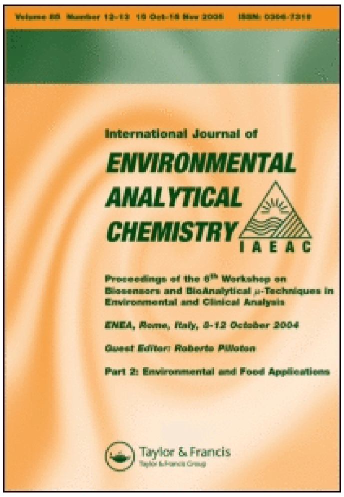

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ANALYTICAL TECHNIQUES FOR THE SEPARATION AND DETERMINATION OF TRANSURANIUM ELEMENT ULTRATRACES IN DEPLETED URANIUM AMMUNITIONS

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It is well known that ammunition containing depleted uranium (DU) was used by NATO during the Balkan conflict. To evaluate the DU origin (natural uranium enrichment or spent nuclear fuel reprocessing) it is necessary to check the presence of activation products (^{236}U, $^{239+240}$Pu, ^{241}Am, ^{237}Np, etc.) in the ammunition.

Every transuranium element (TRU) was separated from the uranium matrix by extraction chromatography with microporous polyethylene (Icorene) supporting suitable stationary phases. Plutonium was separated by tri-*n*-octylamine (TNOA). ^{241}Am was separated by TNOA and di(2ethylhexylphosphoric) acid (HDEHP). Neptunium also was separated by tri-*n*-octylamine using different conditions. After elution, the TRU elements were electroplated and counted by alpha spectrometry. The TRU decontamination factors from uranium were higher than 10^6.

The final chemical yields ranged from 50 to 70%. The detection limit was 1 Bq kg^{-1} for 0.10 g ammunition; $^{239+240}$Pu and ^{241}Am concentrations in two penetrators were 26 and 70 Bq kg^{-1} and <1 and 3.4 Bq kg^{-1}, respectively; the ^{237}Np concentration in one penetrator was 30.1 Bq kg^{-1}.

The presence of these anthropogenic radionuclides in the penetrators indicates that at least part of the uranium originated from the reprocessing of nuclear fuel, although because of their very low concentrations, the radiotoxicological effect is negligible.

Keywords: Depleted uranium; Americium; Neptunium; Plutonium

INTRODUCTION

Depleted uranium (DU) is used in many peaceful and military applications owing to its very high density (19.3 g cm^{-3}) [1,2]. For instance, it is well suited for offensive use in armour-piercing ammunition. Tanks and aircraft can fire depleted uranium ammunition with a calibre of 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

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weapons were fired from NATO aircraft, and it has been reported that over 30 000 rounds with DU were expanded [3].

DU can be (a) a by-product of the natural uranium enrichment process, or (b) derived from the reprocessing of spent nuclear fuel. By reprocessing, ^{235}U can be re-enriched up to 4% and used as reactor fuel. During the chemical reprocessing, the transuranium elements remain partially in the uranium fraction and they can be found both in the enriched uranium and in the by-product DU. In case (a) DU is called "clean DU", in case (b) "dirty DU" because it contains ^{236}U and ultratraces of activation products (^{237}Np, $^{239+240}$Pu and ^{241}Am).

The US Department of Energy (DOE) recently reported [4] that the DU stock for manufacturing munitions may contain trace levels of transuranium elements, which are the most toxic elements. According to a UNEP report the uranium isotope ^{236}U and the plutonium isotopes ^{239}Pu and ^{240}Pu were present in the depleted uranium in very small concentrations [3]. Therefore it is very important to determine the TRU concentration in DU ammunition to evaluate what the health hazard from their presence would be.

The aim of this work was to develop highly selective radiochemical separation techniques to measure by alpha spectrometry ultratraces of transuranium radionuclides in DU penetrators collected in Kosovo. Of course, determination of ^{236}U needs only dissolution, electroplating and alpha spectrometry [5,6]. This counting technique was chosen as it is cheaper than other isotopic techniques such as ICP-MS.

