Abstract It is well known that ammunition containing depleted uranium (DU) was used by NATO during the Balkan conflict. To evaluate the origin of DU (the enrichment of natural uranium or the reprocessing of spent nuclear fuel) it is necessary to directly detect the presence of activation products ($^{236}$U, $^{239}$Pu, $^{240}$Pu, $^{241}$Am, and $^{237}$Np) in the ammunition. In this work the analysis of actinides by $\alpha$-spectrometry was compared with that by inductively coupled plasma mass spectrometry (ICP–MS) after selective separation of ultratrace of transuranium elements from the uranium matrix. $^{242}$Pu and $^{243}$Am were added to calculate the chemical yield. Plutonium was separated from uranium by extraction chromatography, using tri-n-ocetylamine (TNOA), with a decontamination factor higher than $10^6$; after elution plutonium was determined by ICP–MS ($^{239}$Pu and $^{240}$Pu) and $\alpha$-spectrometry ($^{239+240}$Pu) after electroplating. The concentration of Pu in two DU penetrator samples was $7 \times 10^{-12}$ g g$^{-1}$ and $2 \times 10^{-11}$ g g$^{-1}$. The $^{240}$Pu/$^{239}$Pu isotope ratio in one penetrator sample (0.12±0.04) was significantly lower than the $^{240}$Pu/$^{239}$Pu ratios found in two soil samples from Kosovo (0.35±0.10 and 0.27±0.07). $^{241}$Am was separated by extraction chromatography, using di(2-ethylhexyl)phosphoric acid (HDEHP), with a decontamination factor as high as $10^7$. The concentration of $^{241}$Am in the penetrator samples was $2.7 \times 10^{-14}$ g g$^{-1}$ and $<9.4 \times 10^{-15}$ g g$^{-1}$. In addition $^{237}$Np was detected at ultratrace levels. In general, ICP–MS and $\alpha$-spectrometry results were in good agreement.

The presence of anthropogenic radionuclides ($^{236}$U, $^{239}$Pu, $^{240}$Pu, $^{241}$Am, and $^{237}$Np) in the penetrators indicates that at least part of the uranium originated from the reprocessing of nuclear fuel. Because the concentrations of radionuclides are very low, their radiotoxicological effect is negligible.

Keywords Alpha spectrometry · Depleted uranium · Inductively coupled plasma mass spectrometry · Transuranium elements · Uranium-236

Introduction

Depleted uranium (DU) is used in many peaceful and military applications, because of its very high density (19.3 g cm$^{-3}$) [1, 2]. It is, for instance, well suited to offensive use in armour-piercing ammunition. Tanks and aircraft can fire depleted uranium penetrators (jacketed rods of solid metal) of calibre 100–200 mm and 25–30 mm, respectively. The weight of the DU penetrators fired by aircraft is approximately 300 g. During the Kosovo conflict, DU weapons were fired from NATO aircraft, and it has been reported that over 30,000 rounds of DU were used [3]. DU can be a by-product of the uranium enrichment process or it can be derived from the reprocessing of spent nuclear fuel. When the reactor is taken out of operation the removed fuel still contains $^{235}$U. By reprocessing, $^{235}$U can be re-enriched up to 4% and used as reactor fuel. During chemical reprocessing, the transuranium elements remain partially in the uranium fraction and can be found both in the enriched uranium and in its by-product depleted uranium.

Uranium isotope analysis of selected soil samples containing high concentrations of depleted uranium has revealed traces of $^{236}$U [4], an artificial uranium isotope. This presence indicated that part of the DU came from uranium reprocessing. The presence of $^{236}$U in the contaminated soil samples triggered further studies of transuranic elements – $^{239}$Pu, $^{240}$Pu, $^{241}$Am, and $^{237}$Np. In general, measurable concentrations of Pu are present over virtually all the earth’s surface. According to Ganz et al. [5] the natural plutonium concentration in the earth’s crust is approximately $10^{-16}$ g g$^{-1}$ or lower. The median concentration of plutonium produced as a result of nuclear weapons tests is approximately $10^{-13}$ g g$^{-1}$ in the soils of the Northern Hemisphere [6, 7, 8]. Considerably higher concentrations of plutonium and other actinides have been found in re-
gions contaminated by accidental fallout from nuclear re-processing plants and nuclear power plants; e.g. in the Ural region (Russia) and Chernobyl (the Ukraine) [6]. Because ultra-traces of plutonium and $^{241}$Am can usually be found in soils it was advisable to analyse the metallic uranium present in penetrators directly. A decontamination factor (DF) of approximately $10^5$ was sufficient for plutonium measurement by use of $\alpha$-spectrometry. The isotopic ratio $^{239}$Pu/$^{240}$Pu could not, however, be detected by use of this analytical technique, because of the close main alpha energies ($5.15$ MeV and $5.16$ MeV for $^{239}$Pu and $^{240}$Pu, respectively). ICP–MS is, therefore, increasingly used for ultrasensitive isotope analysis of Pu [9, 10]. The main problem of $^{238}$Pu determination in DU penetrators by ICP–MS is uranium hydride formation ($^{238}$U $^{3+}$/$^{238}$U $^{+}$). To reduce isobaric interference a further improvement in the separation technique was required for isotopic analyses of plutonium in DU penetrators by ICP–MS.

The aim of this work was to develop highly selective radiochemical separation techniques for the measurement by alpha spectrometry and ICP–MS of uranium isotope ratios and transuranium radionuclides in two penetrator samples collected in Kosovo.

