Optimisation and application of ICP-MS and alpha-spectrometry for determination of isotopic ratios of depleted uranium and plutonium in samples collected in Kosovo

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

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

The determination of environmental contamination with natural and artificial actinide isotopes and evaluation of their source requires precise isotopic determination of actinides, above all uranium and plutonium. This can be achieved by alpha spectrometry or by inductively coupled plasma mass spectrometry (ICP-MS) after chemical separation of actinides. The performance of a sector-field ICP-MS (ICP-SFMS) coupled to a low-flow micronebulizer with a membrane desolvation unit, "Aridus", was studied with respect to precise isotopic measurements of uranium and plutonium at the ultratrace level. The UH^+/U^+ formation rate was about 3×10^{-5} and a sensitivity for ^{238}U of up to 4×10^9 counts s^{-1} ppm^{-1} was achieved. The limit of quantification (LOQ, $10s$) for ^{236}U and ^{239}Pu using the experimental arrangement described above was 0.6 pg l^{-1} in aqueous solution and 0.13 pg g^{-1} in soil, respectively. ICP-SFMS was used in comparison to alpha spectrometry to measure the U and Pu concentrations and isotopic compositions in two soil samples and in one penetrator collected in Kosovo. ICP-MS permitted the determination of U and Pu isotope ratios including the ^{236}U abundance and $^{240}Pu/^{239}Pu$ ratio at ultratrace levels in soil samples of up to 0.1 g. Depleted uranium ($^{235}U/^{238}U = 0.002\,02 \pm 0.000\,01$) was determined in one penetrator and one soil sample. Pu concentrations of $(5.5 \pm 1.1) \times 10^{-13}$ g g^{-1} and $(4.4 \pm 0.5) \times 10^{-13}$ g g^{-1} ($^{240}Pu/^{239}Pu = 0.35 \pm 0.10$ and 0.27 ± 0.07, respectively) were found in both soil samples from Kosovo. Besides plutonium, ^{236}U (3.1×10^{-5} g g^{-1}) and ^{241}Am (1.7×10^{-12} g g^{-1}) were also detected in the penetrator sample, which indicates the previous existence of neutron-related processes and points to a possible presence of spent reactor uranium in munitions. However, the most probable plutonium contamination sources in analyzed soil samples from Kosovo are mixed fallout including spent reactor fuel due to the Chernobyl nuclear power plant accident in 1986 and plutonium due to nuclear weapon tests. Additional plutonium contamination could not be determined in the Kosovo soil sample containing depleted uranium with a detection limit of about 10^{-13} g g^{-1}.

Introduction

Assessment of the potential health and environmental impact of depleted uranium (DU) used in the Kosovo conflict became recently one of the important tasks of environmental monitoring in the Balkans.[1] In January 2001 the US Department of Energy (DOE) reported that the DU stock for manufacturing munitions might contain trace levels of transuranium elements,[2] some of them highly radiotoxic.[3] According to a UNEP report,[1] the uranium isotope ^{236}U and the plutonium isotopes ^{239}Pu and ^{240}Pu were present in very small concentrations in the depleted uranium of those penetrators analyzed.

^{236}U (half-life 2.3416×10^7 years) is produced from ^{235}U via the (n,γ) reaction. In spent nuclear fuel the $^{236}U/^{238}U$ ratio reaches 2×10^{-3}–5×10^{-3} depending on the reactor type and fuel burn-up history.[4,5] An upper limit of about 6×10^{-10} was found in non-contaminated natural uranium ores for the $^{236}U/^{238}U$ isotope ratio.[6–8] Thus, $^{236}U/^{238}U$ ratios differ in natural ores and spent uranium by seven orders of magnitude and more. ^{236}U may serve as a "fingerprint" for environmental contamination with spent nuclear fuel.[5,9] Plutonium is the most widespread element among the transuranium elements and it is represented, for example, in the Chernobyl fallout by five isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu).[10] Therefore 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).

As conventional radioanalytical techniques such as α-spectrometry or liquid scintillation radiometry[11,12] are often not sensitive enough for the determination of long-lived radionuclides in environmental samples and, furthermore, as it is difficult to distinguish ^{239}Pu and ^{240}Pu by these techniques due to the similarity of their alpha energies (main alpha energies of 5.157 MeV and 5.168 MeV, respectively), different mass spectrometric methods have been proposed for actinide isotopic measurements, such as thermal ionization mass spectrometry (TIMS),[13–16] accelerator mass spectrometry (ASM),[17,18] resonance ionization mass spectrometry (RIMS),[19,20] glow discharge mass spectrometry (GDMS),[21–23] secondary ion mass spectrometry (SIMS),[24–26] inductively coupled plasma mass spectrometry (ICP-MS),[27–30] laser ablation ICP-MS (LA-ICP-MS).[31–33] Sector-field inductively coupled plasma mass spectrometry (ICP-SFMS) is one of the most suitable methods for the isotopic analysis of long-lived radionuclides at the ultra-trace concentration level due to its high sensitivity, good accuracy and precision, and the mostly simple sample preparation procedure.[28] However, the formation of the molecular ions $^{235}U^1H^+$ and $^{238}U^1H^+$ is a limiting factor for the measurement of low concentrations of ^{236}U and ^{239}Pu isotopes in the presence of higher uranium concentrations. ^{235}U and ^{238}U are contained both in reactor fuel and in natural uranium