For the separation and determination of transuranium elements in DU penetrators by alpha spectrometry the following critical points must be taken into account:

- the achievement of very high decontamination factors (DFs), especially for ^{237}Np, which presents an alpha energy very close to that of ^{234}U uranium (from 4.64 to 4.79 MeV);
- the achievement of high chemical yields, as the concentration of TRU elements in DU penetrators is very low;
- the lack of a fully satisfactory yield tracer for ^{237}Np determination: ^{239}Np was used [7], but, as it presents a very short half-life (2.4 d), it needs a regular weekly preparation and standardization which is time consuming and expensive. ^{235}Np can also be used as a tracer [8,9], but it contains some ^{237}Np impurities;
- the possible simultaneous presence of Pu^{4+}, $PuO_2{}^{+}$, $PuO_2{}^{2+}$, Np^{4+}, $NpO_2{}^{+}$ and NpO_2^{2+} in the solution;
- the similar chemical behaviour of uranium, plutonium and neptunium.

To solve these problems extraction chromatography was chosen as the analytical technique for the separation of TRU elements from the uranium matrix.

High decontamination factors were obtained by (a) stabilizing the oxidation state of the TRU elements, (b) the choice of selective stationary phases and eluting agents.

Chromatographic columns of microporous low-density polyethylene (Icorene) supporting a stationary phase were chosen by considering the liquid–liquid extraction literature [10] and some previous applications of reversed-phase partition chromatography to radioecology and radiotoxicology [8–11]. Actually Pu(IV) and Np(IV), but not UO_2^{2+}, form strong anionic complexes in a HNO_3 medium, which can be retained on anion-exchange columns, whereas uranium remains in the eluting solution [5]. TNOA shows better properties than typical strong-base anion-exchange resins because the functional groups are in a liquid form, rather than fixed to a polymeric backbone, with a better mobility to coordinate around target anions. This means that the uptake of these ions is generally higher.

To retain plutonium and neptunium on TNOA columns it is necessary to reduce the higher oxidation states of the two elements to (IV), using $NH_2OH \cdot HCl + NaNO_2$ and $K_2S_2O_5 + FeSO_4$, respectively [5,8,9].

As far as selective Pu and Np elution from the TNOA column is concerned, oxalic acid for Pu and 0.5 M HCl for Np were used, respectively. Oxalic acid can elute Pu by forming a stable complex; 0.5 M HCl can elute Np because in this medium neptunium exists only as a cation.

As far as Am purification from UO_2^{2+} is concerned, an Icorene–TNOA column followed by an Icorene-HDEHP column were used. As a matter of fact $[UO_2(Cl)_4]^{2-}$ can be retained on the anion-exchange column from a HCl medium whereas Am^{3+} remains in the eluting solution. HDEHP is a cation exchanger which can selectively extract cations depending on the pH. At pH 2.4 Am extraction is high and selective: at very low pH (1 M HNO_3) Am can then be eluted from the column [5].

^{242}Pu and ^{243}Am were used as the internal standards for calculation of the final chemical yield. For ^{237}Np a mean final yield (54.0 ± 3.1) was calculated by carrying out multiple analyses on DU after addition of ^{237}Np with a known activity.

EXPERIMENTAL

Apparatus

Alpha spectrometry chain (Canberra Industries, 800 Research Parkway, Meridien, CT 06450, USA) 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).

Electrodeposition apparatus (Carlo Erba, Italy) with perspex cells (25-mm internal diameter); 20-mm diameter stainless-steel disks.

Chromatographic columns (150-mm length and 9-mm diameter).

Standards and Reagents

^{242}Pu, ^{243}Am and ^{237}Np standard solutions were obtained from Amersham International (UK).

Low-density microporous polyethylene powder (Icorene RT 70) was obtained from Verplast srl (Bergamo, Italy).

Di(2-ethylhexylphosphoric) acid (HDEHP) was obtained from Carlo Erba (Milan, Italy), and tri-*n*-octylamine (TNOA) from Sigma-Aldrich (Milano, Italy). All other reagents were analytical grade (Carlo Erba, Italy).

Sample Collection and Dissolution

The two DU 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.

A carefully weighed penetrator fraction was dissolved in 6 M HCl and the solution was taken to dryness. The residue was dissolved in 7.5 M HNO_3 and diluted to 4 M HNO_3.

Chromatographic Column Preparation

Column (A) and (B) for Pu–U and Np–U Separation

Both columns were made of Icorene supporting TNOA. 20 mL 20% TNOA in toluene (v/v) was added to 16 g Icorene; the mixture was stirred for several minutes to get a homogeneous product that was placed in an oven at 40–50°C to evaporate toluene and to obtain a porous powder. 4 g of the Icorene–TNOA powder were mixed with a few millilitres of conc. HNO_3 and transferred into a glass column. The column was then conditioned with 20 mL 7.5 M HNO_3 or 4 M HNO_3 for column (A) and column (B), respectively.

