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Amazigh Ouaksel, Vladimir Vidal, Olivier Proux, Christine Pailles, Jerome Rose, et al.. 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, inPress, 10.1021/acsearthspacechem.3c00217 . hal-04291862

HAL Id: hal-04291862

<https://cnrs.hal.science/hal-04291862v1>

Submitted on 17 Nov 2023

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1 Coupling high-energy resolution fluorescence
2 detected X-ray absorption spectroscopy with
3 microfluidic cells for in situ monitoring of
4 tungsten nanoparticles redox transformation

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11 **Keywords**

12 Tungsten, speciation, redox, HERFD XAS, microfluidic, lab-on chip, in situ monitoring

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19 **Abstract**

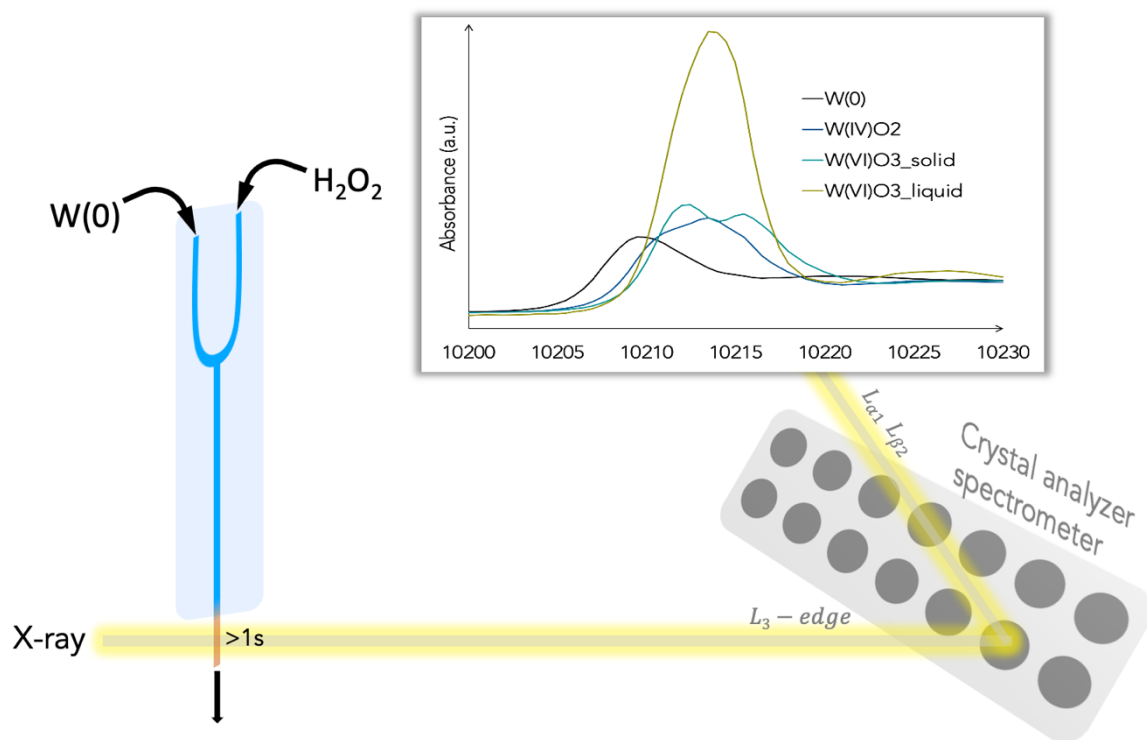
20 Tungsten is a redox-sensitive transition element of strategic importance for many industrial
21 applications. The functionalities of tungsten-based materials are highly dependent on W atomic
22 structure and oxidation state (0, IV and VI), and the same applies to the toxicity of tungsten
23 compounds. However, assessing tungsten speciation and structural changes in complex
24 materials and environmental matrices, poses significant challenges necessitating highly
25 sensitive analysis as well as in situ monitoring at short timescale. We demonstrated that the
26 better energy resolution in HERFD-XAS (energy bandwidth between 1.2 to 1.5 eV) at the L₃-
27 edge with $L_{\alpha 1}$ and $L_{\beta 2}$ emission lines would allow the separation, characterization and
28 quantification of subtle changes in the XAS spectrum associated with specific electronic
29 transitions in W(0), W(IV) and W(VI). Moreover, HERFD-XAS combined with a microfluidic
30 chip proved suitable for in situ monitoring of changes in W redox states with second-scale
31 temporal resolution. We pointed out that such an experimental setup would be particularly
32 useful for providing direct insight into the rapid changes in W speciation that would occur
33 under oxidizing environmental conditions.

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37 Graphical abstract



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40 INTRODUCTION

41 Tungsten (W), a transition element of Group VIb, has proven to be strategic in a variety of
42 fields ranging from catalysis to electronics, due to the high strength and high melting point,
43 resistance to corrosion and electrochromic properties of W metal, oxides, sulfides and alloys ¹.
44 In particular, tungsten compounds are playing an important role in the energy transition ² as
45 tungsten-based materials are used for energy storage technologies (as batteries and
46 supercapacitors), energy efficiency in buildings (as devices for smart windows that
47 dynamically control heat and light transmission), renewable energy technologies (as high-
48 efficiency solar cell and wind turbine components), nuclear energy (as structural materials and
49 neutron reflectors), and in energy-efficient lighting applications (halogen lamps with high
50 luminous efficiency and long lifespan, light-emitting diodes,...) ^{3,4}.

51 Tungsten-based materials functionalities are highly dependent on W atomic structures and
52 oxidation states (W(0), W(IV), W(VI)). But more than the functionalities, the toxicity of
53 tungsten compounds is also speciation-dependent; lower oxidation state compounds being less
54 soluble, less bioavailable, and less toxic compared to those in higher oxidation states as W(VI)
55 ⁵. So far, the rate and mechanisms of metallic tungsten oxidative transformations are more
56 documented in acidic or basic media ⁶⁻⁸ compared to biological or environmental media ⁹⁻¹¹.
57 Investigating thoroughly the electronic structure and local environments of tungsten species in
58 materials and environmental samples is then (i) crucial for unraveling the mechanisms behind
59 their functionalities and (ii) essential to assess potential risks and therefore developing
60 appropriate safety guidelines ^{12,13}.

61 X-ray Absorption Spectroscopy (XAS) has long been a cornerstone technique to probe the
62 oxidation state, coordination environment, ligand identification, and sensitivity to structural
63 changes of metals and metalloids in liquid, solid, and biological matrices. It has been

64 successfully used to identify W speciation in bones ¹³, biological media ¹¹, materials ¹⁴, soils ¹²
65 and catalysts ¹⁵. Two commonly used detection modes in XAS at the W edges are conventional
66 total fluorescence yield mode (conv-XAS) ^{13,16} and High-Energy Resolution Fluorescence
67 Detection mode (HERFD-XAS) ¹⁴. In conv-XAS, detection is typically performed using a
68 solid-state detector (SSD), with energy bandwidth between ~150 to 300 eV, by measuring the
69 main emission lines K_{α} (including both $K_{\alpha 1}$ and $K_{\alpha 2}$) or L_{α} (including both $L_{\alpha 1}$ and $L_{\alpha 2}$). The
70 detection limit with SSD can reach ~10 to 100 $\mu\text{g}\cdot\text{g}^{-1}$ in weight or $<1\text{ mmol}\cdot\text{L}^{-1}$ ¹⁷. In HERFD-
71 XAS, the detection system is based on a crystal analyzer spectrometer (CAS) that allows a
72 better energy resolution (energy bandwidth typically ranging from 0.2 to 2 eV), reduces
73 background contributions, minimizes fluorescence from higher-energy scattering events, and
74 enhances the sensitivity to weak fluorescence signals compared to conv-XAS ^{17,18}. HERFD-
75 XAS is performed by measuring the evolution of the intensity of an emission line of interest or
76 part of it ($K_{\alpha 1}$, $K_{\beta 1,3}$, $L_{\alpha 1}$, $L_{\beta 2}\dots$), the CAS being in most cases optimized at the maximum of
77 this emission line. Conv-XAS and HERFD-XAS can be both used for quantitative
78 determination of the oxidation state or coordination number of an element ¹⁹. However, the
79 higher energy resolution and improved signal-to-noise ratio in HERFD-XAS ²⁰ often lead to
80 more accurate quantitative results, particularly when the sample contains multiple species or
81 subtle spectral changes ¹⁷.

