

Study of the oxidation state of uranium and plutonium in Pu/U hot particles released to the environment

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Particles carrying radionuclides in the environment may result from initial release of particles or from a condensation to form solid particles. Nuclear weapon tests and accidents are important sources of environmental release of hot particles. In order to estimate the origin of dispersed hot particles and their environmental behaviour they must be identified and their chemical composition and state must be determined on the microscopic scale. X-ray spectrometry being non-destructive and providing information on elemental composition and oxidation states, is a complementary technique to the nuclear analytical ones for hot particle studies [1]. The radioactive hot particles investigated were separated from contaminated sediment samples collected during two different campaigns at Thule nuclear accident site (Greenland) [2]. Single radioactive hot particles of 30–100 μm in diameter were localised and identified with a digital autoradiograph, the Beta Camera [3]. All the particles were then analysed as for their size, morphology and surface elemental composition with a SEM with an EDX-system.

The oxidation state of uranium and plutonium in the pre-selected individual Pu/U hot particles was investigated at the micro-fluorescence beamline L at HASYLAB using μ -XANES. 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 μm diameter. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the L_3 absorption edge of U and Pu (17167 and 18060 eV) by stepping the Si(111) monochromator, while recording the $L\alpha$ fluorescent yield of the element of interest using an energy-dispersive GRESHAM Si(Li) detector. The used energy step size varied between 0.5 (edge region) to 2 eV (more than 50 eV above edge). Two different uranium oxide (UO_2 and U_3O_8) as well as Pu(IV) and Pu(VI) crystals prepared and tested in house were used as standards. The diameter of the standard particles was between 5 and 20 μm . The measuring time for each energy point varied from 5 s to 20 s depending on the concentration of the element of interest.

A least-squares fitting method developed originally for arsenic K-edge absorption spectra [4] was used for processing the U and Pu L_3 XANES spectra. Analytical functions were used to model the different fine structures in the spectrum. Oxidation states (IV) and (VI) were considered for the fitting, allowing the determination of the ratio of the two oxidation state forms of U or Pu in the particles. In addition to the measured standard spectra, fluorescence mode standard spectra of U(IV) and U(VI) measured by others at NSLS [5] were also used for the spectrum processing.

The U- L_3 and Pu- L_3 μ -XANES spectra recorded at the centre of four U/Pu particles collected at Thule compared with standard spectra are shown in Fig. 1. The zero of the relative energy scale was set to the inflection point of the U(IV) and Pu(IV) standards respectively. All spectra were processed using the least-squares fitting method described above. Table 1 summarises the fitting results obtained for four individual U/Pu particles. I_w and σ_w denote the intensity and width of the white line. 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 25 % indicating that the particles contained mainly the less mobile form of U. Based on the Pu oxidation state results, two kinds of particles can be distinguished. The particles Thu68-3 and Thu68-5 contain Pu mostly (more than 90 %) in the Pu(IV) form. In the particles Thu68-6 and 975374-5, however, the Pu(VI) form is dominant (67–75 %). No correlation was observed between the U and Pu oxidation states [6].

From the results obtained it might be expected that the behaviour of the particles in the environment as well as in human fluids would be different. Leaching of the particles in environmental media and human body fluids needs to be carried out.

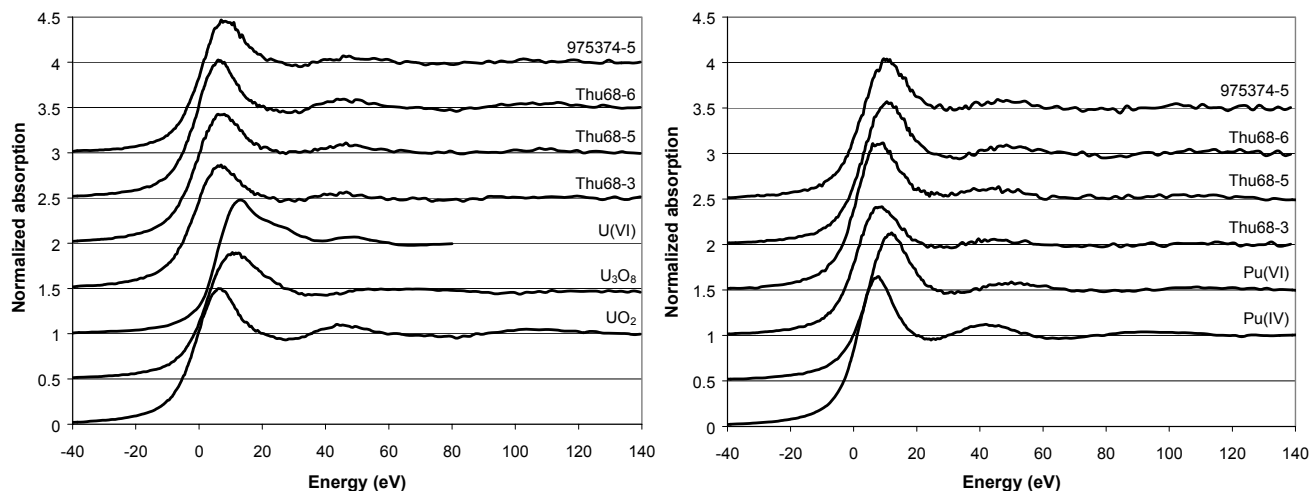


Figure 1: Comparison of μ -XANES spectra of four separated Pu/U particles and the standards, left: U-L₃ edge, right: Pu-L₃ edge

Table 1: Result of least-squares fitting of the U and Pu μ -XANES spectra of four individual Pu/U particles

Particle ID	U(IV) (%)	U(VI) (%)	$I_{w(IV)}$	$I_{w(VI)}$	σ_w	RMS	Pu(IV) (%)	Pu(VI) (%)	$I_{w(IV)}$	$I_{w(VI)}$	σ_w	RMS
Thu68-3	91	9	0.73	0.07	6.97	0.00011	92	8	0.61	0.05	7.13	0.00006
Thu68-5	91	9	0.78	0.08	7.12	0.00011	97	3	0.79	0.03	7.11	0.00017
Thu68-6	100	0	0.91	0.00	6.28	0.00019	25	75	0.23	0.69	6.99	0.00014
975374-5	75	25	0.75	0.25	7.10	0.00014	33	67	0.29	0.57	7.15	0.00018

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