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Plutonium and americium determination in mosses by laser ablation ICP-MS combined with isotope dilution technique

Sergei F. Boulyga[a,b], Donatella Desideri[c], Maria Assunta Meli[c], Corrado Testa[c], J. Sabine Becker[a,*]

[a] Central Department of Analytical Chemistry, Research Center Juelich, 52425 Juelich, Germany
[b] Radiation Physics and Chemistry Problems Institute, Sosny, 220109 Minsk, Belarus
[c] Faculty of Pharmacy, Institute of General Chemistry, Urbino University, Urbino, Italy

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Abstract

Environmental contamination by artificial radionuclides and the evaluation of their sources requires precise isotopic analysis and accurate determination of transuranium elements, above all plutonium and americium. This can be achieved by alpha spectrometry or by inductively coupled plasma mass spectrometry (ICP-MS) after chemical separation of actinides. In the present work, laser ablation (LA) ICP-MS was combined with isotope dilution for the ultratrace level determination of ^{239}Pu, ^{240}Pu and ^{241}Am on the surface of targets after electroplating. ^{242}Pu and ^{243}Am were used as isotope spikes. An overall detection efficiency of better than 10^{-3} counts per atom was achieved for ^{238}U in LA-ICP-MS. The limits of quantification (LOQ, 10σ) for ^{232}Th, U, ^{237}Np and Pu isotopes were comparable with or better than the detection limits of alpha spectrometry for long-lived radionuclides. Thus, the estimated detection limit for Pu was as low as 3.6 fg g^{-1} in soil after chemical separation. Comparison of LA-ICP-SFMS with alpha spectrometry yielded good agreement of Pu concentrations in moss samples at the level of 5×10^{-14} to 2.5×10^{-13} g g^{-1}, but poorer coincidence was observed for ^{241}Am because of very low concentrations (about 2×10^{-14} g g^{-1}). The ^{240}Pu/^{239}Pu isotope ratio was almost constant within experimental errors for all samples analyzed with a weighted average value of 0.212 ± 0.003. The obtained results (global fallout after nuclear weapon tests) confirm once again that mosses are particularly suited for use as bioindicators of environmental contamination.

Keywords: Plutonium; Americium; Bioindicators; Inductively coupled plasma mass spectrometry; Laser ablation

1. Introduction

Determination of the concentration and isotope ratios of actinides is required in environmental monitoring, nuclear safeguards and nuclear forensic studies. For instance, plutonium is the most widespread element among the transuranium elements and it is represented in irradiated nuclear fuel by five isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu) [1]. Knowledge of the isotopic composition of natural and artificial actinides is of great interest for evaluating their source (nuclear power plant accidents, nuclear weapons tests or weapons with depleted uranium) [2–4].

The use of bioindicators to assess the occurrence of airborne pollutants is receiving an ever increasing

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[*] Corresponding author. Tel.: +49-2461-61-2698; fax: +49-2461-61-2560.
E-mail address: s.becker@fz-juelich.de (J.S. Becker).

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attention. In fact, they can provide basic information on the pollution levels of airborne chemical species of present and past times. As is well known, lichens and mosses present a particular interest as bioaccumulators [5–7]. Furthermore, some peat Sphagnum mosses appear to be particularly suitable to investigate atmospheric contamination and may provide a record of the history of atmospheric fallout, especially when collected in appropriate sampling sites (open areas, absence of trees and other vascular plants). From this point of view, the Sphagnum mosses are very interesting and they present some peculiar species which are old enough to be exploited as biological organisms keeping the memory of past pollution events.

Conventional radioanalytical techniques such as alpha spectrometry or liquid scintillation radiometry [3,4] are well established for the determination of most actinide isotopes especially those having a half-life of less than 1000 years, however, they are often not sensitive enough for the determination of long-lived radionuclides in environmental samples. A further limitation of these techniques is that usually only the sum of ^{239}Pu and ^{240}Pu activity can be determined due to similar α energies (5.24 and 5.25 MeV, respectively). Implanted passivated junction silicon detectors and special spectra deconvolution software were proposed two decades ago to improve alpha spectrometry resolution [8]. However, this method did not find wide application for the measurement of ^{239}Pu/^{240}Pu activity ratios because of its complexity.