82 This paper aims to demonstrate the added value of HERFD-XAS compared to conv-XAS when
83 deciphering the different oxidation states of W in mixtures. The higher energy resolution in
84 HERFD-XAS would allow the separation and characterization of subtle changes in the XAS
85 spectrum, such as sharp edges, fine structures, and small shifts associated with specific
86 electronic transitions. As such, the better spectroscopic resolution of HERFD-XAS compared
87 to conv-XAS would allow a more precise quantification of the different oxidation states of W
88 in mixtures. For this, we probed the W L_3 -edge by measuring the $L_{\alpha 1}$ and $L_{\beta 2}$ emission lines

89 attributed to the electronic transitions from vacant $3d_{5/2}$ ($L_{\alpha 1}$) and $4d$ ($L_{\beta 2}$) orbitals to $2p_{3/2}$
90 orbital of the transition metal.

91 Both conv- and HERFD-XAS can be performed under in situ or operando conditions, allowing
92 time-resolved monitoring of changes in speciation of metals and metalloids under different
93 experimental conditions. Various devices have been developed over the years for real-time
94 analysis. The dispersive XAS technique, which uses a curved crystal to disperse a
95 polychromatic X-ray beam over the sample, enables a detection speed for a complete EXAFS
96 spectrum of 100 ps per spectrum ²¹. Quick-XAS, which uses a double-crystal monochromator
97 in continuous mode (instead of step mode), also enables rapid acquisition of a complete
98 spectrum for times of the order of a second ²². However, whatever the speed at which spectra
99 are acquired, the signal-to-noise ratio of the spectra represents a real limitation, and in all cases,
100 the sample is constantly evolving during acquisition. The integration of microfluidic chips with
101 XAS has emerged as a promising approach, opening up new avenues for studying, in situ and
102 operando, chemical, physico-chemical and biological systems at a microscale ²³⁻²⁵. Indeed,
103 there has been recently an increasing use of microfluidic cells in environmental applications as
104 water treatment, carbon storage, phosphate immobilization, etc. ²⁶. These miniaturized
105 experimental devices, commonly referred to as "labs on chips," offer ideal micro-platforms to
106 study complex reaction kinetics, diffusion phenomena, and reaction mechanisms under
107 controlled flow conditions, such as mixing, diffusion, and concentration gradients ²⁶.
108 Furthermore, one of the main advantages of microfluidic cells in environmental detection and
109 monitoring analysis is their ability to be easily combined with a wide range of optical,
110 electrochemical, and mass spectrometry detection methods ²⁶. Herein, HERFD-XAS was
111 combined with a microfluid chip for in situ monitoring of changes in W redox states with an
112 enhanced temporal resolution. We suggest that such an experimental set-up would be of interest

113 in providing direct insight into the fast changes (scale of seconds) in W speciation as it might
114 occur in the oxidizing environmental conditions.

115 **EXPERIMENTAL SECTION**

116 **Standard reference compounds and W nanoparticles**

117 Three tungsten reference compounds (W, WO₂, WO₃) were purchased as dry powders from
118 (Merck®). The W powder is 99% certified pure metallic tungsten W(0) with particle sizes
119 smaller than 20 μm and a density ranging from 18.7 to 19.3 g.cm⁻³ at 20 °C. The WO₂ and WO₃
120 powders are micron-sized with a high purity level (trace metal analysis ≤ 150 ppm) of tungsten
121 (IV) dioxide and tungsten (VI) trioxide respectively.

122 For microfluidic experiments, we used a suspension of metallic W nanoparticles (nanoW).
123 They were produced via high-energy planetary ball milling following a previously described
124 protocol^{11,27,28}. These nanoW are crystallized metallic tungsten with an alpha phase structure.
125 Their size distribution is centered on 216 nm (measured by SEM, see SI, Figure S1) and their
126 surface-specific area measured by Brunauer–Emmett–Teller (BET) method²⁹ at 3.2 ± 0.16
127 m².g⁻¹.

128 **X-ray Absorption Near Edge Structure (XANES)**

129 Conv-XANES spectra at the W L₃-edge (10 207 eV) were obtained on the FAME BM30b
130 beamline, French Absorption spectroscopy beamline in Material and Environmental science at
131 the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (Figure 1 top). A
132 Si(220) two-crystal monochromator was used and energy calibration was carried out by setting
133 the first maximum derivative of the XANES spectrum of a W metal foil at 10 207 eV. The
134 monochromator 1st crystal is liquid-nitrogen cooled, allowing to have an optimal energy
135 selectivity, with a 1st crystal rocking curve close to the Darwin width³⁰, i.e. 0.52 eV, and so to

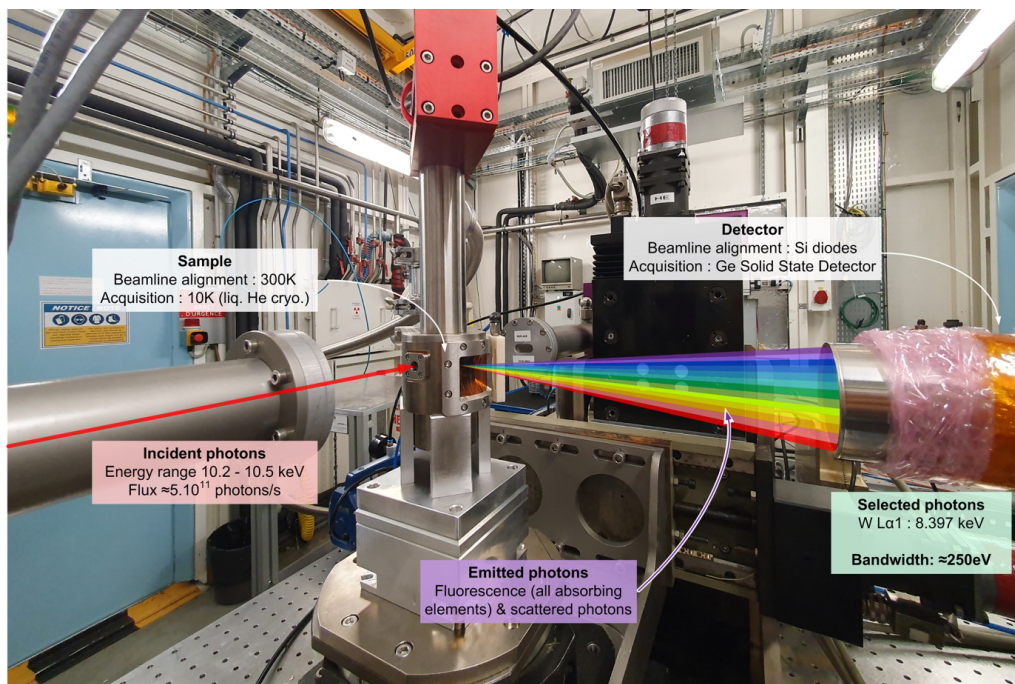
136 obtain spectra with an optimum resolution. For each tungsten reference compounds, 2 to 4
137 spectra were acquired in fluorescence mode using a 30-element Ge semiconductor detector
138 (Canberra).