Column (C) for Am–U Separation

4 g of Icorene–TNOA powder were conditioned with 20 mL 2 M HCl for uranium extraction.

Column (D) for Am Extraction

50 mL 20% HDEHP in *n*-heptane (v/v) were added to 25 g Icorene; the mixture was stirred for several minutes to get a homogeneous product, which was then placed in an oven at 40–50°C to evaporate toluene and to obtain a porous powder. 4 g of the Icorene–HDEHP powder were conditioned with 20 mL of a HCl solution at pH 2.4 for americium extraction.

Plutonium Separation and Determination

After addition of known amounts of ^{242}Pu and ^{243}Am as yield tracers, 2 mL $NH_2OH \cdot HCl$ was added to the original 4 M HNO_3 solution to obtain Pu(III), which was then oxidized to Pu(IV) by adding 5 mL 8 M $NaNO_2$. The solution was heated at 90–95°C to destroy the excess of $NaNO_2$ and then passed through Column (A) at a flow rate of 0.8 mL min^{-1} for plutonium retention. The column was then washed with 200 mL 4 M HNO_3 and the effluent kept for ^{241}Am determination. Plutonium was finally eluted with 18 mL 0.025 M oxalic acid in 0.15 M HNO_3. For better purification of plutonium from uranium this chromatographic operation was repeated. After separation, plutonium was electroplated at pH 1.5–2.0 for 1 h at 550 mA cm^{-2} current density directly from the eluting solution. The chemical yield was $50 \pm 5\%$ for two separation cycles.

Plutonium alpha spectra are showed in Fig. 1(A) (one TNOA column) and Fig. 1(B) (two TNOA columns), respectively.

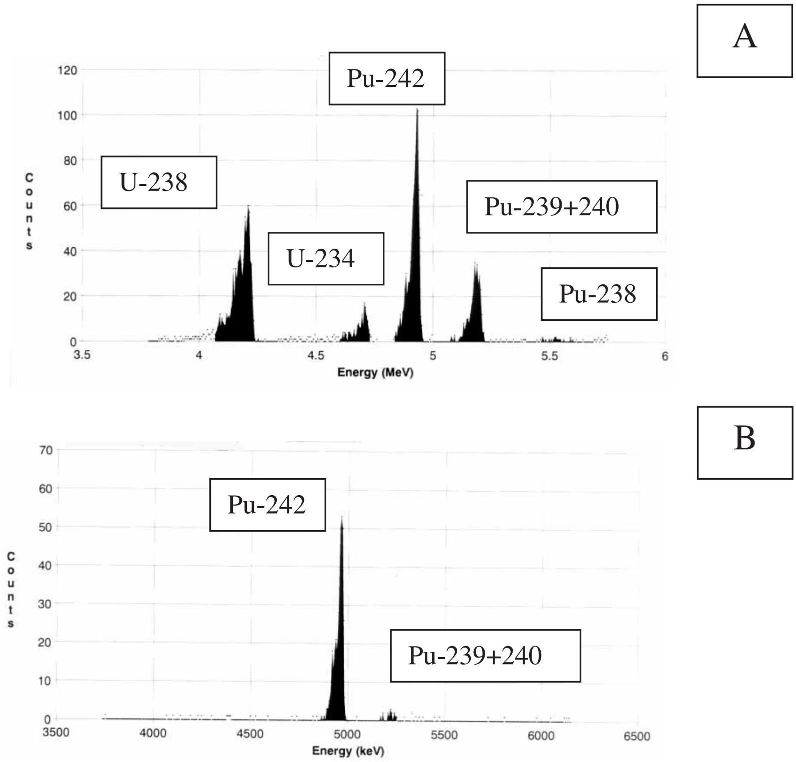

FIGURE 1 Alpha spectra of plutonium separated from a DU penetrator: (A) by one column; (B) by two columns.

Americium Separation and Determination

The americium solution was evaporated to dryness and the residue was dissolved in 150 mL 6 M HCl.

The solution was passed through Column (C) which retains uranium (and iron), but not americium. The column was then washed with 60 mL 6 M HCl. The two effluents were combined and kept for americium determination as follows: (1) the solution was adjusted to pH 2.4 with ammonia and passed through Column D; (2) after washing, americium was eluted with 40 mL 1 M HNO_3; (3) the eluted solution was dried and the residue dissolved in sulphuric acid; (4) americium was electroplated from ammonium sulphate at pH 4 and measured by alpha spectrometry as reported above. The chemical yield was $70 \pm 7\%$.

