

Supplementary material

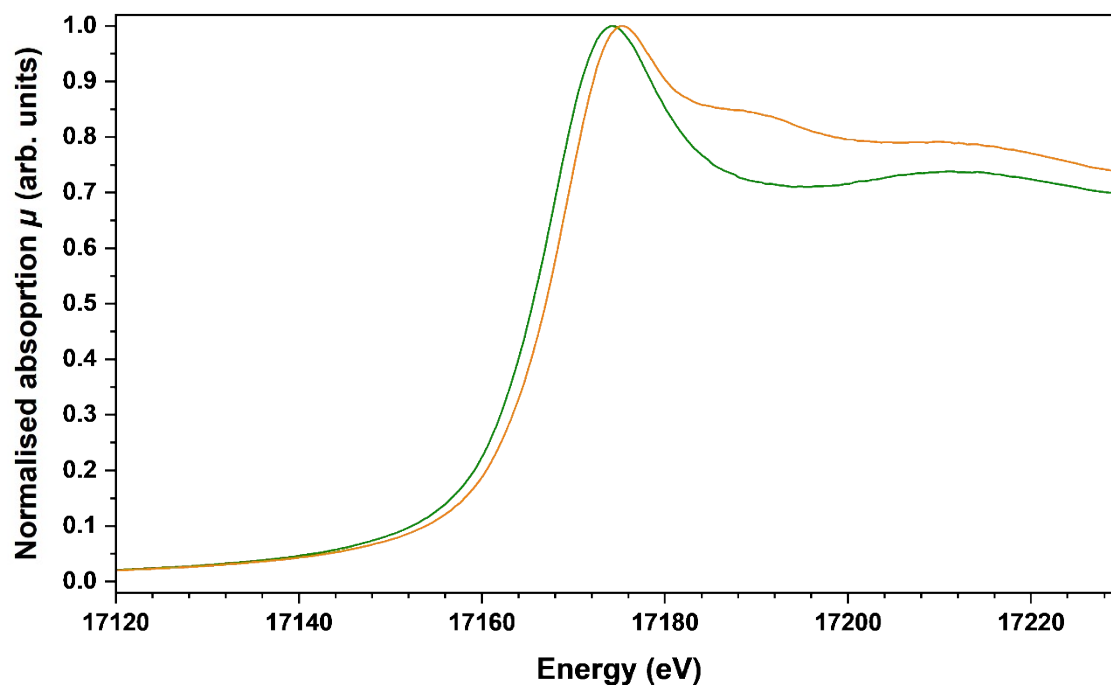


Figure S1. XANES spectra at the U-L₃ edge (fluorescence mode) of reference solutions: uranyl solution in a hydrochloric medium measured at 250°C (orange) and U(IV) solution in a hydrochloric medium measured at room temperature (green). Normalisation was applied at the intensity maximum.