139 HERFD-XANES spectra at the W L_3 -edge with $L_{\alpha 1}$ ($\sim 8\,397$ eV) and $L_{\beta 2}$ ($\sim 9\,961$ eV)
140 emission lines were obtained on the FAME-UHD BM16 beamline, French Absorption
141 spectroscopy beamline in Material and Environmental sciences at Ultra-High Dilution at the
142 European Synchrotron Radiation Facility (ESRF) in Grenoble, France (Figure 1 bottom). The
143 same monochromator than on BM30b is used (liquid-nitrogen cooled Si(220) first crystal),
144 with the same calibration procedure than for the conv-XANES measurements. For the
145 experiment with the $L_{\alpha 1}$ emission line the beam mode at the ESRF was 7/8+1 (200 mA in top-
146 up mode, with a refill every hour) and the CAS used 14 crystals Si(444). For the experiment
147 performed with the $L_{\beta 2}$ emission line the beam mode at the ESRF was 16 bunch (60-70 mA in
148 top-up mode) and the CAS used 14 crystals Si(555). On both cases, the CAS was aligned with
149 central crystal at 90° with respect to the incident beam, and the other distributed at $\pm 30^\circ$ with
150 respect to the central one (Figure 1 bottom).

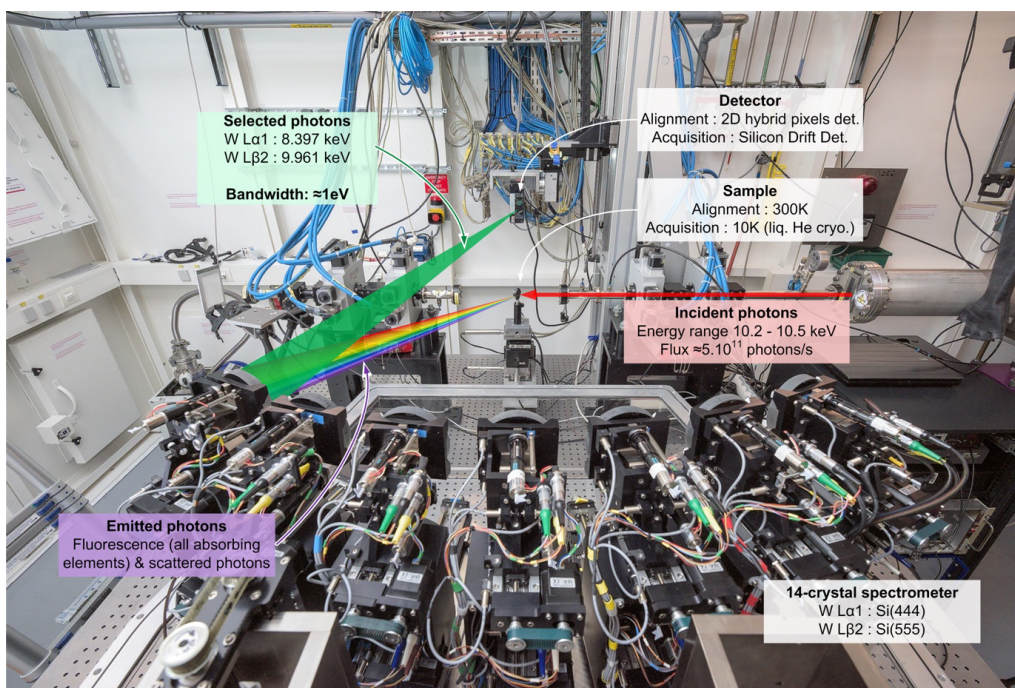
151 Selected photons, diffracted by each crystal analyzer, were collected by either a 2D hybrid
152 pixel detector (S70 ImXpad) for the alignment procedure and for the reference compounds
153 measurements (thanks to its high dynamic range), or an energy-resolved silicon drift detector
154 (AXAS-M Ketek) for the diluted samples measurements (thanks to its energy resolution which
155 allows to discriminate the diffracted photons of interest from the scattered photons due to other
156 emission lines, Thompson and Compton processes). CAS selected energy bandwidths were
157 estimated by measuring the pseudo-elastic peaks corresponding to each reflection, respectively
158 1.2 eV and 1.5 eV for $L_{\alpha 1}$ and $L_{\beta 2}$ (Figure 2 top). After CAS calibration, corresponding non-
159 resonant X-ray emission spectroscopy spectra were measured (Figure 2 bottom). In both cases,

160 positions of the emission lines are found to be independent of the W valence. The emission
161 energy selected by the CAS was then fixed to 8 699.5 eV and 9 964.5 eV for $L_{\alpha 1}$ and $L_{\beta 2}$
162 HERFD-XAS measurements respectively.

163 For both conv- and HERFD-XANES analyses, meticulous care was taken during the
164 preparation of the pellets of the solid reference compounds. Indeed, the quality of XANES
165 spectra with minimal signal-to-noise ratio depends on concentration, homogeneity, and
166 thickness of the samples ^{17,31}. Initially, solid tungsten powders were finely ground and mixed
167 with boron nitride at concentrations of 3000 mg.kg⁻¹ for W, WO₂, and WO₃. The diluted
168 powders were homogenized using a homogenizer (WAB-Turbula[®], Switzerland) and then
169 pressed into 5 mm diameter-pellets. Radiation damages during spectrum acquisition (photo-
170 oxidation and/or reduction) is a critical concern especially for redox-sensitive elements like
171 tungsten ¹¹ under both conventional and HERFD XAS modes. But as the characteristic features
172 of the HERFD-XANES can be more marked than conv-XANES, the consequences of beam
173 damages on the HERFD-XANES shape may appear enhanced ¹⁷. To minimize these radiation
174 damages, pellets analyses were performed using a cryostat at liquid helium temperature and
175 scans (2 to 4 scans per samples) were measured on different areas of the pellets.

