X-ray absorption spectroscopy and actinide electrochemistry: a setup dedicated to radioactive samples applied to neptunium chemistry

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A spectroelectrochemical setup has been developed to investigate radioactive elements in small volumes (0.7 to 2 ml) under oxidation–reduction (redox) controlled conditions by X-ray absorption spectroscopy (XAS). The cell design is presented together with in situ XAS measurements performed during neptunium redox reactions. Cycling experiments on the NpO$_2^{2+}$/NpO$_2^{+}$ redox couple were applied to qualify the cell electrodynamics using XANES measurements and its ability to probe modifications in the neptunyl hydration shell in a 1 mol l$^{-1}$ HNO$_3$ solution. The XAS results are in agreement with previous structural studies and the NpO$_2^{2+}$/NpO$_2^{+}$ standard potential, determined using Nernst methods, is consistent with measurements based on other techniques. Subsequently, the NpO$_2^{+}$, NpO$_2^{2+}$ and Np$^{4+}$ ion structures in solution were stabilized and measured using EXAFS. The resulting fit parameters are again compared with other results from the literature and with theoretical models in order to evaluate how this spectroelectrochemistry experiment succeeds or fails to stabilize the oxidation states of actinides. The experiment succeeded in: (i) implementing a robust and safe XAS device to investigate unstable radioactive species, (ii) evaluate in a reproducible manner the NpO$_2^{2+}$/NpO$_2^{+}$ standard potential under dilute conditions and (iii) clarify mechanistic aspects of the actinyl hydration sphere in solution. In contrast, a detailed comparison of EXAFS fit parameters shows that this method is less appropriate than the majority of the previously reported chemical methods for the stabilization of the Np$^{4+}$ ion.

1. Introduction

In situ X-ray absorption spectroscopy (XAS) in combination with electrochemical techniques is a powerful combination for determining the coordination of metal ions at a controlled oxidation state in various electrolytes (Nockemann et al., 2009; Achilli et al., 2016). Such an in situ approach is nowadays commonly applied for d-block elements and rare earth compounds, but is still very limited for actinide elements (An). These elements display unusual redox properties and complexation behaviour (Brown, 1978). Understanding the equilibria between oxidized and reduced species, the formation of intermediate unstable species and the magnitude of relevant redox couples under the conditions of interest is essential for predicting An chemistry in industrial and natural environments. Specifically, the characterization of intermediate species or unstable oxidation states is of fundamental interest in understanding how the internal structures of An molecular complexes affect their reactivity and the exchange between oxidation states.

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To investigate these reactions at the molecular scale using XAS, a spectroelectrochemical cell was designed at Argonne National Laboratory (USA) (Antonio et al., 1997). The limited volume of this cell (5 ml) allowed for the characterization of radioactive samples using a limited amount of hazardous radionuclide with a concentration range \(10^{-2} \text{ to } 10^{-4} \text{ mol l}^{-1}\) that corresponds to XAS measurements. Thus, this cell has been used to investigate An redox chemistry under acidic conditions (Soderholm et al., 1999), alkaline conditions (Williams et al., 2001) and on frontier elements such as berkelium (Antonio et al., 2002). Subsequent XAS research monitoring actinide and radioactive elements coordination during \textit{in situ} electroactive processes was performed with less active nucleides, such as U (Hennig et al., 2005) or Tc (Antonio et al., 2002; Poineau et al., 2006). Although high-activity samples (Np and Pu) were used in several experiments in recent years, their combination with an electrochemical setup was hampered for various safety reasons. To contribute to this effort and to overcome these limitations, we have developed an electrochemical–XAS setup available for high-activity samples. The setup was designed taking into account specific requirements: (i) a small sample volume to limit radioactivity and permit the study of highly radioactive materials; (ii) the possibility to perform reproducible electrochemical reactions \textit{in situ} (i.e. directly on the beamline) with highly radioactive material during an XAS experiment; (iii) (moderate) flexibility in the choice of working, reference and counter electrodes; (iv) easy access and handling to limit the risk of spillover during sample preparation; (v) tightness and number of barriers satisfying the synchrotron safety requirements for the handling of radioactive samples; and (vi) a small overall size to facilitate transport between the synchrotron facility and actinide laboratories. The cell has been successfully implemented on the MARS beamline at the SOLEIL synchrotron (LLorens et al., 2014). The first set of experiments was performed in 1 \text{ M NHO}_3 to follow \textit{in situ} structural and electronic changes of the neptunium ions under potentiometric control. The results demonstrate the capacities and limits of such a microcell setup and are discussed in comparison with purely Np electrochemistry results (i.e. laboratory scale and no X-ray techniques) (Cohen & Hindman, 1952; Cohen et al., 1954; Takao et al., 2009; Hindman et al., 1958; Sornein et al., 2009; Kihara et al., 1999; Kim et al., 2004, 2005; Cohen, 1961; Zielen et al., 1958) or previous structural XAS studies (Bonin et al., 2009; Allen et al., 1997; Di Giandomenico et al., 2009; Combes et al., 1992; Reich et al., 2000; Soderholm et al., 1999; Hennig et al., 2005; Williams et al., 2001; Den Auwer et al., 1999; Scheinost et al., 2016; Antonio et al., 1997, 2001, 2012; Ikeda-Ohno et al., 2008, 2009).