from environmental samples. 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 higher than plutonium concentration by more than seven orders of magnitude). Therefore a desolvating nebulizer is a powerful tool for reducing molecular ions and improving detection limits for the actinide isotopes mentioned above.[9,34,35] Furthermore, the application of a plasma-shielded torch in ICP-MS[36] was found to be useful for sensitivity improvement.[9,37] A plasma-shielded torch prevents a capacitive coupling from the load coil into the ICP, and the secondary discharge between the ICP and sampling cone is reduced. The production of a narrow ion energy distribution results in a higher transmission and therefore in an increase in sensitivity for ions. On the other hand, it increases the molecule ion formation rate for actinides,[38] and hence isobaric interferences caused by molecular ions, for example of lead, could be expected in the actinide mass range (e.g., PbO_2^+, PbN_2^+).[39]

The aim of this work was the application of a rapid and ultrasensitive isotope analytical procedure based on ICP-MS, in comparison to alpha spectrometry, for the determination of uranium concentration and isotopic composition, and transuranium elements in soil and penetrator samples collected in Kosovo. A low-flow microconcentric nebulizer with membrane desolvation was coupled to an ICP-SFMS instrument fitted with a plasma-shielded torch, and the figures of merit of this instrument were studied for experimental analysis of uranium and plutonium in soil and penetrator samples.

Experimental

ICP-MS measurements

Instrumentation. A double-focusing sector-field ICP-MS instrument (ELEMENT, Finnigan MAT, Bremen, Germany) was used for isotopic ratio measurements of uranium and transuranium elements in penetrator and soil samples after digestion and chemical separation. The ICP torch was shielded with a grounded platinum electrode (GuardElectrode™, Finnigan MAT), which is switched on (ground potential) or off (floating potential) electronically. A microconcentric low-flow nebulizer with membrane desolvation (Aridus, CETAC Technologies Inc., Omaha, NE, USA) was used for solution introduction in ICP-SFMS. A schematic diagram of the ICP-SFMS coupled to the Aridus is presented in Fig. 1. During the optimisation of ICP-SFMS the Aridus was used in the self-aspirating mode. Later on, an aqueous solution was introduced into the Aridus in the continuous flow mode via a syringe pump (Harvard Apparatus, Inc., Holliston, MA, USA) or a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany). Further details of the ICP-SFMS used can be found in refs. 37 and 38.

Standards and reagents. An isotopic standard solution of uranium (CCLU-500 laboratory standard, Nuclear Research Center, Prague, Czech Republic)[40,41] was used for the optimisation of isotope ratio measurements of uranium.
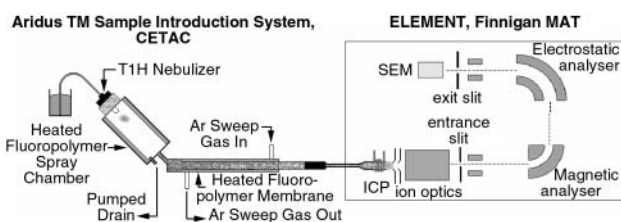
Uranium isotope ratio values for the CCLU-500 laboratory standard have been established by calibration against the NIST-500 SRM by thermal ionization mass spectrometry (TIMS).[40]

For the preparation of a uranium sample solution with a natural isotopic composition, the uranium available in the form of a metal slug (nuclear-free uranium, Merck KGaA, Germany) was first cleaned by etching with concentrated sub-boiled nitric acid. 100 mg of the cleaned sample was subsequently heated on a hot-plate for 2–3 min in 10 ml of sub-boiled nitric acid. The solution was then diluted to 20 ml with high-purity water. Then it was further diluted to the necessary concentrations for determining the isotopic ratio of uranium by ICP-MS with deionised Milli-Q water (18 MΩ cm) obtained from a Millipore Milli-Q-Plus water purifier. The solutions were acidified with 1% sub-boiled HNO_3.

Measurement procedure. Optimisation of experimental parameters of ICP-SFMS was performed with respect to the maximal ion intensity of $^{238}U^+$ and minimal uranium hydride formation rate using a 1 µg l^{-1} natural uranium solution introduced by the Aridus nebulizer. Optimised experimental parameters of the ICP-SFMS coupled to the Aridus are summarized in Table 1. The measured uranium isotopic ratio in soil samples was corrected taking into account the mass discrimination factor (assuming a linear correlation[29,42]), determined experimentally by measuring CCLU-500 standard solution as well as hydride rate: UH^+/U^+ ratios and the dead time of the ICP-SFMS detector.[43] The combined uncertainty of isotopic ratio measurements was calculated according to ref. 44 taking into account standard deviations of the measured ratio, background (including instrument background and interfering hydride ions), uncertainty of the mass discrimination factor and uncertainty associated with the activity of the internal standards (^{242}Pu, ^{243}Am or ^{232}U). In the case of alpha spectrometry, uncertainties associated with background counting, peak counting and the activity of the internal standard were considered.

