

## Supporting Information

# Back-Extraction of Major Actinides from Organic Phase through Precipitation

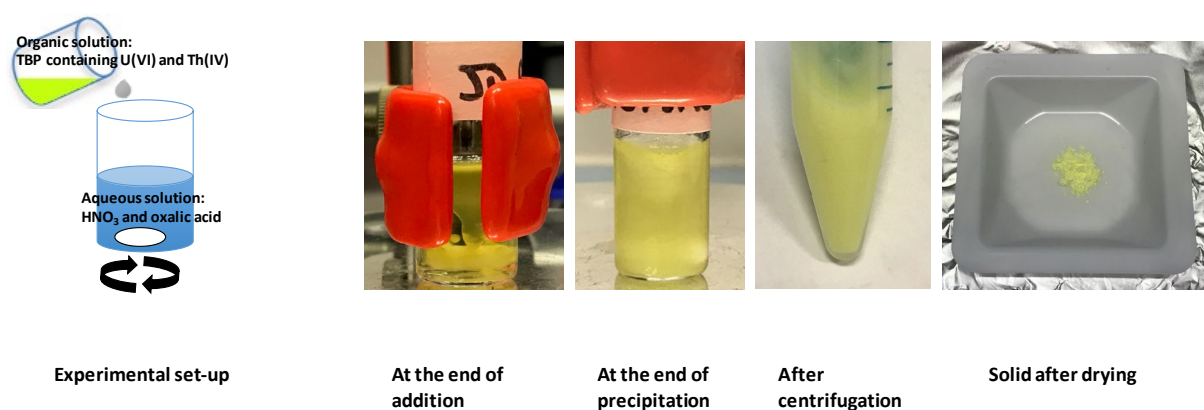
Julie Réaux-Durain,<sup>a</sup> Boushra Mortada,<sup>a</sup> Murielle Bertrand,<sup>b</sup> Jérôme Maynadié,<sup>a</sup> Michaël Carboni,<sup>a</sup> Daniel Meyer<sup>a</sup> and Damien Bourgeois<sup>a\*</sup>

a. ICSM, CEA, CNRS, ENCSM, University of Montpellier, Marcoule, France

b. CEA, DES, ISEC, DMRC, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

\*Corresponding author: [damien.bourgeois@umontpellier.fr](mailto:damien.bourgeois@umontpellier.fr); Tel.: +33 4 66 33 94 92

