



	Experiment title: Chemical state of uranium and thorium in phosphate rock and secondary raw materials for fertilizer production	Experiment number: EV-291
Beamline: ID26	Date of experiment: from: 15.11.2017 to: 21.11.2017	Date of report: 20.02.2018
Shifts: 18	Local contact(s): Rafal Baran	<i>Received at ESRF:</i>
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Report:

We analyzed the chemical state of uranium (U) and thorium (Th) in phosphate rock and secondary raw materials based phosphorus (P) fertilizers by X-ray absorption near edge structure (XANES) spectroscopy.

Uranium and thorium are present in phosphate rock, which is used for mineral fertilizer production, in mass fractions of up to 660 and 220 mg/kg, respectively. These elements can also be found in sewage sludge ash (SSA), which is one of the major secondary raw material for P fertilizers, albeit in lower mass fractions (up to 15 and 10 mg/kg, respectively). Phosphate rock and SSA can be treated thermochemically to reduce its heavy metal content and improve phosphorus bioavailability. However, neither oxidising chlorine conditions nor reducing conditions during the treatment process were suitable to separate U and Th significantly. Therefore, information on the oxidation state and chemical bonding of U and Th in fertilizers is essential to enable a thorough risk assessment of these heavy metals.

We analyzed various P fertilizers on the U and Th L-edge (see Fig. 1 and 2). Different features of the post-edge line were detected for U L-edge HERFD-XANES spectroscopy for the different types of phosphate rock based fertilizer materials (see Fig. 1). Linear combination fitting (LCF) with uranium standards showed that uranium compounds associated to phosphates (e.g. $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$, UO_2HPO_4) are the major U compound of these fertilizers.

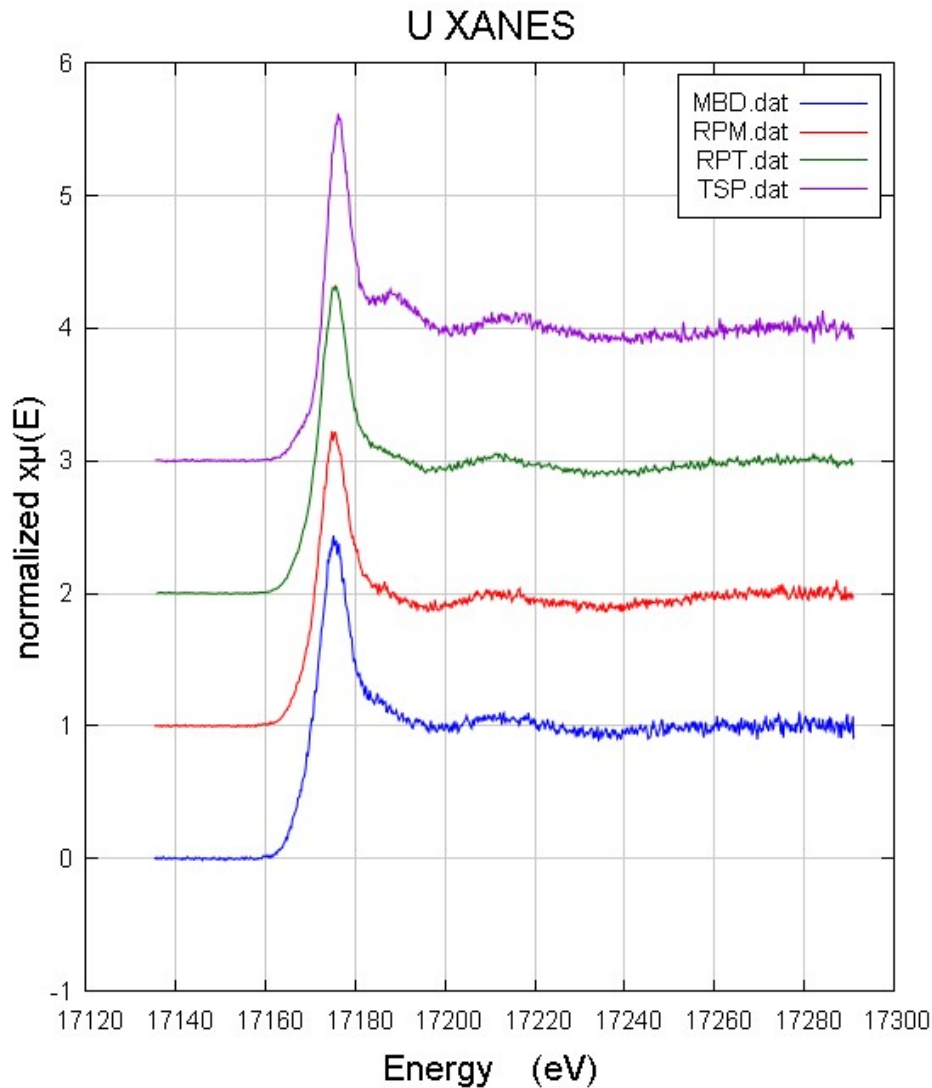


Fig. 1: U L-edge HERFD-XANES spectra of different P fertilizers

Furthermore, different thermochemical treated (various oxidizing and reducing conditions) SSA based P fertilizers were analysed (not shown). However, the U L-edge HERFD-XANES spectra of these fertilizers are very similar. This means that uranium is integrated in the (e.g. phosphate and/or silicate) matrix and is not affected by the treatment processes. This explains why uranium cannot be separated with the used thermochemical treatment processes.

