



	Experiment title: Local structure of PuO _{2+x} nanoparticles formed under acidic conditions	Experiment number: EV-375
Beamline: BM-20	Date of experiment: from: 22.09.2021 to: 25.09.2021	Date of report: 24.01.2022
Shifts: 18	Local contact(s): Kristina Kvashnina, BM20, ESRF Elena Bazarkina, BM20, ESRF	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): * Kristina Kvashnina , ESRF, Grenoble * Anna Romanchuk, Evgeny Gerber, Anastasiya Kuzenkova , Lomonosov Moscow State University		

Report:

Plutonium is one of the most significant elements among actinides due to its high radiotoxicity. Plutonium can migrate at scale of kilometers from previously contaminated sites in the form of intrinsic colloids or “pseudocolloids”. Pu(IV) is highly hydrolysed and demonstrates extremely low solubility. Pu nanoparticles formed during the processes of hydrolysis are appeared to be PuO_{2+x}·nH₂O nanoparticles with size 2-4 nm.¹⁻³ However, the certain structure and stoichiometry of these colloids is still debated.⁴⁻⁷ The complexity of plutonium arises from its chemical properties, as Pu exists in four different oxidation states (III, IV, V and VI) under environmental conditions and all these oxidation states may be presented simultaneously in solution under certain conditions. Moreover, plutonium can easily change its oxidation state due to the values of the standard oxidation-reduction potentials. Therefore presence of oxidation states besides Pu(IV) is an open question and if other oxidation states are present, do they come from precursor solution or exist in nanoparticles.⁸

In our previous work we found that small (2 nm) nanoparticles are formed from the Pu(III), Pu(IV), Pu(V) aqueous solutions at pH 8-12, with the crystal structure close to PuO₂, without any other Pu-O contributions or oxidation states of Pu except Pu(IV).⁹ However there were indirect evidence that Pu at the acidic conditions demonstrates several oxidation states.⁸

We have studied the behaviour of Pu at solid phase and solution with HERFD at Pu M₄ edge to investigate oxidation state of Pu and the local environment. We have measured Pu solution at pH 1 as well as formed under these conditions nanoparticles and bulk PuO₂ used as a reference, the obtained spectra are shown at Fig. 1a. It has been found, that the spectral features of nanoparticles in the solid state can be referred to the corresponding features in the bulk PuO₂, indicating the PuO₂-like structure for nanoparticles. However, the spectrum of solution reveals some additional features, including low energy shoulder at 3.967 keV and peak broadening at 3.971 keV. The shoulder on the left side of the main edge is generally attributed to the presence of a lower oxidation state (i.e. Pu(III)), while peak broadening is an indicator of the presence of Pu(VI), most likely. The exact contribution of each oxidation state of Pu in solution has been achieved with the ITFA-package.¹⁰ The number of principal components needed to reproduce spectra has been determined with principal component analysis (PCA) The contribution of each component has been derived and these contributions are in the order of 30%, 60% and 10% for Pu(III), Pu(IV) and Pu(VI) respectively. Fig. 1b illustrates an individual contribution of each oxidation state. The presence of other oxidation states of Pu besides Pu(IV) arises from disproportionation reactions in the solution, as these reactions are quite intense under these conditions.

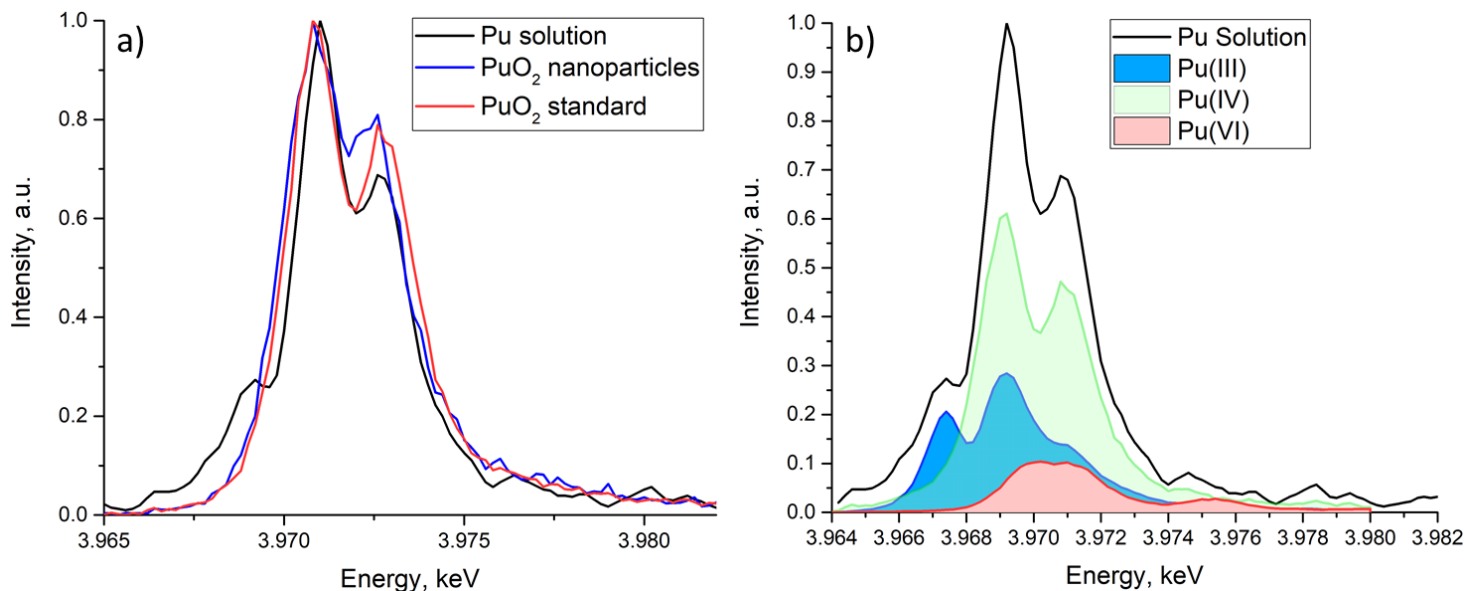


Figure 1. a) Pu M₄ HERFD spectra of solution, extracted PuO₂ nanoparticles and bulk PuO₂, b) contribution of Pu in different oxidation states in the HERFD spectrum of plutonium solution.

Therefore it has been proven, in the wide pH range from 1 to >10 nanoparticles with PuO₂-like structure are formed. In addition, the dominating oxidation state of Pu in HERFD spectra of nanoparticles is Pu(IV), provided nanoparticles have been completely separated from the initial solution (which is especially important in case of acidic conditions), since the latter is the combination of Pu in different oxidation states due to the disproportionation reactions.

These findings have been used in the article which is currently under review in the journal *Environmental Science: Nano*.

Literature

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