### Description of experimental set-up



**Figure S1:** Schematic description and pictures of the precipitation stripping experiments.

### ***Aqueous-Phase Oxalic Precipitation of Uranium***

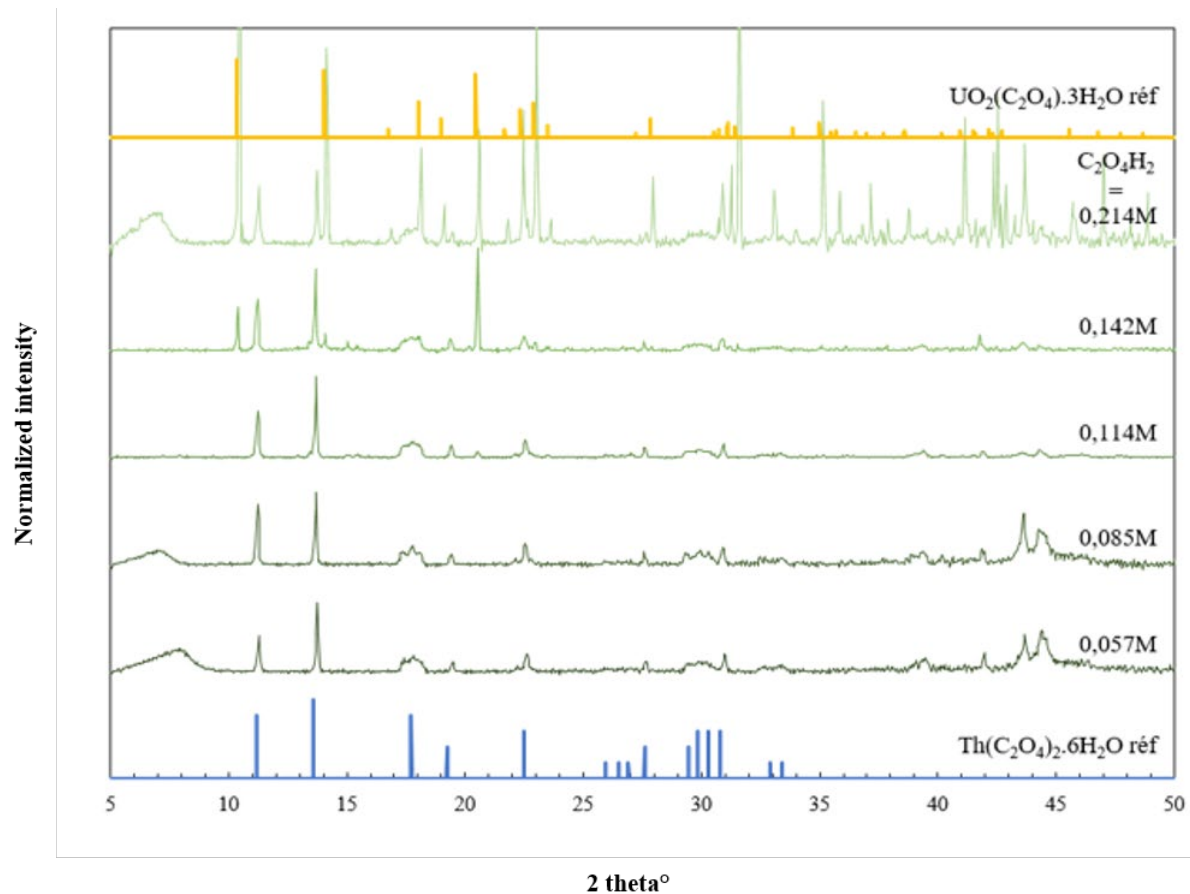
500  $\mu\text{L}$  of an oxalic acid (0.057-0.214 M) solution in  $\text{HNO}_3$  0.1 M were introduced into a 5 mL glass vial. This was followed by the addition of 500  $\mu\text{L}$  of a solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.326 M) in  $\text{HNO}_3$  6 M in a drop-wise manner while stirring at 500 rpm at ambient room temperature. Stirring was maintained for 1 h, after which the aqueous solution and the solid precipitate were separated and recovered through centrifugation. The aqueous phase was stored in an Eppendorf tube for ICP analyses, whereas the solid precipitate was washed with *n*-dodecane, then with heptane and dried at 40  $^\circ\text{C}$  for a few hours.

### ***Aqueous-Phase Oxalic-Co-Precipitation of Uranium and Thorium***

In the aim of comparing the efficiency of the precipitation from the organic phase to that from the aqueous phase, 500  $\mu\text{L}$  of an oxalic acid (0.057-0.214 M) solution in  $\text{HNO}_3$  0.1 M were introduced into a 5 mL glass vial. This was followed by the addition of 500  $\mu\text{L}$  of a solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.326 M) and  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  (0.18 M) in  $\text{HNO}_3$  6 M (while maintaining a U : Th concentration ratio of 9) in a drop-wise manner while stirring at 500 rpm at ambient room temperature. Stirring was maintained for 1 h, after which the aqueous phase and solid precipitate were separated and recovered through centrifugation. The aqueous phase was stored in an Eppendorf tube for ICP analyses, whereas the solid precipitate was washed with minimum aqueous phase and dried at 40  $^\circ\text{C}$  for a few hours.

[C <sub>2</sub> O <sub>4</sub> H <sub>2</sub> ]	0.057 M		0.085 M		0.114 M		0.142 M		0.214 M	
	U	Th	U	Th	U	Th	U	Th	U	Th
Aqueous	100 %	29 %	100 %	N.D.	98 %	N.D.	90 %	N.D.	61 %	N.D.
Solid	N.D.	71 %	N.D.	99 %	2 %	99 %	10 %	99 %	39 %	99 %
(U : Th) <sub>s</sub>	0		0		0.2		0.8		3.3	

