a single electron multiplier (ELEMENT2, Thermo Electron Corp., Bremen, Germany). ^{234}U and ^{230}Th measurements as well as the reverse isotope dilution measurement of the ^{229}Th tracer were carried out in low mass resolution mode (R = 300) with a low-flow microconcentric nebulizer operated in a self-aspirating mode (flow rate was 100 µL min^{-1}) connected to a stable introduction system spray chamber (SIS, Elemental Scientific, Omaha, USA) in order to improve isotope ratio precision. For the production date determinations the precision of the ICP-SFMS measurements is of crucial importance, that is why this combination of sample introduction was chosen. Optimized operating parameters are summarized in **Appendix E**. Prior to analysis of samples the instrument was tuned using a 1 ng g^{-1} multielement solution (Merck, Darmstadt, Germany). The optimization was carried out with respect to maximum uranium sensitivity and low UO^{+}/U^{+} ratio. Sensitivity was approximately 1.0 × 10^{6} cps for 1 ng g^{-1} ^{238}U, UH^{+}/U^{+} and UO^{+}/U^{+} ratios were less than 6 × 10^{-5} and 2 × 10^{-2}, respectively.

For ^{236}U and plutonium analyses a low-flow T1-H nebulizer operated in a self-aspirating mode (flow rate 60 µL min^{-1}) in combination with a desolvation unit (Aridus, CETAC Technologies Inc., Omaha, NE, USA) were used in order to minimize hydride interferences (such as $^{235}U^{1}H^{+}$ and $^{238}U^{1}H^{+}$). As for ^{236}U and plutonium determinations the reduction of the background (deriving from especially $^{235}U^{1}H^{+}$ and $^{238}U^{1}H^{+}$) is more important than the precision of the measurement, sample introduction involving desolvation was chosen for the analysis. As the hydride formation rate (UH^{+}/U^{+}) is approximately one order of magnitude lower using the desolvation than by the conventional sample introduction; thus it results in lower detection limits and more accurate results. Furthermore, possibly occurring oxide interferences (e.g. $^{207}Pb^{16}O_2^{+}$ or $^{209}Bi^{14}N^{16}O^{+}$) of plutonium measurements are also eliminated by the desolvation. Prior to the analysis, the instrument was tuned using a 1 ng g^{-1} uranium standard solution. Sensitivity was about 1.5×10^{6} cps for 1 ng g^{-1} ^{238}U, while UH^{+}/U^{+} and UO^{+}/U^{+} ratios were less than 6.6×10^{-6} and 3×10^{-4}, respectively. Optimized operating parameters are summarized in **Appendix E**. All ICP-SFMS data acquisition parameters, which were the same for both sample introduction systems are also included in **Appendix E**. Concentrations of isotopes of interest were calculated as a function of $^{230}Th/^{229}Th$, $^{236}U/^{233}U$, $^{234}U/^{233}U$, $^{239}Pu/^{242}Pu$, $^{240}Pu/^{242}Pu$ and $^{241}Pu/^{242}Pu$ ratios according to the isotope dilution method. All data were corrected for instrumental mass bias using linear correction [150]. The overall uncertainty was calculated taking into account the uncertainty of the weight measurements, tracer concentrations, measured intensities and half-lives according to ISO/BIPM guide. This standard guide and software based on these instructions were used instead of an own error propagation calculation (in quadrature) for the better traceability of the calculations. However, the combined uncertainty results well agreed for the two types of calculation. The calculations were carried out by the use of commercially available software, GUM Workbench [162].

7.3.7. Figures of Merit of the Method Developed

The sample preparation method developed is based on the procedure optimized for environmental plutonium measurements (**Chapter 5.2.**). However, for nuclear materials higher decontamination from uranium is desirable. In order to avoid suppression of thorium and plutonium ionization in the plasma due to excess uranium concentration and to protect the ICP-SFMS instrument from uranium contamination, the uranium level has to be sufficiently low for the isotope ratio measurements. In case of

^{234}U and ^{236}U measurements, this was achieved by the gravimetric dilution of the sample, while for ^{230}Th and plutonium determinations chemical separation was applied.

For the ^{230}Th concentration measurements, which were used for the production date determination, the decontamination factor (DF) of thorium from ^{238}U (calculated as the ratio of the weight of the ^{238}U before the sample preparation in the sample and thereafter in the measured fraction) was higher than 4×10^{9}. The absolute detection limit (on the basis of three times the standard deviation of method blank) of ^{230}Th and ^{234}U used for production date determinations by ICP-SFMS (calculated for 10 milligram of sample amount for easier comparison) were 0.20 pg (0.15 mBq) and 0.24 pg (5.65×10^{-2} mBq), respectively. The chemical recovery of ^{230}Th sample preparation calculated by the measurement of ^{229}Th tracer was between 53 and 86%. Lower recoveries were found if the uranium concentration was high (above 20 mg mL^{-1}) in the load solution of the first extraction chromatographic separation. This is due to the negative impact of excess U(VI) on the retention of tetravalent actinides [64]. The precision of ^{229}Th/^{230}Th and ^{233}U/^{234}U ratio measurements, which is the most significant parameter for the assessment of total uncertainty for age determination, ranged between 0.67-2.51% at 95% confidence level ($k = 2$) depending on activity level. The minimum age of the uranium oxide material that can be determined depends on the enrichment of the nuclear material, as the ^{234}U concentration is usually proportional to ^{235}U/^{238}U ratio. The higher the ^{234}U enrichment (and usually also the ^{235}U enrichment), the lower the minimum age that can be measured applying the same pre-concentration factor. For example, the detection limit achieved corresponds to 0.15 years (approximately 2 months) according to **Eq. 5.** using 10 mg of natural uranium-oxide sample, though in order to achieve better precision higher sample amount (i.e. higher pre-concentration), analysis of enriched uranium or older sample is necessary.

As the detection limit of ^{236}U is primarily determined not by the pre-concentration, but the concentrations of other uranium isotopes (^{235}U and ^{238}U) in the sample, it is more exact to express it in concentration relative to UO_2. In case of ^{236}U determination chemical separation or higher pre-concentration (i.e. using more concentrated sample aliquot) does not improve the detection limits, as it also increases the background caused by $^{235}U^{1}H^{+}$ interference and overlapping of $^{238}U^{+}$ peak at $m/z = 236$. The effect of $^{235}U^{1}H^{+}$ interference can be expressed by the hydride formation rate ($^{235}U^{1}H^{+}/^{235}U^{+}$), which was approximately 6.6×10^{-6} using the desolvation sample introduction system. If the $^{236}U^{+}/^{235}U^{+}$ ratio is comparable to this value, the effect of

$^{235}U^{1}H^{+}$ interference has to be taken into account with mathematical correction. The effects of $^{235}U^{+}$ and $^{238}U^{+}$ signal on the *m/z* = 236 can be expressed by the so-called abundance sensitivity, which is defined as overlap of a mass peak (e.g. *m/z*) to its adjacent mass peak (*m/z* ± 1 or *m/z* ± 2). For the ELEMENT2 ICP-SFMS instrument, the abundance sensitivities at *m/z* ± 1 and *m/z* ± 2 are approximately 5.0×10^{-6} and 1.5×10^{-6}. As both $^{235}U^{+}$ and $^{238}U^{+}$ can contribute to the background depending on the uranium isotopic composition of the sample, the LOD given was calculated for natural uranium sample. The detection limit of ^{236}U in natural uranium dioxide sample was 1.8 μg g^{-1}, however, it has to be emphasized that it highly depends on the uranium isotopic composition.

For plutonium analyses, the decontamination factor (DF) of plutonium from ^{238}U (calculated as the ratio of the weight of the ^{238}U before the sample preparation in the sample and thereafter in the measured fraction) was higher than 2.5×10^{5}. The absolute detection limits of ^{239}Pu, ^{240}Pu and ^{241}Pu used for the detection of irradiated uranium were 34 fg (78 μBq), 8.5 fg (71 μBq) and 3.4 fg (13 mBq), respectively, calculated for 10 milligram of sample. For plutonium measurements, the recovery ranged between 63 and 89%. Lower recoveries were found if the uranium concentration was high (above 20 mg mL^{-1}) in the load solution of the first extraction chromatographic separation. This is due to the negative impact of excess U(VI) on Pu(IV) retention, similarly to the thorium analysis [64].

The detection limits of ^{230}Th and plutonium measurements can be further improved by higher pre-concentration of the sample. The entire analysis (both sample preparation and ICP-SFMS measurement) can be accomplished within two days, thus significantly faster than gamma or alpha spectrometry. The figures of merit of the method developed are summarized in **Table 28.**

Table 28. Figures of merit of the method developed. [a]: the detection limit is given in concentration.

	^{230}Th determination	**^{234}U determination**	**^{236}U determination**	**Plutonium determination**
Sample preparation				
Sample preparation duration	2 days	3 hours	3 hours	2 days
Decontamination factor from U	$> 4 \times 10^{9}$	NA	NA	$> 2.5 \times 10^{5}$
Chemical recovery	53-86%	NA	NA	63-89%
Absolute detection limit	0.20 pg (0.15 mBq)	0.24 pg (5.5×10^{-2} mBq)	1.8 μg g^{-1} [a]	3.4 – 34 fg
Measurement precision (*k* = 2)	0.8-2.51%	0.67-1.2%	1.1-5.9%	3.2-9.8%
Measurement time	2 days	2 hours	2 hours	2 days
Total uncertainty (*k* = 2)	0.85-2.6%	0.70-1.35%	1.1-6.2%	3.3-23.1%

7.3.8. Analysis of Confiscated Nuclear Materials

The method developed was applied for the production date determination and for the detection of previous irradiation of the confiscated nuclear materials and the Round Robin laboratory intercomparison sample (RR-HEU). The calculated production date results obtained are summarized in **Table 29.** The production dates and ages were calculated using the measured ^{230}Th/^{234}U isotope ratios according to **Eq. 5.** For all age data 01.04.2007 is the reference date. The uncertainties are expressed at 95% confidence level (k = 2) according to ISO/BIPM guide. The production date of the Round Robin sample is in good agreement with the values reported previously (February to July, 1979) by other laboratories in the course of the interlaboratory exercise [163].

Table 29. Production date results of the investigated nuclear materials by the ICP-SFMS method

Sample	^{235}U/^{238}U ratio	Measured ^{230}Th/^{234}U atom ratio	Calculated age (a)	Production date
HU-DEP	0.00258 ± 0.00004	$3.88 \times 10^{-5} \pm 2.8 \times 10^{-6}$	13.7 ± 1.0	August, 1993 (± 12 months)
HU-NAT	0.00713 ± 0.00014	$5.01 \times 10^{-5} \pm 2.4 \times 10^{-6}$	17.73 ± 0.87	July, 1989 (± 10 months)
HU-LEU	0.0255 ± 0.0013	$4.38 \times 10^{-5} \pm 2.8 \times 10^{-6}$	15.51 ± 0.98	September, 1991 (± 12 months)
RR-HEU	10.80 ± 0.17	$7.89 \times 10^{-5} \pm 3.6 \times 10^{-6}$	27.9 ± 1.3	June, 1979 (± 16 months)

The combined uncertainty of the results, which is the most important parameter for nuclear forensics and origin assessment, is similar to the previously reported TIMS [85,89] and alpha spectrometric [40,89] values. However, in the previous studies either higher sample amount was used for the analysis (up to 1 gram of natural uranium oxide), or higher-enriched uranium materials, HEU samples were processed or old samples with high ^{230}Th content were required for the measurements [85,89]. In contrast, the method developed is capable for the precise production date measurement for low-enriched (even for depleted uranium) or young nuclear materials using low sample amount for the analysis.

The measured ^{236}U/^{238}U ratios and plutonium concentrations used for detection of previous irradiation of the investigated samples are summarized in **Table 30.**

Table 30. The measured $^{236}U/^{238}U$ ratios and plutonium concentrations in the investigated samples

Sample	**$^{236}U/^{238}U$ ratio**	**Plutonium concentrations (pg g^{-1})**		
		^{239}Pu	**^{240}Pu**	**^{241}Pu**
HU-DEP	$5.71 \times 10^{-5} \pm 2.1 \times 10^{-6}$	< LOD	< LOD	< LOD
HU-NAT	< LOD	< LOD	< LOD	< LOD
HU-LEU	$4.20 \times 10^{-3} \pm 2.7 \times 10^{-4}$	6.83 ± 0.82	0.400 ± 0.076	< LOD
RR-HEU	$7.91 \times 10^{-2} \pm 2.8 \times 10^{-3}$	6.63 ± 0.27	1.852 ± 0.074	0.276 ± 0.030

According to the measurement data, with the exception of HU-NAT sample, ^{236}U concentration was relatively high in each investigated material. Thus, it can be established that HU-LEU and RR-HEU samples were not only isotopically enriched, but also contain irradiated uranium (for instance, prepared from or mixed with reprocessed spent fuel). As HU-DEP sample also contains relatively high amount of ^{236}U, it is not simply a by-product of the uranium enrichment, but it (or part of it) had been previously irradiated with neutrons. Since the concentration of ^{236}U in HU-NAT sample is very low (lower than 1.8 μg g^{-1}) it is highly probable that it was neither irradiated formerly nor mixed with spent fuel. Beside the high ^{236}U content, HU-LEU and RR-HEU samples have significantly high plutonium content as well. In the RR-HEU (Round Robin intercomparison sample) the measured $^{239+240}Pu$ activity concentration obtained by ICP-SFMS (30.7 ± 1.2 Bq kg^{-1}) agrees well with a previously reported alpha spectrometric result (35 ± 5 Bq kg^{-1}) [164]. This was the only possibility to validate the plutonium results, as reference material with known plutonium content was not available. The trace-level plutonium isotopic composition can be used to further refine the possible provenance of the material (e.g. applying that plutonium isotopic composition is reactor-type and burn-up dependant), however, these assignations require suitable databases possibly in conjunction with reactor-production computer codes, such as ORIGEN or SCALE for more accurate assessment [92]. Nevertheless, these analyses are beyond the scope of this dissertation.

Comparing the ^{236}U and plutonium results, it can be concluded that the presence of ^{236}U is better indicator of previous neutron irradiation, as the complete removal of ^{236}U from the uranium matrix is inextricable, while in most cases plutonium is well-separated from uranium during the reprocessing. However, if higher sample amount is available, plutonium can be determined at very low-level due to the high pre-concentration in contrast to ^{236}U analysis. The improvement of the ^{236}U detection limit is hindered by the inherent problem of the ICP-SFMS technique (similarly to other mass spectrometric techniques) that the ^{236}U mass peak can not be completely separated from the interfering (overlapping) ^{235}U and ^{238}U peaks. Thus, the detection limit achievable is limited. Another advantage of the plutonium measurement in contrast to ^{236}U for the detection of previous irradiation is that as long as it can be measured, it gives further information on the history of the material (such as irradiation conditions, reactor-type) by the plutonium isotopic composition.

7.4. Laser Ablation ICP-SFMS Measurements of Long-lived Radionuclides from Uranium Oxide

7.4.1. Methodology for Laser Ablation ICP-SFMS Measurements

Laser ablation coupled to an ICP-SFMS fulfils eventually all the requirements, which would be desirable for nuclear forensics: besides its excellent detection capabilities, it is not only a quasi non-destructive technique (less than microgram amount of sample is consumed for the analysis), but also it is needless to carry out lengthy and hazardous chemical manipulations with the nuclear materials, which require special laboratory conditions and expertise. Furthermore, as sample preparation is not necessary in most cases, it does not generate nuclear (radioactive) waste. Thus, my aim was to exploit these advantageous characteristics of the laser ablation sample introduction and to develop methods for the production date measurement and for the detection of previous irradiation of uranium-based nuclear materials, which can be used for nuclear forensic investigations.