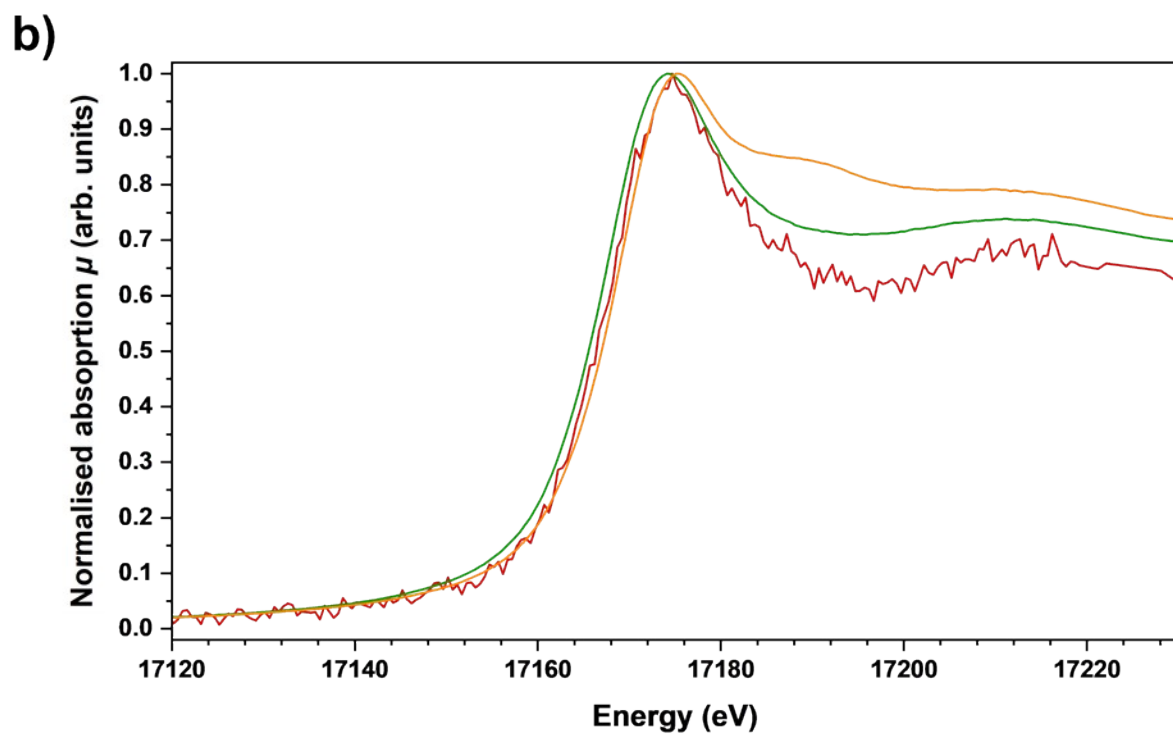
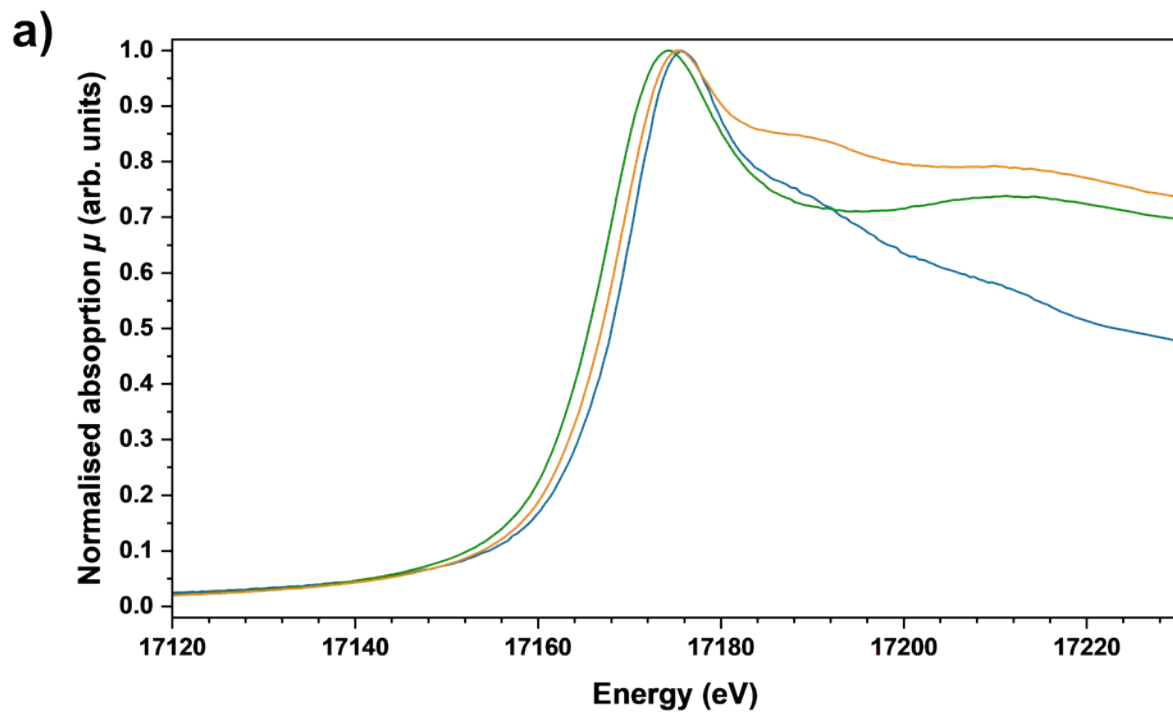


Figure S2. (a) Comparison of the initial spectrum (blue) with the uranium (VI) (orange) and uranium (IV) (green) references. (b) Comparison of the final spectrum (red) with the uranium (VI) (orange) and uranium (IV) (green) references. Normalisation was applied at the intensity maximum.