Alpha spectrometric measurements

The source for alpha spectrometry was obtained by electroplating uranium, plutonium or americium on a stainless-steel disk for 5 h at 600 mA. The alpha spectrometry was performed by 1000–2000 min counting with a 450 mm^2 solid state alpha detector having a 28% counting efficiency, a background of $<10^{-5}$ s^{-1} over the energy region of interest and a resolution (FWHM) of 15–25 keV (^{238}U). A counting time of approximately 1 week is necessary to measure the ^{236}U and ^{235}U concentrations and the ratios $^{236}U/^{238}U$ and $^{235}U/^{238}U$, 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

Table 1 Optimised operating conditions of ICP-SFMS attached to a low-flow microconcentric nebulizer with membrane desolvation (Aridus, CETAC Technologies Inc.)

Rf power/W	1100
Cooling gas flow rate/L min^{-1}	14
Auxiliary gas flow rate/L min^{-1}	1.4
Nebulizer gas flow rate/L min^{-1}	1.1
Sweep gas flow rate/L min^{-1}	3.0–4.0
Solution uptake rate, mL min^{-1}	0.010–0.100
Spray chamber temperature/°C	70
Membrane temperature/°C	160
Total acquisition time per replicate/min	0.6
Number of replicates	10
Mass window (%)	20
Mass resolution, $m/\Delta m$	300

Fig. 1 Schematic diagram of ICP-SFMS coupled to a low-flow microconcentric nebulizer with desolvator (Aridus, CETAC Technologies Inc.).
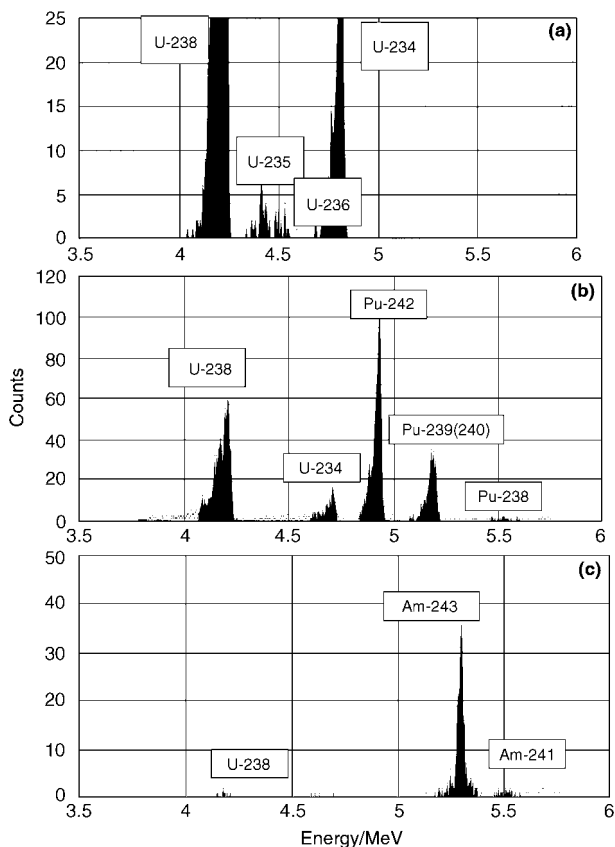
Fig. 2 Alpha spectra of : (a) uranium separated from the soil sample Planik A (counting time, 1 week); (b) plutonium separated from a penetrator (counting time, 2000 min); and (c) americium-241 separated from a penetrator (counting time, 2000 min).

standard. Fig. 2 shows the alpha spectra of uranium, plutonium and americium.

Samples and sample preparation

Soil samples. Soil samples were collected by CISAM (Centro Interforze Studi ed Applicazioni Militari, Livorno, Italy) in November 1999 from a Kosovo site named Planik. The air-dried soil samples were ground, sieved through a 1.0 mm screen for the removal of stones and fragments of plant roots, and carefully mixed. The samples were dried to constant weight at 105 °C for 24 h. 1 g of the sample, after addition of a known activity of ^{232}U as yield tracer, was milled and stirred for 1 h with 20 ml of concentrated HNO_3 and then with 20 ml of concentrated HCl. The residue was treated with warm HF, the solution was evaporated and the residue was boiled with concentrated $HClO_4$; after eliminating $HClO_4$ by warming, the residue was dissolved in 100 ml of 2 M HNO_3 and filtered.[45]