Laser ablation offers an easy possibility for the direct isotope ratio measurements of solid materials, as the ablation and ionization properties of the isotopes of the same element are identical. Thus, determination of ^{236}U/^{238}U ratio, which is one of the indicators of previous irradiation, is relatively straightforward, and can be easily obtained from the measured mass spectrum. However, if the ratio of different elements should be determined, for example ^{230}Th/^{234}U for the production date measurement of nuclear materials according to **Eq. 5.**, several effects have to be considered due to the different chemical properties. Though the intensity ratio of ^{230}Th and ^{234}U signals can be directly obtained from the mass spectrum of the laser ablation ICP-SFMS measurements, correction has to be applied in order to convert it to ^{230}Th/^{234}U atom ratio, which is necessary for age determination (see **Chapter 7.2.** and **Eq. 5.**). The direct determination of ^{230}Th/^{234}U atom ratio from the mass spectrum using laser ablation is hindered by the different ablation and ionization efficiencies of ^{230}Th and ^{234}U, however, this effect for laser ablation ICP-SFMS is not as serious as, for example, for SIMS measurements [165,166]. For the concentration measurement by laser ablation ICP-SFMS, the relative sensitivity factor approach can be applied, which assumes that the sensitivity ratio of two selected elements (either of them is the analyte, the other serves as an internal standard) is constant under the same laser ablation conditions. Thus, if this ratio, called relative sensitivity factor (RSF), is experimentally determined by the analysis of a standard sample, the concentration of the analyte can be calculated by the measurement of the intensity ratios of the two selected elements in the sample, assuming that the RSF is identical. The concentration of the other element (the internal standard) in the sample has to be known for the calculation, and the matrix of the standard should be similar to that of the sample. The RSF method takes into account the differences in the ionization and ablation efficiencies of the elements at fixed conditions (constant laser energy, crater diameter and repetition rate). Mathematically, the RSF value for age determination can be calculated as follows:

$$RSF = \frac{S_{Th-230}}{S_{U-234}} = \frac{I_{Th-230}}{I_{U-234}} \cdot \frac{c_{U-234}}{c_{Th-230}} = \frac{I_{Th-230}}{I_{U-234}} \cdot \frac{N_{U-234}}{N_{Th-230}} \cdot \frac{M_{U-234}}{M_{Th-230}} \qquad \text{Eq. 6.}$$

where $S_{Th\text{-}230}$ and $S_{U\text{-}234}$ are the sensitivities of ^{230}Th and ^{234}U, $I_{Th\text{-}230}$ and $I_{U\text{-}234}$ are the measured intensities of ^{230}Th and ^{234}U, $N_{U\text{-}234}/N_{Th\text{-}230}$ is the atom ratio in the sample, $M_{Th\text{-}230}$ and $M_{U\text{-}234}$ are the molar weights of ^{230}Th and ^{234}U, and $c_{Th\text{-}230}$ and $c_{U\text{-}234}$ are the concentrations of ^{230}Th and ^{234}U in the samples, respectively. If the RSF value is experimentally determined using an uranium oxide standard with known ^{230}Th and ^{234}U content, the $N_{Th\text{-}230}/N_{U\text{-}234}$ atom ratio in the investigated sample can be calculated according to **Eq. 6.** Substituting this calculated ratio into **Eq. 5.** the elapsed time from the last chemical separation or production date can be obtained. For the determination of plutonium concentrations, the same approach can be applied. For this purpose, either a sample with known ^{239}Pu content or a laboratory-prepared uranium oxide matrix spiked with known amount of plutonium (e.g. with ^{242}Pu tracer) can be used as a standard.

7.4.2. Sample Preparation for Laser Ablation Studies

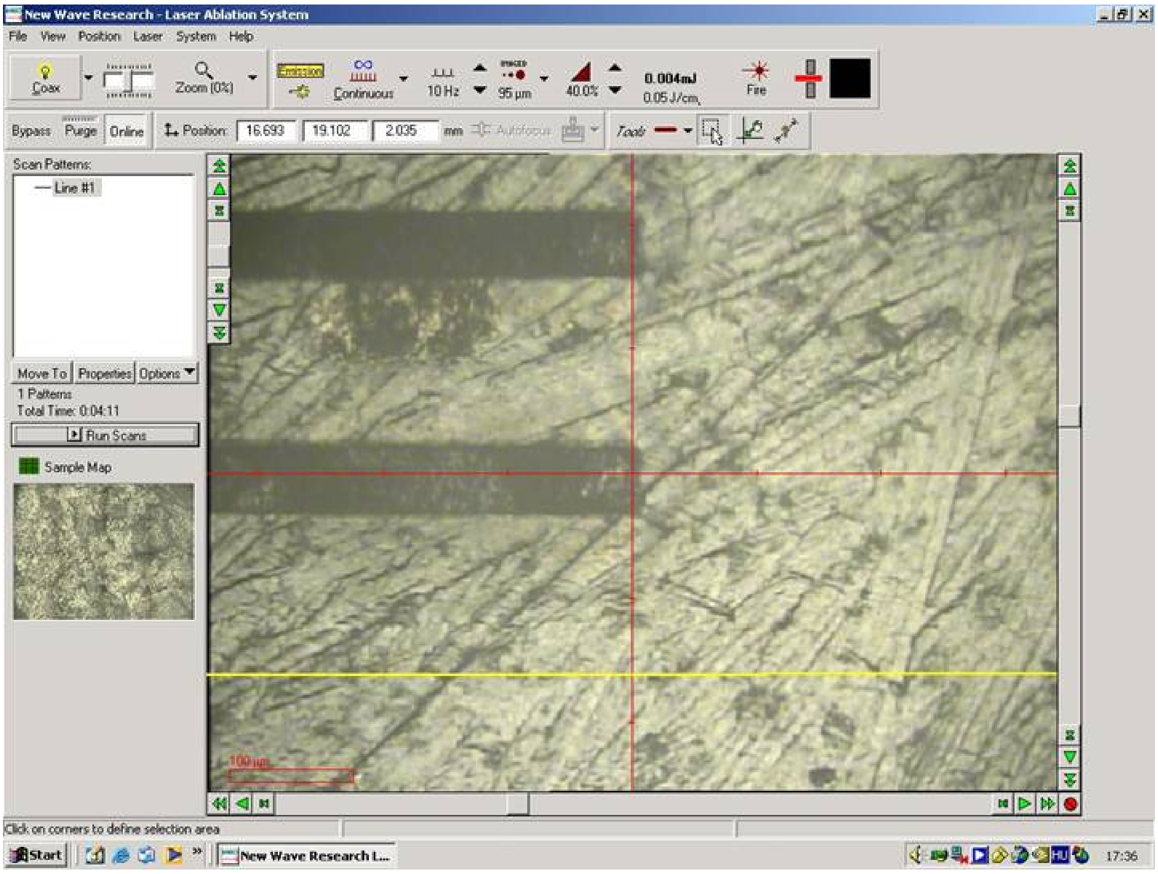
For the laser ablation measurements the same confiscated nuclear materials were used as for the destructive analysis (**Chapter 7.3.2.**). In order to prepare a solid uranium oxide standard for laser ablation studies, an uranium oxide powder was prepared from natural uranyl acetate (Lachema Ltd., Czechoslovakia) by ashing. 1.8 g of

$UO_2(CH_3COO)_2 \cdot 2H_2O$ was placed in a porcelain crucible. The sample was dried at 110 °C for 2 hours, and ashed thereafter by gradually increasing the temperature to 400 °C and holding at that temperature for 3 hours. The uranium oxide, presumably as U_3O_8 according to the uranium content, was thoroughly mixed and homogenized. This natural uranium powder pressed into a pellet was used also for the mass discrimination measurement.

For the laser ablation studies, the uranium oxide powders (the Round Robin HEU sample and the laboratory-prepared natural uranium oxide powder) were pressed hydraulically at a pressure of 20 MPa into a disk-shaped pellet with a diameter of 5 mm and an approximate thickness of 1 mm. Compression time was approximately 3 minutes. Nuclear fuel samples could directly be analysed by laser ablation ICP-SFMS with the exception of the HU-NAT sample due to its cramped geometry and worn surface.

7.4.3. Instrumentation for Laser Ablation ICP-SFMS Measurements

Laser ablation measurements of the samples were carried out using an UP-213 laser ablation system (New Wave, Freemont, USA) using a Nd:YAG laser at a wavelength of 213 nm (**Chapter 4.4.**). The laser ablation appliance was coupled to the ELEMENT2 instrument. The ablated material is transported by argon as a carrier gas into the plasma. Optimization was carried out with respect to maximum $^{238}U^+$ intensity, besides good precision and minimum UO^+/U^+ ratio using a NIST 612 glass reference material (NIST, Gaithersburg, USA). For the production date measurements, line scan was used (scan speed: 5 $\mu m\ s^{-1}$, repetition rate: 10 Hz, laser beam diameter: 95 µm, laser energy: 80% (0.28 mJ)). In case of ^{236}U and plutonium analyses, however, it was not desirable to use such high laser energy and laser beam diameter, as the background ($^{235}U^+$, $^{235}U^1H^+$ and $^{238}U^+$ signals) also increases. Therefore, for the measurement of these nuclides, different laser ablation parameters were applied: line scan with a scan speed of 5 $\mu m\ s^{-1}$, repetition rate: 10 Hz, laser beam diameter: 20 µm, laser energy: 40% (0.14 mJ). Other optimized ICP-SFMS parameters are summarized in **Appendix E**. As an example, the surface of the laboratory-prepared uranium oxide sample with scan lines used for acquisition is shown in **Fig. 21.**



Position: 16.693 19.102 2.035 mm

1 Patterns
Total Time: 0:04:11

Click on corners to define selection area

Fig. 21. Surface of the laboratory-prepared uranium oxide sample with scan lines used for acquisition

For the laser ablation ICP-SFMS measurements low (R = 300) and medium (R = 4000) mass resolutions were employed. Mass calibration of the instrument was verified by the analysis of the NIST 612 reference material.

7.4.4. Optimization of the Laser Ablation Measurements

The ^{230}Th/^{234}U ratio of the investigated uranium-oxide samples necessary for production date determination was measured by the laser ablation ICP-SFMS in chromatographic mode, which means that the intensities of ^{230}Th and ^{234}U signals were recorded as a function of time. The integration allows the elimination of possible drifts and spikes. The ^{230}Th/^{234}U intensity ratio was calculated by the integration of the signals of the isotopes of interest over the selected ranges (**Eq. 7.**):

$$\frac{I_{Th-230}}{I_{U-234}} = \frac{\int_{t_2}^{t_3} I_{Th-230}^{SMP} - \int_{0}^{t_1} I_{Th-230}^{BKG}}{\int_{t_2}^{t_3} I_{U-234}^{SMP} - \int_{0}^{t_1} I_{U-234}^{BKG}} \qquad \text{Eq. 7.}$$

where I^{SMP}_{Th-230} and I^{SMP}_{U-234} are intensities of ^{230}Th and ^{234}U during the ablation period, and I^{BKG}_{Th-230} and I^{BKG}_{U-234} are the intensities of ^{230}Th and ^{234}U during the background measurement, respectively. The first approximately 20 seconds of data acquisition before switching on the laser (t_1) was used for the background correction. Typical chromatographic measurement of UOX-STD sample in low-resolution mode is shown in **Fig. 22.**

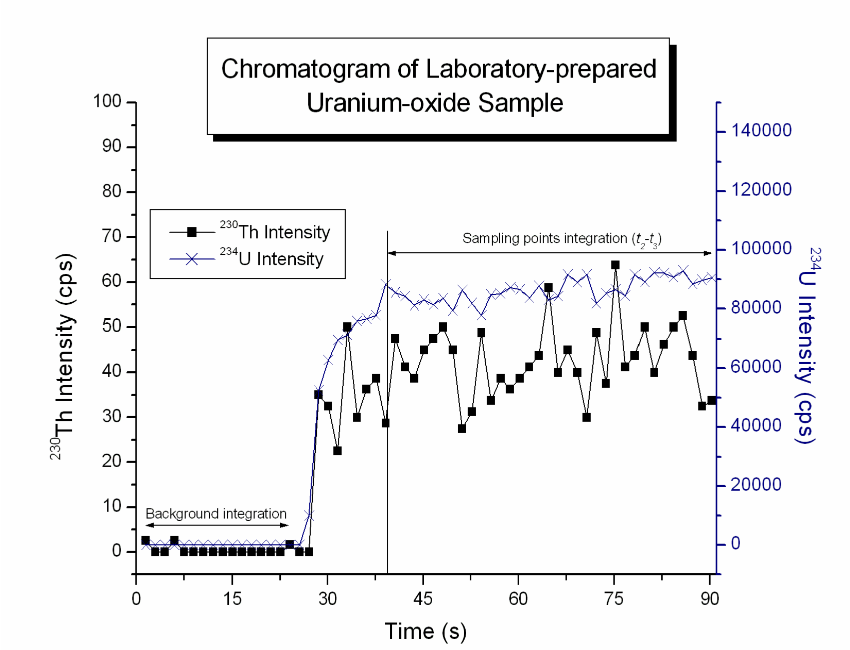


Fig. 22. The typical chromatographic measurement of the laboratory-prepared uranium oxide sample (UOX-STD) in low-resolution mode (R = 300)

The integration limits (t_2 and t_3) for the ablation period were selected within the stabilized signal range.

As the concentrations of ^{230}Th and ^{234}U have already been determined by the destructive isotope dilution ICP-SFMS method described above (**Chapter 7.3.**), the relative sensitivity factors necessary for quantitative analysis for each investigated sample (**Chapter 7.3.2.**) could be calculated according to **Eq. 6.** The calculated RSF values are summarized in **Table 31.**

Table 31. ^{230}Th/^{234}U intensity ratios and relative sensitivity factors measured by LA-ICP-SFMS in low-resolution mode (R = 300).

Sample	Measured ^{230}Th/^{234}U intensity ratio	Calculated RSF values
HU-DEP	$1.30 \times 10^{-3} \pm 9.9 \times 10^{-5}$	33.5 ± 2.6
HU-LEU	$1.16 \times 10^{-4} \pm 5.0 \times 10^{-6}$	2.32 ± 0.19
RR-HEU	$9.05 \times 10^{-5} \pm 1.2 \times 10^{-6}$	1.15 ± 0.06
UOX-STD	$4.96 \times 10^{-4} \pm 1.6 \times 10^{-5}$	2.82 ± 0.08

The laser ablation analysis of HU-NAT could not be carried out because of the cramped geometry of the material and worn surface. The sample was cragged and its outer periphery had a brownish, rusty-like cover. Thus, the rough surface led to highly uneven intensity during laser ablation analysis of this sample.