While the main aim was to check the ability of the setup to proceed safely with the combination of electrochemistry and XAS measurements under confined conditions, a more critical evaluation of the structural results is also proposed. The systematic comparison of the structural EXAFS parameters extracted from (i) this work, (ii) formal works and (iii) theoretical calculations is proposed. This allows for a better understanding of the main benefits of such an electrochemical cell concept, but also some limitations that should not be ignored.

2. MARS electrochemical–XAS setup

The setup was designed to facilitate electrochemical control of a limited volume (700 to 2000 \text{ ml}) of radioactive solution or suspension while at the same time guaranteeing double confinement of these hazardous samples and allowing relatively easy handling in the laboratory and on the beamline. The setup was made of an inner cell and an outer envelope...
The inner cell is made of PEEK, a material that is relatively inert, and thus can be used for acidic, basic and even non-aqueous solutions compatible with this material (such as room-temperature ionic liquids and organic solutions like dodecane or heptane). Two X-ray windows are obtained by locally thinning the inner cell walls down to 200 μm. This design limits the risk of leaking at the X-ray windows, while providing a moderate X-ray attenuation (95% of the X-ray flux transmitted at 17 keV). This cell is enclosed in a secondary containment, also made of PEEK, to prevent dispersion in case of inner cell failure. The inner cell is rotated at 45° with respect to the incident beam, and three windows made of 90 μm Kapton film sealed with three screwed clamping rings to the second envelope provide paths for the incident beam, the transmitted beam and the fluorescence signal. The path length of the transmitted X-ray beam in the inner cell is about 11 mm.

The volumes of liquid that can be introduced in the inner cell vary between 750 (the minimum volume to soak up the windows) and 2000 μl. The bulk solution is steered (600 rpm) by a magnetic bar driven by a stirrer located outside the second envelope. Bulk electrolysis is then performed in the inner cell.

The electrodes are screwed and glued onto the lid of the inner cell to further limit possible leaking of fluids. The nature and distribution of electrodes can be tailored to meet the need of a specific experiment. For example, the working electrode can be made of platinum or any other metallic material, or even carbon. Our conventional reference electrode is an Ag/AgCl microelectrode (World Precision Instruments). However, any other microelectrode could in principle be used, provided it can fit through the inlet (4 mm in diameter) and be reasonably short (a few cm) and sturdy. In a more recent experiment, a homemade reference electrode dedicated to be reasonably short (a few cm) and sturdy. In a more recent experiment, a homemade reference electrode dedicated to be reasonably short (a few cm) and sturdy.