Sector-field inductively coupled plasma mass spectrometry (ICP-SFMS) is one of the most suitable methods for the isotopic analysis of actinides at the ultratrace concentration level due to its high sensitivity, good accuracy and precision and mostly simple sample preparation procedure [9]. However, uranium hydride ions (^{238}U^{1}H^{+}) and other molecular ions, e.g., of lead or rare earth elements, which can be expected in the actinide mass range (e.g., PbO_2^+, PbN_2^+, etc.) [10] are limiting factors for the isotopic measurement of low concentrations of plutonium and americium. For instance, the formation of ^{238}U^{1}H^{+} ions disturbs the ^{239}Pu^{+} measurement even after a chemical separation of uranium (uranium concentration in soil samples is usually significantly higher than plutonium concentration by more than seven orders of magnitude). A complete separation of ultratrace Pu from U is not possible. Therefore, special solution introduction systems such as micronebulizers with desolvators are necessary to reduce molecular ions and improve detection limits for the actinide isotopes mentioned above [10–13]. The application of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has the advantage of direct sampling of solid material surface without dissolution and dilution of samples. This method has been established as a sensitive multielement analytical solid mass spectrometric technique without any restriction with respect to the chemical and physical properties of the solid sample in widely different application fields in geology, materials science and environmental research [14–19]. LA-ICP-MS was applied in our laboratory for the direct determination of long-lived radionuclides at ultratrace concentration levels in solid environmental samples and radioactive waste materials in order to reduce the sample volume, to improve the precision (relative standard deviation) of measurements and the detection limits [20]. It is therefore possible to directly determine, for instance, U at low pg g^{-1} concentration levels in non-conducting, difficult-to-dissolve materials (e.g., concrete). Isotope dilution (ID) mass spectrometry provides accurate results in determining trace amounts of elements in different matrices [21–24] and is widely used in radioanalytical techniques. This approach allows both the correction of element losses during sample preparation and correction of some fractionation effects during sample ablation and ICP-MS measurement, which is usually difficult to control by other techniques. A combination of LA-ICP-MS with the isotope dilution technique is the method of choice for the determination of trace amounts in solid materials. However, the use of LA-ICP-MS for direct analysis of Pu and Am in solid samples does not solve the problem of interferences. Therefore, a chemical separation of analyte by a suitable technique is necessary with the subsequent electroplating of the separated Pu or Am fraction on a stainless steel target, which can be analyzed via LA-ICP-MS and alpha spectrometry. The aim of this work was the application of LA-ICP-MS in comparison to alpha spectrometry for a high-sensitivity isotope analysis of plutonium and americium in moss samples, which are used as bioindicators to assess the occurrence of airborne pollutants.

2. ICP-MS measurements

2.1. Instrumentation

The determination of Pu and Am on stainless steel disks after electroplating was performed by LA-ICP-MS using a commercial laser ablation system LSX 200 from CETAC (CETAC LSX 200, Cetac Technologies, Omaha, NE, USA) coupled to a double-focusing sector-field ICP-MS (ICP-SFMS ELEMENT, Finnigan MAT, Bremen, Germany). The ICP torch was shielded with a grounded platinum electrode (GuardElectrode^{TM}, Finnigan MAT). The ablated material is transported by argon as the carrier gas into the ICP, where the molecules of evaporated and ablated sample material were dissociated and ionized. The ions formed in the ICP were extracted in the sector-field mass spectrometer and separated according to their mass-to-charge ratios. An ultrasonic nebulizer (USN 6000, CETAC Technologies Inc., Omaha, NE, USA) was used for solution introduction in ICP-MS for optimization purposes only. A schematic diagram of the LA-ICP-SFMS is presented in Fig. 1. Further details of the instrumentation used can be found elsewhere [20,25,26].