For plutonium isotope analysis 1 g of the soil sample, after addition of a known activity of ^{242}Pu as yield tracer, was milled and stirred for 1 h with 20 ml of concentrated HNO_3 and then with 20 ml of concentrated HCl. The residue was treated with warm HF, the solution was evaporated and the residue was boiled with concentrated $HClO_4$. After eliminating $HClO_4$ by warming, the residue was dissolved in 100 ml of 7.5 M HNO_3 and filtered.[45]

Uranium separation by extraction chromatography. Uranium was separated by extraction chromatography with a column of microporous polyethylene (Microthene, 50–100 mesh) supporting tri-n-octylphosphine oxide (TOPO). TOPO is a selective extractant in nitric acid medium for tetravalent and hexavalent actinides (Th, U, Pu, Np), and particularly for $UO_2(II)$. The alpha active nuclides of natural thorium, and particularly of

^{230}Th ($E_\alpha = 4.68$ MeV) which could interfere with ^{234}U when being determined *via* alpha spectrometry ($E_\alpha = 4.77$ MeV), were washed out by use of 1 M HCl, then uranium was eluted by 1 M $(NH_4)_2CO_3$ which forms strong uranylcarbonate complexes. The eluting solution was divided into two parts for the alpha spectrometry and for the ICP-SFMS measurements. A source for alpha spectrometry was obtained by electroplating uranium or plutonium on a stainless-steel disk for 5 h at 600 mA. The chemical yield of uranium extraction was $60 \pm 10\%$ (mean $\pm 1s$).

Plutonium separation by extraction chromatography. 2 ml of NH_2OH HCl were 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 nitric solution was passed through a column of Microthene supporting tri-n-octylamine (TNOA) at a flow rate of 0.8 ml min^{-1} for the plutonium retention. The column was washed with 100 ml of 7.5 M HNO_3 and 100 ml of 6 M HCl. Plutonium was eluted with oxalic acid in nitric acid. The eluting solution was divided into two parts for the alpha spectrometry and for the ICP-MS measurements. For the alpha spectrometry the solution was electroplated on a stainless-steel disk 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 below. The chemical yield of plutonium extraction was $50 \pm 5\%$ (mean $\pm 1s$).

Penetrator sample. The penetrator fragment of 0.6 g was dissolved in 6 M HCl. The solution was dried and the residue dissolved with 7.5 M HNO_3 and diluted to 4 M HNO_3. A small part of the solution derived from sample pretreatment was taken to dryness and the residue dissolved in H_2SO_4. Then uranium isotopes were determined by ICP-MS as well as by electroplating and alpha spectrometry. This analysis was performed particularly to detect traces of the ^{236}U isotope ($E_\alpha = 4.49$ MeV).

Plutonium separation. After addition of known activities of ^{242}Pu and ^{243}Am as yield tracers, 2 ml of NH_2OH HCl were 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 4 M HNO_3 leaching solution was passed through a column of Microthene supporting tri-n-octylamine (TNOA) at a flow rate of 0.8 ml min^{-1} for the plutonium retention. TNOA in nitric acid medium retains Pu(IV), but not americium and uranium. The column was washed with 200 ml of 4 M HNO_3 and the two effluents were kept for ^{241}Am determination. Plutonium was eluted with oxalic acid in nitric acid. The chemical yield for plutonium was $52 \pm 4\%$. The decontamination factor (DF) of plutonium from uranium (initial to final uranium concentration ratio) determined by alpha spectrometry (2.0×10^5) is in good agreement with the DF determined by ICP-SFMS (1.7×10^5).

Americium separation. The americium fraction was evaporated and the residue was dissolved in 6 M HCl. The solution was passed through a Microthene-TNOA column conditioned by concentrated HCl. TNOA in HCl medium retains uranium but not americium. The column was washed with 6 M HCl and the two effluents were kept for americium determination. The solution was adjusted to pH 2.4 with ammonia and was passed through a column of microthene-di(2ethylhexyl)-phosphoric acid (HDEHP). After washing, americium was eluted with 1 M HNO_3. The elution solution was dried and the residue dissolved in sulfuric acid. Americium was electroplated from ammonium sulfate at pH 4, as described for uranium, and was measured by alpha spectrometry as reported above. The

chemical yield for americium separation was $70\pm7\%$. The decontamination factor of americium from uranium determined by alpha spectrometry (6.7×10^6) is in good agreement with the DF measured by ICP-MS (6×10^6).

Results and discussion

Performance of ICP-SFMS using a low-flow microconcentric nebulizer for solution introduction

The dependence of the $^{238}U^+$ ion intensity, uranium oxide ion ratio UO^+/U^+ and uranium hydride ion ratio UH^+/U^+ on the experimental parameters of the solution introduction system and ICP-SFMS was studied using $1\,\mu g\,l^{-1}$ uranium solution with a natural isotope composition,[46] introduced by the microconcentric nebulizer with the desolvation unit "Aridus" in a self-aspiration mode with a solution uptake rate of $0.04\,ml\,min^{-1}$.