The counter-electrode was placed in the auxiliary electrode is Pt wire separated from the buck by a tube closed by a porous frit. The reference electrode is a 2 mm-diameter Ag/AgCl microelectrode from World Precision Instrument. Preliminary tests with the counter-electrode bathed directly in the experimental solution failed to achieve quantitative oxidation (or reduction) up to the target oxidation state although the target potentials had been validated previously by spectroelectrochemical UV–Vis absorption spectroscopy. Instead of a progressive change in oxidation state under the applied conditions, competitive side reactions seems to occur and are manifested by important current flow but no significant changes in redox speciation. For the later experiments, the counter-electrode was placed in the frit-sealed tube, which resulted in a reproducible experiment that is presented in the following results.

3. Experimental

3.1. Sample preparation

The sample preparation was performed in a radiochemistry laboratory at the ATALANTE facility (CEA Marcoule, France) in a dedicated glove-box. The purity of the oxidation state of the NpIV stock solution was checked with a UV–Vis spectrometer (Carry). A sample of 0.1 mM NpIV was transferred to the inner cell via a dedicated holder. The filling hole was then closed with a screw and sealed with epoxy glue. Basic tests were performed in the laboratory to check for a correct electrochemical behaviour of the cell. The second envelope was then closed and the cell can be easily shipped due to its relatively small size.

3.2. XAS experiment

The electrochemical cell was installed on the CX3 station of the MARS beamline, which is dedicated to XAS (Jeanson et al., 2009; LLorens et al., 2014). A 13-element HPGe solid-state detector (ORTEC) was used to collect the Np signal in fluorescence mode. The energy calibration of the monochromator was performed at the yttrium K-edge. All measurements were performed at room temperature.

3.3. Bulk electrolysis

Bulk electrolysis was performed over a period of 30 min using a remote-controlled potentiostat (μAutolab, Metrohm) located in the experimental hutch. Chrono-amperometric sequences of 30 min were alternated with acquisition of XAS data. It is worth mentioning that shorter electrolysis times or simultaneous electrolysis–XAS acquisition may artificially suggest hysteresis on Np redox couples under the chosen conditions, a consequence of incomplete or ongoing electrolysis. Moreover, the recorded chronoamperogram, even indicating the exponential shape expected for dilute solution electrolysis, never reached a null current during the experiment, indicating parasitic reactions.

Data processing was carried out using the Athena code (Ravel & Newville, 2005). The E0 energy was set at the maximum of the absorption edge. The EXAFS signal was extracted by subtracting a linear pre-edge background and a combination of cubic spline functions for the atomic absorption background and for normalizing the signal by the Lengeler–Eisenberg procedure. Fourier transforms (FT) were obtained by Fourier transform in k-space over 2.5 and 11 Å−1. Selected FT contributions were fitted in R-space over individual radial distances and Debye–Waller factors (σ2) for every considered distance, using backscattering amplitude and phase shift functions obtained with FEFF8.2 (Rehr & Albers, 2000) performed on structures optimized by density functional theory (DFT) calculations (see §4, DFT calculations). The amplitude reduction factor E02 was set at 0.9. All fitting operations were performed. The R factor (%) and errors in distances were provided by ARTEMIS (Ravel & Newville, 2005).
4. DFT calculations

The geometry and frequency calculations were performed with GAUSSIAN16 (Frisch et al., 2016) at the DFT level of theory. A small core quasi-relativistic effective core potential (RECP-60 electrons) (Cao & Dolg, 2004; Küchle et al., 1994) by the Stuttgart–Cologne group and its corresponding TZ-valence basis set were used for the neptunium ion. The PBE0 functional was used with the def-TZVP (Schäfer et al., 1994) basis sets for O and H atoms. Aqueous solvation effects were taken into account using two explicit hydration shells. Effects beyond the second hydration shell were described through an implicit solvation model. The Integral Equation Formalism Polarizable Continuum Model (IEFPCM) was used as implemented in GAUSSIAN16.

The ab initio Debye–Waller factors ($\sigma^2$) were calculated at 300 K for each scattering path from the dynamical matrix extracted from the DFT frequency calculations with the DMDW module of FEFF9 (Rehr et al., 2010; Rehr & Albers, 2000).