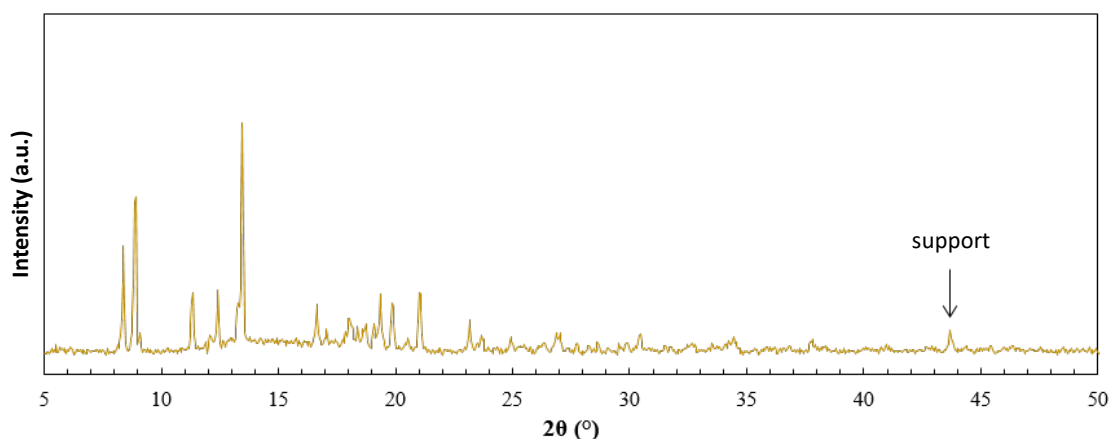
**Table S1.** Variation of the mass percentage of uranium and thorium in the solid precipitate and aqueous phase as a function of the concentration of C<sub>2</sub>O<sub>4</sub>H<sub>2</sub> after aqueous-phase precipitation. Note: [HNO<sub>3</sub>] is fixed at 0.1 M.



**Figure S2.** PXRD patterns of the precipitates obtained from aqueous-phase precipitation of uranium and thorium at variable  $\text{C}_2\text{O}_4\text{H}_2$  concentration and a fixed concentration of  $\text{HNO}_3$  of 0.1 M.

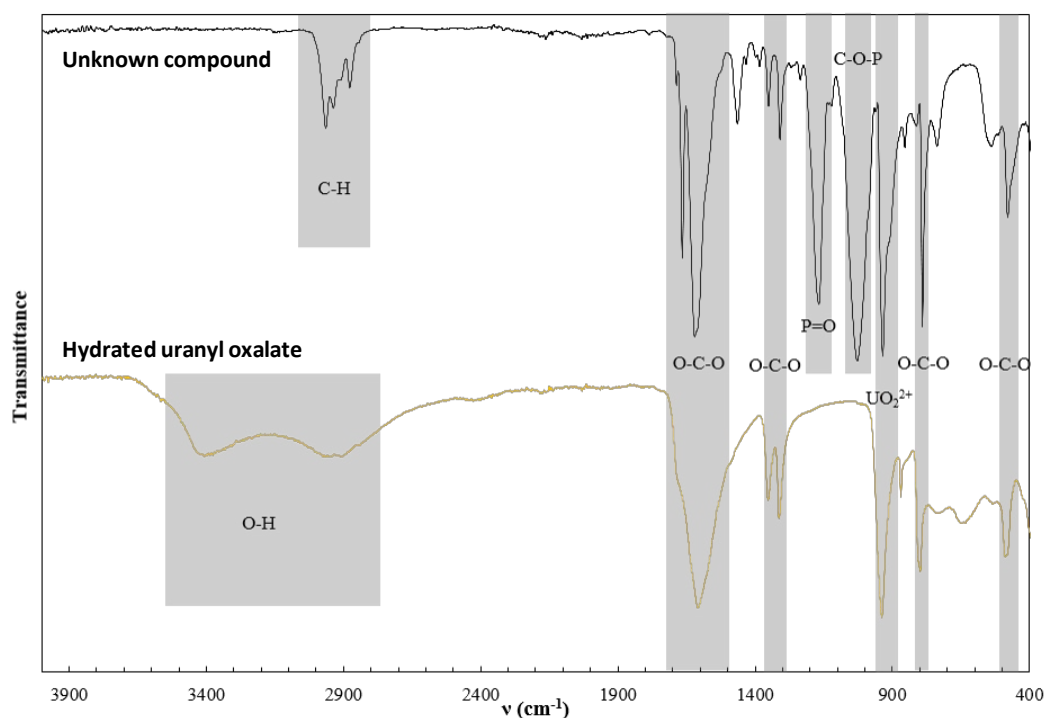
### *Towards the Characterization of the U-TBP-Ox compound*