Surprisingly, the RSF values obtained are significantly different for each sample in spite of the similar matrix composition and far above 1. Such a high discrepancy can not be explained by the difference in ionization potentials or the slightly unlike ablation properties. The ionization potentials of U (E_I = 6.19 eV) and Th (E_I = 6.31 eV) are not significantly different and the high laser power density of 7.1×10^{10} W cm^{-2} also minimizes the elemental fractionation effects [167]. Hence, the difference in the RSF values is expected to be the consequence of the occurring molecular interferences, such as $^{198}Hg^{16}O_2^+$, $^{204}Pb^{12}C^{14}N^+$ or $^{202}Hg^{14}N_2^+$ at m/z = 230. As during the laser ablation the interference components are also introduced into the plasma in contrast to chemical sample preparation, the molecular interferences should be separated from the analytes of interest by instrumental means, i.e. use of higher mass resolution. In order to check the occurrence of interferences, the samples were re-analysed applying higher mass resolution (fixed resolution of R = 4000 for the ELEMENT2 instrument, called medium mass resolution), which is sufficiently high to eliminate most polyatomic interferences (**Appendix A**.). Typical chromatogram display of the laboratory prepared uranium oxide sample (UOX-STD) measured in medium mass resolution mode is shown in **Fig. 23.** The averaged mass spectrum recorded during the laser ablation (t_2 and t_3) is presented in **Fig. 24.**

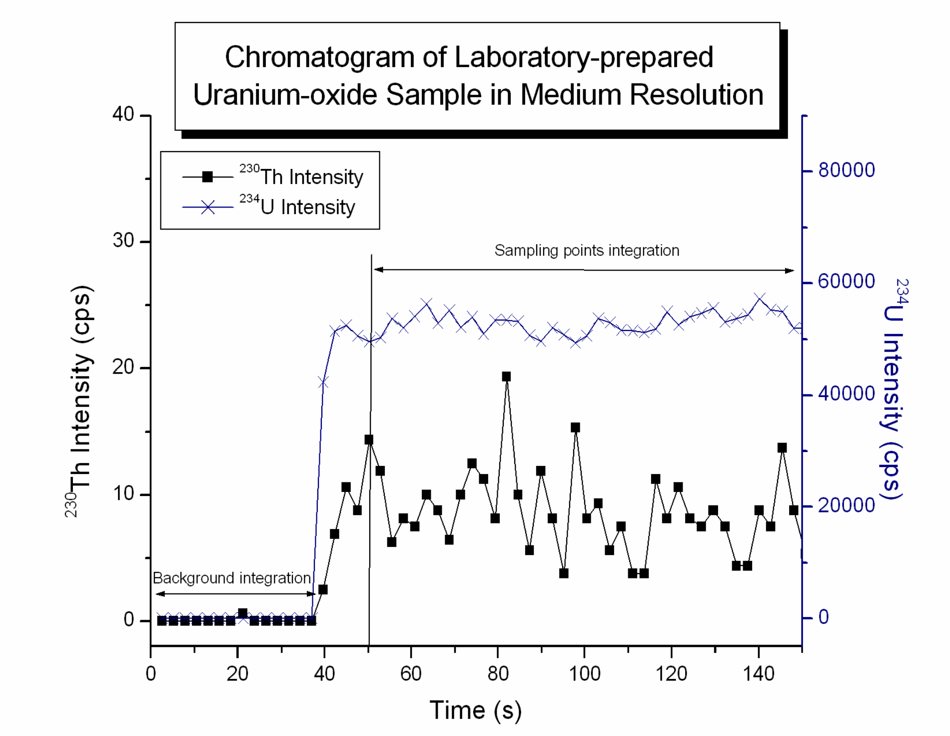


Fig. 23. The typical chromatographic measurement of the laboratory-prepared uranium oxide sample (UOX-STD) in medium resolution mode (*R* = 4000)

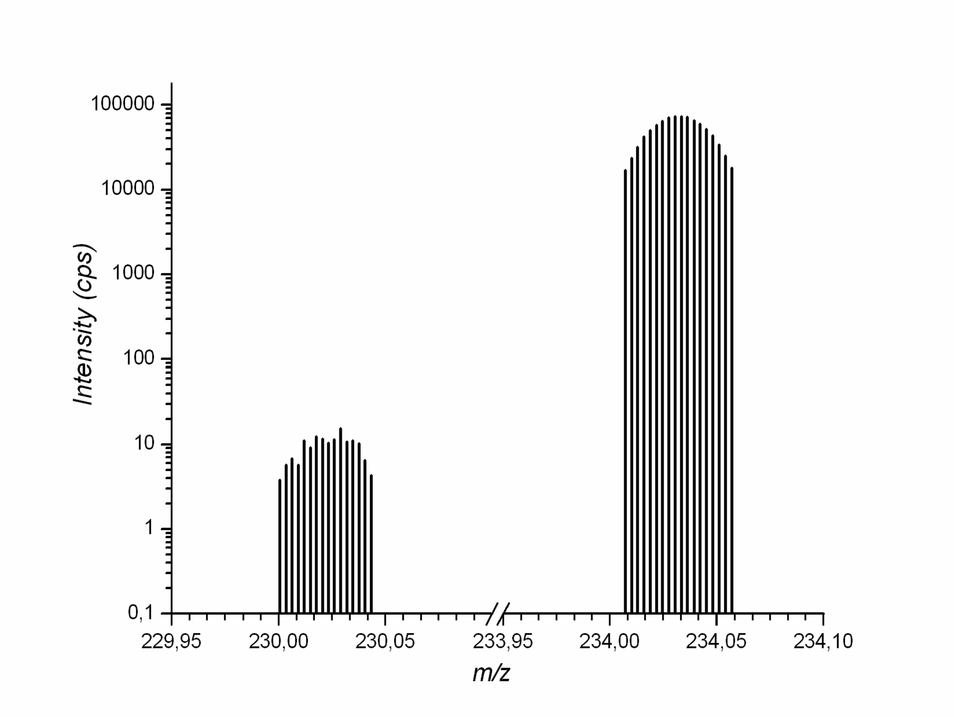


Fig. 24. The averaged mass spectrum of the laser ablation ICP-SFMS analysis in medium resolution mode (*R* = 4000). Integration range: 50-150 s, number of spectra: 36, measured mass regions: 230.016-230.0433 amu and 234.007-234.057 amu

Similarly to the low-resolution measurements, the RSF values were calculated according to **Eq. 6.** and **Eq. 7.** using the previously determined ^{230}Th/^{234}U atom ratio by the destructive method. The RSF values obtained are summarized in **Table 32.**

Table 32. ^{230}Th/^{234}U intensity ratios and relative sensitivity factors measured by LA-ICP-SFMS in medium-resolution mode (R = 4000).

Sample	Measured ^{230}Th/^{234}U intensity ratio	Calculated RSF values
HU-DEP	< LOD ($< 6.5 \times 10^{-6}$)	NA
HU-LEU	$4.23 \times 10^{-5} \pm 6.6 \times 10^{-6}$	0.99 ± 0.16
RR-HEU	$8.61 \times 10^{-5} \pm 5.2 \times 10^{-6}$	1.12 ± 0.03
UOX-STD	$1.73 \times 10^{-4} \pm 2.2 \times 10^{-5}$	0.99 ± 0.09

The values obtained are close to 1 as expected verifying that elevated RSF values in low-resolution mode derive from spectral interferences. Several polyatomic interferences can contribute to the measured signal at m/z = 230, such as ^{204}Pb^{12}C^{14}N^{+}, ^{206}Pb^{12}C$_2^{+}$, ^{206}Pb^{24}Mg^{+}, ^{207}Pb^{23}Na^{+}, ^{198}Hg^{16}O$_2^{+}$ or ^{202}Hg^{12}C^{16}O^{+}. The occurrence of these interferences is probable, as the concentration of Pb, Hg and other trace-level stable impurities is typically in the 1 – 20 µg g^{-1} concentration range. The concentration of the impurities were determined by a destructive UTEVA$^{\text{TM}}$ extraction chromatographic separation method developed in our Institute [168]. The presence of these interferences can be verified in the future, for example, by the medium-resolution measurement of the samples scanning wide mass range around m/z = 230, which enables the separation of the interfering molecular ions and their identification by the accurate mass. This possibility has already been applied for trace-level ^{226}Ra determination and for the identification of interfering polyatomic ions at m/z = 226 [169]. Thus, it can be concluded that for laser ablation measurements use of higher resolution is required to obtain accurate and reliable results for production date measurements. However, it is a great disadvantage of the use of medium mass resolution that the detection limit is higher due to the lower ion transmission.

For ^{236}U and plutonium measurements, low mass resolution (R = 300) was applied, as during the preliminary investigations it was found that the primary interferences derive not from the polyatomic interferences (e.g. ^{235}U^{1}H^{+} and ^{207}Pb^{16}O$_2^{+}$), but from the overlap of the uranium signals (e.g. ^{238}U^{+}). Though use of higher mass resolution (i.e. medium mass resolution) also decrease the overlap (the abundance sensitivity) with a factor of approximately 2, it also results in worse precision. Therefore, for such measurements, low-resolution was used. The intensities of ^{234}U,

^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu and ^{241}Pu signals during the laser ablation ICP-SFMS measurement were recorded as a function of time similarly to the production date measurements. The integration allows the elimination of possible drifts and spikes. The intensity ratios were calculated by the integration of the signals of the isotopes of interest over the selected ranges (**Eq. 7.**) in the same way as described previously. A typical chromatogram display of the laboratory prepared uranium oxide sample (UOX-STD) measured in low mass resolution mode for ^{236}U determination is shown in **Fig. 25.**

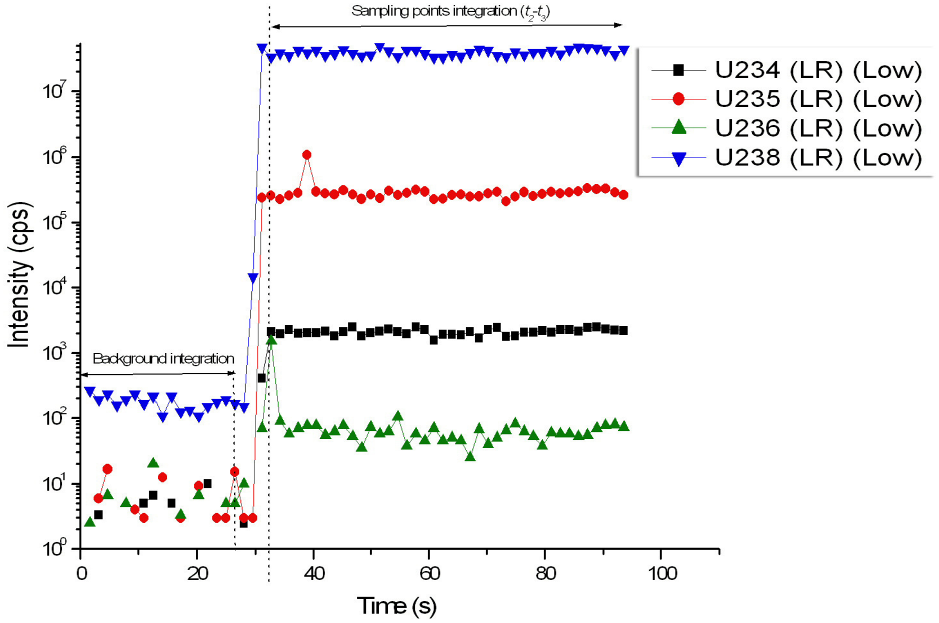


Fig. 25. The chromatogram display of the laboratory prepared uranium oxide sample (UOX-STD) measured in low mass resolution mode for ^{236}U determination

In case of ^{236}U determination, as the use of RSF method is not necessary, the isotope ratios are calculated from the background corrected intensity ratios taking into account the instrumental mass discrimination.

The determination of Pu in the uranium oxide samples by laser ablation ICP-SFMS was not possible due to the very high $^{238}U^+$ interference (overlapping to the adjacent m/z = 239 mass peak). Even the measurement of the Round Robin sample (RR-HEU) with the highest ^{239}Pu and lowest ^{238}U content produced such a low signal at m/z = 239, which agreed with that of measured by the analysis of UOX-STD (natural uranium oxide sample, containing no plutonium) within measurement uncertainty.

7.4.5. Figures of Merit of the Laser Ablation Methods Developed

The measurement capabilities of the laser ablation ICP-SFMS for age determination depend mainly on the ^{230}Th measurements, as usually ^{234}U is present in high amount as a main matrix constituent. The detection limit of ^{230}Th in uranium oxide matrix using the laboratory-prepared standard (on the basis of three times the standard deviation of gas blank and applying the measured ^{230}Th sensitivity the UOX-STD sample) is 33.6 pg g^{-1}, the quantification limit (on the basis of ten times the standard deviation of gas blank) is 88.8 pg g^{-1}. The minimum measurable age that corresponds to the limit of quantification in natural uranium oxide is 0.66 years, though in order to achieve better precision, higher-enriched or older sample is necessary. The precision of isotope ratio measurements, which is the most significant parameter for the assessment of total uncertainty, ranged between 9-35% at 95% confidence level (k = 2) depending on activity level. Though the detection limit and the total uncertainty of laser ablation measurements are much higher than those achievable by the destructive method (**Table 28.**), the method can easily be applied for the characterization of the uranium oxide materials, as sample preparation is not necessary and production date can easily be obtained from the spectra with appropriate precision.

For the detection of the previous irradiation by the measurement of ^{236}U, the same difficulties arise as for the destructive methods. Though the level of ^{235}U^{1}H^{+} interference is less pronounced in case of laser ablation due to the dry aerosol formed, the detection limit is still limited by the effect of other uranium peaks, especially the overlap of the excess ^{235}U^{+} and ^{238}U^{+} signals. Thus, similarly to the destructive method, the detection limit depends on the uranium isotopic composition of the sample. For natural uranium oxide sample (UO_2), the achieved detection limit (calculated on the basis of three times the standard deviation of signal measured at m/z = 236 during the analysis of natural UOX-STD sample (not containing ^{236}U) and applying the measured ^{238}U sensitivity) is 2.34 µg g^{-1}, however, it has to be emphasized that it highly depends on the uranium isotopic composition. The precision of isotope ratio measurements, which is the most significant parameter for the assessment of total uncertainty, ranged between 8 – 27% at 95% confidence level (k = 2) depending on concentration level. It is noteworthy that the achieved detection limit is comparable to that of the destructive method (1.8 µg g^{-1}). This is the consequence of the fact that the detection limit is limited in both cases by the other uranium isotopes. Thus, for the destructive method, chemical separation and pre-concentration can not be used to improve the detection capabilities.

As the laser ablation ICP-SFMS virtually requires no special sample preparation and the dissolution of the sample is not necessary, it is an ideal tool for the detection of previously irradiated uranium, and was found to be a better option for the determination of ^{236}U content in confiscated nuclear materials than the destructive method.

The determination of Pu in the uranium oxide samples by laser ablation ICP-SFMS was not possible due to the very high $^{238}U^+$ interference (overlapping to the adjacent m/z = 239 mass peak). As the overlapping (abundance sensitivity) is typically $(1 – 5) \times 10^{-6}$ for the ELEMENT2 instrument, the maximum ^{239}Pu content, which can be determined in natural UO_2 (^{238}U content is 87.5% by weight) is approximately 8.8 – 44 µg g^{-1}. Though the contribution of $^{238}U^+$ signal can be taken into account with mathematical correction using the abundance sensitivity value, as the uncertainty of the measurement also increases with the correction, it does not improve the detection limit. However, in spite of the high detection limit of the laser ablation ICP-SFMS method, it can easily be used for the rapid characterization (screening) of the uranium oxide material, as sample preparation is not necessary and the estimated plutonium content or an upper value can easily be obtained from the spectra with appropriate precision.