Application of a plasma shielded torch in ICP-SFMS increased the UO^+/U^+ ratio by up to one order of magnitude, but did not alter the uranium hydride ratio. This last effect allowed full use to be made of the advantage of higher sensitivity for uranium (by approximately 10 times), achieving up to $200\,MHz\,ppm^{-1}$ at a solution uptake rate of $0.04\,ml\,min^{-1}$. Fig. 3 presents the dependence of uranium sensitivity, and UO^+/U^+ and UH^+/U^+ ratios on rf power. In contrast to UO^+/U^+, the uranium hydride ratio slightly decreased with decreasing rf power up to 3.3×10^{-5}.

Fig. 4 presents the dependence of uranium sensitivity and UO^+/U^+ and UH^+/U^+ ratios on the sweep gas flow rate and nebulizer gas flow rate. Within the investigated range of gas flow rates the highest sensitivity was observed at a nebulizer gas flow of $1.3\,l\,min^{-1}$ and a sweep gas flow of $3.2\,l\,min^{-1}$ [Fig. 4(a)]. The uranium oxide ion ratio increased both with increasing nebulizer gas flow rate and sweep gas flow rate proportionally to the sum of the two gases [Fig. 4(b)]. A different behavior was observed for the uranium hydride ion ratio [Fig. 4(c)]. Changing the sweep gas flow rate within the range of $3.0–4.0\,l\,min^{-1}$ resulted in a variation of the UH^+/U^+

Fig. 4 Dependence of (a) ^{238}U sensitivity, (b) uranium oxide formation rate, UO^+/U^+, and (c) uranium hydride formation rate, UH^+/U^+, on sweep gas flow rate at different nebulizer gas flow rates. Solution uptake rate of $0.04\,ml\,min^{-1}$. Other experimental parameters are summarized in Table 1.

ratio by up to 30%. The minimum uranium hydride ratio was observed at a nebulizer gas flow of $1.1\,l\,min^{-1}$ and sweep gas flow of $3.6\,l\,min^{-1}$.

Fig. 5 presents the dependence of uranium sensitivity and hydride formation rate on solution uptake rate introduced by the microconcentric nebulizer, Aridus, with a syringe pump. Sensitivity for uranium increased with increasing solution uptake rate, reaching $400\,MHz\,ppm^{-1}$ at a solution uptake rate of $0.1\,ml\,min^{-1}$. However, the overall detection efficiency decreased slightly at a higher solution uptake rate [Fig. 5(a)]. Overall detection efficiency for uranium of 1.1×10^{-3}–0.9×10^{-3} counts per atom was observed using the microconcentric nebulizer, Aridus, at a solution uptake rate of $0.01–0.10\,ml\,min^{-1}$. The uranium hydride formation rate, in practice, did not depend on solution uptake rate [Fig. 5(b)], and the uranium oxide ratio increased at a higher solution uptake rate due to higher water content introduced into the inductively coupled plasma. Along with that, all curves in Figs. 3 and 4 had the same shape at solution uptake rate of $0.10\,ml\,min^{-1}$ introduced by the syringe pump. Therefore rf power, and nebulizer and sweep gas flow rates were optimised in order to combine a sufficiently high sensitivity for uranium at a low hydride formation rate with good precision. An rf power of $1100\,W$, and nebulizer and sweep gas flow rates of $1.1\,l\,min^{-1}$ and $3.5\,l\,min^{-1}$ were chosen for uranium and plutonium isotope ratio measurement in soil samples.