The unknown phase obtained during the oxalic-precipitation of uranium from the organic phase was intended to be further characterized so as to determine its chemical composition and structure. To this end, organic-phase precipitation was realized from a monometallic solution of uranium in the aim of reproducing the impurity following the protocol applied to the co-precipitation of uranium and thorium from a mixture of both actinides. The experimental conditions involved adding 500  $\mu\text{L}$  of the organic solution highly charged with uranium, which was obtained by liquid-liquid extraction of a solution containing  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  0.326 M in  $\text{HNO}_3$  6M by a TBP/*n*-dodecane 1M solution pre-equilibrated with  $\text{HNO}_3$  6M, to 500  $\mu\text{L}$  of an oxalic acid solution of 0.21 M in  $\text{HNO}_3$  0.1 M. The reaction mixture was then stirred for 1 h at room temperature and at 500 rpm. The obtained precipitate was recovered by centrifugation and exhibited a pale yellow color that is similar to the color of  $\text{UO}_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$ , which may also probably indicate that the uranium contained in the material exhibited a +VI oxidation state (unlike U(IV) that is usually green). The diffractogram of the obtained precipitate is represented in Figure S3.



**Figure S3.** PXRD patterns of the precipitate obtained from organic-phase precipitation of uranium only (at  $\text{C}_2\text{O}_4\text{H}_2$  concentration of 0.21 M and  $\text{HNO}_3$  concentration of 0.1 M).

Furthermore, the obtained precipitate was not soluble in different solvents, including water, ethanol, acetone, diethyl ether, toluene, acetonitrile, tetrahydrofuran and even TBP. EDX analysis was also realized and proved the presence of uranium, carbon, oxygen and phosphorous in the precipitate, which is in agreement with the results obtained for the impurity discussed in the main text. Infrared analysis was also realized on the precipitate and the results are represented in Figure S4 and Table S2. The IR spectra reveal that the impurity exhibited several peaks in common with uranyl oxalate obtained from aqueous-phase precipitation (mainly the corresponding to the vibration of the C-O bond) and with the organic phase containing uranyl nitrate in TBP/*n*-dodecane (mainly corresponding to the vibration of the P=O and C-O-P bonds). However, it was complicated to prove the presence of nitrate based on IR analyses.