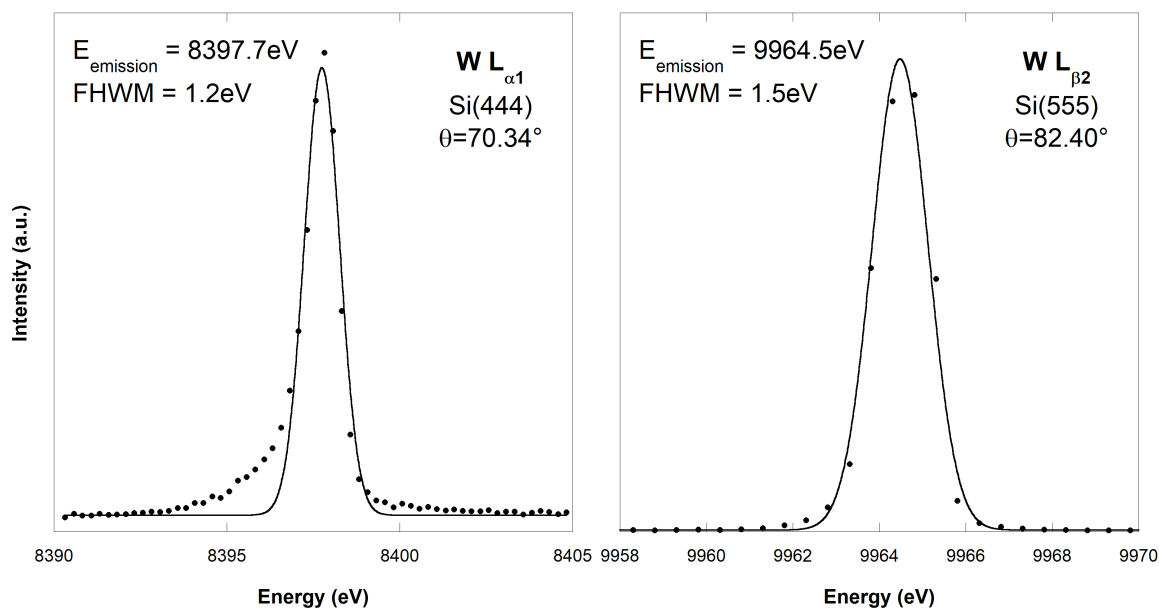


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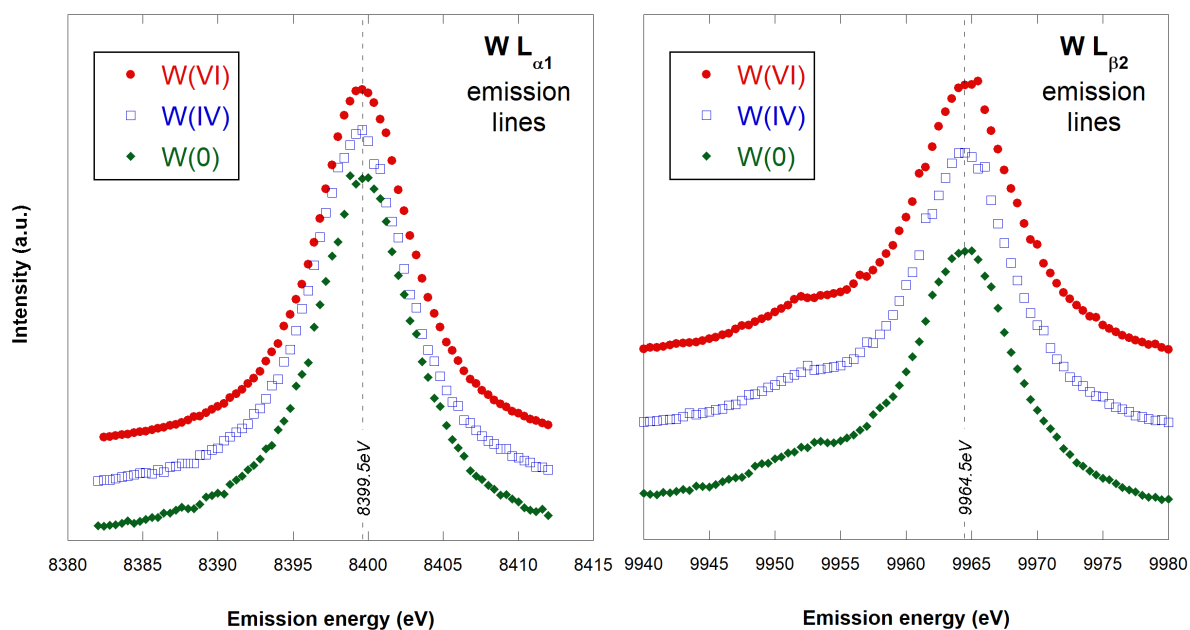


177

178 **Figure 1.** Schemas of the XAS experimental set up of the FAME beamline (BM30b, ESRF)
 179 for conventional total fluorescence yield mode (top) and on the FAME-UHD beamline (BM16,
 180 ESRF) for HERFD detection mode (bottom).



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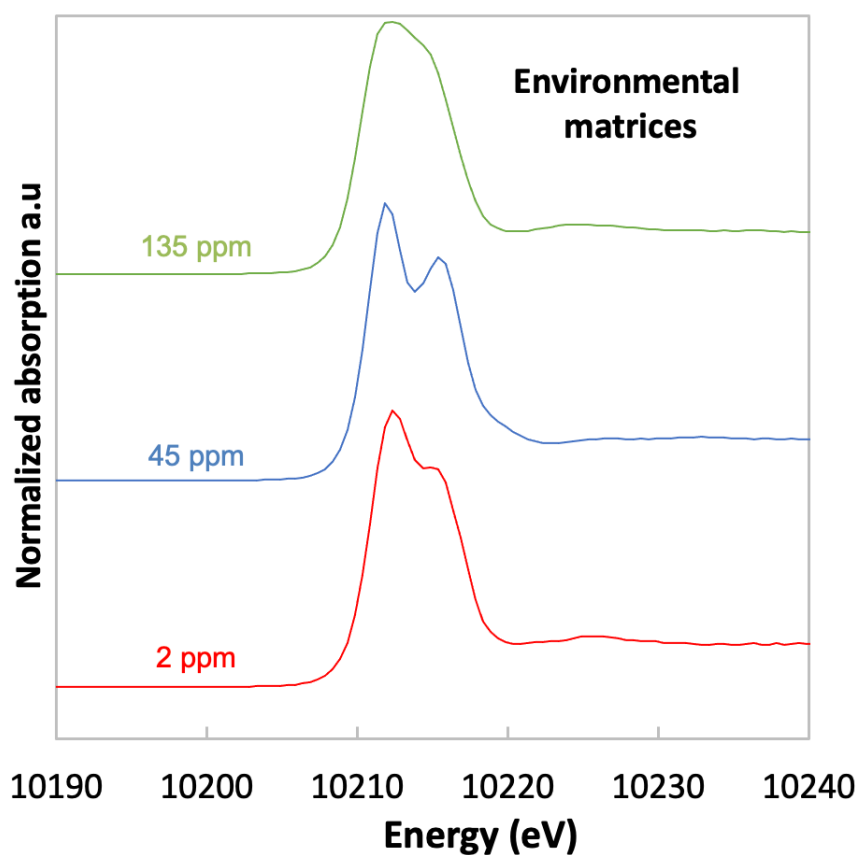
182

183 **Figure 2.** CAS selected energy bandwidths, estimated from the pseudo-elastic peaks and
 184 corresponding to the optimization around the $L_{\alpha 1}$ (left) and $L_{\beta 2}$ (right) emission lines (top).
 185 Non-resonant X-ray Emission Spectroscopy $L_{\alpha 1}$ (left) and $L_{\beta 2}$ (right) spectra of the three
 186 model compounds (bottom). Incident photons energy was fixed to 10 400 eV during XES
 187 acquisition.

188

189 XANES data processing

190 XANES data reduction was performed with ATHENA software ³². To assess whether a better
191 spectroscopic resolution by HERFD-XAS would allow a more accurate quantification of the
192 different oxidation states of W in mixtures compared to conv-XAS, we theoretically-generated
193 3 datasets of more than 30 artificial W multicomponent spectra. These theoretically-generated
194 mixtures were obtained via linear combinations of the conv-XANES or HERFD-XANES ($L_{\alpha 1}$
195 and $L_{\beta 2}$) spectra of the three W reference compounds described above (W, WO₂ and WO₃).
196 Each theoretically-generated mixture was a combination of the three reference compounds,
197 with a minimum contribution of each compound of 10% of the total mixture. A noise
198 corresponding to 2% of the edge step was added to generate theoretical spectra for further
199 Linear Combination Fit (LCF) analysis. This signal-to-noise ratio was estimated on the edge
200 and post-edge regions of experimental XANES spectra measured on environmental samples
201 (sediments, living organisms) containing 2 to 135 mg W.kg⁻¹ (Figure 3). This signal-to-noise
202 is close to the one used in Saurette et al. ³³ and 10 times higher than the one used in Proux et
203 al. ¹⁷. LCF was applied to fit the theoretically-generated spectra with the reference compounds
204 (W, WO₂ and WO₃). For LCF, the uncertainty on the amount of each component was estimated
205 to be approximately 10% of the total amount of the target element ³⁴. Consequently, the
206 attribution of species with values less than 10% should be considered with caution especially
207 if these species do not present striking spectral features.



