Coupling High-Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS) with microfluidic cells for *in situ* monitoring of tungsten nanoparticles redox transformation

Melanie Auffan [a,b], Amazigh Ouaksel [a], Vladimir Vidal [a], Olivier Proux [c], Jerome Rose [a,b],

a. *CEREGE, CNRS, Aix Marseille Univ, IRD, INRAE, Aix-en-Provence 13545, France*
b. *Civil and Environmental Engineering, Duke University, Durham, NC 27708, USA)*
c. *OSUG, UAR 832 CNRS - Univ. Grenoble Alpes, IRSTEA, INRAE, Météo-France, Grenoble 38000, France*

ABSTRACT

Tungsten is a redox-sensitive transition element of strategic importance for many industrial applications. The functionalities of tungsten-based materials are highly dependent on W atomic structure and oxidation state (0, IV and VI), and the same applies to the toxicity of tungsten compounds. However, assessing tungsten speciation and structural changes in complex materials and environmental matrices (*e.g.* sediments, biota), poses significant challenges necessitating highly sensitive analysis as well as *in situ* monitoring at short timescale.

Conventional XANES spectra at the W L_3-edge (10 207 eV) were obtained on the FAME BM30b beamline (French Absorption spectroscopy beamline in Material and Environmental science) at the ESRF, Grenoble, France using a Si(220) two-crystal monochromator. HERFD-XANES spectra at the W L_3-edge with $L_{\alpha1}$ (~8 397 eV) and $L_{\beta2}$ (~ 9 961 eV) emission lines were obtained on the FAME-UHD BM16 beamline (French Absorption spectroscopy beamline in Material and Environmental sciences at Ultra-High Dilution) at the ESRF with a similar monochromator than on BM30b. For the experiment with the $L_{\alpha1}$ emission line, the Crystal Analyzer Spectrometer (CAS) used 14 crystals Si(444) while for the experiment performed with the $L_{\beta2}$ emission line the CAS used 14 crystals Si(555).

We demonstrated that the better energy resolution in HERFD-XAS (energy bandwidth between 1.2 to 1.5 eV) at the L_3-edge with $L_{\alpha1}$ and $L_{\beta2}$ emission lines would allow the separation, characterization and quantification of subtle changes in the XAS spectrum associated with specific electronic transitions in W(0), W(IV) and W(VI). Moreover, HERFD-XAS combined with a microfluidic chip proved suitable for *in situ* monitoring of changes in W redox states with second-scale temporal resolution.

We pointed out that such an experimental setup would be particularly useful for providing direct insight into the rapid changes in W speciation that would occur under oxidizing environmental conditions.

REFERENCES

Ouaksel, A., Vidal, V., Proux, O., Pailles, C., Rose, J., & Auffan, M. (2023). Coupling High-Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy with Microfluidic Cells for in Situ Monitoring of Tungsten Nanoparticles Redox Transformation. ACS Earth and Space Chemistry, 7(12), 2353-2363.

Ouaksel, A., Carboni, A., Slomberg, D., Vidal, V., Proux, O., Santaella, C., ... & Auffan, M. (2025). Behavior and fate of ITER-like tungsten nanoparticles in freshwater ecosystems produced during operation and maintenance. Journal of Hazardous Materials, 488, 137201.