The americium alpha spectrum after radiochemical separation from DU is shown in Fig. 2.

Neptunium Separation and Determination

The 7.5 M HNO_3 sample solution was diluted to 4 M HNO_3. After adding 200 mg $FeSO_4$ and 700 mg $K_2S_2O_5$ to reduce Np to Np(IV) the solution was stirred for 30 min and passed through Column (B) at a flow rate of 0.8 mL min^{-1}. The column

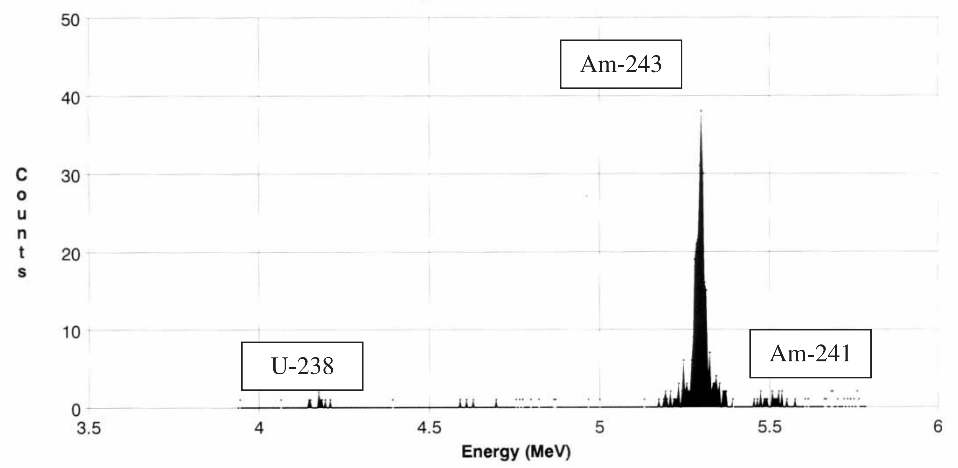

FIGURE 2 Alpha spectrum of americium separated from a DU penetrator.

was then washed with 200 mL 4 M HNO_3 at the same flow rate. Neptunium was eluted with 10 mL water and then with 80 mL 0.5 M HCl. The eluates were combined and taken to dryness. The residue was dissolved in conc. HNO_3 and water was added to obtain 4 M HNO_3. To improve the purification of Np from uranium the chromatographic procedure was repeated as follows: (1) after adding 200 mg $FeSO_4$ and 700 mg $K_2S_2O_5$ to reduce Np to Np(IV) the solution was stirred for 30 min and passed through Column (B); (2) the column was then washed with 200 mL 4 M HNO_3; (3) neptunium was eluted with 10 mL water and then with 80 mL 0.5 M HCl. Finally the eluted solutions were taken to dryness, the residue dissolved in conc. H_2SO_4 and the pH adjusted to 4 with ammonia. The solution was transferred into an electrolytic cell and the electroplating was performed for 5 h at 600 mA on a stainless-steel disk.

A counting time of at least 168 h was necessary to measure the ^{237}Np concentration by alpha spectrometry. The associated uncertainty depends on the background counting, the peak counting and the mean final chemical yield (54.0 ± 3.1%) obtained in the preliminary tests. The detection limit was 0.5 Bq kg^{-1} for 0.10 g of DU ammunition.

Figure 3 shows the alpha spectra of neptunium separated from DU, after addition of a known activity of ^{237}Np, by one column and by two columns Icorene–TNOA: the DF values were 3.0×10^4 and 2.6×10^6, respectively. In spite of this very high DF, a small activity of ^{238}U and consequently of ^{234}U remains in ^{237}Np sources, but the ^{238}U and ^{237}Np alpha peaks, having different energies, are well resolved and it is possible to obtain the ^{234}U/^{238}U ratio by alpha spectrometry of DU [5] to get the contribution of ^{234}U to the ^{237}Np peak. Figure 4 shows the alpha spectrum of ^{237}Np separated from the DU penetrator.

