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Depleted uranium particles in selected Kosovo samples

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Abstract

Selected soil samples, collected in Kosovo locations where DU ammunition was expended during the 1999 Balkan conflict, have been investigated by secondary ion mass spectrometry (SIMS), X-ray fluorescence imaging using a micro-beam (μ-XRF) and scanning electron microscopy equipped with an energy dispersive X-ray fluorescence detector (SEM-EDXRF), with the objective to test the suitability of these techniques to identify the presence of small DU particles and measure their size distribution and the $^{235}U/^{238}U$ isotopic ratio (SIMS). Although the results do not permit any legitimate extrapolation to all the sites hit by the DU rounds used during the conflict, they indicated that there can be "spots ' where hundreds of thousands of particles may be present in a few milligrams of DU contaminated soil. The particle size distribution showed that most of the DU particles were <5 μm in diameter and more than 50% of the particles had a diameter <1.5 μm. Knowledge on DU particles is needed as a basis for the assessment of the potential environmental and health impacts of military use of DU, since it provides information on possible re-suspension and inhalation.

Keywords: Depleted uranium; DU; DU particle size; DU particle size distribution; SIMS; SEM-EDXRF

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1. Introduction

In a previous article in this Journal (Danesi et al., 2003), we reported results on the isotopic composition of uranium and plutonium in soil samples collected in Kosovo in November 2000 by IAEA during a UNEP-led field mission aimed at making an environmental assessment of depleted uranium (DU) from ammunition used during the 1999 Kosovo conflict.

Here we report the results of an investigation on the DU particles present in selected samples. The information has been obtained by secondary ion mass spectrometry (SIMS), X-ray fluorescence imaging using a micro-beam (μ-XRF) and scanning electron microscopy equipped with an energy dispersive X-ray fluorescence detector (SEM-EDXRF). The objective of the present study was to test the suitability of these three micro-analytical techniques in obtaining information on the presence of DU particles in selected Kosovo soil samples and measure their size distribution. All three techniques permit identification of the presence of uranium in the samples and in principle can give information on the particle size. Moreover SIMS also permits measurement of the $^{235}U/^{238}U$ isotopic ratio.

2. Experimental

The measurements were been performed on two samples, that exhibited relatively high DU concentrations. The concentration of the uranium isotopes in these two samples (sample # 11 and # 12) were shown in Table 1 (Danesi et al., 2003). The $^{235}U/^{238}U$ values reported in this work were measured by IMS.

2.1. Sample treatment

When received the two samples were visibly heterogeneous, containing stones, large agglomerates of soil and pieces of vegetation. After drying, each sample was sieved into two fractions, a "coarse" fraction (>3 mm) and a "fine" fraction (<3 mm). Individual aliquots of the "fine" fraction were prepared for the measurements.

2.2. SIMS measurements

The sample to be measured was prepared by suspending portions of the "fine" fractions in 1 ml of reagent-grade heptane in a glass vial. The vial was placed in an ultrasonic bath for 1 min to disperse the particles and to break up agglomerates. An Eppendorf pipette was used to transfer approximately 100 μl of heptane suspension onto a heated pyrolytic graphite planchet of 2.5 cm diameter.

In SIMS an energetic beam of focused ions (in our case O_2^+ at 12–15 keV) was directed at the sample surface in a high vacuum environment. The transfer of momentum from the impinging primary ions to the sample caused sputtering of the surface atoms and molecules. The sputtered uranium ions were analyzed by an imaging mass spectrometer equipped with a position sensitive detector. The secondary ions

Table 1
Isotopic composition of the two samples studied (Danesi et al., 2003)[a]

#	Location	Sample	U-234 mg.kg^{-1}	U-235 mg.kg^{-1}	U-236 mg.kg^{-1}	U-238 mg.kg^{-1}	U-235/U-238
11	Ceja Mountain underneath a jacket	Soil core, 0–5 cm	0.024±0.001	7.06±0.20	0.099±0.003	4040±65	0.00203±0.00002
12	Same, underneath a jacket	Soil core, 5–10 cm	0.0080±0.0003	2.35±0.05	0.033±0.001	1285±19	0.00182±0.00002