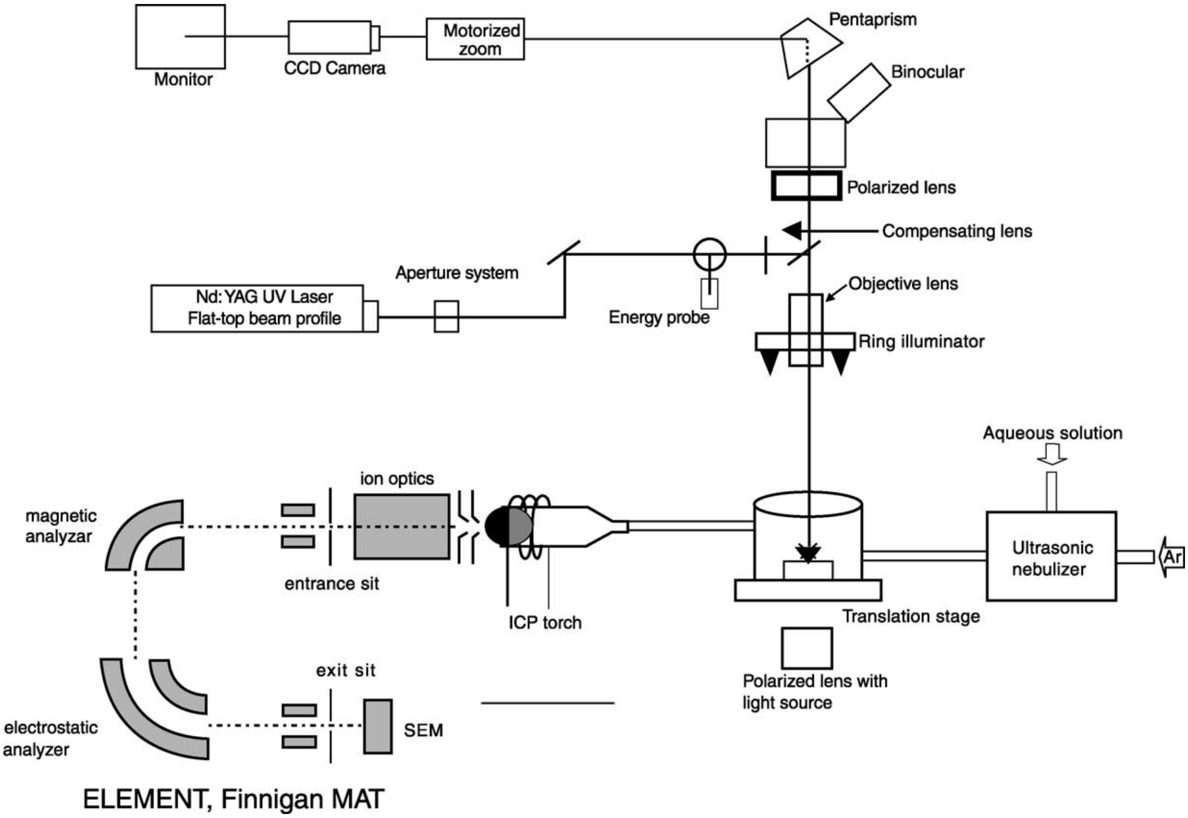

Fig. 1. Schematic diagram of ICP-SFMS coupled to a laser ablation system LSX 200 (CETAC Technologies Inc.). An ultrasonic nebulizer was used for solution introduction in ICP-MS for optimization purposes only.

2.2. Standards and reagents

Isotope standard reference materials U-020 and U-015 (National Institute of Standards and Technology (NIST)) and isotopic standard solution of uranium (CCLU-500 Laboratory Standard, Nuclear Research Center, Prague, Czech Republic [27]) were used for the optimization of isotope ratio measurements because of a lack of certified Pu or Am isotope standards. Uranium isotope ratios for the CCLU-500 standard were established ($^{234}U/^{238}U = 0.011122$, $^{235}U/^{238}U = 0.99991$, $^{236}U/^{238}U = 0.002789$) by calibration against the NIST-500 SRM using TIMS. The solutions were diluted to the necessary concentrations for determining the isotopic ratio of uranium by ICP-MS with deionized Milli-Q water (18 MΩ) obtained from a Millipore Milli-Q-Plus water purifier and acidified to 1% subboiled HNO_3. Targets for laser ablation were prepared by evaporating 0.2 ml of isotope standard solution on a stainless steel disk (spot square of about 1 cm^2).

2.3. Measurement procedure

Optimization of experimental parameters of ICP-SFMS was performed with respect to the maximal ion intensity of $^{238}U^+$ using a 0.1 $\mu g\,l^{-1}$ natural uranium solution introduced by the ultrasonic nebulizer. Optimized experimental parameters of the LA-ICP-SFMS are summarized in Table 1. Laser ablation was performed with a Nd:YAG laser ($\lambda = 266$ nm, laser energy 4.0 mJ, laser crater diameter 300 μm, scan speed 1 mm/s). The measured plutonium or americium isotopic ratio was corrected taking into account the mass discrimination factor (assuming a linear correlation [21,28]) determined experimentally by measuring CCLU-500 standard solution as well as hydride rate UH^+ ratios and the dead time of the detector of ICP-SFMS [29]. The combined uncertainty of the measured concentration (specific activity) was calculated according to EURACHEM/CITAC Guide [30] taking into account standard deviations of the measured ratio, background (including instrument background and interfering hydride ions), uncertainty of mass discrimination factor and uncertainty associated with the activity of the internal standards (^{242}Pu, ^{243}Am).

Table 1
Optimized operating conditions of ICP-SFMS attached to the laser ablation system LSX 200 (CETAC Technologies Inc.)