5. Results

5.1. NpVI/NpV

The first electrolysis experiment was performed with an initial NpV solution. XANES and EXAFS spectra were recorded after 30 min of electrolysis for each potential step at 850, 950, 1000, 1025 and 1150 mV/(Ag/AgCl) in the oxidation (anodic) direction, and at 1150, 1050, 975, 950, 925, 900, 875, 800 and 750 mV/(Ag/AgCl) in the reduction (cathodic) direction (Fig. 2). All XANES spectra display a white line, which is shifted from 17616 to 17619.5 eV as NpV is oxidized to NpVI. The high-energy shoulder of the absorption edge, located near 17628 eV and attributed to multiple scattering in the neptunyl moiety, is also shifted to higher energy, i.e. 17634 eV, consistent with a trans-dioxo structure for both +V and the +VI oxidation states. Conversely, a shift of the white line and of the shoulder back to their initial values is measured during the reduction steps of NpVI back to NpV. From NpV to NpVI, the white line increases in intensity. An isosbestic point at 17617.7 eV repeats itself in both the oxidation and the reduction sequences, suggesting that only two components were simultaneously present in solution for each sequence. Transitional spectra were reproduced by linear combination fits using the two extrema spectra for NpV and NpVI, resulting in NpV/VI ratios for each potential. A direct estimation of the redox species is only possible if there is no change in the experimental setup during the data acquisition except for the imposed potential in the solution.

The relative NpV/VI concentrations are determined with a linear combination fit from the two extrema spectra. This can be used in a Nernst plot as $\log([\text{NpVI}]/[\text{NpV}])$ plotted as a function of the applied potential (Fig. 3). Both data sets from the oxidation (red) and reduction (blue) experiments are well aligned within error bars. This evidences the reversibility of the NpVI/VI redox system, confirming that the electrochemical setup operates as expected. From the Nernst plot, a formal potential of the NpVI/VI redox couple in 1 M NHO3 is determined by linear regression (Fig. 3, red and blue dotted lines), according to

$$E = E^{0'} + (2.3RT/nF) \log([\text{NpVI}]/[\text{NpV}])$$

where $E$ is the potential, $E^{0'}$ is the apparent standard potential, $R$ is the perfect gas constant (J mol$^{-1}$ K$^{-1}$), $T$ is temperature (K), $n$ is the number of electrons in the reaction, $F$ is the Faraday constant and [NpVI] and [NpV] are the relative concentrations in NpVI and NpV, respectively, as determined by the linear combination fit of the neptunium L3-edge spectra.

The slopes, ranging between 55.5 and 58.2 mV ($\pm 8$ mV), are in reasonable agreement with a single electron transfer (expected value of 59 mV at $T = 298$ K). The two formal potentials obtained from the oxidation and reduction experi-
ments are 918.7 and 918.4 mV/(Ag/AgCl), respectively. Herein, the Np\(^{VI}\)/Np\(^{V}\) formal potential given with a maximum uncertainty of 10 mV is in good agreement with similar studies performed in perchloric acid (Soderholm et al., 1999; Antonio et al., 2001) or recent work from Chatterjee et al. (2017) in nitric acid using equivalent spectrophotometric methods.