[a] Concentrations were reported on a dry weight basis. The U-235/U-238 values were measured by SIMS (this work).

of uranium were counted and the counts and position stored in the memory. An image was thus constructed over several seconds of integration, showing the intensity of a particular U isotope as a function of position. Superimposing the ^{235}U images with that of ^{238}U yielded enrichment of the various particles detected. The technique permited measurement of the isotopic composition of several thousand U-containing μm sized particles present in an area of several mm^2 in about 4–5 h.

The measurements were carried out with a Cameca-IMS-4f instrument equipped with a resistive anode encoder detector system for ion counting of mass-resolved ion images. A special software package (PSEARCH, Charles Evans and Associates, Redwood City, CA) was used to acquire data for the isotope ^{235}U and ^{238}U in fields of 150 μm diameter on the sample planchet. The *x* and *y* co-ordinates of each ion striking the detector were then registered giving spatially resolved images for each isotope of interest. A typical search consisted of an array of 10×10 or 20×20 fields of 150 μm diameter. The software identified the U-containing particles in each field and calculated the $^{235}U/^{238}U$ ratio for each identified particle. The uncertainty of the $^{235}U/^{238}U$ ratio measurement for a given particle was limited by the total number of ion counts collected. In the case of our samples the uncertainty was in the range of ±10%. The possible presence of isobaric interference on the ^{235}U signal was checked by measuring the ^{233}U and ^{234}U mass positions.

2.3. μ-XRF measurements

With this technique, different points of the sample were irradiated by a narrow primary X-ray beam. At each point an X-ray fluorescence spectrum was collected, the concentration of a particular element versus position was obtained and a concentration map was drawn. The X-ray beam was supplied by a 3kW X-ray tube and concentrated by a polycapillary optical unit to a spot size of about 30 μm. The sample was positioned by four stepper motors (one for rotation and three for translation) with reproducibility better than 1 μm for translations in the range of 25 mm. A video image of the sample with a spatial resolution of a few microns per pixel was projected on a monitor screen using an optical microscope, a CCD camera and a video capture board. The fluorescence X-rays were detected by a high resolution Si/Li detector (FWHM of 165 eV at 5.9 keV) connected to standard front-end electronics.

Particles from the "fine" fractions of the samples were glued on the plastic sample holder, covering a surface of several tens of mm^2 .The sample holders were placed perpendicularly to the primary beam and the fluorescence X-rays were detected at 45° with a collimator. The samples were scanned at various steps of 7–50 μm with preset counting time of 50 s per pixel.

2.4. SEM-EDXRF measurements

This technique permits an automated search for particles containing high Z elements using the back-scattered electron signal. The size range of the particles that can be detected depends on the applied magnification and the image matrix. In this case 250× magnification and a matrix of 1024×800 pixels matrix was used. This

permitted detection of particles having diameters >~0.9 μm. The SEM instrument used was a Philips XL-30 equipped with an EDAX Model DX-4 energy dispersive X-ray spectrometer with SUTW Si(Li) detector. For each particle identified by SEM, the spectrum was measured by the EDX spectrometer to obtain information about a number of selected elements including U. The entire spectrum of each particle was obtained and the M-alpha X-ray line at 3.17 keV and the L-alpha X-ray line at 13.6 keV were used for calculating the U content in the particles. A typical EDX spectrum of a uranium-containing particle is shown in Fig. 1.

The samples to be measured were prepared by gently tapping an aluminum SEM stub covered with a double-sided adhesive carbon disk into the "fine' fraction of the original samples. This ensured that the physical integrity of the sample was maintained. An iDXac (version 2,20) software was used to perform an automated search for particles containing high-Z elements using the back-scattered electron signal. The automated search identified about 1000 uranium-containing particles in each sample. Each automatic measuring session (for single stub or particle) lasted about 30 h.