ICP-MS	
rf power (W)	1150
Cooling gas flow rate ($l\,min^{-1}$)	18
Auxiliary gas flow rate ($l\,min^{-1}$)	1.1
Nebulizer gas flow rate ($l\,min^{-1}$)	1.1
Total acquisition time per single analysis (min)	1.05
Mass window (%)	20
Mass resolution ($m/\Delta m$)	300
Laser ablation system	
Laser type	Nd:YAG laser
Wave length (nm)	266
Laser energy (mJ)	5
Pulse (ns)	5
Pulse frequency (Hz)	20
Nebulizer	
Solution uptake rate ($ml\,min^{-1}$)	2.1
USN heating temperature (°C)	140
USN cooling temperature (°C)	3

3. Alpha spectrometric measurements

3.1. Instrumentation and measurement procedure

The source for alpha spectrometry and LA-ICP-MS was obtained by electroplating plutonium or americium on a stainless steel disk for 1.5–5 h at 600 mA. The alpha spectrometry was performed for 1000–2000 min counting with a 450 mm^2 solid state alpha detector having a 28% counting efficiency, a background $<10^{-5}\,s^{-1}$ over the energy region of interest and a resolution (FWHM) of 15–25 keV (^{238}U). A counting time of approximately 1–3 days is necessary to measure the $^{239+240}Pu$ and ^{241}Am depending on the background and peak intensity count rates. In alpha spectrometry the associated uncertainty depends on background counting, peak counting, and activity of the internal standard.

3.2. Standard and reagent

^{242}Pu and ^{243}Am were supplied by Amersham International Ltd. (UK). Low-density polyethylene powder (Icorene RT 70) was supplied by VERPLAST SRL (Bergamo, Italy). Tri-*n*-octylammine (TNOA) was supplied by Sigma Aldrich Srl (Milano, Italia) and di(2-ethyl-hexyl) phosphoric acid (HDEHP) by Carlo Erba (Milano, Italy). All the other reagents were analytical grade (Carlo Erba).

4. Samples and source preparation

4.1. Sampling and sample pretreatment

Moss samples were collected from a bog in the eastern Italian Alps (1500 m a.s.l.: a peat core of mosses was sampled by digging a rectangular trench having thickness 30 cm and a section of 150 cm^2. This core was frozen prior to sectioning. Fragments of vascular plants were carefully removed from the sample before drying at 85 °C. The samples were finally cut into 1–2 cm sections and analyzed separately to obtain the distribution curves of vertical concentrations. For plutonium and americium isotope analysis 1–2 g of the samples were placed in a ceramic crucible with a 6 cm internal diameter. After the addition of a known activity of ^{242}Pu and ^{243}Am as yield tracers, the samples were ashed in the muffle at 600 °C for 20 h. After cooling, two leachings were carried out for 30 min with 30 ml of 6 M HCl each. The leaching solutions were combined and filtered.

4.2. Plutonium separation by extraction chromatography

Two milliliter of NH_2OH HCl was added to obtain Pu(III), which was then oxidized to Pu(IV) by adding 5 ml of 8 M $NaNO_2$. The solution was evaporated at 90–95 °C to destroy the excess of $NaNO_2$. The chloride solution was passed through a column of Microthene supporting TNOA at a flow rate of 0.8 ml min^{-1} for the plutonium retention. TNOA in HCl medium retains uranium, iron, plutonium but not americium. The column was washed with 100 ml 7.5 M HNO_3 and 100 ml of 6 M HCl. The column effluent was retained for americium analysis. Plutonium was eluted with oxalic acid in nitric acid. Then, it was electroplated on a stainless steel disk with a diameter of 12 mm at pH 1.5–2.0 for 90 min at a current density of 550 mA cm^{-2}. Plutonium activity was measured by alpha spectrometry as described above.

4.3. Americium separation

The solution was adjusted at pH 2.4 with ammonia and was passed through a column of Microthene-di(2-ethylhexyl) phosphoric acid (HDEHP). After washing with 60 ml of 0.1 M HNO_3 americium was eluted with 20 ml of 1 M HNO_3. The elution solution was dried and the residue dissolved in sulphuric acid. Americium was electroplated from ammonium sulphate at pH 4 and it was measured by alpha spectrometry as reported above.

5. Results and discussion

5.1. Optimization of LA-ICP-MS

The dependence of $^{238}U^+$ ion intensity on experimental parameters of LA-ICP-SFMS was studied by the ablation of targets prepared by precipitating known amounts of uranium isotopic standard solutions on stainless steel disks with a spot of 1 cm^2. Fig. 2 presents the dependence of uranium sensitivity on nebulizer gas flow and rf power. Sensitivity for $^{238}U^+$ ions of about 1.3×10^{16} cps/(g cm^{-2}) was achieved at an ablation rate of 0.3 mm^2 s^{-1} at optimal nebulizer gas flow (1.1 l min^{-1}) and rf power (1150 W). This corresponded to an absolute sensitivity for uranium as high as 1.8×10^{-3} counts per atom of ^{238}U deposited on the target surface. It is rather interesting to note that this value determined for LA-ICP-SFMS was similar to the value of absolute sensitivity for uranium observed when using the same ICP-SFMS instrument for determining uranium in liquid samples