A relatively high uranium sensitivity of $4\times10^9\,counts\,s^{-1}\,ppm^{-1}$ together with the low instrumental
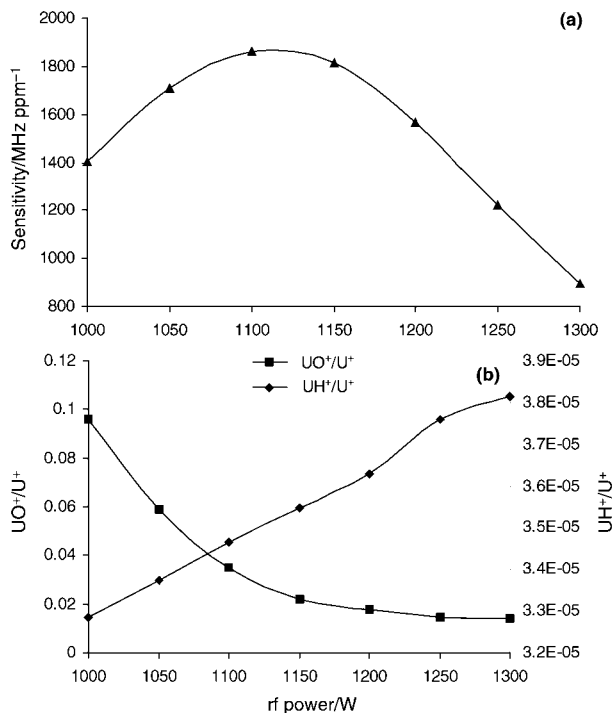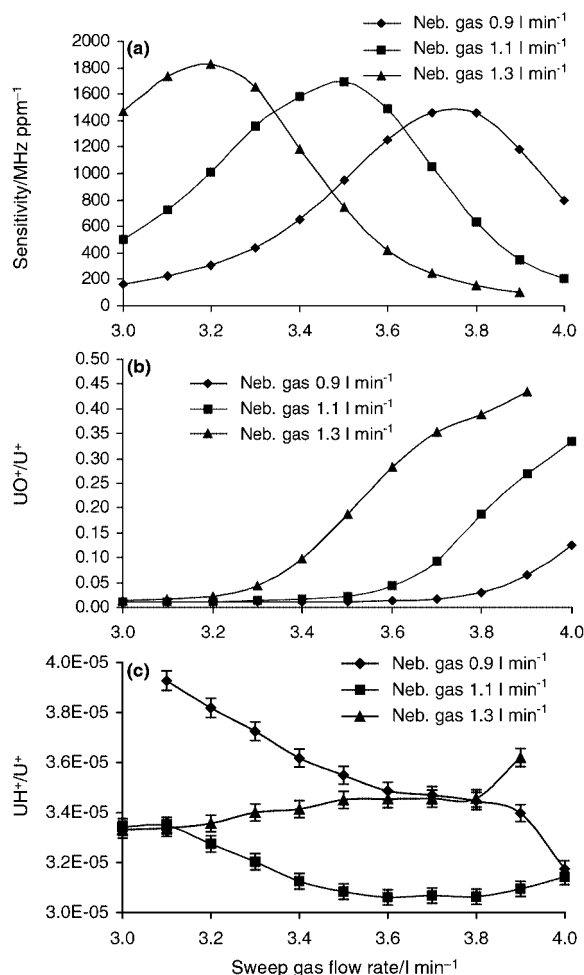

Fig. 3 Dependence of (a) ^{238}U sensitivity and (b) uranium oxide formation rate, UO^+/U^+, and uranium hydride formation rate, UH^+/U^+, on rf power. Solution uptake rate of $0.04\,ml\,min^{-1}$. Other experimental parameters are summarized in Table 1.
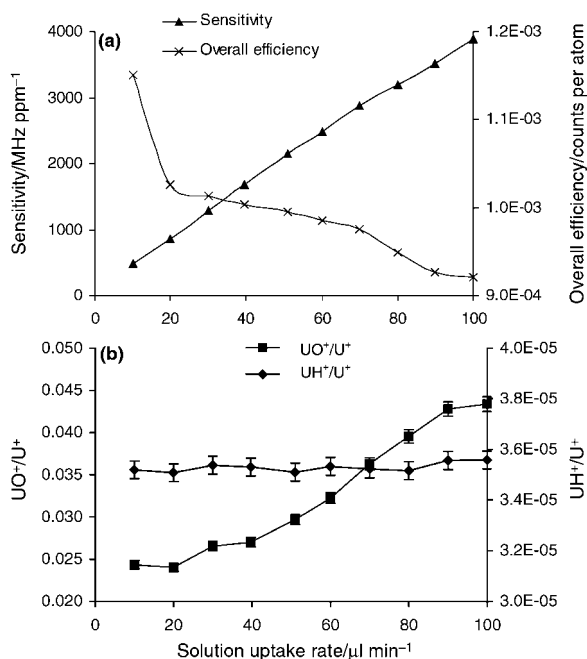
Fig. 5 Dependence of (a) sensitivity and overall detection efficiency and (b) uranium oxide ratio, UO^+/U^+, and uranium hydride ratio, UH^+/U^+, on solution uptake rate. The experimental parameters are summarized in Table 1.

background of ICP-SFMS in the high mass range and a uranium hydride ratio as low as 3×10^{-5} allowed a limit of quantification (LOQ, 10s) for ^{236}U of 0.6 pg l^{-1} to be achieved (measured in Milli-Q water under 10s criteria, measurement time 6 min, solution uptake rate 0.1 ml min^{-1}). However, the uranium hydride formation ($^{238}U^1H^+/^{238}U^+$) remained the main factor affecting ^{239}Pu measurement in real samples due to the higher abundance of ^{238}U (500 times higher than ^{235}U abundance in depleted uranium). After uranium separation the LOQ for ^{239}Pu using the experimental arrangement described above was 0.6 pg l^{-1} in aqueous solution and 0.13 pg g^{-1} in soil. Mass discrimination per mass unit for uranium was 1.2% under the experimental conditions described above.