7.4.6. Analysis of Confiscated Nuclear Materials by Laser Ablation ICP-SFMS

The methods developed were applied for the characterization (production date measurement and the detection of previous irradiation) of the confiscated nuclear materials. For the production date calculations, the laboratory-prepared uranium oxide sample was used as a standard for the RSF determination applying medium mass resolution (R = 4000) in order to avoid polyatomic interferences. The calculated RSF value of 0.99 ± 0.09 was used for the determination of ^{230}Th/^{234}U ratio of the investigated uranium oxide samples according to **Eq. 6.** By the use of this ratio, the production date can be determined for each confiscated sample (**Table 33.**).

Table 33. Production date results of the investigated nuclear materials by the laser ablation ICP-SFMS method

Sample	Calculated age (a)	Production date
HU-DEP	> 2.3	Earlier, than November, 2004
HU-LEU	16.1 ± 3.0	February, 1991 (± 3 years)
RR-HEU	30.4 ± 3.8	October, 1976 (± 3.8 years)

The age results of uranium oxides obtained agree with those measured by the destructive isotope dilution ICP-SFMS method (**Table 29.**) and also with the previously reported values for the Round Robin interlaboratory comparison sample (RR-HEU). Though the precision of laser ablation ICP-SFMS technique is inferior to that of the liquid sample introduction, the uncertainty of the measured production date is usually adequate for nuclear forensic purposes.

Measurements of ^{236}U and plutonium isotopes, which are characteristic of previous neutron irradiation, were also carried out for the investigated samples. The measured $^{236}U/^{238}U$ ratios and plutonium concentrations, which give information on the previous irradiation of the investigated samples, are summarized in **Table 34.**

Table 34. The measured $^{236}U/^{238}U$ ratios and plutonium concentrations by laser ablation ICP-SFMS in the investigated samples

Sample	**$^{236}U/^{238}U$ ratio**	**Plutonium concentrations (pg g^{-1})**		
		^{239}Pu	**^{240}Pu**	**^{241}Pu**
HU-DEP	$6.48 \times 10^{-5} \pm 1.1 \times 10^{-5}$	< LOD	< LOD	< LOD
HU-LEU	$4.25 \times 10^{-3} \pm 3.1 \times 10^{-4}$	< LOD	< LOD	< LOD
RR-HEU	$8.47 \times 10^{-2} \pm 7.6 \times 10^{-3}$	< LOD	< LOD	< LOD

The $^{236}U/^{238}U$ isotope ratios of the investigated uranium oxides agree with those measured by the destructive isotope dilution ICP-SFMS method (**Table 30.**). Though the uncertainties obtained are inferior to that of the destructive method similarly to the production date measurements, this is still appropriate for nuclear forensics. Plutonium concentrations were below the detection limit in all samples, due to the relatively high detection limit achievable by laser ablation ICP-SFMS. Therefore, for these types of nuclear materials (uranium-based materials with low plutonium content), the plutonium measurement can only be used as a screening. However, for samples with relatively high plutonium content (such as MOX samples) this method seems to be a viable option in the future by the adaptation of the methodology developed (**Chapter 7.4.1.**).

7.5. Novelty and the Significance of the Methods Developed for the Analysis of Nuclear Materials

Novel analytical methods have been developed for the production date measurement and for the detection of previous irradiation from the most important nuclear materials, uranium-based matrices by ICP-SFMS methods. The methods give basic information on the nuclear material (age and history of the nuclear material), which can be used for nuclear forensic purposes and help authorities to deduce the origin of the nuclear material. The procedures are less tedious and more rapid than the previously described methods in the literature. These methods, due to their very low detection limits, can be used even if limited sample amount is available. For the production date measurement, the capabilities of the method in comparison with the previously described methods can be easily demonstrated and expressed mathematically. The detection capabilities of production date methods depend not only on the ^{234}U enrichment and but also on the age of the material, thus for the accurate comparison of the methods reported, both of these parameters have to be taken into account. The ratio of ^{230}Th and ^{234}U in the material can be expressed using the formerly applied notations as follows:

$$\frac{N_{Th-230}}{N_{U-234}} = \frac{\lambda_{U-234}}{\lambda_{Th-230} - \lambda_{U-234}}(1 - e^{(\lambda_{U-234} - \lambda_{Th-230})t}) \qquad \text{Eq. 8.}$$

Converting the corresponding nuclide number into mass gives

$$e^{(\lambda_1 - \lambda_2)t} = 1 - \frac{m_{230}}{m_{234}} \cdot \frac{M_{234}}{M_{230}} \cdot \frac{\lambda_2 - \lambda_1}{\lambda_1} \qquad \text{Eq. 9.}$$

where m_{230} and m_{234} are the weight of ^{230}Th and ^{234}U in the samples, and M_{230} and M_{234} are the molar mass of ^{230}Th and ^{234}U, respectively. Taken the Taylor series of the exponential function, we can obtain the following equation for the exponential part:

$$e^{(\lambda_1 - \lambda_2)t} = \sum_{n=0}^{\infty} \frac{[(\lambda_1 - \lambda_2)t]^n}{n!} = 1 + (\lambda_1 - \lambda_2)t + \frac{[(\lambda_1 - \lambda_2)t]^2}{2!} + \ldots \qquad \text{Eq. 10.}$$

As λ_1-λ_2 << 1, the first two members of the Taylor series (its Taylor polynomial of one) are good approximation of the exponential function. Thus, a more simple formula can be obtained for the age after rearranging the equation:

$$t = \frac{m_{230}}{m_{234}} \cdot \frac{M_{234}}{M_{230}} \cdot \frac{1}{\lambda_1} \qquad \text{Eq. 11.}$$

Therefore, the slope of the variation of ^{230}Th and ^{234}U weight ratio as a function of time is proportional (and almost equals to) λ_1. This can also be noticed in **Fig. 19.** Substituting the ^{230}Th and ^{234}U detection limits of a certain analytical technique for m_{230} and m_{234}, respectively, into **Eq. 11.**, the minimal measurable age can be determined, which corresponds to a certain ^{234}U content (enrichment)[*]. However, as it was mentioned beforehand, the minimal age that can be measured by an analytical technique depends also on ^{234}U enrichment, and not only the age. Therefore, **Eq. 11.** has to be converted into a formula, which contains also ^{234}U abundance (*f*). The formula is given for UO_2 materials, which is the most frequently investigated compound.

$$t = \frac{m_{230}}{M_{UO_2}} \cdot \frac{1}{0.8815 \cdot f} \cdot \frac{M_{234}}{M_{230}} \cdot \frac{1}{\lambda_1} = c_{230} \cdot \frac{1}{f} \cdot K \qquad \text{Eq. 12.}$$

where M_{UO2} is the weight of the UO_2 material used for the analysis, f is the isotope abundance of ^{234}U, c_{230} is the concentration of ^{234}U in the nuclear material and K is a constant (4.08×10^5 year^{-1}). Substituting the ^{230}Th detection limit of a certain analytical method into **Eq. 12.**, a simple formula can be obtained, which gives the minimal age and/or ^{234}U enrichment that can be measured with the technique:

$$t_{\min} \cdot f_{\min} > LOD_{Th-230} \cdot K \qquad \text{Eq. 13.}$$

Thus, if the ^{230}Th detection limit of an analytical method is known, one can predict the minimal age and/or ^{234}U enrichment, which is necessary for the production date measurement. For instance, the detection limit of the destructive ICP-SFMS method is 0.20 pg using 10 milligram of sample. Thus, for natural uranium sample ($f = 0.000055$) the minimal age that can be measured is 0.15 years. Similarly, for a 10-year-old sample the ^{234}U isotope abundance has to be at least 8.2×10^{-7} for the analysis (highly depleted uranium is sufficient). This expression (**Eq. 13.**) offers a more exact and descriptive comparison of production date methods. The capabilities of different production date methods developed for uranium oxide materials as a function of ^{234}U isotopic abundance and sample age are illustrated in **Fig. 26.**

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[*] It would be more appropriate to use the limit of quantification instead of the limit of detection. However, the methods reported in the literature did not specify only the detection limit. Therefore, I also used the limit of detection by reason of the comparability.

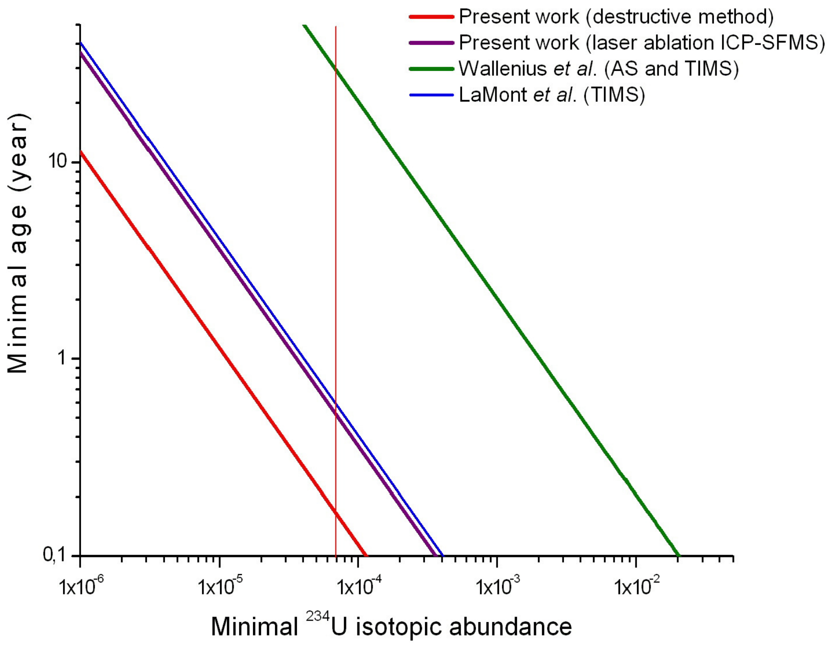

Fig. 26. The comparison of the capabilities of methods developed for production date determination. The natural abundance of ^{234}U ($f = 0.000055$) is also included in the diagram

For instance, in case of natural uranium samples, the minimum ages that can be determined are 37.1 years and 0.74 years applying the method reported by Wallenius *et al.* [89] and LaMont *et al.* [85], respectively. The main disadvantage of the procedure developed by Wallenius *et al.* is that high ^{230}Th amount (5 – 10 ng) is necessary for the analysis, which also implies that high sample amount has to be processed. In comparison, by the destructive method presented in this dissertation, the production date determination can be carried out using a much younger sample with a minimal age of 0.15 year. This low detection limit compared to the other methods can also be utilized to decrease the sample amount required for the analysis, and also results in the improvement in the uncertainty of the results. The minimal measureable age by the laser ablation ICP-SFMS method is 0.25 year, which is comparable to that of reported by LaMont *et al.* and significantly lower than that of reported by Wallenius *et al.*, though the total uncertainty of the laser ablation ICP-SFMS method is worse. However, as this method consumes the lowest sample amount (approximately a few microgram) and can be carried out virtually without sample preparation (it does not require the dissolution of the sample), it is the preferential method for nuclear forensic studies at the first stage of the investigation. Nevertheless, if better precision is required to specify the provenance of the material more precisely, the destructive method developed can be the optimal choice.

For the detection of previous irradiation in uranium-based nuclear materials the measurement of both ^{236}U and plutonium isotopes is suitable. The detection limits of the methods are comparable or lower than those of the previously reported procedures (**Table 13.**). However, these developed methods can be carried out faster and using lower sample amount. According to my results obtained for the characterization of illicit nuclear materials, it can be concluded that the presence of ^{236}U is better indicator of previous neutron irradiation, as the complete removal of ^{236}U from the uranium matrix is inextricable, while in most cases plutonium is well-separated from uranium during the reprocessing. However, if higher sample amount is available, plutonium can be determined at very low-level by the destructive method developed due to the high degree of pre-concentration. Another advantage of the plutonium measurement in contrast to ^{236}U for the detection of previous irradiation is that as long as it can be measured, it gives further information on the history of the material (such as irradiation conditions, reactor-type) by the plutonium isotopic composition. The determination of Pu in the investigated uranium oxide samples by laser ablation ICP-SFMS was not possible due to the very high $^{238}U^+$ interference (overlapping to the adjacent m/z = 239 mass peak). However, in spite of the high detection limit of the laser ablation ICP-SFMS method for plutonium measurement, it can be easily used for the rapid characterization (screening) of the uranium oxide material, as sample preparation is not necessary and an estimated plutonium content or an upper value can be easily obtained from the spectra with appropriate precision. The laser ablation ICP-SFMS measurement of ^{236}U is hindered by the same difficulties as for the destructive methods (by the interference of $^{235}U^+$ and $^{238}U^+$ signals), which resulted in that the achieved detection limit is comparable to the destructive method. Thus, since the laser ablation virtually requires no special sample preparation and the dissolution of the sample is not necessary, it was found to be a better option for the determination of ^{236}U content and for the detection of previously irradiated uranium in confiscated nuclear materials than the destructive method.

8. Summary

The aim of my Ph.D. study was to develop and implement novel analytical methods for the measurement of long-lived radionuclides by inductively coupled plasma sector-field mass spectrometry. The dissertation deals with two main application fields of these radionuclides. The first part of my thesis presents novel analytical methods developed for the measurement of the most significant artificial transuranics, plutonium and americium, and discusses various applications of these procedures. By the use of these methods, the determination of plutonium (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu) and americium (^{241}Am) concentrations and isotope ratios in environmental samples can be carried out easier and faster than by the previously reported procedures. I applied the methods for the analysis of various samples taken from higher-contaminated and less-contaminated sites. By the use of the results, I investigated the applicability of origin assessment of environmental plutonium contamination by the different plutonium isotope ratios and determined the sensitivities of the isotope ratios. If the contamination derives from several sources, I could calculate the qualitative contribution of the sources to the plutonium content in the sample using models. I also investigated the effect of various parameters on the uncertainty of the final result. For release date assessment of environmental plutonium, I developed a model, which is based on the isotope ratio measurement of ^{241}Pu ($T_{1/2}$ = 14.35 a) and its progeny, ^{241}Am ($T_{1/2}$ = 432.2 a).

The second part of the dissertation discusses the application possibilities of long-lived radionuclides for the characterization of illicit nuclear materials for nuclear forensic purposes. I developed an analytical method for the determination of production date (age) of uranium-based nuclear materials by the isotope dilution ICP-SFMS measurement of ^{230}Th/^{234}U ratio. It is important information for the assessment of the provenance of confiscated nuclear materials, whether it contains previously neutron-irradiated (reprocessed) uranium. Therefore, I worked out the sample preparation method in such a way that allows the detection of previous irradiation by the measurement of ^{236}U and Pu isotopes in addition to the age determination from the same sample. Besides the destructive methods, I developed quasi non-destructive laser ablation ICP-SFMS methods for the production date measurement and for the determination of those radionuclides, which are characteristic of previous irradiation. By the use of the methods developed, the analyses can be carried out faster and with lower sample consumption than by the procedures described in the literature.