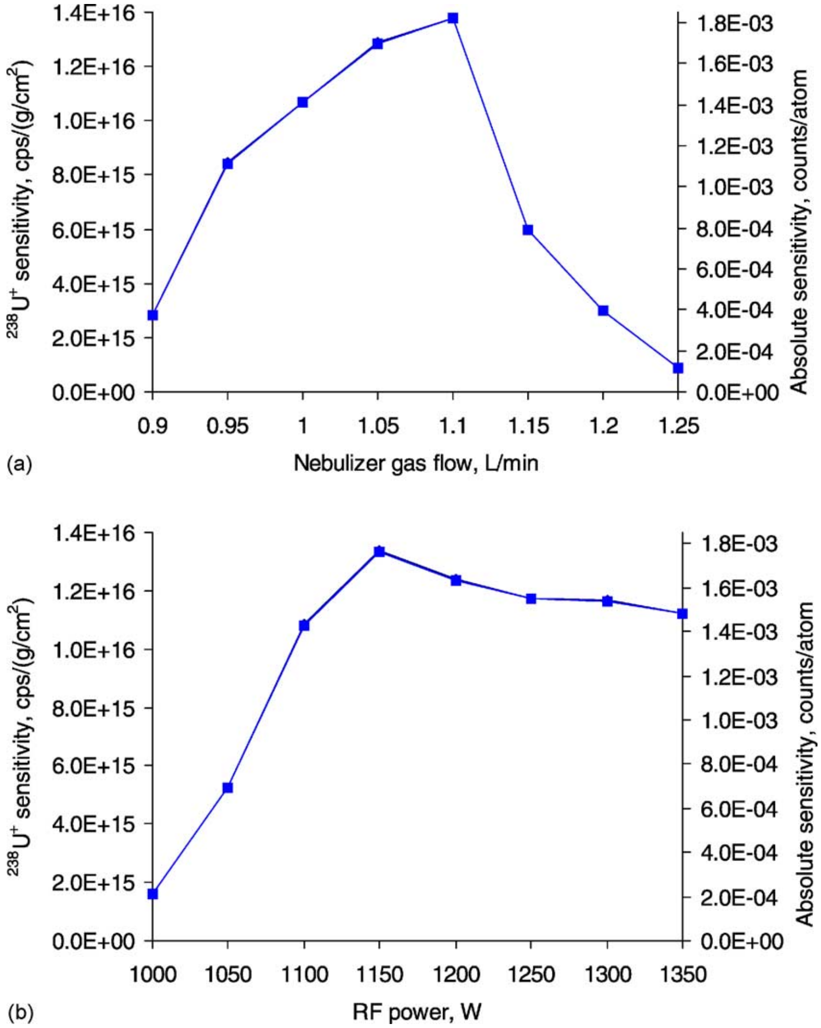

Fig. 2. Dependence of ^{238}U sensitivity (cps/(g cm^{-2}) and absolute sensitivity (counts/atom) measured by LA-ICP-MS on (a) nebulizer gas flow rate and (b) rf power. Ablation rate, 0.3 mm^2 s^{-1}; the other experimental parameters are summarized in Table 1.

introduced via micronebulizers. Thus, the application of microconcentric nebulizer with the Aridus desolvator in ICP-SFMS yielded the absolute sensitivity of 1.1×10^{-3} counts per atom, whilst direct injection high-efficiency nebulizer (DIHEN)® yielded the absolute sensitivity of 1.4×10^{-3} counts per atom [31,32]. The sensitivity in ICP-SFMS with aqueous sample introduction depends among other things on nebulization efficiency, atomization and ionization grade, ion sampling efficiency, ion transfer and detection efficiency. In the case of DIHEN (which works without a spray chamber at low solution uptake rate) the liquid sample is delivered to the ICP in its entirety, i.e., nebulization efficiency is close to 100%. Hence, the main sources of ion losses are connected with ion scattering in the plasma–vacuum interface region and in the ion transmission system of the mass spectrometer due to space charge effects. Similar values of absolute sensitivity obtained both with laser ablation and with liquid sample introduction show that laser ablation provides an effective sample introduction of uranium from the target surface with efficiency close to that of the direct injection of liquid samples. Absence of water matrix in the case of LA-ICP-SFMS would probably result in a reduced space charge effect in the plasma, however, ablated target material is introduced into ICP. On the other hand, the results obtained might point to a possible limit of ion transmission on the plasma-detector path, which is typical of the applied ICP-SFMS. In addition, reduced uranium hydride formation rate ($^{238}U^{1}H^{+}/^{238}U^{+} = 1.8 \times 10^{-5}$ was close to the abundance sensitivity for the ICP-SFMS instrument used [33]) was observed in LA-ICP-MS due to the absence of any water or water vapor during sample ablation.

