Confocal µ-XANES analysis of the Pu oxidation state distribution in environmental radioactive particles

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Introduction

Radioactive substances released to the environment are mostly in the form of particles. These particles continuously interact with the surrounding environment in different ways. Some environmental processes can lead to dissolution and release of particle bound elements into the biosphere. Other processes, such as sedimentation, may permanently immobilize the particles and particle associated elements from any further interactions with the environment. In order to improve understanding of the long-term impacts of radioactive pollution, it will be important to continue to develop new and improved techniques to determine to the form, nature and potential reactivity of radioactive particles in the environment. We have previously published the results of gamma spectrometry, SEM, 2D µ-XRF, and SIMS experiments on plutonium particles derived from atmospheric nuclear (safety) tests [1]. Here we present the results of µ-XANES analysis on one of these particles.

Methods

XANES is a technique that utilizes a shift in the absorption edge energy of a particular atom in the presence in neighbouring atoms interacting with its outer electrons. In principle, the presence of the more electronegative atom produces partial, positive charging of the central atom and thus increasing its ionization energy. With XANES, the energy of ionization at the inner shell of an atom is measured and information on its charge (oxidation state) can be extracted. For example, XANES spectra of Pu_2O_3 and PuO_2 are shown in fig. 1.

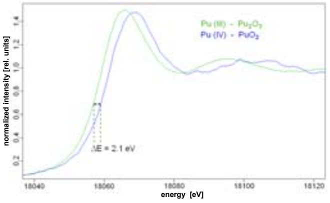

Fig. 1. XANES spectra of plutonium at different oxidation states.

Confocal µ-XRF spectrometer (HASYLAB, Doris storage ring, beam line L; Hamburg, Germany) with Si (111) monochromator was used to acquire the XANES spectra in fluorescence mode. In the fig. 2 the general scheme of the set up and the confocal geometry are presented. The dimensions of confocal spot were found by scanning with 2.5 µm thick Nb foil. A value of 20 µm was obtained as defined by the FWHMs of measured intensity profiles.

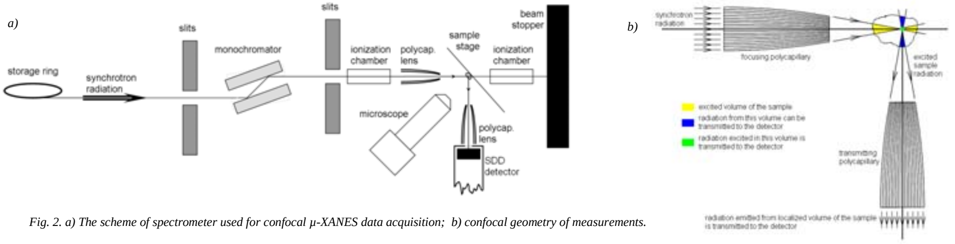

Fig. 2. a) The scheme of spectrometer used for confocal µ-XANES data acquisition; b) confocal geometry of measurements.

During the first measurements a small shift was observed (see fig. 3) when XANES spectra collected at the maximum intensity and close to particle surface were compared.

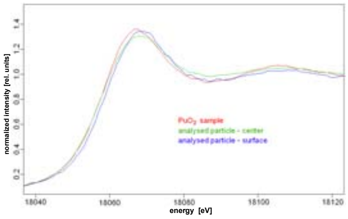

Fig. 3. XANES spectra of a plutonium particle recorded at different spots relative to a Pu (IV) spectrum.

In order to measure the distribution of Pu oxidation state in the particle, a 2D scan with the sample through the confocal spot of the system was performed. The step size of the energy scan across the sectioned particle area was set to 5 µm. To keep time of measurements at a reasonable level, the energy steps were increased up to 2 eV in the edge range and up to 15 eV outside the edge. For each of the energies, the XRF spectrum was recorded for 3 s. From the XRF spectra, Pu La net intensities were extracted to create the XANES data.

As a standard procedure, XANES data are normally fitted with a function consisting of arc tangent step across a small number of gaussian peaks (see fig. 4.). However, this procedure is not applicable where spectra contain a relatively low number of measurement points. In this case, to fit the XANES dataset, a simple linear fit is used (fig. 4.).

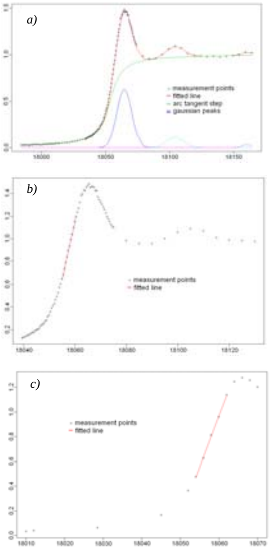

Fig. 4. XANES spectra collected from: a) PuO_2 ample, fitted with full model; b) PuO_2 sample, fitted with simple model, c) particle, fitted with simple model.

From the fitting procedure, three parameters were saved for each measurement point: the energy, its uncertainty, and the height of the absorption edge. The uncertainty of the measured energy was calculated as a standard uncertainty from the fit. The measurement repeatability was not included in the uncertainty estimate. From a series of ten different XANES spectra recorded for PuO_2 under the same conditions, the repeatability of the measurements was equal to 0.026 eV. The height of absorption edge was measured as the difference between summed count numbers from three points just after and before the edge. This value describes the distribution of Pu within the sample. Maps of described factors distribution are presented in fig. 5.

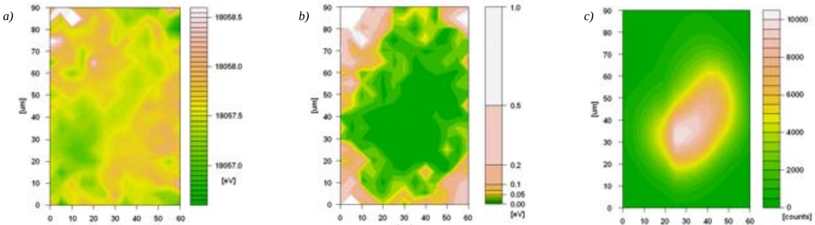

Fig. 5. Distribution maps of: a) Pu L_{III} absorption edge energy; b) uncertainty of the edge energy measurement; c) measured intensity of Pu L_α line.

Conclusions

From the obtained distribution map only small variations, not larger than ca. 0.5 eV, in the Pu L_{III} absorption edge energy can be observed within the sectioned particle area. This is much less than the 2.1 eV variation observed when comparing Pu III and Pu IV spectra. We conclude, plutonium within the whole sample is present at oxidation state +4 with the variations less than 0.25 units, and appears to be irregularly distributed without correlation to the sample shape.

Bibliograpy

[1] Jernström J, Eriksson M, Simon R, Tamborini G, Bildstein O, Carlos Marquez R, Kehl S R, Hamilton T F, Ranebo Y, Betti M (2006) *Characterization and source term assessments of radioactive particles from Marshall Islands using non-destructive analytical techniques*. ***Spectrochim Acta B* 61**:971

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