9. Összefoglalás

Doktori (Ph.D.) munkám célja új analitikai módszerek kidolgozása és alkalmazása volt hosszú felezési idejű radionuklidok mérésére induktív csatolású plazma mágneses szektorral ellátott tömegspektrometriával (ICP-SFMS). Az értekezés ezen nuklidok alkalmazásának két fő területével foglalkozik. Az első terület a legjelentősebb mesterséges transzurán radionuklidok, a plutónium és amerícium környezeti mintákból történő meghatározására kidolgozott új analitikai módszereket és alkalmazásukat mutatja be. A kidolgozott analitikai módszerekkel az irodalomban korábban leírt módszereknél gyorsabb és egyszerűbb mintaelőkészítés után határozható meg környezeti minták plutónium (^{238}Pu, ^{239}Pu, ^{240}Pu és ^{241}Pu) és amerícium (^{241}Am) koncentrációja és izotóparánya. A módszereket alkalmaztam több különböző helyről származó, transzuránnal erősebben és kevésbé szennyezett minta analízisére. Irodalmi adatok és a kapott eredmények alapján megvizsgáltam a plutónium-szennyezés eredet-meghatározási lehetőségeit különböző izotóparányok alapján, és meghatároztam az egyes izotóparányok érzékenységét. Modell alapján mennyiségileg megadtam több forrásból származó plutónium-szennyezés esetén az egyes komponensek plutónium-hozzájárulását a vizsgált mintákban, és vizsgáltam a különböző paraméterek hatását az eredmény bizonytalanságára. A környezetbe került plutónium-szennyezés idejének becslésére modellt dolgoztam ki, amely a ^{241}Pu ($T_{1/2}$ = 14,35 év) és leányelemének, a ^{241}Am ($T_{1/2}$ = 432,2 év) izotóparányának mérésén alapszik.

Az értekezés második része a hosszú felezési idejű radionuklidok alkalmazási lehetőségeit tárgyalja lefoglalt nukleáris minták karakterizálása céljából, amelyek felhasználhatók a törvényszéki eljárás során. Módszert dolgoztam ki urán-oxid alapú nukleáris anyagok gyártási idejének meghatározására (kormeghatározás) a ^{230}Th/^{234}U arány mérése alapján. Mivel a lefoglalt nukleáris anyagok származási helyének meghatározásánál fontos kiegészítő információ, hogy a minta tartalmaz-e korábbi neutron-besugárzásból (reprocesszálásból) származó uránt, ezért olyan mintaelőkészítést dolgoztam ki, amely azonos mintából teszi lehetővé a kormeghatározás és a korábbi neutron-besugárzás kimutatását a ^{236}U és plutónium-izotópok mérése révén. A kidolgozott roncsolásos módszer mellett lézerablációs ICP-SFMS módszereket fejlesztettem ki a gyártási idő és korábbi neutron-besugárzásra jellemző nuklidok meghatározására, amelyek révén az irodalomban leírt módszereknél egyszerűbben és kisebb mintamennyiség felhasználásával elvégezhető az elemzés.

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References

[1] *Ionizing radiation: Sources and biological effects*, United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York, 1982.

[2] G.R. Choppin, J.-O. Liljenzin, J. Rydberg, *Radiochemistry and Nuclear Chemistry*, Butterworth-Heinemann, 2nd edition, Oxford, UK, 1995.

[3] J.K. Cochran, H. Feng, D. Amiel, A. Beck, Natural radionuclides as tracers of coastal biogeochemical processes, *Journal of Geochemical Exploration*, **88(1-3)** (2006) 376-379.

[4] L. Coppola, M. Roy-Barman, S. Mulsow, P. Povinec, C. Jeandel, Thorium isotopes as tracers of particles dynamics and deep water circulation in the Indian sector of the Southern Ocean (ANTARES IV), *Marine Chemistry*, **100(3-4)** (2006) 299-313.

[5] A.J. Pietruszka, R.W. Carlson, E.H. Hauri, Precise and accurate measurement of Ra-226-Th-230-U-238 disequilibria in volcanic rocks using plasma ionization multicollector mass spectrometry, *Chemical Geology*, **188(3-4)** (2002) 171-191.

[6] P. van Calsteren, L. Thomas, Uranium-series dating applications in natural environmental science, *Earth-Science Reviews*, **75** (2006) 155-175.

[7] F. Vanhaecke, G. de Wannemacker, L. Moens, P. van den Haute, The use of sector field ICP-mass spectrometry for Rb-Sr geochronological dating, *Fresenius Journal of Analytical Chemistry*, **371** (2001) 915-920.

[8] *Ionizing radiation: Sources and biological effects*, United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York, 1993.

[9] *Up-to-date Methods of Analytical Chemistry*, (in Hungarian), Gy. Záray (ed.), Akadémiai Kiadó, Budapest, 2006.

[10] J.S. Becker, Inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation ICP-MS for isotope analysis of long-lived radionuclides, *International Journal of Mass Spectrometry*, **242(2-3)** (2005) 183-195.

[11] J.S. Becker, Mass spectrometry of long-lived radionuclides, *Spectrochimica Acta Part B*, **58(10)** (2003) 1757-1784.

[12] *Classification of Radioactive Waste*, Safety Series No. 111-G-1.1, International Atomic Energy Agency, Vienna, 1994.

[13] *Euratom: Commission Recommendation of 15 September 1999 on a classification system for solid radioactive waste (99/669/EC)*, 1999.

[14] D.M. Taylor, Environmental plutonium - creation of the universe to twenty-first century mankind, in: *Radioactivity in the Environment, Volume 1: Plutonium in the Environment (ed. A. Kudo)*, Elsevier Science Ltd., 2001, 1-14.

[15] P. Ormai, A. Fritz, J. Solymosi, I. Gresits, E. Hertelendi, Z. Szucs, N. Vajda, Z. Molnar, P. Zagyvai, Inventory determination of low and intermediate level radioactive waste of Paks nuclear power plant origin, *Journal of Radioanalytical and Nuclear Chemistry*, **211(2)** (1996) 443-451.

[16] P.E. Warwick, I.W. Croudace, J.S. Oh, Radiochemical determination of Am-241 and Pu(alpha) in environmental materials, *Analytical Chemistry*, **73(14)** (2001) 3410-3416.

[17] M.S. Baxter, S.W. Fowler, P.P. Povinec, Observations on Plutonium in the Oceans, *Applied Radiation and Isotopes*, **46(11)** (1995) 1213-1223.

[18] M.E. Ketterer, K.M. Hafer, V.J. Jones, P.G. Appleby, Rapid dating of recent sediments in Loch Ness: inductively coupled plasma mass spectrometric measurements of global fallout plutonium, *Science of the Total Environment*, **322(1-3)** (2004) 221-229.

[19] D. Schaumlöffel, R. Lobinski, Isotope dilution technique for quantitative analysis of endogenous trace element species in biological systems, *International Journal of Mass Spectrometry*, **242(2-3)** (2005) 217-223.

[20] G. Rädlinger, K.G. Heumann, Iodine Determination in Food Samples Using Inductively Coupled Plasma Isotope Dilution Mass Spectrometry, *Analytical Chemistry*, **70(11)** (1998) 2221-2224.

[21] S. Winkler, I. Ahmad, R. Golser, W. Kutschera, K.A. Orlandini, M. Paul, A. Priller, P. Steier, A. Valenta, C. Vockenhuber, Developing a detection method of environmental Pu-244, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **223-24** (2004) 817-822.

[22] *The International Chernobyl Project, Technical Report, Assessment of Radiological Consequences and Evaluation of Protective Measures*, Report by an International Advisory Committee, International Atomic Energy Agency, Vienna, 1991.

[23] A. Aarkrog, H. Dahlgaard, S.P. Nielsen, A.V. Trapeznikov, I.V. Molchanova, V.N. Pozolotina, E.N. Karavaeva, P.I. Yushkov, G.G. Polikarpov, Radioactive inventories from the Kyshtym and Karachay accidents: Estimates based on soil samples collected in the South Urals (1990-1995), *Science of the Total Environment*, **201(2)** (1997) 137-154.

[24] A.C. Chamberlain, Emissions from Sellafield and activities in soil, *Science of the Total Environment*, **177** (1996) 259-280.

[25] E.P. Hardy, P.W. Krey, H.L. Volchok, Global Inventory and Distribution of Fallout Plutonium, *Nature*, **241** (1973) 441-445.

[26] M. Yamamoto, A. Tsumura, Y. Katayama, T. Tsukatani, Plutonium isotopic composition in soil from the former Semipalatinsk nuclear test site, *Radiochimica Acta*, **72(4)** (1996) 209-215.

[27] M.J. Micholas, K.L. Coop, R.J. Estep, Capability and limitation study of DDT passive-active neutron waste assay instrument, in: *LA-12237-MS, Los Alamos National Laboratory*, 1992, Los Alamos.

[28] *Ionizing radiation: Sources and biological effects*, United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York, 1998.

[29] S.F. Boulyga, J.S. Becker, Isotopic analysis of uranium and plutonium using ICP-MS and estimation of burn-up of spent uranium in contaminated environmental samples, *Journal of Analytical Atomic Spectrometry*, **17** (2002) 1143 - 1147.

[30] M.E. Ketterer, K.M. Hafer, J.W. Mietelski, Resolving Chernobyl vs. global fallout contributions in soils from Poland using Plutonium atom ratios measured by inductively coupled plasma mass spectrometry, *Journal of Environmental Radioactivity*, **73(2)** (2004) 183-201.

[31] A.S. Krivokhatsky, Y.V. Dubasov, E.A. Smirnova, N.V. Skovorodkin, V.G. Savonenkov, B.M. Alexandrov, E.L. Lebedev, Actinides in the near Release from the Chernobyl Npp Accident, *Journal of Radioanalytical and Nuclear Chemistry*, **147(1)** (1991) 141-151.

[32] J.M. Kelley, L.A. Bond, T.M. Beasley, Global distribution of Pu isotopes and Np-237, *Science of the Total Environment*, **238** (1999) 483-500.

[33] Council for Nuclear Fuel Cycle (Japan), Can Reactor Grade Plutonium Produce Nuclear Fission Weapons?, *Plutonium*, **34** (2001) 3-7.

[34] MARLAP Workgroup, Chapter 14: Separation Techniques, in: *Multi-Agency Radiological Laboratory Analytical Protocols Manual*, U. S. Environmental Protection Agency, July 2004, 1-226.

[35] G.H. Coleman, *The Radiochemistry of Plutonium*, National Academy of Sciences, National Research Council, U. S. Atomic Energy Commission, Livermore, California, 1965.

[36] J.M. Peterson, M.M. MacDonell, L.A. Haroun, F.A. Monette, R.D. Hildebrand, *Radiological and Chemical Fact Sheets to Support Health Risk Analyses for Contaminated Areas*, Argonne National Laboratory, Environmental Science Division, Chicago, 2007.

[37] M.W. Huntley, Sequential separation of americium, curium, plutonium, neptunium and uranium in various matrices from the electrometallurgic treatment of spent-nuclear fuel, *Radiochimica Acta*, **89(10)** (2001) 605-612.

[38] R.D. Lloyd, S.C. Miller, G.N. Taylor, F.W. Bruenger, W. Angus, W.S.S. Jee, Comparison of internal emitter radiobiology in animals and humans, *Health Physics*, **72(1)** (1997) 100-110.

[39] K. Mayer, M. Wallenius, I. Ray, Nuclear forensics - a methodology providing clues on the origin of illicitly trafficked nuclear materials, *Analyst*, **130(4)** (2005) 433-441.

[40] M. Wallenius, K. Mayer, I. Ray, Nuclear forensic investigations: Two case studies, *Forensic Science International*, **156(1)** (2006) 55-62.

[41] G. Tamborini, D. Phinney, O. Bildstein, M. Betti, Oxygen isotopic measurements by secondary ion mass spectrometry in uranium oxide microparticles: A nuclear forensic diagnostic, *Analytical Chemistry*, **74(23)** (2002) 6098-6101.

[42] C. Mahan, S. Bonchin, D. Figg, D. Gerth, C. Collier, Chromatographic extraction of plutonium and inorganic impurity analysis using ICP-MS and ICP-AES, *Journal of Analytical Atomic Spectometry*, **15** (2000) 929-935.

[43] C.T. Nguyen, J. Zsigrai, Basic characterization of highly enriched uranium by gamma spectrometry, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **246(2)** (2006) 417-424.

[44] C.T. Nguyen, J. Zsigrai, Gamma-spectrometric uranium age-dating using intrinsic efficiency calibration, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **243(1)** (2006) 187-192.

[45] D. Desideri, M.A. Meli, C. Roselli, C. Testa, S.F. Boulyga, J.S. Becker, Determination of U-236 and transuranium elements in depleted uranium ammunition by alpha-spectrometry and ICP-MS, *Analytical and Bioanalytical Chemistry*, **374(6)** (2002) 1091-1095.

[46] C.H. Lee, M.Y. Suh, K.S. Choi, J.S. Kim, B.C. Song, K.Y. Jee, W.H. Kim, Separation of fission products from spent pressurized water reactor fuels by anion exchange and extraction chromatography for inductively coupled plasma atomic emission spectrometric analysis, *Analytica Chimica Acta*, **428(1)** (2001) 133-142.

[47] M. Eriksson, *On Weapons Plutonium in the Arctic Environment (Thule, Greenland), Ph.D. Thesis*, Riso National Laboratory, Roskilde, Denmark, 2002.

[48] U. Nygren, I. Rodushkin, C. Nilsson, D.C. Baxter, Separation of plutonium from soil and sediment prior to determination by inductively coupled plasma mass spectrometry, *Journal of Analytical Atomic Spectrometry*, **18(12)** (2003) 1426-1434.

[49] N.L. Elliot, G.A. Bickel, S.H. Linauskas, L.M. Paterson, Determination of femtogram quantities of ^{239}Pu and ^{240}Pu in bioassay samples by thermal ionization mass spectrometry, *Journal of Radioanalytical and Nuclear Chemistry*, **267(3)** (2006) 637-650.

[50] M.V. Zoriy, C. Pickhardt, P. Ostapczuk, R. Hille, J.S. Becker, Determination of Pu in urine at ultratrace level by sector field inductively coupled plasma mass spectrometry, *International Journal of Mass Spectrometry*, **232(3)** (2004) 217-224.

[51] A.E. Eroglu, C.W. McLeod, K.S. Leonard, D. McCubbin, Determination of plutonium in seawater using co-precipitation and inductively coupled plasma mass spectrometry with ultrasonic nebulisation, *Spectrochimica Acta Part B*, **53(6-8)** (1998) 1221-1233.

[52] T.C. Kenna, Determination of plutonium isotopes and neptunium-237 in environmental samples by inductively coupled plasma mass spectrometry with total sample dissolution, *Journal of Analytical Atomic Spectroscopy*, **17** (2002) 1471-1479.

[53] S.H. Lee, J. Gastaud, J.J. La Rosa, L.L.W. Kwong, P.P. Povinec, E. Wyse, L.K. Fifield, P.A. Hausladen, L.M. Di Tada, G.M. Santos, Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques, *Journal of Radioanalytical and Nuclear Chemistry*, **248(3)** (2001) 757-764.

[54] S.H. Lee, J. La Rosa, J. Gastaud, P.P. Povinec, The development of sequential separation methods for the analysis of actinides in sediments and biological materials using anion-exchange resins and extraction chromatography, *Journal of Radioanalytical and Nuclear Chemistry*, **263(2)** (2005) 419-425.

[55] W.S. Moore, D.F. Reid, Extraction of radium from natural waters using manganese impregnated acrylic fibers, *Journal of Geophysical Research*, **90** (1973) 6983-6994.