5.1.1. EXAFS analysis. From electrolysis experiments and analysis of XANES spectra, we demonstrated that the setup provides a fairly robust and reliable method to isolate Np\(^{VI}\) and Np\(^{V}\) oxidation states by electrolysis. With the potentials set at 1150 and 750 mV/(Ag/AgCl), we expect to stabilize pure species for EXAFS analysis. This controlled potential may stabilize the Np oxidation state upon long EXAFS measurements, thereby balancing for the \textit{in situ} photooxidation due to beam damage. The purpose of the following section is to evaluate whether the electrochemically purified solution results in a more reliable solution to isolate both neptunium oxidation-state ions in a simple solution. In order to compare the results with previous EXAFS measurements on similar systems, we propose to compare the significant fit parameters (CN and DWF) on a single plot. First, Fig. 4 shows the \(k^3\)-weighted EXAFS oscillations and Fourier transform (FT) for both Np\(^{V}\) and Np\(^{VI}\)-stabilized solutions. Neptunyl ions hydrates show two main oscillations corresponding to two FT peaks typical for hydrated actinyl oxocation (Allen et al., 1997; Bolvin et al., 2001; Di Giandomenico et al., 2009; Takao et al., 2009). The structural parameters from simple two oxygen shell EXAFS fits are summarized in Table 1. The coordination spheres of Np\(^{VI}\) and Np\(^{V}\) are formed by two O atoms from the neptunyl moiety (O\(_{yl}\)) at short \(R_{(Np-O_{yl})}\) distances of 1.75 and 1.82 Å, respectively, and by about 4.4 and 4.9 equatorial O atoms (O\(_{eq}\)) from water molecules at longer \(R_{(Np-O_{eq})}\) distances of 2.41 and 2.51 Å, respectively. Overall, these results are in line with published values and confirm that a single oxidation state predominates in solution. Distances correspond to the values reported in the literature within a maximum deviation of 0.02 Å (Combes et al., 1992; Allen et al., 1997; Antonio et al., 1997, 2001; Den Auwer et al., 1999; Reich et al., 2000; Bolvin et al., 2001; Williams et al., 2001; Kim et al., 2004; Denecke et al., 2005; Kim et al., 2005; Ikeda-Ohno et al., 2008; Di Giandomenico et al., 2009; Hennig et al., 2009; Takao et al., 2009). However, the hydration numbers (N\(_{Oeq}\)) are known to be much less accurately determined from the EXAFS fits and are still actively discussed. For Np\(^{VI}\), the N\(_{Oeq}\) values from previous EXAFS measurements range between 4.6 and 5.3. For Np\(^{V}\), the N\(_{Oeq}\) values are between 3.6 and 5.2.

The large dispersions reported in the literature are likely due to the mathematical correlation observed in a fitting procedure between the number of scattering atoms in a given shell (\(N\)), the Debye–Waller factor (\(\sigma^2\)) and the value of the total amplitude reduction factor (\(S_0^2\)). Although there is no physical meaning between these physical parameters, upon an EXAFS fit the three parameters \(N\), \(S_0^2\) and \(\sigma^2\) result in similar effects on the oscillation amplitudes. It is therefore difficult to

Table 1

| Path       | \(N\) | \(R\) (Å) | \(\sigma^2\) |
|------------|------|---------|------------|
| Np\(^{VI}\) | O\(_{yl}\) | 2*      | 1.75 (1)   |
| \(\Delta E_0\) = 5 eV | O\(_{H2O}\) | 4.6 (7) | 2.41 (2) |
| \(R\) factor 2.1% | | | | |
| Np\(^{V}\) | O\(_{yl}\) | 2*      | 1.82 (1)   |
| \(\Delta E_0\) = -1 eV | O\(_{H2O}\) | 4.9 (6) | 2.51 (2) |
| \(R\) factor 1.8% | | | | |

Figure 3

Nernst plots obtained from XANES measurements. Red diamonds correspond to the oxidizing experiment and blue diamonds to the reducing experiment. The dashed lines are the linear regression.

Figure 4

Experimental FT EXAFS signal (line) and best fits (open circles) obtained after 30 min electrolysis at 1150 mV/(Ag/AgCl) (blue) and at 750 mV/(Ag/AgCl) (red). The inset is the corresponding \(k^3\)-weighted EXAFS oscillations.
address coordination numbers from a single EXAFS signal with perfect accuracy, especially if the \( k \) range is short.

In order to estimate the magnitude of these correlations and allow a good comparison between previous EXAFS fits performed under different conditions (i.e. fixed or floating \( R \) and \( \sigma^2 \)), a more complete EXAFS data analysis is proposed hereafter. This analysis follows a method proposed by Ikeda-Ohno et al. (2008). \( N_{Oeq} \) is successively fixed from 3 to 6 and, for each coordination number step, a best fit is performed. This results in the determination of a conditional \( \sigma^2 N \) plot, as proposed by Ikeda-Ohno et al. (2008) (Fig. 5). The best \( N_{Oeq} \) and \( \sigma^2 \) combinations (corresponding to Table 1; values for \( \text{Np}^V \) and \( \text{Np}^VI \)) are plotted as triangles in Fig. 5.