RESULTS

The $^{239+240}$Pu specific activity concentrations results were 0.070 ± 0.014 and 0.026 ± 0.005 Bq g^{-1} for Sample I and Sample II, respectively (Table I): for comparison,

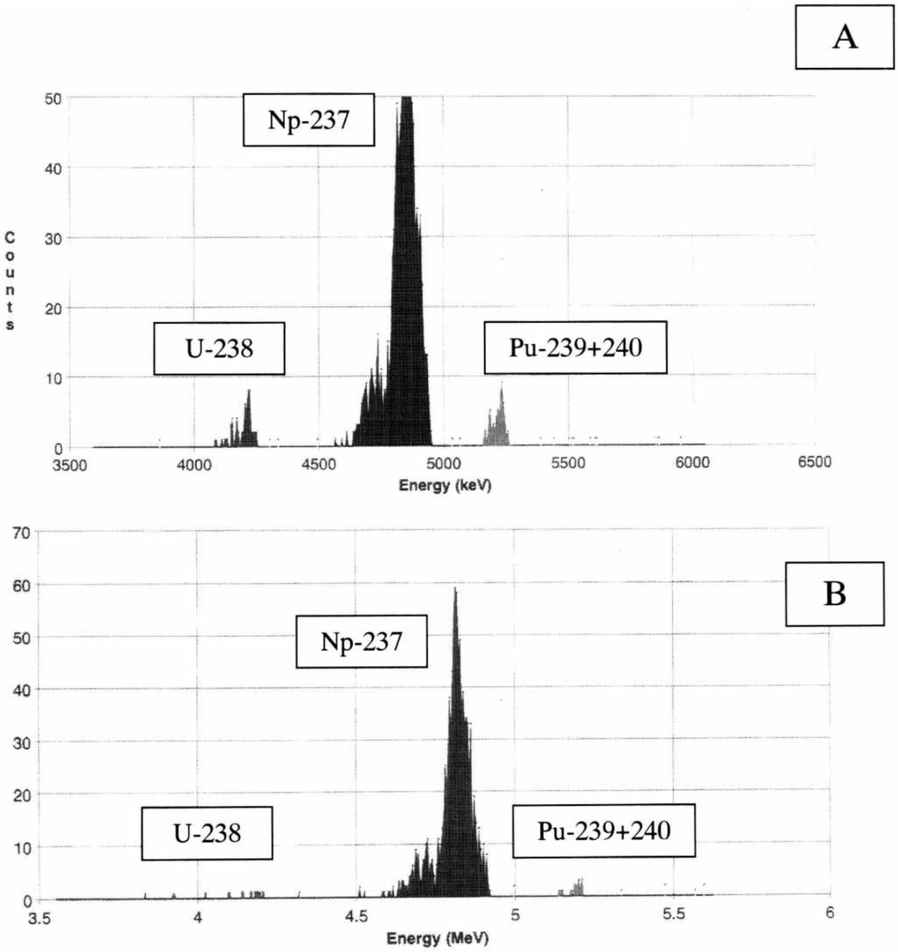

FIGURE 3 Alpha spectra of neptunium separated from a DU penetrator sample with a known activity of ^{237}Np added: (A) separation Np/U by one Icorene–TNOA column; (B) separation Np/U by two Icorene–TNOA columns.

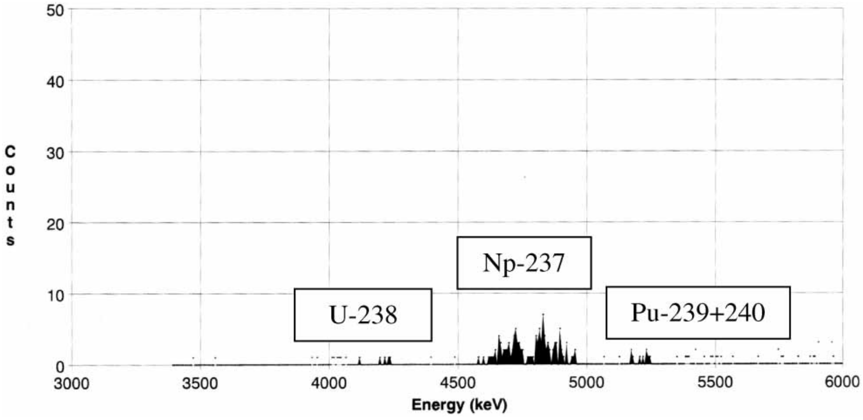

FIGURE 4 Alpha spectrum of neptunium separated from a DU penetrator sample.

a plutonium concentration for DU penetrators ranging from <0.001 to $0.13\,\mathrm{Bq\,g^{-1}}$ has been reported [3]. Plutonium to uranium activity ratios are also summarized in Table I: a limitation of alpha spectrometry is that only the sum of ^{239}Pu and ^{240}Pu can be obtained, owing to the similar alpha energies of the two isotopes (5.24 and 5.25 MeV, respectively). In this case, ICP-MS could be used for the individual determination of the two Pu isotopes [5,6].