[56] K. Norisuye, K. Okamura, Y. Sohrin, H. Hasegawa, T. Nakanishi, Large volume preconcentration and purification for determining the ^{240}Pu/^{239}Pu isotopic ratio and ^{238}Pu/$^{239+240}$Pu alpha-activity ratio in seawater, *Journal of Radioanalytical and Nuclear Chemistry*, **267(1)** (2006) 183-197.

[57] S.H. Lee, J. Gastaud, J.J. La Rosa, L.L.W. Kwong, P.P. Povinec, E. Wyse, L.K. Fifield, P.A. Hausladen, L.M. Di Tada, G.M. Santos, Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques, *Journal of Radioanalytical and Nuclear Chemistry*, **248** (2001) 757-764.

[58] P. Lindahl, P. Roos, E. Holm, H. Dahlgaard, Studies of Np and Pu in the marine environment of Swedish-Danish waters and the North Atlantic Ocean, *Journal of Environmental Radioactivity*, **82(3)** (2005) 285-301.

[59] J. Zheng, M. Yamada, Investigating Pu and U isotopic compositions in sediments: a case study in Lake Obuchi, Rokkasho Village, Japan using sector-field ICP-MS and ICP-QMS, *Journal of Environmental Monitoring*, **7(8)** (2005) 792-797.

[60] M. Ayranov, U. Krahenbuhl, H. Sahli, S. Rollin, M. Burger, Radiochemical separation of actinides from environmental samples for determination with DF-ICP-MS and alpha spectrometry, *Radiochimica Acta*, **93(5)** (2005) 249-257.

[61] H. Rameback, M. Skalberg, A separation procedure for the analysis of Sr-90, Eu-154, and the actinides Np-237, Pu-239, Am-241 and Cm-244, *Journal of Radioanalytical and Nuclear Chemistry*, **240(2)** (1999) 661-663.

[62] H. Rameback, M. Skalberg, Separation of neptunium, plutonium, americium and curium from uranium with di-(2-ethylhexyl)-phosphoric acid (HDEHP) for radiometric and ICP-MS analysis, *Journal of Radioanalytical and Nuclear Chemistry*, **235(1-2)** (1998) 229-233.

[63] M. Momoshima, H. Kakiuchi, Y. Maeda, E. Hirai, T. Ono, Identification of the contamination source of plutonium in environmental samples with isotopic ratios determined by inductively coupled plasma mass spectrometry and alpha-spectrometry, *Journal of Radioanalytical and Nuclear Chemistry*, **221(1-2)** (1997) 213-217.

[64] E.P. Horwitz, Dietz M., Chiarizia R. , Diamond H., Maxwell S.L., Nelson M., Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste Solutions, *Analytica Chimica Acta*, **310** (1995) 63-78.

[65] E.P. Horwitz, Extraction Chromatography of actinides and Selected Fission Products: Principles and Achievement of Selectivity, *www.eichrom.com*,

[66] C. Pin, J.S. Zalduegui, Sequential Separation of Light Rare-Earth Elements, Thorium and Uranium by Miniaturized Extraction Chromatography: Application to Isotopic Analyses of Silicate Rocks, *Analytica Chimica Acta*, **339(1-2)** (1997) 79-89.

[67] S.L. Maxwell, Rapid method for Ra-226 and Ra-228 analysis in water samples, *Journal of Radioanalytical and Nuclear Chemistry*, **270(3)** (2006) 651-655.

[68] N. Vajda, J. La Rosa, R. Zeisler, P. Danesi, G. Kis-Benedek, A novel technique for the simultaneous determination of ^{210}Pb and ^{210}Po using a crown ether, *Journal of Environmental Radioactivity*, **37(3)** (1997) 355-372.

[69] A.P. Vonderheide, M.V. Zoriy, A.V. Izmer, C. Pickhardt, J.A. Caruso, P. Ostapczuk, R. Hille, J.S. Becker, Determination of Sr-90 at ultratrace levels in urine by ICP-MS, *Journal of Analytical Atomic Spectometry*, **19(5)** (2004) 675-680.

[70] C.-S. Kim, C.-K. Kim, J.-I. Lee, K.J. Lee, Rapid determination of Pu isotopes and atom ratios in small amounts of environmental samples by an on-line sample pre-treatment system and isotope dilution high resolution inductively coupled plasma mass spectrometry, *Journal of Analytical Atomic Spectrometry*, **15** (2000) 247-262.

[71] M.V. Zoriy, Z. Varga, C. Pickhardt, P. Ostapczuk, R. Hille, L. Halicz, I. Segal, J.S. Becker, Determination of Ra-226 at ultratrace level in mineral water samples by sector field inductively coupled plasma mass spectrometry, *Journal of Environmental Monitoring*, **7(5)** (2005) 514-518.

[72] Y. Muramatsu, S. Yoshida, K. Tagami, S. Uchida, W. Rühm, ICP-MS analysis of environmental plutonium, in: *Radioactivity in the Environment, Volume 1: Plutonium in the Environment (ed. A. Kudo)*, Elsevier Science Ltd., 2001, 63-77.

[73] P.C. Zoriy MV, Ostapczuk P, Hille R, Becker JS, Determination of Pu in urine at ultratrace level by sector field inductively coupled plasma mass spectrometry, *International Journal of Mass Spectrometry*, **232(3)** (2004) 217-224.

[74] C.S. Kim, C.K. Kim, J.I. Lee, K.J. Lee, Rapid determination of Pu isotopes and atom ratios in small amounts of environmental samples by an on-line sample pre-treatment system and isotope dilution high resolution inductively coupled plasma mass spectrometry, *Journal of Analytical Atomic Spectrometry*, **15(3)** (2000) 247-255.

[75] A.H. Thakkar, Rapid sequential separation of actinides using Eichrom's extraction chromatographic material, *Journal of Radioanalytical and Nuclear Chemistry*, **248(2)** (2001) 453-456.

[76] P.E. Warwick, I.W. Croudace, R. Carpenter, Review of analytical techniques for the determination of Americium-241 in soils and sediments, *Applied Radiation and Isotopes*, **47(7)** (1996) 627-642.

[77] J.J. La Rosa, W. Burnett, S.H. Lee, I. Levy, J. Gastaud, P.P. Povinec, Separation of actinides, cesium and strontium from marine samples using extraction chromatography and sorbents, *Journal of Radioanalytical and Nuclear Chemistry*, **248(3)** (2001) 765-770.

[78] R.P. Bernabee, D.R. Percival, F.D. Hindman, Liquid-Liquid-Extraction Separation and Determination of Plutonium and Americium, *Analytical Chemistry*, **52(14)** (1980) 2351-2353.

[79] M. Agarande, S. Benzoubir, P. Bouisset, D. Calmet, Determination of Am-241 in sediments by isotope dilution high resolution inductively coupled plasma mass spectrometry (ID HR ICP-MS), *Applied Radiation and Isotopes*, **55(2)** (2001) 161-165.

[80] S.F. Boulyga, D. Desideri, M.A. Meli, C. Testa, J.S. Becker, Plutonium and americium determination in mosses by laser ablation ICP-MS combined with isotope dilution technique, *International Journal of Mass Spectrometry*, **226(3)** (2003) 329-339.

[81] M. Rodriguez, J.L. Gascon, J.A. Suarez, Study of the interferences in the determination of Pu, Am and Cm in radioactive waste by extraction chromatography, *Talanta*, **45(1)** (1997) 181-187.

[82] S. Salminen, J. Paatero, T. Jaakkola, J. Lehto, Americium and curium deposition in Finland from the Chernobyl accident, *Radiochimica Acta*, **93(12)** (2005) 771-779.

[83] M. Pimpl, R.H. Higgy, Improvement of Am and Cm determination in soil samples, *Journal of Radioanalytical and Nuclear Chemistry*, **248(3)** (2001) 537-541.

[84] D.M. Beals, S.P. LaMont, J.R. Cadieux, C.R. Shick, G. Hall, *Determination of Trace Radionuclides in SRS Depleted Uranium*, U.S. Department of Energy, Office of Scientific and Technical Information, Oak Ridge, 2002.

[85] S.P. LaMont, G. Hall, Uranium Age Determination by Measuring the ^{230}Th/^{234}U Ratio, *Journal of Radioanalytical and Nuclear Chemistry*, **264(2)** (2005) 423-427.

[86] M. Wallenius, K. Mayer, Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry, *Fresenius Journal of Analytical Chemistry*, **366(3)** (2000) 234-238.

[87] D. Desideri, M.A. Meli, C. Roselli, C. Testa, Analytical techniques for the separation and determination of transuranium element ultratraces in depleted uranium ammunitions, *International Journal of Environmental Analytical Chemistry*, **84(5)** (2004) 331-339.

[88] S.F. Boulyga, C. Testa, D. Desideri, J.S. Becker, Optimisation and application of ICP-MS and alpha-spectrometry for determination of isotopic ratios of depleted uranium and plutonium in samples collected in Kosovo, *Journal of Analytical Atomic Spectrometry*, **16(11)** (2001) 1283-1289.

[89] M. Wallenius, A. Morgenstern, C. Apostolidis, K. Mayer, Determination of the Age of Highly Enriched Uranium, *Analytical and Bioanalytical Chemistry*, **374** (2002) 379-384.

[90] A. Morgenstern, C. Apostolidis, K. Mayer, M. Wallenius, Uranium Age Determination: Separation and Analysis of ^{230}Th and ^{231}Pa, in: *Advances in Destructive and Non-destructive Analysis for Environmental Monitoring and Nuclear Forensics*, International Atomic Energy Agency, Vienna, 2002, 367-369.

[91] A. Morgenstern, C. Apostolidis, R. Carlos-Marquez, K. Mayer, R. Molinet, Single-column extraction chromatographic separation of U, Pu, Np and Am, *Radiochimica Acta*, **90(2)** (2002) 81-85.

[92] M. Wallenius, P. Peerani, L. Koch, Origin determination of plutonium material in nuclear forensics, *Journal of Radioanalytical and Nuclear Chemistry*, **246(2)** (2000) 317-321.

[93] Y.F. Yu, B. Salbu, H.E. Bjornstad, Recent Advances in the Determination of Low-Level Plutonium in Environmental and Biological-Materials, *Journal of Radioanalytical and Nuclear Chemistry*, **148(1)** (1991) 163-174.

[94] N.A. Talvitie, Electrodeposition of actinides for alpha spectrometric determination, *Analytical Chemistry*, **43(11)** (1971) 1827.

[95] C.W. Sill, Precipitation of actinides as fluorides or hydroxide for high-resolution alpha spectrometry, *Nuclear and Chemical Waste Management*, **7** (1987) 201-215.

[96] J.W. Mietelski, J. Dorda, B. Was, Pu-241 in samples of forest soil from Poland, *Applied Radiation and Isotopes*, **51(4)** (1999) 435-447.

[97] L.C. Sun, Y.-H. Xue, Methods for applying plutonium fission track analysis, in: *Radioactivity in the Environment, Volume 1: Plutonium in the Environment (ed. A. Kudo)*, Elsevier Science Ltd., 2001, 79-89.

[98] G. Espinosa, K. Meyers, R.B. Gammage, Soil Measurements by Nuclear Track Detectors, *Radiation Measurements*, **25(1-4)** (1995) 401-404.

[99] A. Kerkapoly, *Investigation of Hot Particles*, Ph.D. Thesis (in Hungarian), Institute of Nuclear Techniques, Budapest University of Technology and Economics, 2005.

[100] N. Dacheux, J. Aupiais, Determination of uranium, thorium, plutonium, americium, and curium ultratraces by photon electron rejecting alpha liquid scintillation, *Analytical Chemistry*, **69(13)** (1997) 2275-2282.

[101] M. Ristic, S. Degetto, T. Ast, C. Cantallupi, Sample preparation for the determination of Am-241 in sediments utilizing gamma-spectroscopy, *Journal of Environmental Radioactivity*, **59(2)** (2002) 179-189.

[102] N. Dacheux, J. Aupiais, O. Courson, C. Aubert, Comparison and improvement of the determinations of actinide low activities using several alpha liquid scintillation spectrometers, *Analytical Chemistry*, **72(14)** (2000) 3150-3157.

[103] K. Mayer, G. Rasmussen, M. Hild, E. Zuleger, H. Ottmar, S. Abousahl, E. Hrnecek, Application of Isotopic Fingerprinting in Nuclear Forensic Investigations: a Case Study, in: *Advances in Destructive and Non-destructive Analysis for Environmental Monitoring and Nuclear Forensics*, International Atomic Energy Agency, Vienna, 2002, 63-70.

[104] P.P. Povinec, Ultra-sensitive radionuclide spectrometry: Radiometrics and mass spectrometry synergy, *Journal of Radioanalytical and Nuclear Chemistry*, **263(2)** (2005) 413-417.

[105] T.M. Beasley, J.M. Kelley, T.C. Maiti, L.A. Bond, Np-237/Pu-239 atom ratios in integrated global fallout: a reassessment of the production of Np-237, *Journal of Environmental Radioactivity*, **38(2)** (1998) 133-146.

[106] M. Betti, S. Giannarelli, T. Hiernaut, G. Rasmussen, L. Koch, Detection of trace radioisotopes in soil, sediment and vegetation by glow discharge mass spectrometry, *Fresenius Journal of Analytical Chemistry*, **355(5-6)** (1996) 642-646.

[107] M. Miyabe, M. Oba, M. Kato, I. Wakaida, K. Watanabe, Development of RIMS apparatus for isotope analysis of calcium in nuclear waste materials, *Journal of Nuclear Science and Technology*, **43(4)** (2006) 305-310.

[108] N. Erdmann, G. Herrmann, G. Huber, S. Kohler, J.V. Kratz, A. Mansel, M. Nunnemann, G. Passler, N. Trautmann, A. Turchin, A. Waldek, Resonance ionization mass spectroscopy for trace determination of plutonium in environmental samples, *Fresenius Journal of Analytical Chemistry*, **359(4-5)** (1997) 378-381.

[109] C. Gruning, G. Huber, P. Klopp, J.V. Kratz, P. Kunz, G. Passler, N. Trautmann, A. Waldek, K. Wendt, Resonance ionization mass spectrometry for ultratrace analysis of plutonium with a new solid state laser system, *International Journal of Mass Spectrometry*, **235(2)** (2004) 171-178.

[110] B.A. Bushaw, W. Nortershauser, P. Muller, K. Wendt, Diode-laser-based resonance ionization mass spectrometry of the tong-lived radionuclide Ca-41 with < 10(-12) sensitivity, *Journal of Radioanalytical and Nuclear Chemistry*, **247(2)** (2001) 351-356.

[111] S.L. Oughton DH, Fifield LK, Cresswell RG, Salbu B, Day P, Accelerator mass spectrometry measurement of Pu-240/Pu-239 isotope ratios in Novaya Zemlya and Kara Sea sediments, *Applied Radiation and Isotopes*, **61(2-3)** (2004) 249-253.

[112] E. Hrnecek, P. Steier, A. Wallner, Determination of plutonium in environmental samples by AMS and alpha spectrometry, *Applied Radiation and Isotopes*, **63(5-6)** (2005) 633-638.

[113] J.E. McAninch, T.F. Hamilton, T.A. Brown, T.A. Jokela, J.P. Knezovich, T.J. Ognibene, I.D. Proctor, M.L. Roberts, E. Sideras-Haddad, J.R. Southon, J.S. Vogel, Plutonium measurements by accelerator mass spectrometry at LLNL, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **172** (2000) 711-716.