For \( \text{Np}^V \) (Fig. 5, red dashed line) and \( \text{Np}^VI \) (Fig. 5, blue dashed line) the \( \sigma^2 \) values were found to vary approximately linearly with \( N_{Oeq} \) for \( \text{Np}^V \). The \( \text{Np}^V \) trend is similar to that reported by Ikeda-Ohno et al. (2008) for \( \text{Np}^V \). The corresponding \( R \) factors follow a parabolic variation (not shown) with a minimum at \( N_{Oeq} = 4.9 \) for \( \text{Np}^V \) and a minimum at \( N_{Oeq} = 4.6 \) for \( \text{Np}^VI \). However, for both \( \text{Np}^V \) and \( \text{Np}^VI \), reasonable fit parameters were obtained for all tested \( N_{Oeq} \) values (i.e. \( R_F < 5\% \) and \( \sigma^2 < 0.015 \AA^2 \)). This is the reason why this semi-empirical methodology was applied to compare the data with previous results whatever the method used to fit the data. Since the fit can be performed assuming multiple \( N_{Oeq} \) values, a relevant comparison with any single data point from previous reports needs to be achieved toward the full \( N_{Oeq} \) range.

On Fig. 5, the grey diamonds are previous fit parameters determined under similar chemical conditions (i.e. noncomplexing and acidic solution). Both \textit{ex situ} measurements (i.e. chemical preparation) (Hennig et al., 2009; Ikeda-Ohno et al., 2008; Di Giandomenico et al., 2009; Allen et al., 1997; Reich et al., 2000; Combes et al., 1992) and \textit{in situ} measurements by spectroelectrochemistry (Antonio et al., 2001) are compared with \( \text{Np}^V \) and \( \text{Np}^VI \) fit parameters from this work. For a given \( N_{Oeq} \) value, the \( \sigma^2 \) values (dashed blue and red lines) determined in this work are comparable with or lower than previously published \( \sigma^2 \) parameters. This is a good indication for a lower disorder/higher purity in this work where \( \text{Np}^V \) and \( \text{Np}^VI \) were purified electrochemically.

Concomitantly, a comparison of the \( \text{Np}^V \) and \( \text{Np}^VI \) structures is in agreement with the expected changes in the neptunyl ion coordination. The \( \sigma^2 \) values tend to be lower for \( \text{Np}^VI \) than for \( \text{Np}^V \) for a given \( N_{Oeq} \). This result agrees well with the decrease in atomic charge and bonding strength between water and neptunyl units from \( \text{Np}^VI \) to \( \text{Np}^V \) (Choppin & Rao, 1984; Denning, 2007).

At this stage, we conclude that the sample preparation, as well as the continuous application of electrochemical potential, is a good way to maintain a pure oxidation state during X-ray measurements resulting in a low conformational \( \sigma^2 \). However, this better oxidation-state purification does not solve the difficult question of the hydration structure of actinyl ions in solution. To evaluate this point further, additional information may be extracted to narrow down the actual \( N_{Oeq} \) values. With this same aim, Ikeda-Ohno et al. (2008) suggested that the \( N_{Oeq} \) values be derived from the more accurately determined interatomic distances applying the bond valence model (Brown, 1978). Although this approach proved to be satisfying for the well-known coordination chemistry of \( \text{U}^VI \), application to \( \text{Np} \) is plagued by the limited number of crystallographic references and by uncertainties in the valence unit and the charges of the neptunyl moieties, so that \( N_{Oeq} \) values still range between 4 and 6. Another way to constrain the accurate coordination number is to associate EXAFS analysis with quantum chemical calculations (Vila et al., 2012). For some actinide molecular compounds, it is possible to generate EXAFS metrical parameters from a DFT calculation (Acher et al., 2016, 2017; Dalodière et al., 2018). The calcula-