### Experimental

**Apparatus**

Alpha spectrometry (Canberra Industries, 800 Research Parkway, Meriden, CT 06450, USA) was performed with a 450 mm$^2$ solid-state alpha detector with a 28% counting efficiency; a background of <10$^{-5}$ s$^{-1}$ over the energy region of interest and resolution (FWHM) of 15–25 keV ($^{238}$U).

A double-focusing sector-field ICP–MS (ICP–SFMS Element, Finnigan MAT, Bremen, Germany) was used for isotopic ratio measurements of uranium and transuranium radionuclides in penetrator samples after digestion and chemical separation. The ICP torch was shielded with a grounded platinum electrode (Guard Electrode, Finnigan MAT). A microconcentric low-flow nebulizer with membrane desolvation (Ardis, CETAC Technologies, Omaha, Nebraska, USA) was used for solution introduction in ICP–SFMS. Aqueous solution was introduced into the Ardis in the continuous flow mode by use of a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany). Optimization of the experimental conditions for ICP–SFMS was performed for the maximum ion intensity of $^{235}$U and minimum rate of uranium hydride formation using a $1 \mu$g L$^{-1}$ natural uranium solution introduced by the Ardis nebulizer. The measured uranium isotopic ratio was corrected taking into account the mass discrimination factor (assuming a linear correlation [11, 12]) determined experimentally by measuring CCLU-500 laboratory standard solution, the hydride UH+/U$^{+}$ ratio, and the dead time of the detector of the ICP–SFMS [13]. The combined uncertainty of isotopic ratio measurements was calculated as described elsewhere [14], 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 standard ($^{242}$Pu, $^{243}$Am, or $^{235}$U). Further details of the ICP–SFMS and the measurement procedure used can be found elsewhere [9].

**Standards and reagents**

The $^{242}$Pu and $^{233}$Am solutions were supplied by Amersham International (UK). The isotope composition of $^{242}$Pu and $^{233}$Am solutions was measured by ICP–MS to prove the isotope purity and avoid possible contamination of samples with coexisting isotopes. Low-density polyethylene powder (Icorene RT70) was supplied by Verplast SRL (Bergamo, Italy). Tri-$n$-octylamine (TNOA) was supplied by Sigma–Aldrich (Milano, Italia) and di(2-ethylhexyl)phosphoric acid (HDEHP) by Carlo Erba (Milano, Italy). All other reagents were analytical grade (Carlo Erba). An isotopic standard solution of uranium (CCLU-500 laboratory standard, Nuclear Research Centre, Prague, Czech Republic) was used to optimise the uranium isotope ratio measurement by ICP–MS. Uranium isotope ratio values for the CCLU-500 laboratory standard were established by calibration against the NIST-500 SRM, by thermal ionization mass spectrometry (TIMS) [15]. A uranium solution with natural isotopic composition was prepared as described elsewhere [16].

**Samples**

The two penetrators were supplied by CISAM (Centro Interforze Studi ed Applicazioni Militari, S. Piero a Grado, Livorno, Italy; Sample I) and by National Research Centre for Environment and Health, Neuherberg, Germany (Sample II). Both penetrators were collected in Kosovo.

**Column preparation**

Columns A and B for Pu-U and Am-U separation

Both columns were prepared from microporous polyethylene powder (Icorene) supporting TNOA. TNOA in toluene (20% v/v, 20 mL) was added to Icorene (16 g) and the mixture was stirred for several minutes to furnish a homogeneous product which was then placed in an oven at 40–50°C to evaporate the toluene and furnish a porous powder.

To prepare column A 4 g Icorene-TNOA powder was mixed with a few millilitres of conc. HNO$_3$ and transferred to a glass column. The column was conditioned with HNO$_3$ (7.5 mol L$^{-1}$, 20 mL) for plutonium extraction and uranium elimination (Pu-U separation).

To prepare column B 4 g Icorene-TNOA powder was mixed with a few millilitres of conc. HCl and transferred to a glass column where it was conditioned with HCl (2 mol L$^{-1}$, 20 mL) for uranium extraction (Am-U separation).

**Column C for Am extraction**

Column C was the Icorene-di(2-ethylhexyl)phosphoric acid (HDEHP) column and was used for Am extraction. HDEHP in n-heptane (20% v/v, 50 mL) was added to Icorene (25 g) and the mixture was stirred for several minutes to furnish a homogeneous product which was then placed in an oven at 40–50°C to evaporate toluene and to furnish a porous powder. Icorene–HDEHP powder (4 g) was mixed with a few millilitres of concentrated HCl and transferred into a glass column. Column C was conditioned with 20 mL HCl at pH 2.4 for americium extraction.

**Sample preparation**

Figure 1 shows a schematic diagram of the analytical technique described above for the determination of radionuclides in penetrator samples. Carefully weighed penetrator fragments were dissolved in 6 mol L$^{-1}$ HCl. The solution was evaporated to dryness and the residue dissolved in 7.5 mol L$^{-1}$ HNO$_3$ and diluted to 4 mol L$^{-1}$ HNO$_3$.

**Determination of uranium isotopes**

A small part of the solution derived from sample dissolution was used to determine uranium isotope ratios both by ICP–MS [9] and alpha spectrometry. This analysis was performed specifically to detect traces of the $^{238}$U isotope (E$x$=4.49 MeV).