The limits of quantification (LOQ) for actinide isotopes were estimated from the mass spectrum of the blank stainless steel disks using the 10σ criterion considering the measured $^{238}U^{+}$ ion sensitivity S on synthetic standard targets with known uranium amount. The LOQ is given by $(m_b + 10\sigma_b)/S$, where m_b is the mean value of the blank intensity, cps, and σ_b is the standard deviation of five independent measurements of the blank value, cps. As no certified standards for other actinides (except U and Th) were available in this study, it was assumed that all actinides from Th to Am have approximately equal sensitivities. Table 2 summarizes the absolute LOQ (Bq per sample) provided by LA-ICP-SFMS for actinide isotopes in comparison to the detection limits of alpha spectrometry. It should be noted that these LOQs can only be achieved if no interference occurs, i.e., the elements which could cause isobaric interferences must be separated before mass spectrometric measurement (for instance, isobaric interferences of ^{241}Pu and ^{241}Am or interference of peak tails of highly abundant ^{238}U with neighboring isotopes of Np and Pu might limit the capability of the mass spectrometric method). In general, the theoretically estimated LOQ values are better than the detection limits of alpha spectrometry for radionuclides with half-lives longer than 10^{3} years. However, when measuring real samples the LOQs found for ^{239}Pu (0.2 mBq) and ^{243}Am (1.4 mBq) were higher than the estimated values by approximately 20 and 3 times, respectively. The LOQ for ^{239}Pu was affected by the peak tail and UH^{+} ions originating from ^{238}U residue on the targets, which raised background intensities. In addition, sensitivities for ^{242}Pu and ^{243}Am isotopes were lower than expected due to losses of these radionuclides during

Table 2
Estimated limits of quantification of LA-ICP-MS for actinide isotopes deposited on stainless steel plates after chemical separation

Isotope	Half-life (year)	Limit of quantification ($g\,g^{-1}$)	Limit of quantification (Bq)	
		LA-ICP-MS	LA-ICP-MS	Alpha spectrometry
^{230}Th	7.54×10^{4}	3.8×10^{-15}	2.9×10^{-6}	2.0×10^{-5}
^{232}Th	1.41×10^{10}	6.8×10^{-15}	2.8×10^{-11}	5.0×10^{-5}
^{233}U	1.59×10^{5}	3.8×10^{-15}	1.4×10^{-6}	–
^{234}U	2.44×10^{5}	3.8×10^{-15}	8.8×10^{-7}	2.0×10^{-5}
^{235}U	7.04×10^{8}	4.9×10^{-15}	3.9×10^{-10}	2.0×10^{-5}
^{236}U	2.34×10^{7}	4.0×10^{-15}	9.5×10^{-8}	3.0×10^{-5}
^{238}U	4.47×10^{9}	7.1×10^{-15}	8.8×10^{-11}	5.0×10^{-5}
^{237}Np	2.14×10^{6}	3.8×10^{-15}	1.0×10^{-7}	2.0×10^{-5}
^{238}Pu	87.7	–	–	8.0×10^{-5}
^{239}Pu	2.41×10^{4}	3.9×10^{-15}	9.0×10^{-6}	5.0×10^{-5}
^{240}Pu	6.56×10^{3}	3.7×10^{-15}	3.1×10^{-5}	
^{241}Pu	1.49×10^{1}	3.8×10^{-15}	1.4×10^{-2}	–
^{242}Pu	3.87×10^{5}	3.6×10^{-15}	5.1×10^{-7}	2.0×10^{-5}
^{244}Pu	8.26×10^{7}	3.6×10^{-15}	2.4×10^{-9}	–
^{241}Am	4.32×10^{2}	3.7×10^{-15}	4.7×10^{-4}	8.0×10^{-5}
^{243}Am	7.37×10^{3}	3.6×10^{-15}	2.7×10^{-5}	4.0×10^{-5}

chemical extraction, which resulted in a lower nuclide amount on the target than expected (i.e., added to the sample). Furthermore, non-homogeneous distribution of radionuclides on the stainless steel disks was observed by LA-ICP-SFMS with higher concentration on the spot periphery, whilst sample ablation was mainly performed in the spot center.

In order to determine the precision and accuracy of the analytical method, six measurements of uranium isotope ratios were performed when ablating specially prepared synthetic targets with deposited CCLU-500 and NIST U-020 isotopic standards. Mass discrimination per mass unit (MD) and dead time were determined experimentally by measuring $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratios in CCLU-500 ($^{235}\mathrm{U}/^{238}\mathrm{U} = 0.99991$) and NIST U-020 ($^{235}\mathrm{U}/^{238}\mathrm{U} = 0.020808$), respectively. The measured $^{236}\mathrm{U}/^{238}\mathrm{U}$ and $^{234}\mathrm{U}/^{238}\mathrm{U}$ isotope ratios in isotope standards and relative standard deviations are summarized in Table 3. The isotope ratios in NIST U-020 were as low as 10^{-4} and their precision and accuracy were within 3% due to low counting statistics. For isotope ratios in the 10^{-3} to 10^{-2} range, the precision and accuracy were significantly better (accuracy was between 0.21 and 0.67%). This result was found to be satisfactory for isotopic measurements of plutonium and americium, as Pu and Am isotope ratios in deposited samples were not lower than 10^{-3}.