The decontamination factors (DF = original uranium/final uranium) of plutonium from uranium are given also in Table I. It is necessary to repeat the chromatographic separation of plutonium from uranium when the final determination technique is ICP-MS: as a matter of fact this better DF can reduce the isobaric interference due to uranium hydride (^{238}UH^{+}) formation [5].

Table II summarizes the results for americium activity concentrations, the americium to plutonium and americium to uranium ratios and the DF.

^{237}Np was analysed only in penetrator I (Table III). The DF was very high ($>10^6$). Plutonium does not interfere because the alpha peaks of $^{239+240}$Pu (5.15 MeV) and of ^{238}Pu (5.50 MeV) are well resolved from that of ^{237}Np (4.77 MeV). Also ^{241}Am does not interfere because it is not retained on the Icorene–TNOA column.

According to the UNEP Report [3] the relevant radiological risk is "insignificant" if the corresponding dose or concentration intake are lower than 1 mSv, or below the WHO health standards, respectively. On the basis of the activity concentrations measured in the penetrators the corresponding radiological risks appear not to be significant.

TABLE I Plutonium concentrations, isotope ratios and DF

Penetrator	*$^{239+240}$Pu* (Bq kg^{-1})	*$^{239+240}$Pu/^{238}U*	*DF*
Sample I	70 ± 14	5.7×10^{-6}	2.1×10^{5}
Sample II	26 ± 5.2	2.1×10^{-6}	$>4.0 \times 10^{6}$[a]

DF = Original U/Residual U.
[a] Double separation.

TABLE II ^{241}Am concentrations, isotope ratios and DF

Penetrator	*^{241}Am* (Bq kg^{-1})	*^{241}Am* (g g^{-1})[a]	*^{241}Am /$^{239+240}$Pu* (*activity*)	*^{241}Am/^{238}U* (*activity*)	*^{241}Am/^{238}U* (*mass*)[a]	*DF*
Sample I	3.4	2.7×10^{-14}	0.048	2.7×10^{-7}	2.7×10^{-14}	1.0×10^{7}
Sample II	<1.2	$<9.4 \times 10^{-15}$	–	–	–	$>4.0 \times 10^{6}$

[a] Mass concentration was calculated through the isotope's specific activity.

TABLE III ^{237}Np concentration, isotope ratios and DF

Penetrator	*^{237}Np* (Bq kg^{-1})	*^{237}Np* (g g^{-1})[a]	*^{237}Np/$^{239+240}$Pu* (*activity*)	*^{237}Np/^{238}U* (*activity*)	*^{237}Np/^{238}U* (*mass*)[a]	*DF*
Sample I	30.1 ± 2.4	1.1×10^{-9}	0.43	2.0×10^{-6}	1.1×10^{-9}	8.1×10^{6}

[a] Mass concentration was calculated through the isotope's specific activity.

CONCLUSIONS

From the results it is possible to draw the following conclusions

- The suggested procedures are sufficiently simple, given the real difficulties of separating ultratraces of transuranium elements from a uranium sample.
- Good recoveries, very high decontamination factors from uranium and good sensitivities can be obtained.
- The analysed DU penetrators contain ultratraces of transuranium radionuclides, indicating that at least part of the uranium has originated from the reprocessing of nuclear fuel.
- The amounts of these TRU isotopes are very low and not significant in terms of the overall radioactivity of the penetrator.

As the transuranium element content is very low and distributed over very large areas, it cannot cause significant environmental contamination. Therefore, even considering local impact and particularly unfavourable situations, transuranium concentrations cannot be the source of relevant radiological contaminations, as indicated also by a specific UNEP report [3].

In conclusion the danger from "dirty DU" is 1.5–2 times higher than that from "clean DU"; this increase is almost completely due to the different composition of uranium isotopes (^{236}U presence and ^{234}U/^{238}U higher in dirty DU) and less than 1% of the dose contribution would be caused from transuranium elements [12] if all TRU contained in the reprocessed uranium had been introduced into the enrichment cascades.

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