Determination of uranium and plutonium isotopic composition in soil samples and in a DU penetrator

ICP-MS and alpha spectrometry were used to determine the uranium isotopic composition in one DU penetrator and soil samples collected in Kosovo. Table 2 presents results of measurements of uranium isotope ratios in the penetrator sample and in a soil sample with the uranium isotopic composition depleted in ^{234}U and ^{235}U (compared to natural isotopic composition, $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios are

Table 3 Plutonium concentrations and isotopic ratios in two soil samples from the Kosovo region (ICP-SFMS)

	Sample A	Sample B
Depleted uranium	Yes	No
LOD of ^{239}Pu and ^{240}Pu in soil/g g^{-1}	1.3×10^{-13}	2.7×10^{-14}
Weight of soil sample/mg	99.85	502.3
Concentration of ^{239}Pu in soil/g g^{-1}	$(4.1 \pm 0.8) \times 10^{-13}$	$(3.5 \pm 0.4) \times 10^{-13}$
Concentration of ^{240}Pu in soil/g g^{-1}	$(1.4 \pm 0.3) \times 10^{-13}$	$(9.4 \pm 1.4) \times 10^{-14}$
Measured $^{240}Pu/^{239}Pu$ atomic ratio	0.35 ± 0.10	0.27 ± 0.07
Calculated $^{240}Pu/^{239}Pu$ for Chernobyl fuel[10]	0.42	
Measured $^{240}Pu/^{239}Pu$ in Chernobyl vicinity[48]	0.33	

5.54×10^{-5} and 7.25×10^{-3}, respectively; and compared to that of depleted uranium, $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios are 1.0×10^{-5} and 2.00×10^{-3}, respectively[1]). Measurements of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios in a soil sample from the Kosovo region by ICP-SFMS and alpha spectrometry coincided within experimental errors and were close to the isotopic composition of metallic depleted uranium, *i.e.*, the fraction of depleted uranium[1] in the soil sample is near to 100%. The uranium concentration in the contaminated sample was 158 μg g^{-1} in comparison to that in non-contaminated samples from the same region of about 1 μg g^{-1}. ^{236}U was also detected in this soil sample containing depleted uranium, which indicates a previous existence of neutron-related processes and points to a possible presence of spent nuclear uranium in DU munitions. However, the $^{236}U/^{238}U$ ratio measured in the soil sample (2.8×10^{-6}) was about 10 times lower than that found in the DU penetrator in this work (3.1×10^{-5}) and in ref. 1 ($^{236}U/^{238}U$ weight ratio was 2.4×10^{-5} to 2.6×10^{-5}). On the contrary the $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotopic ratios coincided in the soil sample, DU penetrator and metallic DU (Rockwell, USA) measured for comparison. The results obtained by ICP-SFMS and alpha spectrometry on metallic uranium are in good agreement; the $^{235}U/^{238}U$ atomic ratio measured here is close to the ratio of $(2.02 \pm 0.03) \times 10^{-3}$ determined by TIMS.[43]

Table 3 presents plutonium measurements in two Kosovo soil samples. The first sample (A) contained depleted uranium (see Table 2), and the second one (B) was collected at the Kosovo site which was free from DU contamination. In soil sample A, ^{239}Pu and ^{240}Pu were detected although the concentration of ^{240}Pu was close to the LOQ (10s criterion) level. The total Pu concentration was $(5.5 \pm 1.1) \times 10^{-13}$ g g^{-1}, and the ratio of $^{240}Pu/^{239}Pu$ was 0.35 ± 0.10. In soil sample B, which did not contain depleted uranium, the Pu concentration ($^{239}Pu + ^{240}Pu$) was $(4.4 \pm 0.5) \times 10^{-13}$ g g^{-1}. Due to the higher

Table 2 Uranium isotopic ratios measured by ICP-SFMS and alpha spectrometry in a Kosovo soil sample containing DU, in a Kosovo DU penetrator and in metallic DU in comparison to isotopic composition of natural uranium

	Isotope ratio	Method	
		ICP-SFMS	α-Spectrometry
Soil sample A (Kosovo)	$^{234}U/^{238}U$	$(7.9 \pm 0.6) \times 10^{-6}$	$(7.3 \pm 0.5) \times 10^{-6}$
	$^{235}U/^{238}U$	$(2.02 \pm 0.01) \times 10^{-3}$	$(2.4 \pm 0.4) \times 10^{-3}$
	$^{236}U/^{238}U$	$(2.8 \pm 0.8) \times 10^{-6}$	
Penetrator sample (Kosovo)	$^{234}U/^{238}U$	$(8.0 \pm 0.5) \times 10^{-6}$	$(6.6 \pm 0.2) \times 10^{-6}$
	$^{235}U/^{238}U$	$(2.02 \pm 0.01) \times 10^{-3}$	$(1.9 \pm 0.2) \times 10^{-3}$
	$^{236}U/^{238}U$	$(3.1 \pm 0.4) \times 10^{-5}$	$(3.2 \pm 0.5) \times 10^{-5}$
Depleted uranium	$^{234}U/^{238}U$	$(8.8 \pm 1.2) \times 10^{-6}$	$(7.8 \pm 0.4) \times 10^{-6}$
	$^{235}U/^{238}U$	$(2.07 \pm 0.01) \times 10^{-3}$	$(2.2 \pm 0.5) \times 10^{-3}$
Natural uranium[6-8,46]	$^{234}U/^{238}U$	5.54×10^{-5}	
	$^{235}U/^{238}U$	7.25×10^{-3}	
	$^{236}U/^{238}U$	1.2×10^{-11}–5.6×10^{-10}	

