ESRF	**Experiment title:** Determination of actinide local chemical environnement and valence state in Plutonium(IV) or Uranium(VI) gels with citric acid or glycine	**Experiment number**: CH-6592
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Report:

Aim of the experiment

The aim of this experiment is to investigate uranium and plutonium valence state and local environnement in gels prepared by dehydration of a nitric solution containing Pu(IV) and/or U(VI) and organic ligands (citric acid or glycine). The study of this gels is of particular interest because they constitute the reactive material for Solution Combustion Synthesis of plutonium and uranium oxides. In this scope, several gels were prepared in Atalante (CEA Marcoule) with glycine or citric acid in various amounts. Uranium and plutonium oxides were also prepared by SCS in order to confirm the uranium and plutonium's valence state at the end of the combustion of the gels. More specifically, EXAFS was conducted in order to probe the Pu and U local environments in gels and oxides. Moreover, HERDF-XANES on simple and mixed actinides gels was used to determine oxidation state of U and Pu.

Results

HERFD measurements on gel containing plutonium and citric acid or glycine allowed to observe differences in plutonium oxidation state according to the organic ligand used in the gel. Especially, recorded spectra for CA/Pu mixtures show a reducing effect of citric acid on plutonium(IV) (Figure 1) whereas in gels containing glycine, plutonium was found to remain at +IV oxidation state.

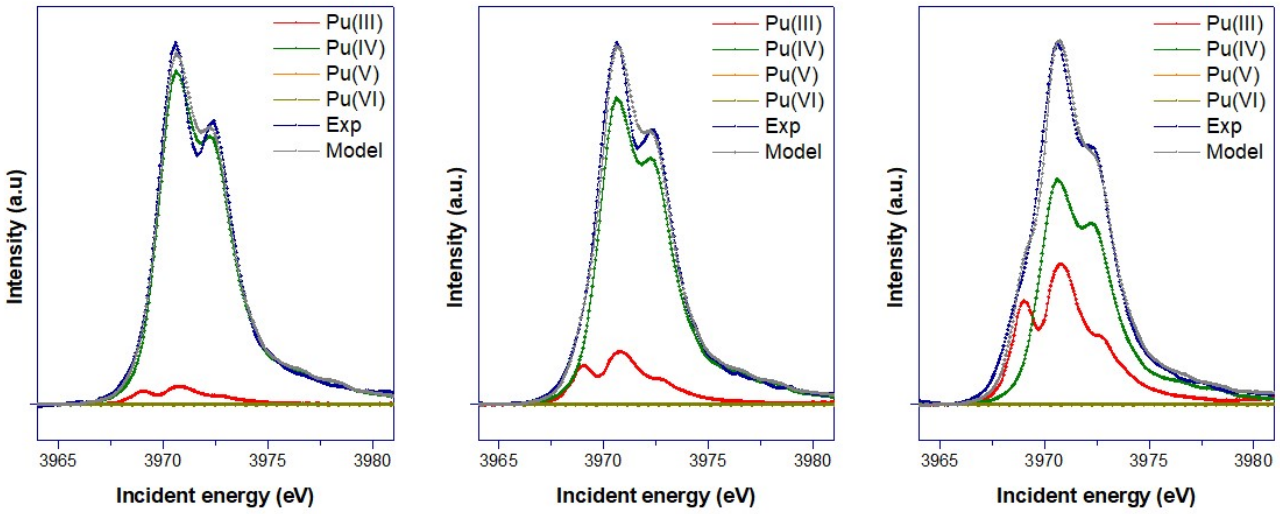
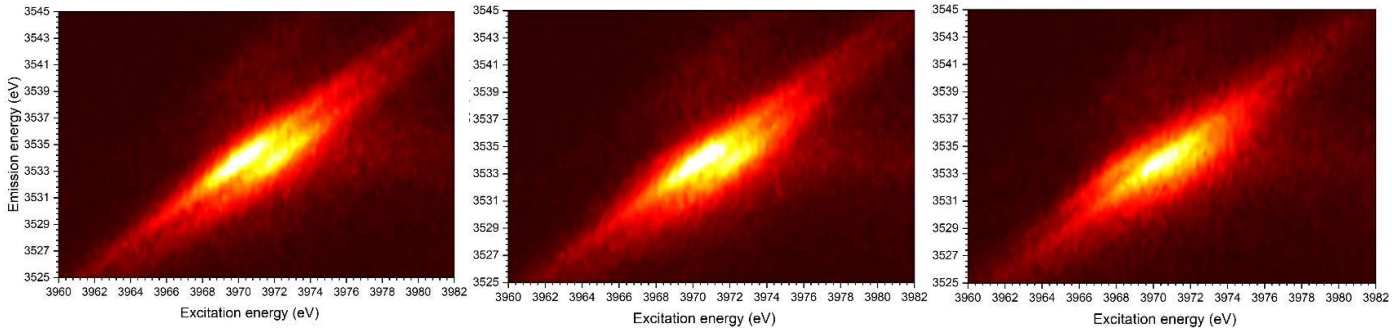


Figure 1: Deconvolution of the HERFD spectra recorded on gel containing plutonium and citric acid

RIXS maps confirmed the results observed on HERFD spectra for gel containing plutonium and citric acid.



Concerning gels containing uranium, HERFD spectra also show a reducing effect of citric acid on U(VI) during the dehydration of the gel. On the other hand, the use of glycine did not show evidence of a change in uranium oxidation state during the gelation.

HERFD analysis on the oxides produced by calcination of the gel (SCS method) allow to confirm oxidation state of uranium and plutonium after the combustion.

The collected EXAFS data from the gels, after processing, will allow us to determine the chemical environment of cations within the gels. These insights will aid in detecting potential differences between gels containing citric acid or glycine. The impact of the cation's oxidation state will also be investigated (Pu(IV) and U(VI)). These findings will be complemented by additional synchrotron analyses to provide a substantial body of results, including the gel without ligands (uranium or plutonium nitrates undergoing the same chemical treatment as ligand-containing gels). The objective is to elucidate the structure of the complexes present in the gel, aiming to explain why their thermal decomposition is more favorable than that of the nitrate alone.

This work shows differences in gels caused by the nature of the fuel used for the combustion (citric acid and glycine). These differences have to be linked to the caracteristics of the actinide(s) oxide powder after the combustion in order to determine which parameters influences the combustion and to help understanding mechanism at stake during ignition of the gel.