3. Results

3.1. SIMS measurements

This technique gave excellent information on the isotopic ratio of the particles. However, considerable uncertainty exists in the measured particle size. Typical PSEARCH images for the two uranium isotopes ^{235}U and ^{328}U are shown in Fig. 2 a and b. When these two images were superimposed, images of the particles were obtained (Fig. 2 c.). In sample # 12 the PSEARCH software identified a total of 318 U-containing particles in area of 1.15 mm^2. Eighty six had sufficient ion counts (i.e. >20 counts for ^{235}U and ^{328}U) to be further processed. The distribution of the $^{235}U/^{328}U$ atom ratio in the particles of a sub-sample of sample # 12 (Fig. 3) indicated

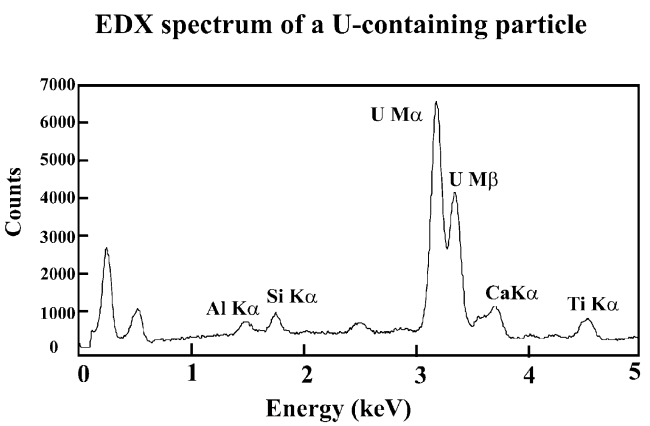

Fig. 1. Measurements by SEM-EDXRF. Typical spectrum of a depleted uranium particle.

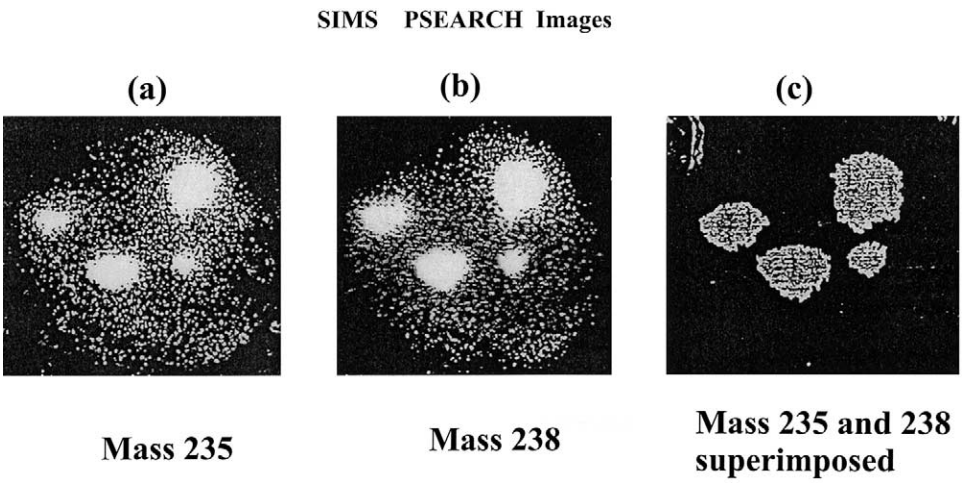

Fig. 2. Measurements by SIMS. Typical PSARCH images for the two uranium isotopes ^{235}U (a) and ^{238}U (b) and for the DU particles (c). In (c) the images were superimposed and edited by the instrument software. The field of view is about 150 μm.