[114] R.N. Taylor, T. Warneke, J.A. Milton, I.W. Croudace, P.E. Warwick, R.W. Nesbitt, Multiple ion counting determination of plutonium isotope ratios using multi-collector ICP-MS, *Journal of Analytical Atomic Spectrometry*, **18(5)** (2003) 480-484.

[115] R. Chiappini, J.M. Taillade, S. Brebion, Development of a high-sensitivity inductively coupled plasma mass spectrometer for actinide measurement in the femtogram range, *Journal of Analytical Atomic Spectrometry*, **11(7)** (1996) 497-503.

[116] L. Halicz, J.S. Becker, C. Pickhardt, I. Gavrieli, A. Burg, A. Nishri, I.T. Platzner, Characterization of natural water resources in Israel by inductively coupled plasma mass spectrometry, *International Journal of Mass Spectrometry*, **249** (2006) 296-302.

[117] J.S. Becker, ICP-MS: determination of long-lived radionuclides, *Spectroscopy Europe*, **14(6)** (2002) 1-7.

[118] E.J. Wyse, S.H. Lee, J. La Rosa, P. Povinec, S.J. de Mora, ICP-sector field mass spectrometry interferences of plutonium isotopes: recognizing and resolving potential interferences, *Journal of Analytical Atomic Spectrometry*, **16** (2001) 1107-1111.

[119] U. Nygren, H. Rameback, D.C. Baxter, C. Nilsson, Lanthanide phosphate interferences in actinide determination using inductively coupled plasma mass spectrometry, *Journal of Analytical Atomic Spectrometry*, **20(6)** (2005) 529-534.

[120] C.-S. Kim, C.-K. Kim, K.J. Lee, Determination of Pu isotopes in seawater by an on-line sequential injection technique with sector field inductively coupled plasma mass spectrometry, *Analytical Chemistry*, **74** (2002) 3824-3832.

[121] J.B. Truscott, P. Jones, B.E. Fairman, E.H. Evans, Determination of actinide elements at femtogram per gram levels in environmental samples by on-line solid phase extraction and sector-field-inductively coupled plasma-mass spectrometry, *Analytica Chimica Acta*, **433** (2001) 245-253.

[122] V.N. Epov, K. Benkhedda, R.J. Cornett, R.D. Evans, Rapid determination of plutonium in urine using flow injection on-line preconcentration and inductively coupled plasma mass spectrometry, *Journal of Analytical Atomic Spectrometry*, **20(5)** (2005) 424-430.

[123] M.V. Zoriy, L. Halicz, M.E. Ketterer, C. Pickhardt, P. Ostapczuk, J.S. Becker, Reduction of UH^+ formation for U-236/U-238 isotope ratio measurements at ultratrace level in double focusing sector field ICP-MS using D_2O as solvent, *Journal of Analytical Atomic Spectrometry*, **19(3)** (2004) 362-367.

[124] S.F. Boulyga, M. Tibi, K.G. Heumann, Application of isotope-dilution laser ablation ICP-MS for direct determination of Pu concentrations in soils at pg g(-1) levels, *Analytical and Bioanalytical Chemistry*, **378(2)** (2004) 342-347.

[125] P. Evans, S. Elahi, K. Lee, B. Fairman, A rapid and accurate method for the determination of plutonium in food using magnetic sector ICP-MS with an ultra-sonic nebuliser and ion chromatography, *Journal of Environmental Monitoring*, **5(1)** (2003) 175-179.

[126] C.S. Kim, C.K. Kim, Determination of Pu isotopes in eawater by an on-line sequential injection technique with sector field inductively coupled plasma mass spectrometry, *Analytical Chemistry*, **74(15)** (2002) 3824-3832.

[127] M. Agarande, S. Benzoubir, A.M. Neiva-Marques, P. Bouisset, Sector field inductively coupled plasma mass spectrometry: another tool for plutonium isotopes and plutonium isotope ratios determination in environmental matrices, *Journal of Environmental Radioactivity*, **72** (2004) 169-176.

[128] M.V. Zoriy, P. Ostapczuk, L. Halicz, R. Hille, J.S. Becker, Determination of Sr-90 and Pu isotopes in contaminated groundwater samples by inductively coupled plasma mass spectrometry, *International Journal of Mass Spectrometry*, **242(2-3)** (2005) 203-209.

[129] Y. Muramatsu, S. Uchida, K. Tagami, S. Yoshida, T. Fujikawa, Determination of plutonium concentration and its isotopic ratio in environmental materials by ICP-MS after separation using ion-exchange and extraction chromatography, *Journal of Analytical Atomic Spectrometry*, **14(5)** (1999) 859-865.

[130] S. Stürup, H. Dahlgaard, S.C. Nielsen, High resolution inductively coupled plasma mass spectrometry for the trace determination of plutonium isotopes and isotope ratios in environmental samples, *Journal of Analytical Atomic Spectrometry*, **13** (1998) 1321-1326.

[131] P. Evans, S. Elahi, K. Lee, B. Fairman, A rapid and accurate method for the determination of plutonium in food using magnetic sector ICP-MS with an ultra-sonic nebuliser and ion chromatography, *Journal of Environmental Monitoring*, **4** (2002) 1-6.

[132] T.C. Kenna, F.L. Sayles, The distribution and history of nuclear weapons related contamination in sediments from the Ob River, Siberia as determined by isotopic ratios of plutonium and neptunium, *Journal of Environmental Radioactivity*, **60** (2002) 105-137.

[133] B.G. Ting, R.S. Pappas, D.C. Paschal, Rapid analysis for plutonium-239 in urine by magnetic sector inductively coupled plasma-mass spectrometry using Aridus desolvation introduction system, *Journal of Analytical Atomic Spectrometry*, **18** (2003) 795-797.

[134] V.N. Epov, K. Benkhedda, D. Brownell, R.J. Cornett, R.D. Evans, Comparative study of three sample preparation approaches for the fast determination of americium in urine by flow injection ICP-MS, *Canadian Journal of Analytical Sciences and Spectroscopy*, **50(1)** (2005) 14-22.

[135] S. Richter, A. Alonso, J. Truyens, H. Kühn, A. Verbruggen, R. Wellum, Evaluating the status of uranium isotope ratio measurements using an inter-laboratory comparison campaign, *International Journal of Mass Spectrometry*, **264(2-3)** (2007)

[136] S. Richter, S.A. Goldberg, Improved techniques for high accuracy isotope ratio measurements of nuclear materials using thermal ionization mass spectrometry, *International Journal of Mass Spectrometry*, **229(3)** (2003) 181-197.

[137] S.K. Aggarwal, G. Chourasiya, R.K. Duggal, R. Rao, H.C. Jain, Experimental evaluation of plutonium-239 spike for determining plutonium concentration by isotope dilution- thermal ionization mass spectrometry, *International Journal of Mass Spectrometry and Ion Processes*, **69(2)** (1986) 137-151.

[138] M. Betti, L.A. de las Heras, Glow discharge spectrometry for the characterization of nuclear and radioactively contaminated environmental samples, *Spectrochimica Acta Part B*, **59(9)** (2004) 1359-1376.

[139] S.F. Boulyga, J.L. Matusevich, V.P. Mironov, V.P. Kudrjashov, L. Halicz, I. Segal, J.A. McLean, A. Montaser, J.S. Becker, Determination of U-236/U-238 isotope ratio in contaminated environmental samples using different ICP-MS instruments, *Journal of Analytical Atomic Spectrometry*, **17(8)** (2002) 958-964.

[140] J.M. Barrero Moreno, M. Betti, J.I. Garcia Alonso, Determination of Neptunium and Plutonium in the Presence of High Concentrations of Uranium by Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry, *Journal of Analytical Atomic Spectrometry*, **12(3)** (1997) 355.

[141] S. Röllin, Z. Kopatjtic, B. Wernli, B. Magyar, Determination of lanthanides and actinides in uranium materials by high-performance liquid chromatography with inductively coupled plasma mass spectrometric detection, *Journal of Chromatography A*, **739** (1996) 139-149.

[142] I. Günther-Leopold, J. Kobler Waldis, B. Wernli, Z. Kopajtic, Measurement of plutonium isotope ratios in nuclear fuel samples by HPLC-MC-ICP-MS, *International Journal of Mass Spectrometry*, **242** (2005) 197-202.

[143] T. Bíró, Experience and current activities at the Institute of Isotopes, Budapest, related to nuclear safeguards and forensics, *ESARDA Bulletin*, **35** 36-41.

[144] *http://www.natur.cuni.cz/ugmnz/icplab/slab0.html*,

[145] L.A. Currie, Limits for qualitative detection and quantitative determination, *Analytical Chemistry*, **40** (1968) 586.

[146] S. Ballestra, *Intercomparison of radionuclide measurements in mixed seaweeds sample IAEA-308*, International Laboratory of Marine Radioactivity, International Atomic Energy Agency, Monaco, 1989.

[147] P.P. Povinec, P.P. Pham, *Report on the intercomparison run IAEA-384 - Radionuclides in Fangataufa Lagoon Sediment*, IAEA/AL/126 International Atomic Energy Agency, Monaco, 2000.

[148] P.P. Povinec, P.P. Pham, *Report on the intercomparison run IAEA-385 - Radionuclides in Irish Sea Sediment*, International Atomic Energy Agency, Monaco, 2000.

[149] *United Nations Scientific Committee on the Effects of Atomic Radiation, Ionizing Radiation: Sources and Biological Effects*, United Nations, New York, 1982.

[150] K.G. Heumann, S.M. Gallus, G. Rädlinger, J. Vogl, Precision and accuracy in isotope ratio measurements by plasma source mass spectrometry, *Journal of Analytical Atomic Spectrometry*, **13** (1998) 1001-1008.

[151] J. Paatero, T. Jaakkola, S. Kulmala, Lichen (sp. Cladonia) as a deposition indicator for transuranium elements investigated with the Chernobyl fallout, *Journal of Environmental Radioactivity*, **38(2)** (1998) 223-247.

[152] P.J. Kershaw, D.S. Woodhead, M.B. Lovett, K.S. Leonard, Plutonium from European Reprocessing Operations - Its Behavior in the Marine-Environment, *Applied Radiation and Isotopes*, **46(11)** (1995) 1121-1134.

[153] M. Yamamoto, A. Tsumura, Y. Katayama, T. Tsukatani, Plutonium isotopic composition in soil from the former Semipalatinsk Nuclear Test Site, *Radiochimica Acta*, **72** (1995) 209-215.

[154] L.E. De Geer, The Radioactive Signature of the Hydrogen Bomb, *Science and Global Security*, **2** (1991) 351-363.

[155] J. Molero, J.A. Sanchez-Cabeza, J. Merino, J.V. Batlle, P.I. Mitchell, A. Vidalquadras, Particulate Distribution of Plutonium and Americium in Surface Waters from the Spanish Mediterranean Coast, *Journal of Environmental Radioactivity*, **28(3)** (1995) 271-283.

[156] K. Bunzl, W. Kracke, W. Schimmack, Vertical Migration of Pu-239 + Pu-240, Am-241 and Cesium-137 Fallout in a Forest Soil under Spruce, *Analyst*, **117(3)** (1992) 469-474.

[157] S.F. Boulyga, M. Zoriy, M.E. Ketterer, J.S. Becker, Depth profiling of Pu, Am-241 and Cs-137 in soils from southern Belarus measured by ICP-MS and alpha and gamma spectrometry, *Journal of Environmental Monitoring*, **5(4)** (2003) 661-666.

[158] P. Bossew, M. Gastberger, H. Gohla, P. Hofer, A. Hubmer, Vertical distribution of radionuclides in soil of a grassland site in Chernobyl exclusion zone, *Journal of Environmental Radioactivity*, **73(87-99)** (2004)

[159] M.O. Mboulou, C. Hurtgen, K. Hofkens, C. Vandecasteele, Vertical distributions in the Kapachi soil of the plutonium isotopes (Pu-238, Pu-239,Pu-240, Pu-241), of Am-241, and of Cm-243,Cm-244, eight years after the Chernobyl accident, *Journal of Environmental Radioactivity*, **39(3)** (1998) 231-237.

[160] C. Testa, S. Degetto, G. Jia, R. Gerdol, D. Desideri, M.A. Meli, F. Guerra, Plutonium and americium concentrations and vertical profiles in some Italian

mosses used as bioindicators, *Journal of Radioanalytical and Nuclear Chemistry*, **234(1-2)** (1998) 273-276.

[161] H. Cheng, H.L. Edwards, J. Hoff, C.D. Gallup, D.A. Richards, Y. Asmerom, The half-lives of uranium-234 and thorium-230, *Chemical Geology*, **169** (2000) 17-33.

[162] GUM Workbench, Version 1.2.4, Metrodata GmbH, Grenzach-Wyhlen, Germany, 1999.

[163] G.B. Dudder, R.C. Hanlen, G.M.J. Herbillon, International Working Group Round Robin Tests, in: *Advances in Destructive and Non-destructive Analysis for Environmental Monitoring and Nuclear Forensics*, International Atomic Energy Agency, Vienna, 2002, 41-51.

[164] Z. Málek, F. Sus, Report on the Recent Progress at the Central Analytical Laboratory (NRI, Rez plc.) for Upgrading Capabilities for Identification of Illicit Nuclear Materials, in: *Advances in Destructive and Non-destructive Analysis for Environmental Monitoring and Nuclear Forensics*, International Atomic Energy Agency, Vienna, 2002, 53-61.

[165] J.S. Becker, H.J. Dietze, State-of-the-art in inorganic mass spectrometry for analysis of high-purity materials, *International Journal of Mass Spectrometry*, **228(2-3)** (2003) 127-150.

[166] G. Tamborini, M. Wallenius, O. Bildstein, L. Pajo, M. Betti, Development of a SIMS method for isotopic measurements in nuclear forensic applications, *Mikrochimica Acta*, **139(1-4)** (2002) 185-188.

[167] J.S. Becker, C. Pickhardt, H.J. Dietze, Laser ablation inductively coupled plasma mass spectrometry for the trace, ultratrace and isotope analysis of long-lived radionuclides in solid samples, *International Journal of Mass Spectrometry*, **202(1-3)** (2000) 283-297.

[168] Z. Stefánka, Z. Varga, Determination of trace impurities in highly enriched uranium oxide samples by inductively coupled plasma mass spectrometry in combination with extraction chromatography, *15th Radioanalytical Conference*, 23-28 April 2006, Mariánské Lázne, Czech Republic.