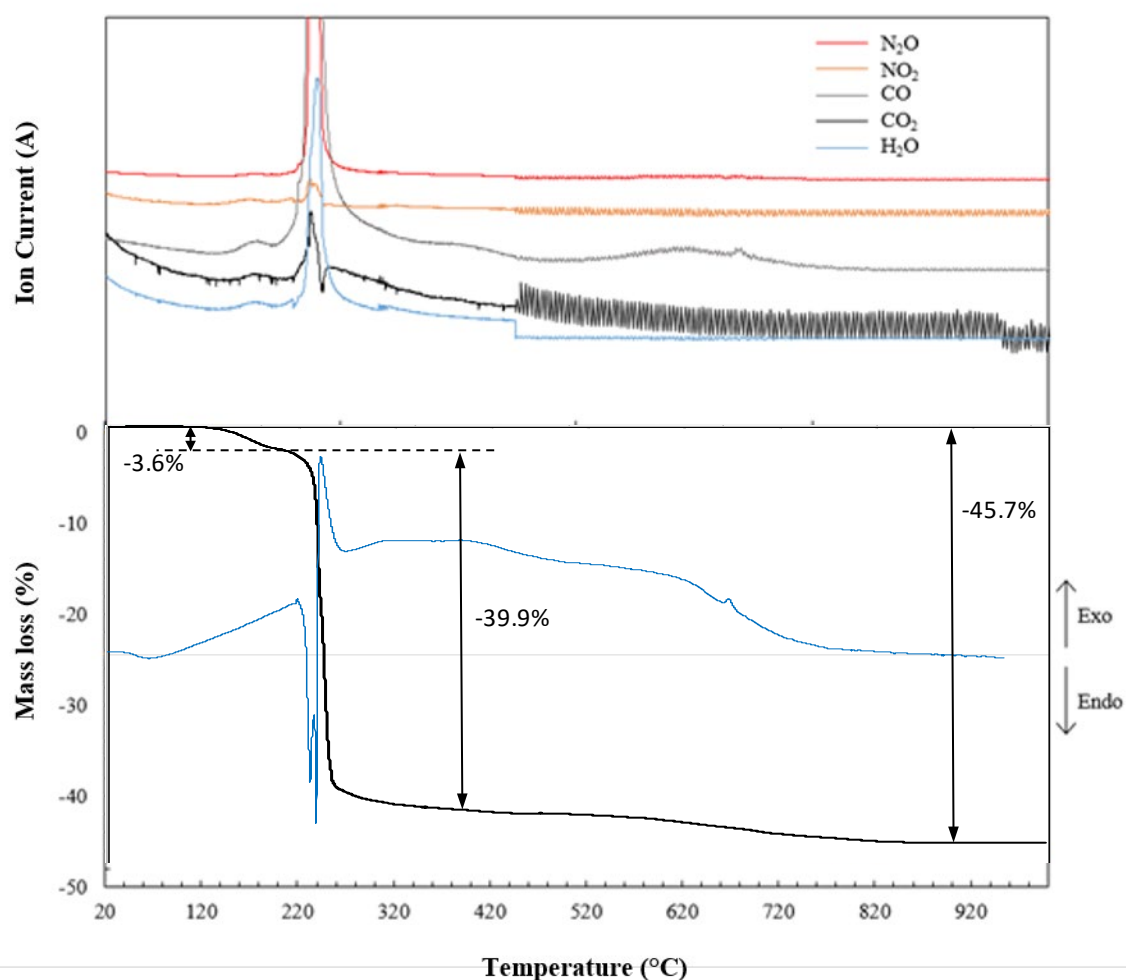


**Figure S4.** Infrared spectra of the impurity and uranyl oxalate trihydrate.

Vibration (cm <sup>-1</sup> )	Organic phase TBP-UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Uranyl oxalate trihydrate	Impurity (mixed composite compound)
$\nu_{\text{asym}}$ O-H (H <sub>2</sub> O)		3400 + 2940 (broad peak)	
$\nu$ C-H (TBP)			3000-2840*
$\nu_{\text{asym}}$ C-O and $\delta$ O-H (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> and H <sub>2</sub> O)		1670	1685 + 1665
$\nu_{\text{asym}}$ C-O and $\nu$ C=O (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )		1607	1618 (broad peak)
$\nu_{\text{asym}}$ ONO (NO <sub>3</sub> <sup>-</sup> )	1527		1525
$\nu$ C-H (TBP)	1466		1463
$\nu_{\text{sym}}$ O-C-O (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )		1351	1350
$\nu_{\text{sym}}$ O-C-O (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )		1312	1309
$\nu_{\text{sym}}$ ONO (NO <sub>3</sub> <sup>-</sup> )	1276		1266
$\nu$ P=O (TBP bonded to U)	1188		1167
$\nu$ C-O-P (TBP)	1028		1026
$\nu_{\text{asym}}$ UO <sub>2</sub> <sup>2+</sup>	939	938	934
$\delta$ H-O-H + $\delta$ O-C-O + $\nu_{\text{sym}}$ C-O (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> and H <sub>2</sub> O)		868	853
?			810
$\delta$ O-C-O (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )		802-797	790
?		725 (broad peak)	735
?		636	
?		532	536
$\delta$ O-C-O (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )		484	478

**Table S2.** Variation frequencies of the bonds and attributions to species present in a TBP solvent rich in uranium, uranyl oxalate trihydrate and in the impurity (mixed composite) obtained from organic-phase precipitation of uranium. \* indicates the presence of more than one peak. Note that these attributions are based on references [1-4].