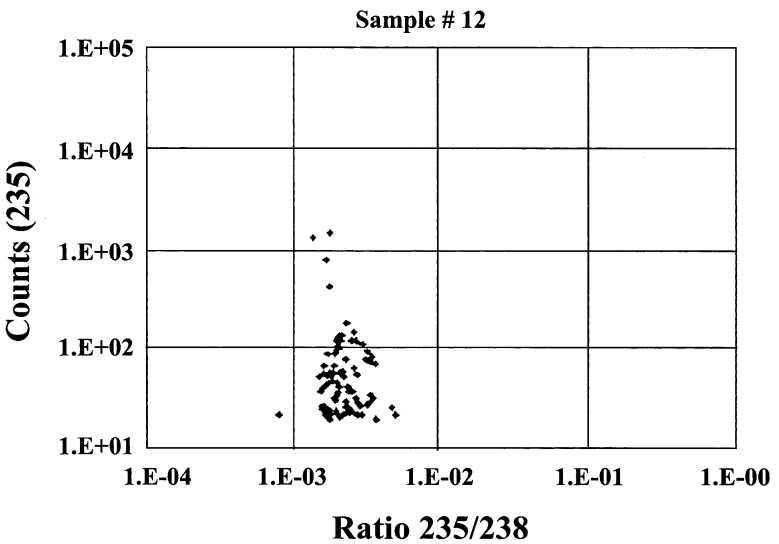

Fig. 3. Measurements by SIMS. Distribution of the $^{235}U/^{238}U$ atom ratio in the particles of sample # 11.

a single population having an average value of 0.00182±0.00002. Fig. 3 is displayed in a logarithmic scale in order to show the absence of particle populations with very different isotopic ratios (e.g. natural U from the soil). For sample # 11 a total of 5282 particles was found in an area of 7.0 mm^2. Out of these 1226 had sufficient ion counts to be further processed. For this sample a single population having an average value of 0.00203±0.00002 of the $^{235}U/^{328}U$ atom ratio was calculated. The

$^{235}U/^{328}U$ atom ratios were obtained by computing the weighed mean of the isotope ratios of the single particles and the deviation of that mean value. Statistical weights of single particle isotope ratios were obtained from counting statistics of the accumulated ^{235}U and ^{238}U ion counts. Both values of the $^{235}U/^{328}U$ atom ratio confirmed that the samples consisted of DU having the same isotopic composition as that of the armor-piercing ammunition used in the 1999 Kosovo conflict (Bleise et al., 2003). The technique gave only a rough estimate of the most frequent diameter of the U-particles (<15 μm).

3.2. μ-XRF measurements

The technique does not provide information on the isotopic composition and only gives information on the size of uranium particles if they are smaller than the beam diameter. In order to confirm the presence of uranium the two samples (# 11 and # 12) were first analyzed with a large beam (0.7 mm in diameter). The spectra at each different pixel were summed up to produce a cumulative spectrum. The uranium L_α characteristic X-ray confirmed the presence of uranium in both samples. The elemental maps of uranium were then constructed by analyzing the two samples with a finer beam (35 μm) by summing up at each pixel the counts in the energy range 13.4–13.6 keV.

The elemental maps of the samples covered an area of approximately 4 mm×4 mm (sample #11) and 2 mm×2 mm (sample # 12). The optical image of the scanned area of sample # 11 is shown in Fig. 4a. When this map was super-imposed onto the U elemental map, information was obtained on how uranium was distributed in the material visible in the optical image. The elemental map of uranium of sample # 11 is shown in Fig. 4b. The elemental map of sample # 12 was qualitatively similar to that of sample # 11. The several red spots in the elemental maps indicate the presence of high uranium concentrations, possibly in the form of particles on top of a relatively homogeneous background containing many other small particles. As an example the uranium elemental map around one of the more intense red spots of sample #11 is shown in detail in Fig. 5a. The width of the net peak areas of the uranium L_α X-ray lines (Full Widths at Half Maximum=FHWM) of these small spots gave some information on the size of the uranium particles. An example of a two-dimensional cross section along the *x*-axis of the elemental map of Fig. 5a is shown in Fig. 5b. The Gaussian curves obtained in this way were characterized by an FWHM of about 30 μm (close to the beam size) indicating that the size of the uranium spots (particles) was in the micron range.