[169] Z. Varga, Ultratrace-level radium-226 determination in seawater samples by isotope dilution inductively coupled plasma mass spectrometry, *Analytical and Bioanalytical Chemistry*, (in press)

List of Publications

Papers in connection with the dissertation, published in peer-reviewed journals

1. Z. Varga, Application of inductively coupled plasma mass spectrometry for low-level environmental Am-241 analysis, Analytica Chimica Acta, 2007, **587**, 165-169
2. Z. Varga, G. Surányi, N. Vajda, Z. Stefánka, Rapid sequential determination of americium and plutonium in sediment and soil samples by ICPSFMS and alpha-spectrometry, Radiochimica Acta, 2007, **95**, 81-87
3. Z. Varga, Surányi, G., Production date determination of uranium-oxide materials by inductively coupled plasma mass spectrometry, Analytica Chimica Acta, 2007, **599**, 16-23
4. Z. Varga, G. Surányi, N. Vajda, Z. Stefánka, Improved sample preparation method for environmental plutonium analysis by ICP-SFMS and alpha-spectrometry, Journal Radioanalytical Nuclear Chemistry, 2007, **274**, 87-94
5. Z. Varga, Surányi, G., Vajda, N., Stefánka, Z., Determination of plutonium and americium in environmental samples by inductively coupled plasma sector field mass spectrometry and alpha spectrometry, Microchemical Journal, 2007, **85**, 39-45
6. Z. Varga, G. Surányi, N. Vajda, Z. Stefánka, Rapid methods for the determination of long-lived radionuclides in environmental samples by ICP-SFMS and radioanalytical techniques, Czechoslovakian Journal of Physics, 2006, **56**. Suppl. D., D177
7. Z. Varga, Origin and Release Date Assessment of Environmental Plutonium by Isotopic Composition, Analytical and Bioanalytical Chemistry (accepted, in press)

Other papers published in peer-reviewed journals

1. M. Zoriy, Z. Varga, C. Pickhardt, P. Ostapczuk, R. Hille, L. Halicz, I. Segal, J. S. Becker, Determination of ^{226}Ra at ultratrace level in mineral water samples by sector field inductively coupled plasma mass spectrometry, Journal of Environmental Monitoring, 2005, **7**, 514-518

2. Z. Varga, Ultra-trace Level Radium-226 Determination in Sea-Water Samples by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry, Analytical and Bioanalytical Chemistry (accepted, in press)
3. Z. Varga, Preparation and Characterization of Manganese-dioxide Impregnated Resin for Radionuclide Pre-concentration, Applied Radiation and Isotopes, 2007, **65**, 1095-1100
4. K. Gméling, K. Németh, U. Martin, N. Eby, Z. Varga, Boron Concentrations of Volcanic Fields in Different Geotectonic Settings, Journal of Volcanology and Geothermal Research, 2007, **159**, 70-84
5. Horváth, A. Beck, A. Sárkány, Gy. Stefler, Z. Varga, O. Geszti, L. Tóth, L. Guczi, Silica-supported Au Nanoparticles Decorated by TiO2: Formation, Morphology, and CO Oxidation Activity, The Journal of Physical Chemistry B, 2006, **110**, 15417-15425

Other papers

Varga Zsolt, Myroslav V. Zoriy, J. Sabine Becker, Mintaelőkészítési módszerek ^{226}Ra ásványvizekből induktív csatolású plazma tömegspektrometriával történő meghatározására, Fizikai Szemle, 2005/4, 140-143 (in Hungarian)

International Conferences

Varga, Z., T. Bíró, Z. Stefanka, Determination of Long-lived Radionuclide Impurities in Uranium-oxide, 29th ESARDA Annual Meeting, Aix en Provence, Franciaország, 22-24 May, 2007 (oral presentation)

Stefánka, Z., R. Katona, Z. Varga, T. Bíró, Investigation of Uranium-oxide Samples using ICP-SFMS: Determination of Impurities and Isotope Ratios, 29th ESARDA Annual Meeting, Aix en Provence, Franciaország, 22-24 May, 2007 (oral presentation)

Varga, Z., N. Vajda, Z. Stefánka, Applicability of Transuranic Isotope Ratios for Origin Assessment, 29th ESARDA Annual Meeting, Aix en Provence, Franciaország, 22-24 May, 2007 (poster)

Varga, Z., Z. Stefanka, Ultratrace-Level Environmental Transuranic Analysis by ICP-SFMS for Origin Assessment, 2007 Winter Conference on Plasma Spectrochemistry, Taormina, Olaszország, 2007 (oral presentation)

Zaray, Gy., Zs. Varga, V. G. Mihucz, E. Tatar, I. Virag, R. van Grieken, M. Kazmer, Investigation of Uranium Pollution in a Former Uranium Mining Area in Hungary, 2007 Winter Conference on Plasma Spectrochemistry, Taormina, Olaszország, 2007 (oral presentation)

Stefánka, Zs., Zs. Varga, T. Bíró, Investigation of Uranium Oxide Samples Using ICP-SFMS: Determination of Impurities and Isotope Ratios, 2007 Winter Conference on Plasma Spectrochemistry, Taormina, Olaszország, 2007 (oral presentation)

Varga, Z., Ultra-trace Level Ra-226 Analysis by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry, 2007 Winter Conference on Plasma Spectrochemistry, Taormina, Olaszország, 2007 (poster)

Varga, Z., G. Suranyi, N. Vajda, Z. Stefanka, Assessment of Possible Sources of Artificial Long-Lived Radionuclides in Environmental Samples by Measurement of Isotopic Composition, 10th Environmental Radiochemical Analysis, Oxford, United Kingdom, 2006 (poster)

Varga, Z., G. Suranyi, Z. Stefanka, Environmental long-lived radionuclide analysis by inductively coupled plasma mass spectrometry and radioanalytical methods, 1st European Chemistry Congress, Budapest, Hungary, 2006. (poster)

Varga, Z., G. Suranyi, N. Vajda, Z. Stefanka, Rapid methods for the determination of long-lived radionuclides in environmental samples by ICP-SFMS and radioanalytical techniques, 15th Radiochemistry Conference, Marianske Lázne, Czech Republic, 2006. (oral presentation)

Stefanka, Z., Varga, Z., Determination of trace impurities in highly enriched uranium oxide samples by inductively coupled plasma mass spectrometry in combination with extraction chromatography, 15th Radiochemistry Conference, Marianske Lázne, Czech Republic, 2006. (poster)

Zoriy, M., Z. Varga, C. Pickhardt, P. Ostapczuk, R. Hille, L. Halicz, I. Segal and J. S. Becker, Determination of Ra-226 in mineral and groundwater samples at ultratrace level by sector field inductively coupled plasma mass spectrometry, European Winter Conference on Plasma Spectrochemistry, Budapest, 2005 (Poster)

Varga, Z., Stefánka, Z., Rapid sequential methods for separation and pre-concentration of anthropogenic radionuclides followed by a-spectrometry and ICP-SFMS detection, XII. Italian-Hungarian Spectrochemical Symposium, 2005 (oral presentation)

Hungarian Conferences

Varga Zsolt, Stefánka Zsolt, Bíró Tamás, Radionuklidok elemzése induktív csatolású plazma tömegspektrometriával, Centenáriumi Vegyészkonferencia, Sopron, 2007. május 29 - június 1. (előadás)

Varga Zsolt, Stefánka Zsolt, Környezeti transzuránok tömegspektrometriás és radiokémiai analízise, Őszi Radiokémiai Napok, Siófok, 2006. (előadás)

Stefánka Zsolt, Varga Zsolt, Bíró Tamás, Urán-oxid minták vizsgálata induktív csatolású plazma tömegspektrometria segítségével: elemanalízis és izotóparány-meghatározás, Őszi Radiokémiai Napok, Siófok, 2006. (előadás)

Osváth Szabolcs, Oroszlány Endre, Varga Zsolt, Csernobili eredetű biológiai és környezeti minták vizsgálata, Sugárvédelmi Tanfolyam, Balatonkenese, 2006. (poszter, Poszter-díj).

Stefánka Zsolt, Varga Zsolt, Vajda Nóra, Bíró Tamás, Radionuklidok meghatározása környezeti mintákban induktív csatolású plazma tömegspektrometria segítségével, Sugárvédelmi Tanfolyam, Balatonkenese, 2006. (előadás)

Varga Zsolt, Stefánka Zsolt, Az induktív csatolású plazma tömegspektrometria felhasználási lehetőségei nukleáris minták analízisére, IV. Nukleáris Technikai Szimpózium, Budapest, 2005. (előadás)

Varga Zsolt, Vajda Nóra, Stefánka Zsolt, Plutónium meghatározása induktív csatolású plazma tömegspektrometriával, Őszi Radiokémiai Napok, Mátraháza, 2005. (előadás, Hevesy György Előadói Nívódíj 3. hely)

Stefánka Zsolt, Varga Zsolt, Mintaelőkészítési módszerek radionuklidok alfa spektrometriával és ICP-MS-sel történő meghatározásához, Környezetvédelmi Analitikai és Technológiai Konferencia, Eger, 2005. (előadás)

Varga Zsolt, Myroslav V. Zoriy, J. Sabine Becker, Mintaelőkészítési módszerek ^{226}Ra ásványvizekből induktív csatolású plazma tömegspektrometriával történő meghatározására, 48. Magyar Spektrokémiai Vándorgyűlés, Hajdúszoboszló, 2005. (előadás)

Z. Varga, Zoriy, M., Becker, J. S., Mintaelőkészítési módszerek Ra-226 ásványvizekből induktív csatolásù plazma tömegspektrometriával történő meghatározására, III. Nukleáris Technikai Szimpózium, Budapest, 2004. (előadás)

Varga Zsolt Bór mérése induktív csatolású plazma optikai emissziós spektrometriával, 46. Magyar Spektrokémiai Vándorgyűlés, Szeged, 2003. (előadás)

Appendixes

Appendix A

Possible isobaric interferences of plutonium analysis and mass resolution required to separate from the analyte peak

Possible interferences on *m/z* = 239:

Interference	Mass resolution required
$^{238}U^+$ overlap	Not applicable
$^{238}UH^+$	37054
$^{207}Pb^{16}O_2^+$	2765
$^{208}Pb^{31}P^+$	2350
$^{207}Pb^{32}S^+$	2287
$^{206}Pb^{33}S^+$	2250
$^{202}Hg^{37}Cl^+$	2089

Interference	Mass resolution required
$^{204}Hg^{35}Cl^+$	2177
$^{205}Tl^{34}S^+$	2176
$^{203}Tl^{36}Ar^+$	2129
$^{201}Hg^{38}Ar^+$	2006
$^{199}Hg^{40}Ar^+$	1967
$^{204}Pb^{35}Cl^+$	2168

Possible interferences on *m/z* = 240:

Interference	Mass resolution required
$^{238}UH_2^+$	21662
$^{208}Pb^{16}O_2^+$	2750
$^{209}Bi^{31}P^+$	2409
$^{208}Pb^{32}S^+$	2284
$^{207}Pb^{33}S^+$	2255
$^{206}Pb^{34}S^+$	2153
$^{205}Tl^{35}Cl^+$	2172
$^{204}Pb^{36}Ar^+$	2120

Interference	Mass resolution required
$^{204}Hg^{36}Ar^+$	2128
$^{203}Tl^{37}Cl^+$	2077
$^{202}Hg^{38}Ar^+$	1993
$^{200}Hg^{40}Ar^+$	1955

Possible interferences on *m/z* = 241:

Interference	Mass resolution required
$^{206}Pb^{35}Cl^+$	2123
$^{204}Pb^{37}Cl^+$	2044
$^{241}Am^+$	1.09×10^7
$^{209}Bi^{32}S^+$	2309
$^{208}Pb^{33}S^+$	2217
$^{203}Tl^{38}Ar^+$	1979
$^{201}Hg^{40}Ar^+$	1941

Interference	Mass resolution required
$^{207}Pb^{34}S^+$	2131
$^{206}Pb^{35}Cl^+$	2123
$^{205}Tl^{36}Ar^+$	2097
$^{205}Tl^{36}S^+$	2090
$^{204}Hg^{37}Cl^+$	2052
$^{209}Bi^{16}O_2^+$	2783

Possible interferences on *m/z* = 242:

Interference	Mass resolution required
$^{207}Pb^{35}Cl^+$	2097
Cross contam.	Not applicable
$^{206}Pb^{36}Ar^+$	2097

Interference	Mass resolution required
$^{202}Hg^{40}Ar^+$	1917

Appendix B

Optimized ICP-SFMS operating parameters for environmental plutonium analysis (Chapter 5.2.)

Element2 ICP-SFMS Instrument	
RF power, W	1245
Cooling gas flow rate, L min^{-1}	15.6
Auxiliary gas flow rate, L min^{-1}	0.85
Nebulizer gas flow rate, L min^{-1}	1.095
Resolution	300
Runs and passes	20*1
Mass window, %	20
Samples per peak	250
Search window, %	5
Integration window, %	80
Scan type	E-Scan
Aridus Sample Introduction System with T1-H nebulizer	
Solution uptake rate, µL min^{-1}	60
Spray chamber temperature, °C	70
Membrane temperature, °C	160
Sweep gas flow rate, L min^{-1}	5.20

Appendix C

Optimized ICP-SFMS operating parameters for environmental ^{241}Am analysis (Chapter 5.3.)

Element2 ICP-SFMS Instrument	
Forward power, W	1425
Cooling gas flow rate, L min^{-1}	13.8
Auxiliary gas flow rate, L min^{-1}	0.75
Nebulizer gas flow rate, L min^{-1}	0.730
Sample introduction conditions (MCN-6000)	
Solution uptake rate, µL min^{-1}	60
Spray chamber temperature, °C	105
Membrane temperature, °C	160
Sweep gas flow rate, L min^{-1}	2.85
Data acquisition	
Resolution	300
Runs and passes	40 x 1
Mass window, %	5
Samples per peak	250
Search window, %	60
Integration window, %	5
Sampling time, s	0.1
Integration type	Average
Scan type	E-Scan
Measured isotopes	^{208}Pb, ^{209}Bi, ^{238}U, ^{239}Pu, ^{241}Am, ^{242}Pu, ^{243}Am

Appendix D

Optimized ICP-SFMS operating parameters of the sequential method (Chapter 5.4.)

Element2 ICP-SFMS Instrument	
RF power, W	1263
Cooling gas flow rate, L min^{-1}	15.3
Auxiliary gas flow rate, L min^{-1}	0.89
Nebulizer gas flow rate, L min^{-1}	1.025
Resolution	300
Runs and passes	20 x 1
Mass window, %	20
Samples per peak	250
Search window, %	5
Integration window, %	80
Scan type	E-Scan
Aridus in combination with T1-H nebulizer	
Solution uptake rate, µL min^{-1}	60
Spray chamber temperature, °C	70
Membrane temperature, °C	160
Sweep gas flow rate, L min^{-1}	5.15

Appendix E

Optimized ICP-SFMS operating parameters for the destructive and laser ablation ICP-SFMS analysis of nuclear materials
(Chapter 7.3. and 7.4.)

Optimized ICP-SFMS operating parameters		
	Liquid sample introduction	**Laser ablation**
Forward power, W	1275	1275
Cooling gas flow rate, L min^{-1}	15.95	15.95
Auxiliary gas flow rate, L min^{-1}	1.21	1.21
Nebulizer gas flow rate, L min^{-1}	0.975	1.040
Sample introduction conditions (for Th and ^{234}U determinations)		
Solution uptake rate, µL min^{-1}	100	NA
Aridus in combination with T1-H nebulizer (used for ^{236}U and Pu determinations)		
Solution uptake rate, µL min^{-1}		60
Spray chamber temperature, °C		70
Membrane temperature, °C		160
Sweep gas flow rate, L min^{-1}		5.00
Data acquisition		
Resolution	300	300, 4000
Runs and passes	5 x 10	60 x 1
Mass window, %	5	120
Samples per peak	100	20
Search window, %	60	60
Integration window, %	5	80
Sampling time, s	0.08 (^{229}Th, ^{230}Th, ^{233}U, ^{234}U) 0.01 (^{235}U, ^{238}U)	0.1 (^{230}Th) 0.01 (^{234}U)
Integration type	Average	Average
Scan type	E-Scan	E-Scan
Measured isotopes	^{229}Th, ^{230}Th, ^{232}Th ^{233}U, ^{234}U, ^{235}U, ^{238}U	^{234}U, ^{230}Th