5.2. *Plutonium and americium determination in moss samples*

LA-ICP-SFMS and alpha spectrometry were used to determine the concentration of $^{239}\mathrm{Pu}$, $^{240}\mathrm{Pu}$ and $^{241}\mathrm{Am}$ and plutonium isotopic composition in moss samples. Table 4 presents results of measurements of plutonium isotope ratios in moss samples with LA-ICP-SFMS and alpha spectrometry. The concentration of $^{239}\mathrm{Pu}$ and $^{240}\mathrm{Pu}$ isotopes in 10 moss samples analyzed varied between 0.03 and 10 Bq/kg, which corresponded to a plutonium concentration of 7.5×10^{-15} to 2.5×10^{-13} g g^{-1}. The $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ isotope ratio was almost constant within experimental errors with the weighted average value of 0.212 ± 0.003. Higher values found for samples 16 and 17 are due to their low activity concentration and consequently to a higher experimental error. In general, the $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ ratios measured in the present work correspond to the plutonium isotope ratio in fallout from weapons tests and they are lower than the $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ ratio calculated for the fourth Chernobyl reactor at the time of the accident [1] and the $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ ratios experimentally measured in the vicinity of Chernobyl [34]. This conclusion is also confirmed by $^{238}\mathrm{Pu}/^{239+240}\mathrm{Pu}$ activity ratios (0.028) and $^{241}\mathrm{Am}/^{239+240}\mathrm{Pu}$ activity ratios (0.3) measured by alpha spectrometry (see Table 4). Specific activity of $^{239}\mathrm{Pu}$ and $^{240}\mathrm{Pu}$ isotopes measured using LA-ICP-SFMS and alpha spectrometry coincided within 10% for all the analyzed samples excluding samples 9 and 10, where the ratio of activity measured by alpha spectrometry to activity measured by LA-ICP-SFMS was 0.82 and 0.76, respectively. In any case, these results were within experimental errors, thus supporting the correct uncertainty evaluation when measuring plutonium isotope ratios.

Results of $^{241}\mathrm{Am}$ measurements in three samples are also presented in Table 4. The LOQ (in activity

Table 3
Measured and recommended isotopic ratios $^{236}\mathrm{U}/^{238}\mathrm{U}$ and $^{234}\mathrm{U}/^{238}\mathrm{U}$ in laboratory isotopic standard solution CCLU-500 and NBS U-020 isotopic standard solution (concentration = 10 ppb) deposited on stainless steel targets and analyzed by LA-ICP-SFMS

Measured $^{234}\mathrm{U}/^{238}\mathrm{U}$ ratio	RSD ($n = 6$), %	Recommended $^{234}\mathrm{U}/^{238}\mathrm{U}$ ratio	Accuracy (%)
1.1099×10^{-2}	1.2	1.1122×10^{-2} (CCLU-500)	−0.21
1.293×10^{-4}	2.7	1.2756×10^{-4} (NBS U-020)	1.4
Measured $^{236}\mathrm{U}/^{238}\mathrm{U}$ ratio	RSD (%)	Recommended $^{236}\mathrm{U}/^{238}\mathrm{U}$ ratio	Accuracy (%)
2.77×10^{-3}	1.3	2.789×10^{-3} (CCLU-500)	−0.67
1.639×10^{-4}	3.1	1.6856×10^{-4} (NBS U-020)	−2.8

Table 4
Plutonium and americium specific activities and isotope ratios in moss samples (1–2 g) obtained by alpha spectrometry and LA-ICP-MS