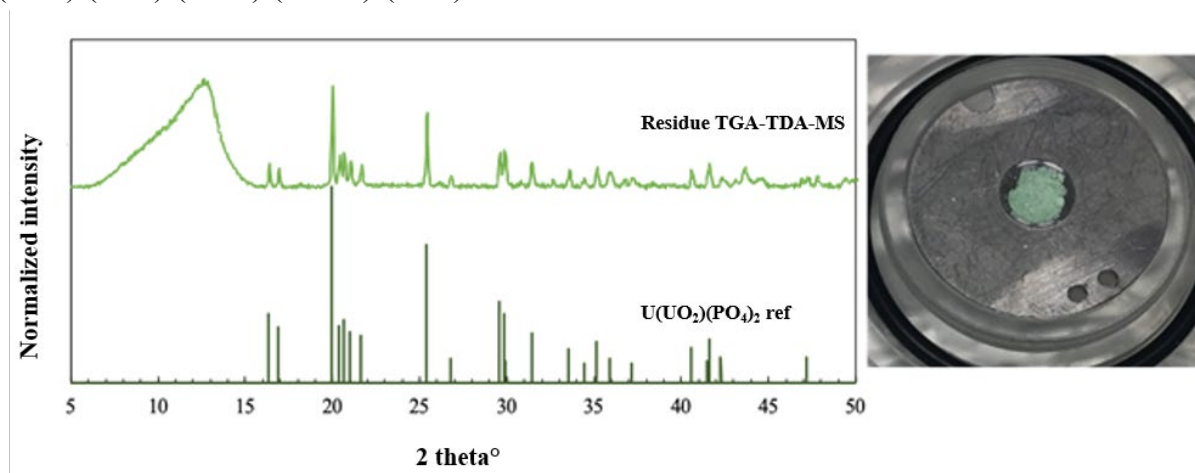
Thermogravimetric and thermodifferential analyses coupled with mass spectrometry (TGA-TDA-MS) were also carried out on the impurity. The analyses were realized under air flow between 22-1000°C with a heating rate of 5°C/minute. Based on Figure S5, these analyses reveal a total percentage mass loss of 45.7%, compared to a theoretical mass loss of 31.9% for uranyl oxalate trihydrate when calcined under air, which confirms that the impurity consists of a higher percentage of organic material compared to uranyl oxalate trihydrate. [5] Furthermore, the liberation of CO, CO<sub>2</sub> and water vapor molecules during the analysis is an additional proof of the presence of oxalate in the impurity, whereas the formation of NO and NO<sub>2</sub> gases confirms the presence of nitrates or nitric acid.



**Figure S5.** TGA-TDA-MS analysis of the mixed composite compound U-Ox-TBP obtained from organic-phase precipitation of uranium.

Finally, the residue obtained after calcination to 1000°C was a grey-to-green powder, which when analyzed with XRD (Figure S6) revealed the presence of peaks characteristic of a mixed-uranium-phosphate compound  $U(UO_2)(PO_4)_2$  containing both U (IV) and (VI). Thus, the impurity can be assumed to be a mixed composite consisting of uranium, oxalate, nitrate or nitric acid and TBP, with a preliminary composition that can be denoted as U-TBP-Ox.

Therefore, based on whether nitrate or nitric acid is present in the mixed composite, its chemical formula can be either  $(U^{IV})_a(UO_2)_b(C_2O_4)_c(NO_3)_d(TBP)_e$  or  $(U^{IV})_a(UO_2)_b(C_2O_4)_c(HNO_3)_d(TBP)_e$ .



**Figure S6.** PXRD patterns of the residue obtained from TGA-TDA-MS analysis and of the mixed-uranium-phosphate compound  $U(UO_2)(PO_4)_2$  (left side). The grey powder corresponding to the residue is also represented (right side).

## References

- [1] N.D. Dahale, K.L. Chawla, N.C. Jayadevan and V. Venugopal, *X-ray, thermal and infrared spectroscopic studies on lithium and sodium oxalate hydrates*, *Thermochim. Acta* 293 (1997), pp. 163–166.
- [2] P.A. Giesting, N.J. Porter and P.C. Burns, *Uranyl oxalate hydrates: structures and IR spectra*, *Z. Für Krist. - Cryst. Mater.* 221 (2006).
- [3] N. Dahale, K. Chawla and V. Venugopal, *X-ray, thermal and infrared spectroscopic studies on potassium, rubidium and caesium uranyl oxalate hydrates*, *J. Therm. Anal. Calorim.* 61 (2000), pp. 107–117.
- [4] E.A. Smirnova, E.M. Pazukhin and A.S. Krivokhatskii, *Size and shape of thorium oxalate crystals as function of preparation conditions*, *Sov. Radiochem.* 30 (1988), pp. 24–29.
- [5] H. Tel, M. Bülbül, M. Eral and Y. Altaş, *Preparation and characterization of uranyl oxalate powders*, *J. Nucl. Mater.* 275 (1999), pp. 146–150.