3.3. SEM-EDXRF measurements

This technique, although unable to provide information on the isotopic composition of the sample, gave excellent information on the particles' dimensions and size distribution. Most of the identified particles were in the size range of 1 to 8 μm in diameter. Some larger particles, up to 40 μm, were also detected. The automatic search routine identified 1338 uranium containing particles in sample # 11 and 713

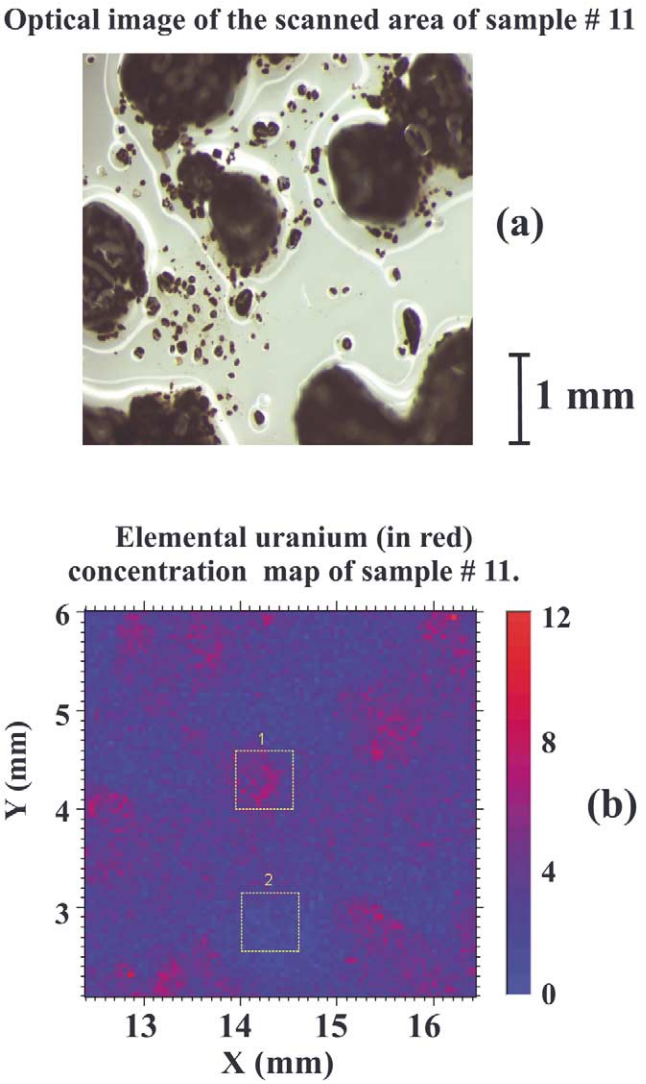

Fig. 4. Measurements by μ-XRF. (a) Optimal image of the scanned area of sample # 11. (b) Elemental uranium (in red) concentration map of sample # 11. The intensity of the red colour is proportional to the U concentration. The squares indicate areas where cumulative spectra were collected.

particles in sample # 12. The particle diameter distribution is shown in Fig. 6. The data indicate that most particles were less than 5 μm in diameter, with more than 50% of them below 1.5 μm. The uranium-containing particles were usually associated with larger soil particles containing mainly Si. SEM images of large uranium containing particles, superimposed on soil particles, are shown as light areas in Fig. 7a and b. The large particles were about 8 to 10 μm in diameter. Several smaller U