Sample	Alpha spectrometry		Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)						Alpha spectrometry
	Specific activity (Bq/kg)		Concentration (pg g^{-1})		Specific activity (Bq/kg)			Isotope ratio	LA-ICP-MS
	^{238}Pu	$^{239+240}$Pu	^{239}Pu	^{240}Pu	^{239}Pu	^{240}Pu	$^{239+240}$Pu	^{240}Pu/^{239}Pu	$^{239+240}$Pu
9	0.16 ± 0.10	5.2 ± 0.8	±1.72	±0.35	3.63 ± 0.54	2.68 ± 0.40	6.31 ± 0.94	0.20 ± 0.02	0.82
10	0.14 ± 0.09	5.6 ± 0.8	±1.88	±0.46	3.88 ± 0.58	3.51 ± 0.52	7.39 ± 1.10	0.25 ± 0.03	0.76
11	0.20 ± 0.07	6.74 ± 0.82	±2.05	±0.40	4.31 ± 0.65	3.11 ± 0.46	7.42 ± 1.11	0.20 ± 0.02	0.91
12	0.16 ± 0.08	6.86 ± 0.92	±2.38	±0.49	4.37 ± 0.66	3.26 ± 0.47	7.63 ± 1.13	0.20 ± 0.02	0.90
13	0.30 ± 0.09	8.06 ± 0.99	±3.86	±0.77	4.43 ± 0.66	3.23 ± 0.45	7.66 ± 1.11	0.20 ± 0.02	1.05
14	0.30 ± 0.12	10.1 ± 1.4	±4.81	±0.93	5.52 ± 0.82	3.88 ± 0.56	9.40 ± 1.38	0.19 ± 0.02	1.07
15	0.12 ± 0.05	5.67 ± 0.66	±2.75	±0.50	3.16 ± 0.45	2.09 ± 0.31	5.25 ± 0.76	0.18 ± 0.02	1.08
16	<0.04	1.41 ± 0.24	±0.67	±0.185	0.77 ± 0.14	0.78 ± 0.14	1.55 ± 0.28	0.27 ± 0.05	0.91
17	<0.04	0.24 ± 0.05	±0.107	±0.031	0.12 ± 0.03	0.13 ± 0.03	0.25 ± 0.06	0.29 ± 0.06	0.96
18	<0.04	0.13 ± 0.3	<0.03	<0.01	<0.07	<0.09			
19	<0.04	0.03 ± 0.02	<0.03	<0.01	<0.07	<0.09			
	^{241}Am		^{241}Am		^{241}Am				^{241}Am
13	2.02 ± 0.33		±0.065		4.1 ± 1.3				0.49
14	2.80 ± 0.45		±0.061		3.9 ± 1.2				0.72
15	1.49 ± 0.24		±0.044		2.8 ± 0.9				0.53

units) of LA-ICP-MS for ^{241}Am is significantly higher than that for ^{239}Pu because of the relatively short half-life of the americium radionuclide ($T_{1/2} = 432$ years). The measured concentrations (2.8–4.1 Bq/kg corresponding to 2.2×10^{-14} to 3.2×10^{-14} g g^{-1}) were close to LOQ and the estimated uncertainty was 30–35%. Comparison of LA-ICP-MS with alpha spectrometry only yielded coincidence for sample 14, whilst systematically higher results were observed for all samples in LA-ICP-MS. This might be due to unknown interference with a molecule ion with $m/z = 241$ originating from the ablated target material. A further investigation of possible interference with molecular ions from the targets analyzed using a mass resolution of 4000 was impossible because the sensitivity was not satisfactory at higher resolution.

Maximum Pu and Am concentrations should correspond to the period 1960–1965 which was characterized by heavy radioactive pollution due to several above-ground nuclear weapons tests [2,3]. This conclusion is based on the fact that this kind of moss (*Sphagnum* mosses) can 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 fallout caused by nuclear facility accidents and from nuclear weapons tests. They are long-lived plants and they can play an important role in cycling naturally or artificially enhanced radionuclides in the atmosphere for a long period. Dating by ^{210}Pb determination in the different sections is now in progress.

6. Conclusions

LA-ICP-SFMS applied in this study offered a possibility for plutonium isotope measurements in environmental samples at a concentration level of 5×10^{-14} to 2.5×10^{-13} g g^{-1}. The overall detection efficiency for ^{238}U of 1.8×10^{-3} counts per atom was close to the overall detection efficiency observed in ICP-SFMS with liquid solution introduction when using micronebulizers DIHEN or Aridus. In addition, a reduced uranium hydride formation rate was observed in LA-ICP-SFMS due to the absence of any water or water vapor during sample ablation. Experiments showed a good agreement between LA-ICP-SFMS and alpha spectrometry results when measuring Pu isotopes, but worse coincidence was observed for ^{241}Am. In general, isotope dilution LA-ICP-SFMS allowed plutonium isotope ratio measurement with good accuracy and precision, avoiding possible errors associated with losses during sample preparation. However, plasma instability, inhomogeneous distribution of analyte on target sample and instability of the laser ablation rate affected the precision and accuracy of isotope analysis. Application of multiple ion collector LA-ICP-SFMS is proposed in future work to avoid these effects.

From the results obtained for the moss samples we can conclude that the environment at the sites analyzed has been contaminated with artificial transuranium elements. The probable Pu contamination source was the global fallout after nuclear weapons tests in the sixties. The anthropogenic radionuclide concentrations (^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Am) in the samples are extremely low and these mosses appeared to be particularly suitable for investigating atmospheric contamination with actinides and to provide a record of the history of atmospheric fallout [3,35].

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