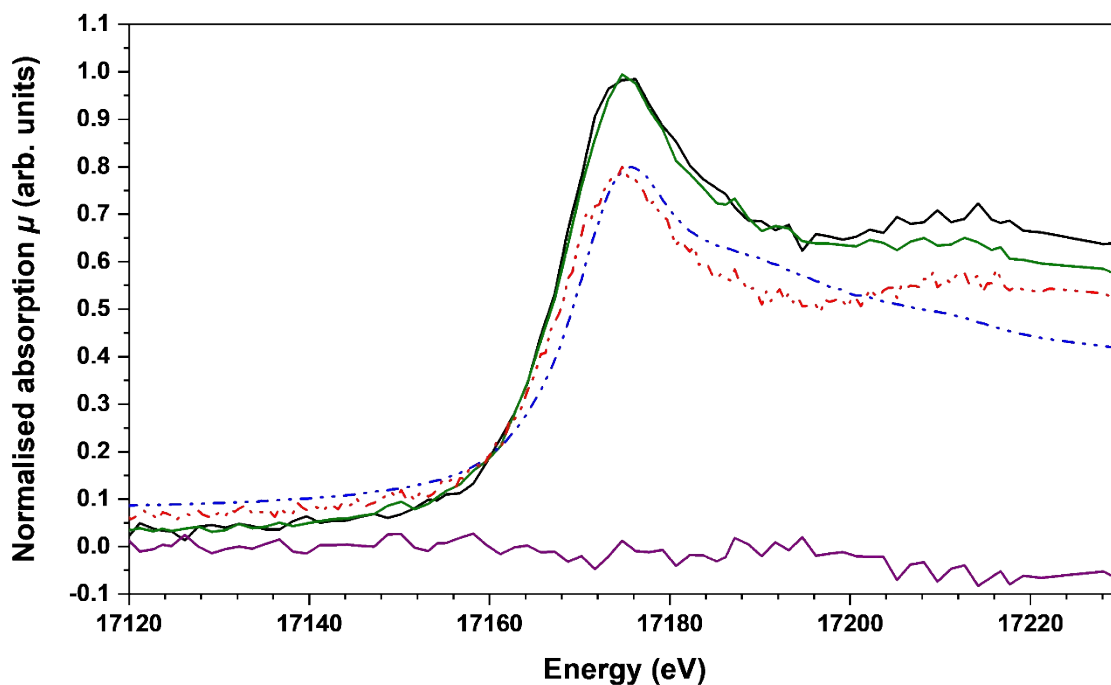


Figure S3. Illustration of the linear combination fitting methodology used to qualitatively estimate the contribution of uranium (IV) and uranium (VI) during hydrothermal treatment. The experimental spectrum recorded during conversion is shown in black. The two references used for the linear combination are the spectrum recorded at the start of the experiment (in blue), reflecting the contribution of uranium (VI), and the spectrum recorded at the end of the experiment (in red), for uranium (IV). The fitted function is in green, while the purple curve represents the residual plot.