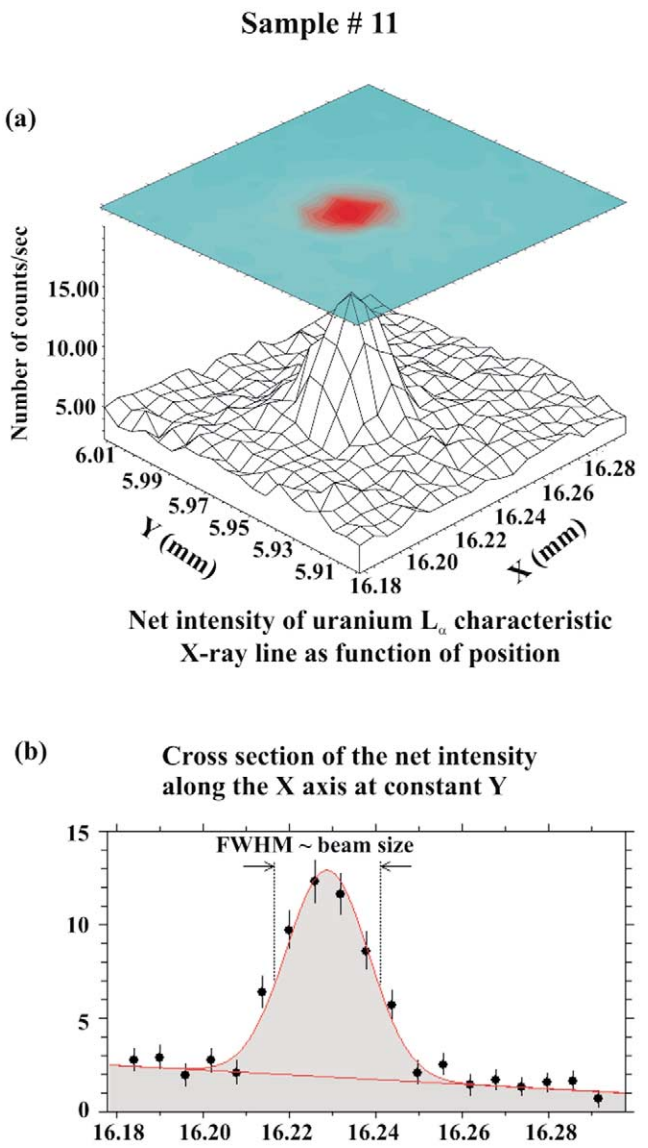

Fig. 5. Measurements by μ-XRF. (a) Detailed elemental uranium concentration map around one of the intense red spots of sample # 11. (b) Two-dimensional cross section along the X-axis of the elemental map (a) at constant Y. The FWHM (Full Width at half Maximum) is about 30 μm.

particles of diameter 1 to 2 μm were also clearly visible. However it must be mentioned that since the number and size of inactive particles (without uranium) in the samples can be large, thereby making small DU particles covered by them invisible, the information obtained here is restricted to the particles visible in the SEM images.

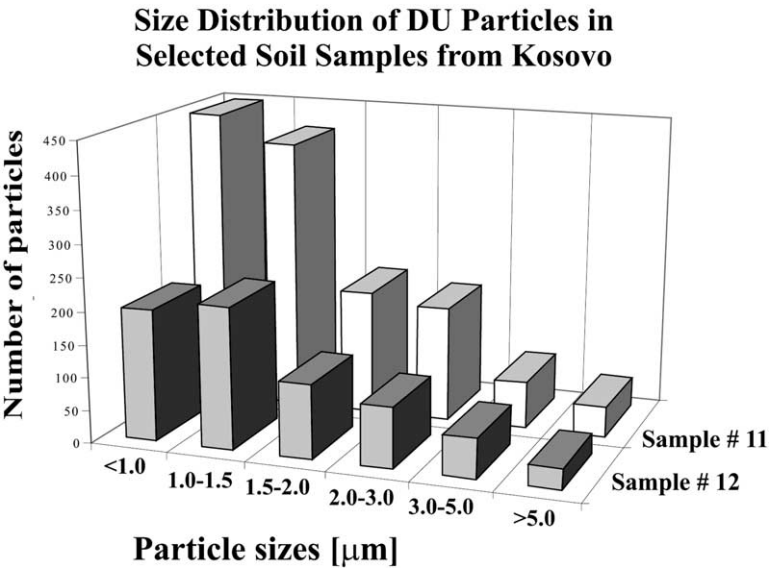

Fig. 6. Measurements by SEM-EDXRF. Size distribution of the DU particles in samples # 11 and #12.

