

Study of the oxidation state of depleted uranium particles in soil using micro-XANES

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Depleted uranium (DU) due to its physical properties (e.g. high density that is about twice that of lead) is used in munitions designed to penetrate armour plate and is also used to reinforce military vehicles such as tanks. DU munitions have been recently used during the Gulf war, in Bosnia Herzegovina and in Kosovo conflicts. In addition, DU has a number of civilian applications. It is employed in counterweights or ballast in aircraft; radiation shield in medical equipment; as containers for the transport of radioactive material and chemical catalyst [1]. The Boeing 747-258F that crashed into a block of flats in Amsterdam in October 1992 carried 282 kg of DU counterweights. The Boeing-747 crashed near Stansted airport in England in January 2000, was estimated to be carrying *ca.* 425 kg of DU counterweights [2]. Both civilian and military employment of DU can produce aerosol that generates microparticles uranium bearing. Therefore, a dispersion and redeposition of these microparticles in the environment can occur. In order to understand transport and dispersion mechanisms of DU as weathering rates, mobilisation and biological uptake, of microparticles containing DU, it is important to determine the oxidation state of uranium in the microparticles.

The samples were collected by the UNEP expedition conducted in September 2000 in the Kosovo area. The samples investigated consisted of two soil specimens collected at 0-5 cm depth. After collection the samples were dried, homogenised and sieved at the IAEA analytical laboratories of Seibersdorf.

The experiments were performed at the micro-fluorescence beamline L at HASYLAB. The white beam of a bending magnet was monochromatized by a Si(111) double monochromator. A polycapillary half-lens (X-ray Optical Systems) was employed for focusing a beam of $1 \times 1 \text{ mm}^2$ down to a spot size of $15 \text{ }\mu\text{m}$ diameter. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the L_{III} absorption edge of uranium (17167 eV) by stepping the Si(111) monochromator. The fluorescence yield was detected at an angle of 90° to the incoming beam using an energy-dispersive HPGe detector. Soil particles taken in the Kosovo war area containing around 1 wt% of uranium of 20-40 μm diameter were selected for XANES measurements. U_3O_8 particles as well as a thin UF_4 foil ($34 \text{ }\mu\text{g/cm}^2$, Micromatter) were used as standards. All measurements were carried out using an 1 eV step size. The measuring time for each point varied from 2 s (standard particles) to 60 s (soil particles).

The XANES spectra were processed using a least-square fitting method developed by Osán et al. [3] originally for arsenic K-edge absorption spectra. Fluorescence mode standard spectra of U(IV) and U(VI) measured by Duff et al. [4] at NSLS were also used for the spectrum processing. The energies and intensities of the white line and multiple scattering peak, as well as the parameter of the arctangent step for U(IV) and U(VI) were determined using the standard spectra. The ratios of the different oxidation state forms in the particles were calculated using these parameters fixed in the fitting function. Figure 1 shows two examples of the least squares fitting of the XANES spectra of individual particles recorded at the U L_{III} edge.

As a preliminary result of 1 day user beam and 1 day test beam, Table 1 summarizes the fitting results obtained for six individual soil particles. I_w and σ_w denotes the intensity and width of the white line, while I_s and σ_s correspond to the height and width of the multiple scattering peak. The indices (IV) and (VI) are indicating the oxidation state. The table indicates that uranium is present in the particles mostly in the U(IV) form, the maximum ratio of U(VI) to the total U content was obtained as 24 % indicating that the particle contained mainly the less mobile form of U.

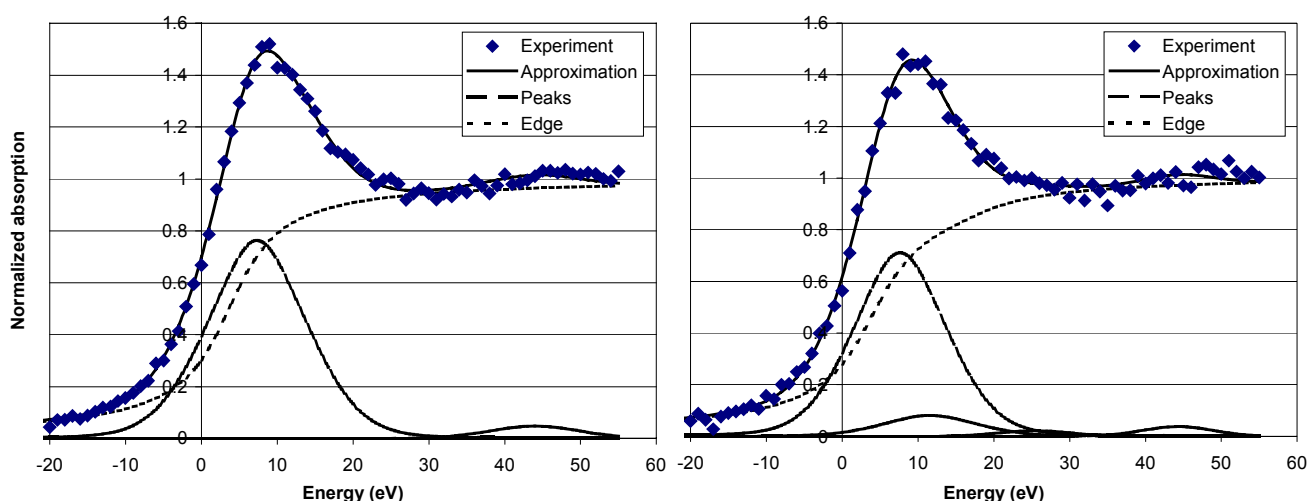


Figure 1: Least squares fitting of the spectra of single particles, (a) Kosovo 4a and (b) Kosovo 4b. The zero of the energy scale was set to the inflection point of the U(IV) standard.

Table 1: Results of least squares fitting of the U-L_{III} XANES spectra of six individual soil particles*

	U(IV) (%)	U(VI) (%)	$I_{u(IV)}$	$I_{u(VI)}$	σ_u (eV)	$I_{s(IV)}$	$I_{s(VI)}$	σ_s (eV)	RMS error
Kosovo 1a	100	0	0.887	0.000	7.789	0.081	0.000	19.560	0.029
Kosovo 1b	79	21	0.817	0.222	6.323	0.115	0.158	6.068	0.023
Kosovo 4a	100	0	0.763	0.000	6.882	0.048	0.000	5.967	0.019
Kosovo 4b	90	10	0.711	0.081	6.363	0.038	0.022	4.656	0.025
Kosovo 4c	92	8	0.736	0.065	6.801	0.072	0.031	5.370	0.031
Kosovo 4d	77	23	0.663	0.200	6.015	0.078	0.121	5.249	0.030

*RMS: root mean square

The measurements performed on these particles showed that the techniques employed is suitable for the determination of the oxidation state of uranium in microparticles. The results indicate that even though the uranium is mainly present in the oxidation state (IV), still a small fraction is found at the oxidation state (VI) which might contribute in mobilisation of uranium in the environment. More data are necessary in order to predict mobilisation mechanisms. In the continuation of the project we plan to collect XANES spectra of a higher number of particles originating from different areas contaminated with radioactive particles.

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