208

209 **Figure 3.** HERFD-XANES (W L₃-edge with $L_{\alpha 1}$ emission) spectra of environmental matrices
 210 (macrophytes, and sediments initially contaminated with nanoW). The total W concentration
 211 in these samples were ranged between 2 to 135 mg W.kg⁻¹.

212 **Microfluidic device design and HERFD-XAS measurements**

213 The microfluidic cell used was manufactured by stereolithography (3D Printer, Formlabs Inc.)
 214 using a Clear resin[®] in order to be X-ray-compatible via an X-ray-transparent window at the
 215 cell outlet. The cell contained Y-shaped input channels (800 μm radius tubes) joining into to a
 216 115 mm long channel connected to a Kapton tube (10 mm length, 750 μm internal radius).
 217 HERFD-XAS measurements were performed in the Kapton window at the L₃-edge with $L_{\beta 2}$
 218 emission line with X-ray beam dimensions of 200 μm x 100 μm. The microfluidic unit was set
 219 vertically and perpendicularly to the X-ray beam on an x-y-z stage for precise manipulation

220 and alignment, and in Bragg conditions for the detection by the CAS (see SI, Figure S2). To
221 precisely control fluid flow rates and to probe different reaction times at a second scale the
222 flow was controlled in the two channels by a peristaltic pump (BT100S-1, Lead Fluid).

223 The first channel of the microfluidic device was connected to a suspension containing the
224 nanoW at a concentration of 1.14 g of W.L⁻¹ diluted in Volvic[®] water with 2 mmol.L⁻¹ of
225 potassium hydrogen phthalate (C₈H₅KO₄). The pH and Eh of this suspension were 4.6 ± 0.1
226 and 163 ± 1 mV. The potassium hydrogen phthalate (C₈H₅KO₄) was used to prevent the
227 oxidation of the nanoW and to stabilize the pH around 4³⁵. To confirm such a chemical stability,
228 this nanoW suspension was circulated in the microfluidic device in closed-loop mode for 3h.
229 In this control experiment, the Eh (142 ± 1 mV) and the pH remained stable (pH between 4.6
230 ± 0.1 at t₀ and 4.9 ± 0.1 at t_{3h}). No change in the shape or intensity of the HERFD-XANES
231 spectra were observed over time (see SI, Figure S3) confirming the chemical stability of the
232 nanoW during at least 3h.

233 The second channel of the microfluidic device was connected to a 0.8% H₂O₂ solution. By
234 adjusting the flows in the two channels at 204, 102, 76, 61 μL.s⁻¹ we monitored the oxidation
235 state of nanoW after 0.75 s, 1.5 s, 2 s, and 2.5 s of interaction with H₂O₂. For the shorter and
236 longer reaction time points of 0.75 s and 2.5 s, the Reynolds numbers in the cell were 213 and
237 64 respectively, indicating a laminar flow regimen³⁶. For each reaction timepoint, 2 to 3 scans
238 (9 min / scan) were averaged to obtain the final HERFD-XANES spectrum. In such
239 configuration, the nanoW exposure to the X-ray beam is 1.2 to 4.2 ms (100 μm of beam height)
240 minimizing beam damage.

241 Additionally, longer reaction times of 10, 19 and 28 min were examined. In that purpose, the
242 microfluidic device was used in a closed-loop mode: the two input channels and the cell outlet
243 were connected to the same beaker with a constant flow rate of 220 μL.s⁻¹ in the cell . Forty

244 mL of the nanoW suspension (at 1.14 g W.L⁻¹ diluted in Volvic[®] water and with 2 mmol.L⁻¹ of
245 potassium hydrogen phthalate) were mixed with 0.5 mL of H₂O₂ (30%). pH at 4.4 ± 0.1 and
246 Eh 153 ± 1 mV were measured right after the mixing and reach 3.32 and 213 mV respectively
247 at the end of the 28 min-experiment. In that setup, each HERFD-XANES spectra acquisition
248 last 9 minutes with a one-minute delay prior starting data acquisition. LCF was applied on the
249 first derivatives of the spectra acquired in closed-loop mode. These LCF were performed using
250 the spectra of W(0), WO₂ (IV), and WO₃ (VI) solid reference compounds, and the spectra of
251 dissolved W(VI) obtained after dissolution of WO₃ in milli-Q water followed by an
252 ultrafiltration at 3 KDa (Amicon).

253 **RESULTS and DISCUSSION**

254 **Contribution of HERFD-XANES to the detection and quantification of different** 255 **oxidation states of W in mixtures**

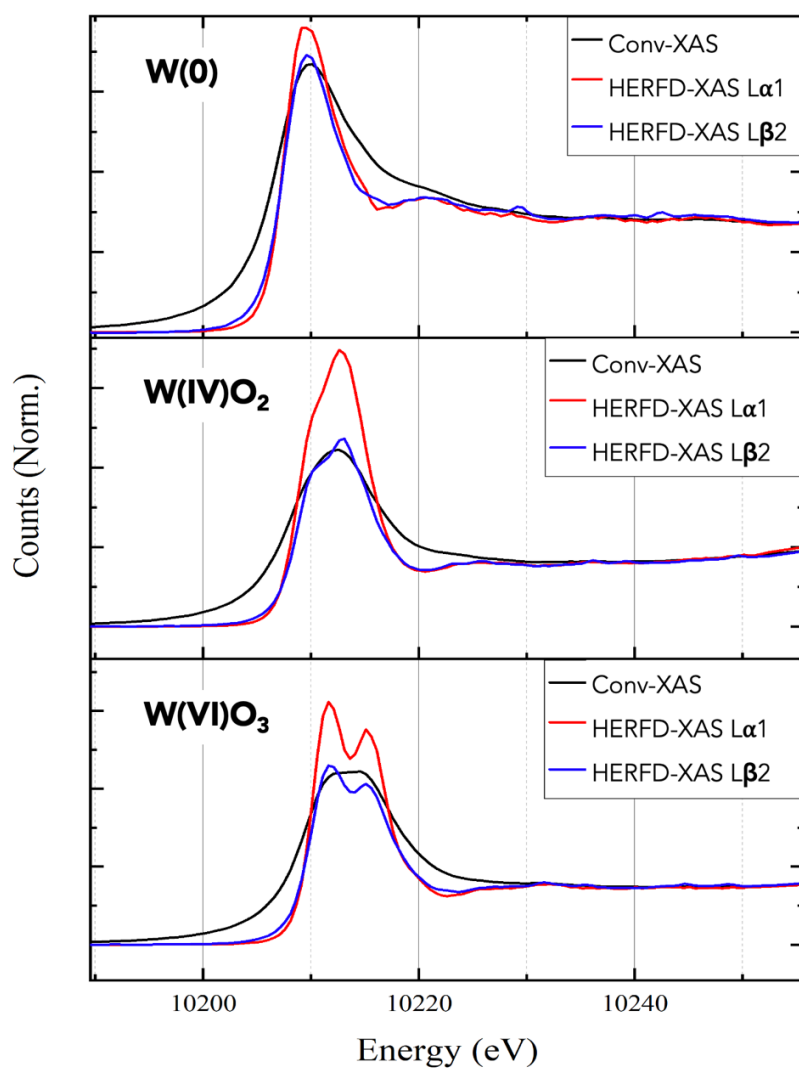
256 The W L₃-edge spectra obtained using the three previously described fluorescence
257 measurements mode and for three W model compounds (W, WO₂, and WO₃) are gathered on
258 Figure 4. The first observation one can make is that, for a given model compound, the spectral
259 resolution of the conventional spectrum is lower than the HERFD ones. Such improvement is
260 well-known and well documented since the first paper by Hämäläinen et al.³⁷. Briefly, this was
261 attributed to the relevant core-hole lifetimes involved in the processes. In conventional mode,
262 the final state has a core-hole on the 2p_{3/2} level with a lifetime of 4.81 eV³⁸. In HERFD mode,
263 the final state has a core-hole on the 3d_{5/2} level (case of L_{α1}-HERFD measurement) with a
264 lifetime of 1.7 eV, or on the 4d ones (case of L_{β2}-HERFD measurement) with a lifetime of
265 around (4 eV)³⁸; the fluorescence lines corresponding to the 3d_{5/2} → 2p_{3/2} (L_{α1}) and 4d →
266 2p_{3/2} (L_{β2}) transitions. HERFD measurements are possible when the energy bandwidth of the
267 fluorescence measurement is lower than these characteristics lifetimes, which is the case here.