The particles were found to consist mostly of uranium (>90 wt%) and to contain Ti as an impurity (~1 wt%).

4. Conclusions

The data obtained by SIMS confirmed that the samples contained small uranium particles having a single isotopic population with a $^{235}U/^{328}U$ atom ratio of about 0.002, corresponding to the composition of DU used in ammunition. The measurements performed by μ-XRF gave only some coarse information on the size of the uranium particles, the reason being that the particles were in general smaller than the diameter of the beam used (35 μm).

Better information on the particle size was obtained by SEM-EDXRF. Thousands of particles were identified in both sub-samples, indicating that several hundred thousands or a million particles can be present in a few milligrams of DU contaminated soil. The particle size distribution showed that most of the DU particles were <5 μm in diameter in concurrence with what was previously reported (Harley et al., 1999; US AEPI, 1995). In addition, more than 50% of the particles had a diameter <1.5 μm. This means that the DU particles display a large surface area for dissolution processes and have a potential for re-suspension and inhalation under arid conditions.

The presence of about 1% Ti is in good agreement with information by Bukowski et al. (1993) that DU penetrators were hardened by reducing carbon content and alloying with titanium at a concentration of ~0.8% by weight.

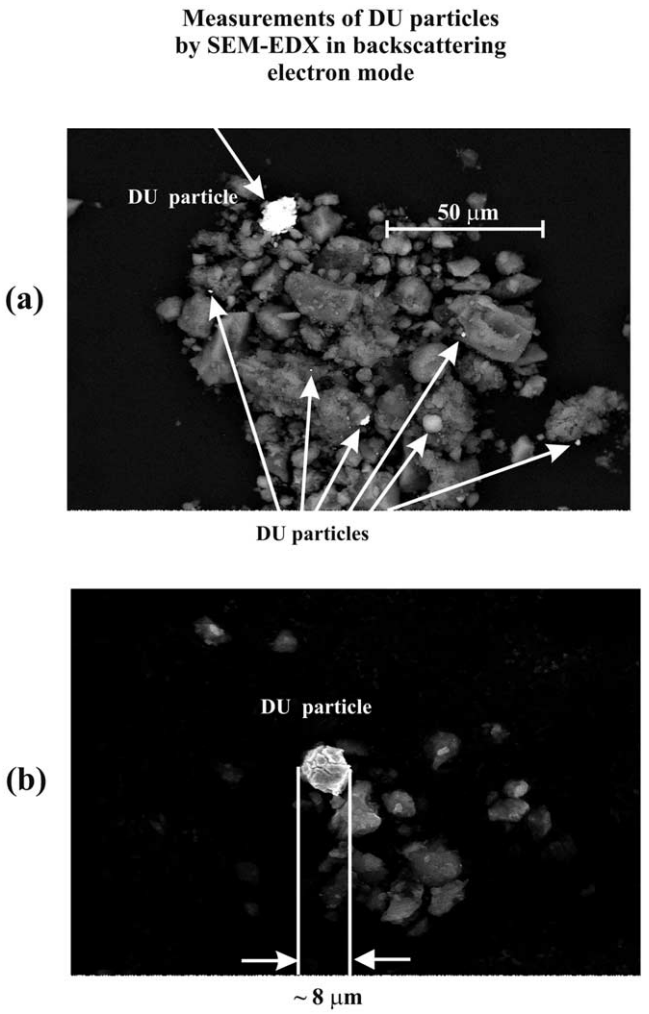

Fig. 7. Measurements by SEM-EDXRF. Images of DU particles (light areas) in samples # 12.

The results obtained on only two samples obviously do not permit any legitimate extrapolation of the findings of this work to all the 112 sites hit by the 30,000 DU rounds used during the 1999 Kosovo conflict. However, the results provide important input on DU particle size needed for an assessment of environmental impact and potential human exposures due to military use of DU. For a full assessment, additional in-depth investigations on concentrations and size distribution of DU particles are needed for the different targets and soils affected by different types of DU ammunition.

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