Thorium L-edge HERFD-XANES spectroscopy showed almost no differences of the Th compounds in the various P fertilizers (Fig. 2). The spectra come close to the spectrum of thorium phosphate ($\text{Th}_3(\text{PO}_4)_4$). However, not so many thorium standards were available than for uranium. Thus, different Th compounds could not completely be excluded.

Summarized, we were able to determine the chemical state of uranium and thorium in various P-fertilizers. A paper of these results is in preparation and will be submitted to the Journal of Hazardous Materials.

Th XANES

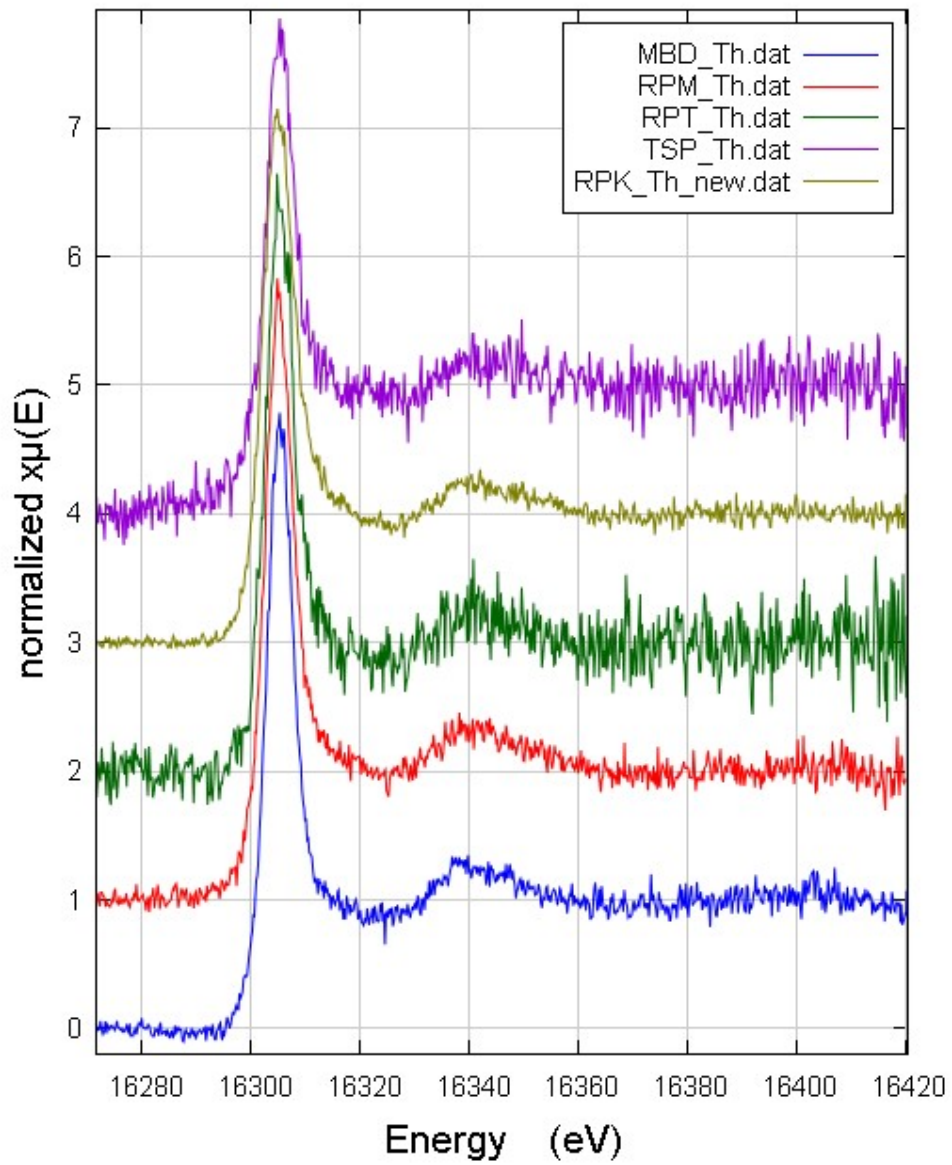


Fig. 2: Th L-edge HERFD-XANES spectra of different P fertilizers