sample weight (0.5 g in sample B in comparison to 0.1 g in sample A), the LOD for Pu was about 5 times lower (2.7×10^{-14} g g^{-1}). The isotope measurement of Pu in sample B yielded a ^{240}Pu/^{239}Pu ratio of 0.27 ± 0.07. Specific activities of ^{239}Pu $+^{240}$ Pu in two Kosovo soil samples, calculated from ICP-MS measurements, was 2.1 and 1.6 Bq kg^{-1}, respectively. This activity range corresponded to the plutonium specific activity in soil found in central Italy, using alpha spectrometry, after contamination with fallout from Chernobyl in 1986 (^{239}Pu $+^{240}$Pu activity was in the range of 0.2–1.5 Bq kg^{-1} in uncultivated soil samples).[47]

The ^{240}Pu/^{239}Pu ratio measured in the present work in both soil samples from Kosovo is close to the ^{240}Pu/^{239}Pu ratio calculated for the fourth Chernobyl reactor at the time of the accident[10] and to the ^{240}Pu/^{239}Pu ratio experimentally measured in the vicinity of Chernobyl.[48] However, it should be noted that, in the present study, it was impossible to achieve better precision of the measured isotopic ratio due to a very low Pu concentration in small samples of 0.1–0.5 g.

Alpha spectrometric determination of ^{241}Am in the penetrator sample using ^{243}Am as a spike yielded a specific activity of 0.0034 Bq g^{-1}. This value was lower than the detection limit of ICP-SFMS taking into account the relatively short half-life of ^{241}Am ($T_{1/2} = 432$ yr). The measured value is lower by several orders of magnitude than the specific activity of ^{241}Am in DU armour plates (0.7 Bq g^{-1}), reported in ref. 49. When determining plutonium, a separation factor for uranium of 5.7×10^{-6} was achieved. Taking into account the hydride formation rate, the LOQ of ^{239}Pu in the uranium penetrator sample after extraction was 1.1×10^{-9} g g^{-1}, corresponding to a specific activity of 2.3 Bq g^{-1}. Alpha spectrometry yielded a $^{239+240}$Pu activity of 0.070 Bq g^{-1} in the penetrator, which corresponds within experimental error to that in DU armour plate ($^{239+240}$Pu activity of 0.10 Bq g^{-1}) reported in ref. 49. For comparison, the activity of plutonium in the penetrators examined in ref. 1 varied from less than 0.001 to 0.013 Bq g^{-1}. The isotopic ratio was not investigated because ^{240}Pu could not be resolved from ^{239}Pu by alpha spectrometry due to close main alpha lines (5.157 MeV and 5.168 MeV for ^{239}Pu and ^{240}Pu, respectively). Thus, a further improvement in the separation technique is required for isotopic analysis of Pu in uranium samples using ICP-MS.

Conclusions

The ICP-SFMS technique with a shielded torch and the microconcentric nebulizer with desolvator, "Aridus", applied in this study offered high absolute sensitivity for uranium, and a low uranium hydride formation rate. A difference in behavior of uranium oxide ion formation UO$^+$/U$^+$ and uranium hydride ion formation UH$^+$/U$^+$ was observed. Thus, the uranium hydride ion ratio was not altered by the shielded plasma torch, which allowed full use to be made of the advantage of higher sensitivity for uranium by the application of the shielded torch in ICP-SFMS. The overall detection efficiency of 10^{-3} counts per atom and low hydride formation rate (UH$^+$/U$^+$ ratio of 3×10^{-5}) obtained using ICP-SFMS with a shielded torch coupled to Aridus made it possible to detect depleted uranium and permitted the isotopic determination of ^{236}U and plutonium at ultratrace levels in soil samples of up to 0.1 g. This might be especially important in environmental monitoring if only small sample are available, for instance for analysis of aerosol particles or atmospheric precipitation. The limits of determination for ^{236}U and ^{239}Pu were as low as 0.6 pg l^{-1} in aqueous solution and 0.13 pg g^{-1} in soil, respectively.

From the results obtained for the Kosovo soil sample contaminated with depleted uranium, we can conclude that the DU munitions could contain traces of spent uranium because non-natural ^{236}U and transuranic elements are present in depleted uranium. However, the most probable Pu contamination sources in soils at the Kosovo sites were mixed fallout including spent reactor fuel due to the Chernobyl accident, along with nuclear weapons test fallout and possibly depleted uranium. The experimental results show that the soil sample contaminated with depleted uranium did not contain a markedly higher plutonium concentration in comparison to a soil sample with a natural uranium isotopic composition. The anthropogenic radionuclide concentrations (^{236}U, $^{239+240}$Pu and ^{241}Am) in the penetrator are very low, which makes their effect negligible from a radiotoxicological point of view.

Experiments showed good agreement between ICP-SFMS and alpha spectrometry results due to the preliminary separation procedures providing high decontamination factors.

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