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**Figure 5**

\( \sigma^2 N \) plots from the \( \text{Np}^VI \) and \( \text{Np}^V \) fits. Blue and red dashed lines are the \( \sigma^2 \) variation as a function of \( N_{Oeq} \) for \( \text{Np}^VI \) and \( \text{Np}^V \), respectively. Previous reported single-point fit values are given as grey diamonds (Antonio et al., 2001; Ikeda-Ohno et al., 2008, 2009; Hennig et al., 2009; Di Giandomenico et al., 2009; Combes et al., 1992; Allen et al., 1997; Reich et al., 2000; Scheinost et al., 2016; Denecke et al., 2005). The open circles are DFT-calculated parameters.
In HNO₃ solution, the Np IV ion is difficult to stabilize due to previous XANES measurements, the Np XANES spectra are displayed on Fig. 4. Consistent with five water molecules, 2.41 and 2.42 Å bond lengths are observed for Np VI and Np V, respectively. However, this trend is obviously not due to the correlation of EXAFS fit parameters since the normalized Np—O bond lengths with the measurements. This type of correlation provides distances and σ² values ab initio from a selected structure. The NpO₂(H₂O)₄(H₂O)₈⁺, NpO₂(H₂O)₆(H₂O)₁₀²⁻, NpO₂(H₂O)₄(H₂O)₈⁺ and NpO₂(H₂O)₆(H₂O)₁₀⁻ complexes in the presence of a continuum solvent model were selected to produce the parameters reported in Table 2. The accuracy of the optimized geometry was checked by direct comparison of Np—O bond lengths with the measurements. This type of calculation provides an estimated value for the thermal σ² for a given coordination number and for both Np V and Np VI. It was possible to compare it with the experimental fit values obtained from the fit and the calculation, respectively. Overall, the results support the fact that five water molecules coordinate both the Np V and the Np VI ions.

5.2. Np V/Np IV

To evaluate further the electrochemistry setup, a second electrolysis experiment was performed following the previous one. After stabilizing the +V oxidation state by a 1 h electrolysis at 750 mV/(Ag/AgCl), the Np V purity was checked again using XANES and EXAFS. Next, the Np IV reduction was investigated by a stepwise decrease of the applied potential to 0, −100, −150, −200 and −250 mV/(Ag/AgCl). In HNO₃ solution, the Np IV ion is difficult to stabilize due to its reoxidation with HNO₂ in equilibrium with nitrate ions. The corresponding FT displays a single peak which can be reliably modelled with a single Np—O coordination shell. The structural parameters from this fit are summarized in Table 3. The best fit values correspond to approximately 9.5 O atoms (from water molecules), with an average R(Np-O) distance of 2.39 Å.

The Np—O distance corresponds to the values reported in the literature of 2.37–2.41 Å (Combes et al., 1992; Allen et al., 1997; Reich et al., 2000; Williams et al., 2001; Bolvin et al., 2001; Williams et al., 2001; Hindman et al., 1949; Sjoblom & Hindman, 1951; Sullivan et al., 1976; Cohen, 1976).
Antonio et al., 2001). The $N_{\mathrm{H}_{2}O}$ value also falls within the range of previous EXAFS results for Np IV aqua complexes, i.e. between 8.7 and 11.6 (Combes et al., 1992; Allen et al., 1997; Reich et al., 2000; Williams et al., 2001; Bolvin et al., 2001; Antonio et al., 2001).

As for NpV and NpVI, a clear correlation between $\sigma^2$ and $N_O$ can be drawn with restricted $N_O$ fits. Fixing $N_O$ from 8 to 11 allows the determination of the corresponding $\sigma^2$. These values approximately align as a function of $N_O$ (Fig. 8, green dashed line), together with the best fit values (triangle). The corresponding data determined previously on analogous systems are compared (grey diamond). Interestingly, almost all previous studies report a lower $\sigma^2$ value for a given $N_O$ compared with the present report. The more distorted geometry of the 8 to 11 water molecule coordination shell results in $\sigma^2$ values (from 0.0065 to 0.012 Å$^2$) much larger than observed for the neptunyl hydration shell. This time the comparison with previous studies clearly indicates a residual disorder in the neptunium coordination sphere for the in situ prepared Np$^{4+}$. This may be explained by either (i) a residual NpO$_2^{2+}$ contribution in the EXAFS spectrum, (ii) over-reduction resulting in the formation of Np$^{3+}$ with a coordination shell at about 2.5 Å (Antonio et al., 2001; Brendebach et al., 2009) or (iii) complexation of Np$^{IV}$ by nitrate (by analogy with Pu$^{IV}$ chemistry in nitric acid this must be quite insignificant; Allen et al., 1996), or a combination of points (i), (ii) and (iii).