268 In conventional mode, different absorption features are observed at approximately 10 209, 10
269 213, and 10 214 eV for W(0), W(IV)O₂, and W(VI)O₃ respectively. Despite these shifts in
270 energy, these 3 spectra did not exhibit any marked features. In HERFD mode, a significant
271 shift of the absorption energy was observed between the HERFD-XANES spectra of W(0) (10
272 207eV) and W(IV)O₂ (10 212 eV) with sharper features compared to conv-XANES. Moreover,
273 the HERFD-XANES spectrum of W(VI)O₃ exhibited a splitting of the white line not detected
274 in conv-XANES, with two distinct peaks at 10 211 and 10 215 eV. Similar sharper features
275 and white line splitting were observed with both $L_{\alpha 1}$ and $L_{\beta 2}$ emission lines. The spectral
276 resolution is slightly better using the $L_{\alpha 1}$ emission line than the $L_{\beta 2}$ one and definitely better
277 when compared with the conventional mode, which is consistent with the fact that the
278 corresponding probed core-hole lifetimes evolve in the same way: 1.7 eV ($L_{\alpha 1}$ -HERFD-mode)
279 < 4eV ($L_{\beta 2}$ -HERFD-mode) < 4.81eV (conv-mode).

280 XANES around the W L₃-edge consists of electron transitions from 2p_{3/2} orbitals to vacant 5d
281 orbitals. The two peaks in the white line of W(VI)O₃ are due to the splitting of the 5d states
282 into 5d(t_{2g}) and 5d(e_g) sub-bands¹⁶. In our experimental configuration, the HERFD-XANES
283 spectra were sufficiently resolved to distinguish the splitting of the white line which
284 characterizes the octahedral coordination of W(VI) in WO₃ powders. These findings are
285 consistent with a previous study on the thermochromic phase transition in CuMo_{1-x}W_xO₄ solid
286 solutions at the W L₃-edge using resonant X-ray emission spectroscopy¹⁴. These authors
287 highlighted that the crystal-field splitting energy for octahedral coordination is approximately
288 3-4 eV. Herein, the obtained value is completely coherent with this splitting.

289 Such features can also be observed on HERFD-XANES spectra (W L₃-edge with $L_{\alpha 1}$ emission)
290 of environmental samples (macrophytes and sediments containing 2 to 135 mg W.kg⁻¹) initially
291 contaminated with nanoW (Figure 2). In these samples, the white lines are shifted to energies

292 corresponding to oxidized form of W with more or less marked splitting. In environmental
293 sciences, such a precise discrimination of the local structure around the W atom allowed by
294 HERFD-XAS is crucial since different tungsten oxidation states (0, IV, or VI) and different
295 coordination (tetrahedral or octahedral) can be evidenced.



296

297 **Figure 4.** XANES spectra of W(0), W(IV)O₂ and W(VI)O₃ standard reference compounds
298 obtained at the W L₃-edge in both conventional and HERFD modes with L_{α1} and L_{β2} emission
299 lines respectively.

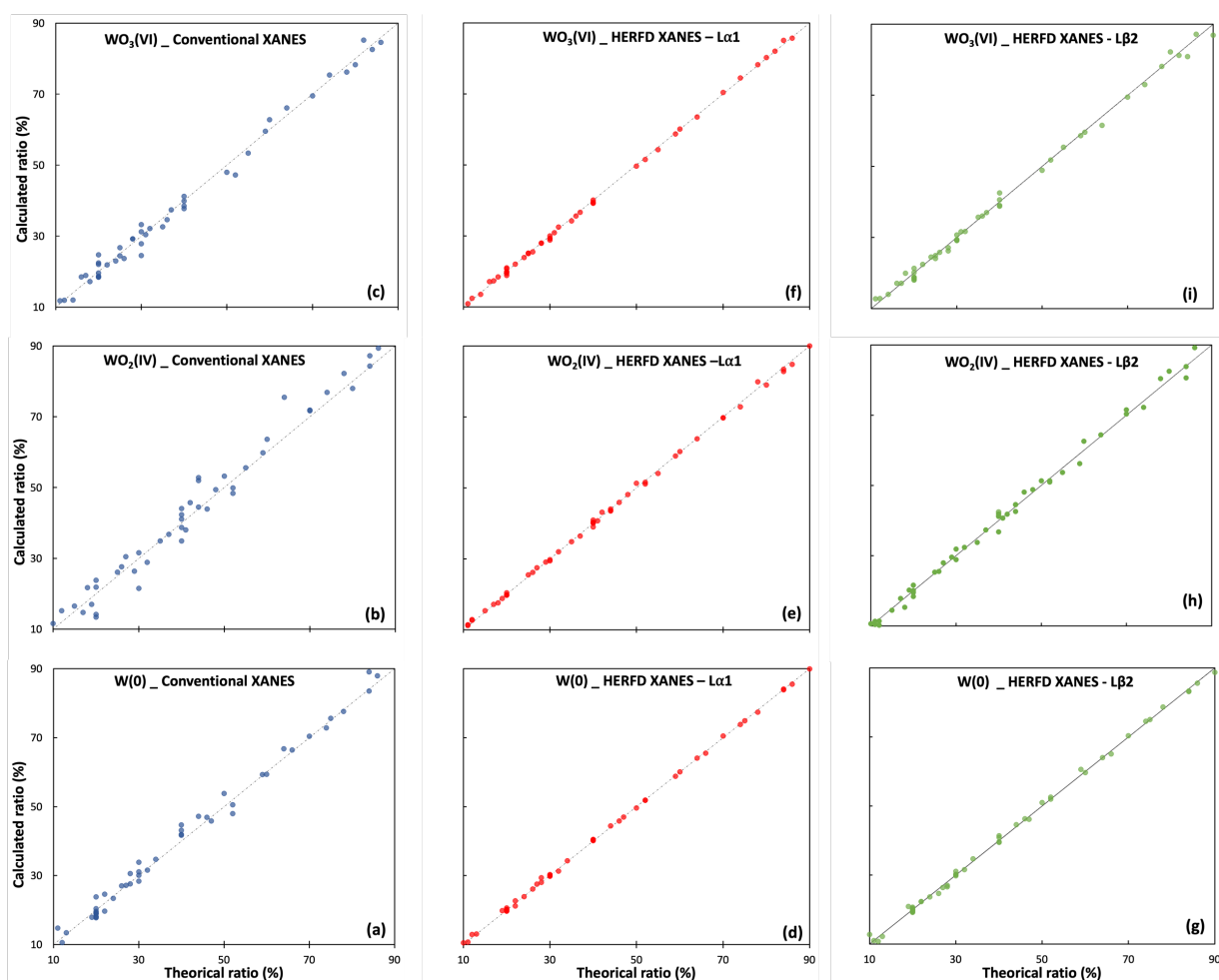
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301 **Quantitative comparison of HERFD and conventional XANES spectroscopy**