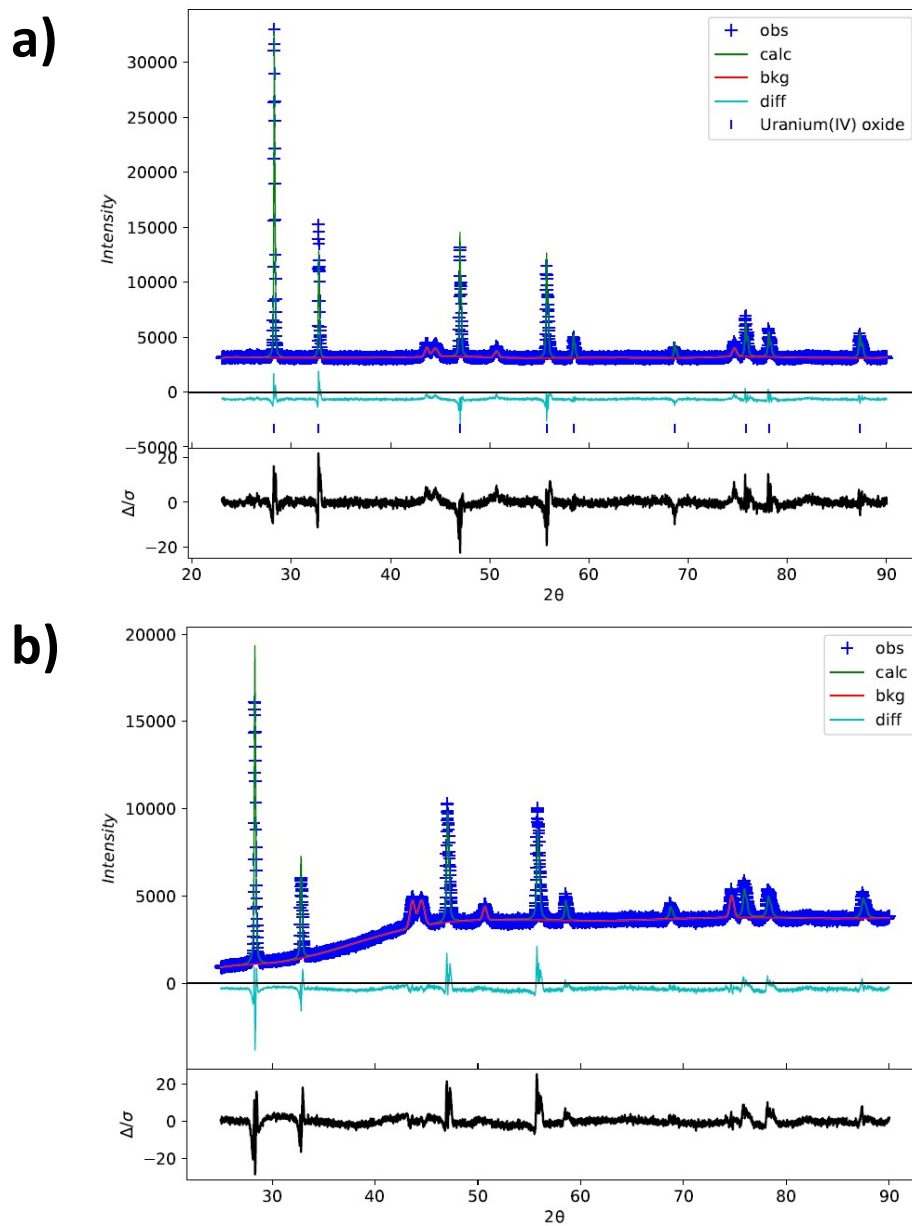


Figure S4. Rietveld refinement plots of the XRD data collected on UO_{2+x} samples prepared by hydrothermal conversion of a U(VI) – oxalate mixture ($T = 250^\circ\text{C}$, $R = 3$, $\text{pH} = 0.8$) during a) 24 hours and b) 168 hours. The blue crosses represent the experimental data, the red line accounts for the subtracted background, and the green line for the calculated pattern. The residue is plotted in black.

Table S1. Rietveld refinement results for PXRD patterns of UO_{2+x} samples formed by hydrothermal conversion of a U(VI) – oxalate mixture ($T = 250^\circ\text{C}$, $R = 3$).

Effect of the initial pH					
Initial pH	Rwp (%)	Average crystallite size UO_{2+x} (μm)	Average crystallite size U_3O_8 (μm)	Wt.% UO_{2+x}	Wt.% U_3O_8
0.8	3.976	3	-	100	-
1.0	5.180	2	10	66.3	33.7
Effect of treatment duration					
Time (hours)	Rwp (%)	Average crystallite size UO_{2+x} (μm)	Average crystallite size U_3O_8 (μm)	Wt.% UO_{2+x}	Wt.% U_3O_8
18	33.963	10	10	61.5	38.5
24	3.976	3	-	100	-
48	61.525	N.D.	-	100	-
72	8.026	1	-	100	-
168	5.276	3	-	100	-