### Table 3

Parameters from Np$^{IV}$ EXAFS fits.

| Path      | CN   | R       | $\sigma^2$ |
|-----------|------|---------|------------|
| $S_k^1$ 1$^+$ | 9.5 (16) | 2.39 (2) | 0.0095 (15) |
| $\Delta E_{\mathrm{c}}$ | 4 eV |

$R$ factor 3.8%  

![Figure 7](image-url)  
Experimental $k^3$-weighted EXAFS oscillations (line) and best fits (open circles) obtained after 30 min electrolysis at $-250$ mV (green).

![Figure 8](image-url)  
Plot of the $\sigma^2$ values as a function of coordination number from the EXAFS fit (dashed line) and comparison with previously reported values (Antonio et al., 2001; Ikeda-Ohno et al., 2008, 2009; Hennig et al., 2009; Di Giandomenico et al., 2009; Combes et al., 1992; Allen et al., 1997; Reich et al., 2000; Scheinost et al., 2016; Denecke et al., 2005) (grey diamonds). The triangle shows the best fit results from this work.

### 6. Conclusions

The main aim of this study was to develop a spectro-electrochemical cell and to qualify this setup for further applications on radioactive samples. During the experiment, it was possible to investigate the neptunium coordination during redox processes in a simple $1 \, \text{M} \, \text{HNO}_3$ solution.

The technical parameters of the microcell design are presented herein and its first application to transuranic elements, performed safely, are reported. The cell design minimizes the volume of radioactive solution and facilitates transport and handling on the beamline. Low actinide concentration and volume minimize the sample activity and allows XANES and EXAFS measurements within a reasonable timescale. From an electrochemistry point of view, such a static confinement concept is not ideal. On one hand, cycling the NpO$_2^{2+}$/NpO$_2^{3+}$ redox couple was quite possible and resulted in reliable standard potential determination. It was then possible to measure both NpV and NpVI EXAFS spectra under fully consistent conditions. This was a good opportunity to compare the Np$^{V}$ and Np$^{VI}$ hydration spheres, and to implement a statistical comparison with formal literature results, as well as theoretical models. The evolution in the equatorial actinyl hydration is well characterized and is consistent with theoretical expectations. Moreover, a detailed comparison with previous structural data using EXAFS established that the stabilization of Np$^{V}$ and Np$^{VI}$ oxidation by in situ electrochemistry appears to be the most reliable way to maintain a pure oxidation state during X-ray measurements.

On the other hand, the reduction to Np$^{IV}$ never fully succeeded in maintaining pure Np$^{IV}$ in solution. From the point of view of electrochemistry, a clear offset in the expected standard potential must be applied to begin the Np$^{V}$ reduction. The resulting Np$^{IV}$ EXAFS spectra reveal hydrated Np$^{IV}$...
as the main species, but comparison with a previous chemically stabilized NpIV solution indicates a more disordered coordination sphere. Altogether, it seems that, while the results are fully satisfying for the oxidized neptunium species, the cell must be used with care to study reduced neptunium forms. As a final point, this cell, primarily designed to confine radioactive samples for user safety, was also efficient for performing measurements on nonradioactive samples. Its design for radioactive samples appears to be versatile and extremely convenient for preventing moisture and oxygen contaminating air-sensitive samples in the reverse direction. By doing so, the in situ XAS stabilization and characterization of LnIV in room-temperature ionic liquid samples was made possible with this cell (Bengio et al., 2018, 2020) and other applications of this kind are expected.

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