302 Following the approaches outlined by Proux et al. and Saurette et al.^{17,33} LCF analysis were
303 carried out on the 3 sets of theoretically-generated spectra acquired in conventional, HERFD
304 $L_{\alpha 1}$ and HERFD $L_{\beta 2}$ modes respectively. Then the standard errors between the theoretical
305 percentage of compounds used and the percentages obtained by LCF were calculated (Figure
306 5 and Table 1). The standard errors ranged from 1.2 to 2.3 % for the conventional mode while
307 they were ≤ 0.4 % and ≤ 0.9 % for the $L_{\alpha 1}$ and $L_{\beta 2}$ HERFD modes respectively. For W(0)
308 quantification, the standard errors for $L_{\alpha 1}$ and $L_{\beta 2}$ HERFD datasets were 4.5 and 2.5 times
309 lower than conv-mode. For W(IV)O₂ quantification, the standard errors for $L_{\alpha 1}$ and $L_{\beta 2}$
310 HERFD datasets were 6 and 2.6 times lower than conv-mode. For W(VI)O₃ quantification, the
311 standard errors for $L_{\alpha 1}$ and $L_{\beta 2}$ HERFD datasets were 4 and 1.5 times lower than conv-mode.
312 Such improvements in the precision of LCF were already observed in the literature when using
313 HERFD-XANES spectra at the As and Hg-edges compared to conv-XANES spectra. Proux et
314 al.¹⁷ observed a 8-fold improvement in precision when applying LCF to reconstruct 50
315 theoretical spectra, using HERFD-XANES spectra of four mercury reference compounds.
316 Saurette et al.³³ calculated the standard error of the LCF with 8 As reference compounds
317 (reconstruction of 3500 computer-generated arsenic mixtures) of the HERFD-XANES and
318 compared to the LCF of the transmission-XANES spectra. The authors observed an
319 improvement in the precision of the LCF when using HERFD-XANES for 4 out of the 8 As
320 reference compounds investigated. These improvements are in good agreement with our study.

321 The XANES signal of W(IV)O₂ is particularly interesting to consider since it shows the highest
322 improvement in term of quantification using HERFD-XANES. Indeed, spectra reconstruction
323 using LCF is greatly influenced by the spectral features of the reference compounds. Herein,
324 HERFD-XANES spectra of W(IV)O₂ reference compound were sharper and exhibited higher

325 spectral resolution compared to the conventional mode which resulted in a more precise
326 detection and quantification. This is of major interest, as it enables the W(IV) oxidation state
327 (important intermediary product during the tungsten oxidation and dissolution) to be
328 distinguished from other oxidation states and quantified when studying oxidative
329 transformations of tungsten.



330

331 **Figure 5.** Comparison of the theoretically percentage used to create the theoretically-generated
332 spectra versus the percentages determined from LCF. Results from conv-mode are in blue,
333 from $L_{\alpha 1}$ HERFD-mode in red, and from $L_{\beta 2}$ HERFD-mode are in green. LCF that perfectly
334 replicated the data would result in points that align along a line with a slope of 1 (grey dashed
335 line).

336 **Table 1.** Standard errors in percentage for LCF results for each W reference compound, in all
337 theoretically-generated mixtures (conv-XANES and HERFD-XANES). A lower value
338 indicates LCF results close to the theoretical mixture composition.

XANES ACQUISITION MODE	W(0)	W(IV)O ₂	W(VI)O ₃
CONVENTIONAL	1.3	2.3	1.2
HERFD $L_{\alpha 1}$	0.3	0.4	0.3
HERFD $L_{\beta 2}$	0.5	0.9	0.8

339

340 HERFD-XAS and microfluidic coupling for improved temporal resolution and 341 monitoring of short kinetics transformation of W compounds

342 In addition to discriminate and quantify the different oxidation stages of W in mixtures, XAS-
343 HERFD can also respond to another challenge in environmental sciences: understanding the
344 tungsten oxidation process on short timescales *in situ*. Indeed, tungsten oxidation kinetics and
345 mechanisms can be complex in the environment, involving multistep reactions and
346 intermediate species formation¹¹. These complexities arise from the multiple oxidation states
347 of W, but also from the variations in environmental conditions in term of pH, Eh, temperature,
348 illumination, ionic strength, as well as the presence of other aqueous species or biota. All these
349 parameters may enhance or inhibit W oxidation and consequently its impacts of human and
350 environmental health^{39,40}.

351 Recently, Sanles-Sobrido et al.¹¹ proposed a pathway explaining the oxidation of metallic W
352 particles in biological media with three interfaces defined between the W(0) particle core, a
353 WO₂ subsurface layer, a WO₃ surface layer and W aqueous species¹¹. The authors highlighted
354 that even if WO₂ solid phase is not thermodynamically stable in these biological media (pH>6
355 and positive Eh)⁴¹, it can be considered as an important intermediary product during the

356 tungsten oxidation and dissolution^{11,42}. However, Anik and Cansizoglu⁴³ did not mention WO₂
357 in the dissolution process of WO₃ in more acidic solutions⁴³. It is noteworthy that in both
358 Sanles-Sobrido et al.¹¹ and Anik and Cansizoglu⁴³ the reaction kinetics are studied at an hour-
359 scale (first time point at 2h and 30 min respectively). Herein, we studied whether the
360 combination of XAS-HERFD at the W L₃-edge with microfluidic chips would provide an
361 interesting platform for time-resolved and *in situ* monitoring of the tungsten oxidation kinetics.

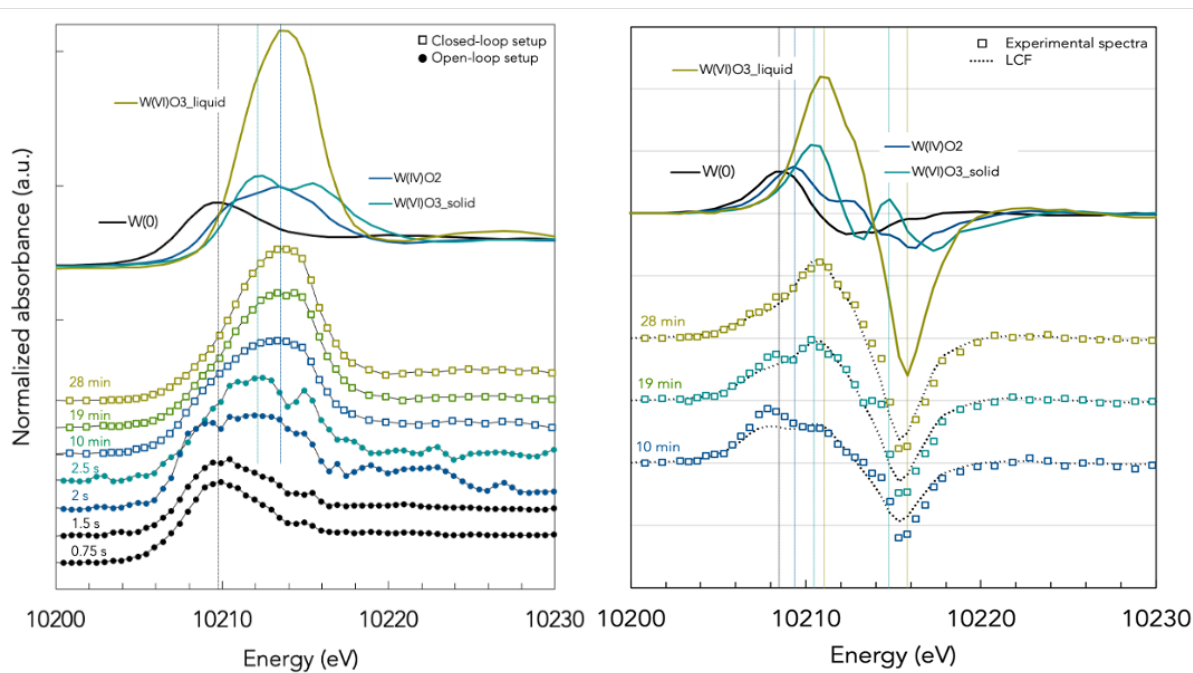
362 The microfluidic cell described above has been set at the end station of the FAME-UHD
363 beamline. The flow was controlled in the two channels to maintain fluid flow rates between
364 204 and 61 $\mu\text{L}\cdot\text{s}^{-1}$ and to test different reaction times between nanoW (injected in one channel)
365 and H₂O₂ (injected in the second channel) at the second- and minute-scale (Figure 6 left). Of
366 course, these experimental conditions are far from environmentally relevant ones, but they
367 allow us (i) to ensure about the chemical stability of the nanoW at t_0 using the potassium
368 hydrogen phthalate buffer and (ii) to adjust the oxidation kinetics of these nanoW using H₂O₂
369 to a few seconds to test the validity of the proposed approach.

370 We first used the microfluidic cell in a closed-loop setup. The XANES spectra given in figure
371 6 at 10 min, 19 min, and 28 min highlighted respectively the transformation occurring between
372 1-10 minutes, 10-19 min, and 19-28 minutes of interaction between nanoW and H₂O₂. These
373 three spectra were characterized by one large white line shifted to energy corresponding to
374 oxidized species of W. The first derivatives of these experimental HERFD-XANES spectra
375 were fitted using LCF of the spectra of the reference compounds (Figure 6 right). Based on
376 O'Day et al.⁴⁴, the uncertainty on the quantification of each contribution is assumed to be about
377 20%. From LCF, metallic W and dissolved W(VI) were detected in the suspension whatever
378 the sampling time at the limit of the uncertainty. The proportion of metallic W decreased from
379 65 % \pm 13 (at 10 min) to 39 % \pm 8 (at 28 min) and the proportion of dissolved W(VI) increased
380 from 35 % \pm 7 (at 10 min) to 61 % \pm 12 (at 28 min). Sanles Sobrido et al.¹¹ proposed an

381 oxidative dissolution model limited by diffusion from the surface. In such a case, we estimated
382 that the metallic core of the nanoW would be shrunk by ~14 nm between 1 and 10 minutes and
383 by ~29 nm between 19-28 minutes.

384 Using the open-loop setup, the first reaction timepoint analyzed was at 0.75 s. Between 0.75 to
385 1.5 s, we did not observe significant change in the oxidation state of nanoW which remained
386 centered on the absorption energy of the W(0) reference compounds. After 2s, an oxidation of
387 the nanoW in contact with H₂O₂ is visible with an enlargement of the white line and shift
388 toward higher absorption energies in line with the signature of W(IV)O₂ and W(VI)O₃
389 reference compounds. In particular, the splitting of the white line at 2.5s could highlight the
390 presence of W(VI) with an octahedral geometry ¹⁶. At the end of the XAS acquisition in the
391 open-loop mode, the final pH and Eh were measured at 2.9 ± 0.1 and 261 ± 2 mV respectively.
392 This acidification is related to the protons that are released during the W(0) oxidation in W(VI)
393 in contact with H₂O₂. However, the low signal-to-noise ratio limit deeper discussion and
394 possible quantification using LCF. Indeed, such open-loop setup is relevant to acquire
395 information on changes of nanoW speciation after few seconds of interaction with oxidizing
396 molecules. Although, one drawback to get an acceptable signal-to-noise ratio is that it requires
397 a compromise between the amount of reactant used and the duration of the scans, considering
398 that a minimal fluid flow rate is needed to ensure the particle circulation in the cell.

399 Allowing the manipulation of the flow rate, of the pH/Eh conditions, and the composition of
400 media (e.g. freshwater, saline water, interstitial water, biological media) in the channels, such
401 HERFD- XAS-microfluidic cell coupling would allow precise and reproducible conditions
402 when investigating the W oxidation kinetics and mechanisms at short (second) timescales. Such
403 coupling is opening new perspectives to decipher the underlying mechanisms governing the
404 rapid oxidation of tungsten in biological and environmental media as well as the durability of
405 the W submicronic materials.



406

407 **Figure 6.** HERFD-XANES spectra (left) and first derivatives (right) at the W L_{3} -edge with $L_{\beta 2}$

408 emission line measured at increasing reaction times between a nanoW suspension and H_2O_2

409 solution. Reaction times at the second-scale were obtained with the microfluidic cell in open-

410 loop setup (\bullet) while those at the minute-scale were obtained with the closed-loop setup (\square).

411 Experimental XANES spectra are compared with W(0), $WO_2(IV)$, and $WO_3(VI)$ solid

412 reference compounds, and with dissolved W(VI) reference obtained after dissolution of WO_3

413 in milli-Q water followed by an ultrafiltration at 3 KDa. First derivatives of the experimental

414 XANES spectra were fitted using linear combination fits (LCF) of the previously cited

415 reference compounds.

416

417

418

419 CONCLUSION

420 Tungsten can be exposed to diverse environmental conditions, including freshwater, saline

421 water, soil, sediment as well as biota. Each environment has its unique set of chemical species,

422 pH levels, redox potentials, and temperature variations, which can significantly influence the
423 oxidation kinetics and mechanisms. Studying tungsten oxidation in such reactive environments
424 requires carefully designed experiments. This paper highlights the ability of coupling
425 microfluidics with HERFD-XAS to fill this gap. We demonstrated that the high energy
426 resolution in HERFD-XAS would allow the separation, characterization, and quantification of
427 subtle changes in the XAS spectrum, such as sharp edges, energy shifts and white line splitting
428 associated with specific electronic transitions of W. We were able to quantify to which extend
429 the better spectroscopic resolution of HERFD-XAS compared to conv-XAS would allow a
430 more accurate estimation of the different oxidation states of W in mixtures. Moreover, HERFD-
431 XAS has been combined with a microfluid chip for in situ monitoring of changes in W redox
432 states with enhanced temporal resolution. We highlighted that such experimental set-up would
433 be particularly valuable to provide direct insight into the fast changes (scale of seconds) in W
434 speciation that would occur in oxidizing conditions.

435 This study opens new possibilities for monitoring the oxidation–reduction processes at
436 mineral-water interfaces that control the W biogeochemical cycle via electron transfer
437 reactions. In safer by design- or risk assessment-perspectives, understanding the molecular
438 scale process of biogeochemical redox reactions involving W is critical in predicting its fate,
439 mobility, bioavailability, and toxicity in the environment. In the near future, such experimental
440 device could be tuned to tackle the role of organic matter in this process and especially in
441 microbial-mediated transformations. This will be even more important in the context of climate
442 change, during which hotspots for redox reactions are likely to become increasingly active.

443 **ASSOCIATED CONTENT**

444 **Supporting Information.** X-ray Diffractogram and electron microscopy images of the nanoW,
445 microfluidic cell setup on the FAME-UHD beamline, HERFD-XANES spectra of control
446 nanoW suspension are provided in Supporting Information.

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450 **AUTHOR CONTRIBUTIONS**

451 The manuscript was written through contributions of all authors. All authors have given
452 approval to the final version of the manuscript.

453 **ACKNOWLEDGEMENTS**

454 We thank Mickaël Payet from the CEA for providing the metallic tungsten nanoparticles. This
455 work is a contribution to the OSU-Institut Pythéas. The FAME-UHD project is financially
456 supported by the French "grand emprunt" EquipEx (EcoX, ANR-10-EQPX-27-01), the CEA-
457 CNRS CRG consortium and the INSU CNRS institute. FAME and FAME-UHD are members
458 of the REGEF French Research Infrastructure. Finally, the authors acknowledge the CNRS
459 funding for the IRP iNOVE.

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