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The Rossendorf Beam Line ROBL – a dedicated experimental station for XAFS measurements of actinides and other radionuclides

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Summary. X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool for obtaining basic molecular-level information, which is required for a better understanding of the mechanisms responsible for radionuclide transport in the environment. A unique experimental station dedicated to the study of actinides and other radionuclides by XAFS spectroscopy has become operational at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The main characteristics of the Rossendorf Beamline, ROBL, and its radiochemistry end station and selected results obtained on Tc and Np solutions are presented.

1. Introduction

X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool for the determination of molecular-level information on the speciation of elements including radioactive isotopes in solids and solutions [1, 2]. The speciation not only describes the type of the element or radionuclide and its concentration but also its oxidation state and coordination sphere. The structural parameters of the radionuclide surrounding, i.e., bond distances, coordination numbers, and type of neighboring atoms, can be determined by extended X-ray absorption fine structure (EXAFS) spectroscopy. The X-ray absorption near-edge structure (XANES) contains information on the electronic structure and the molecular symmetry of the element [3].

Although EXAFS and XANES spectroscopy have demonstrated their potentials in many areas of research since the mid seventies, they were rarely used in studies on radioactive materials until the mid nineties. Only then it became possible at a few synchrotron light sources in the world to implement protocols and procedures allowing to handle radioactive samples safely at large multi-user facilities [4]. However, these protocols impose restrictions on the activity and type of radionuclides that can be studied and do not, usually, allow for any sample manipulation.

The Rossendorf Beamline (ROBL) is unique in that sense that it operates the first experimental station dedicated to XAFS spectroscopy on radioactive elements at a synchrotron light source in Europe. In addition to all the advantages offered by a third-generation synchrotron light source as the ESRF, the uniqueness of ROBL is also due to the possibility of sample manipulation in a specially designed glove box before or during the measurement.

The first XAFS spectra of uranium samples were collected at ROBL in August 1998, followed by the first XAFS measurements on neptunium and technetium samples in November 1998. Since the beamline was still in commissioning, some of the experiments were designed to test ROBL's technical capabilities for XAFS measurements. After describing the main features of ROBL that are relevant to actinide studies, this paper will highlight selected results obtained on Tc and Np solutions using XAFS spectroscopy.

2. Beamline optics

ROBL has been constructed and is operated by Forschungszentrum Rossendorf at the ESRF bending-magnet port BM 20. The usable energy range at ROBL is 5 to 35 keV. The beamline optics are of standard design corresponding to this energy range and consisting of two mirrors and a double-crystal monochromator (DCM) of fixed-exit type, several slits, attenuators, and beam position monitors [5]. Two bendable mirrors installed before and after the DCM suppress beam contamination due to higher harmonics and collimate and focus the beam vertically. The DCM can be equipped either with a pair of Si(111) or Si(311) crystals. Due to the large heat load of the white synchrotron beam, the first mirror and the first Si crystal are water cooled. For the Si(311) crystals, it will be possible to sagitally focus the beam at the sample by bending the second crystal. The standard beam size at the sample is $20 \times 3\ \text{mm}^2$ ($h \times v$). The size of the focused beam is $\leq 0.5 \times 0.5\ \text{mm}^2$. The calculated integrated flux for the focused beam is 6×10^{11} photons/s at an energy of 20 keV and 200 mA electron-beam current.

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3. Radiochemistry experimental station

The radiochemistry experimental station, which is inside the lead-shielded Radiochemistry Hutch (RCH), has been designed to perform XAFS spectroscopy of solid and liquid non-sealed radioactive samples. According to the safety requirements of a radiochemistry laboratory, the radioactive samples are positioned inside a glove box. The glove box is equipped with several 125-μm thick polyimide windows to transmit the X-ray beam and the fluorescence radiation. Two sample positioners can be installed alternately at a standard sample position. The first sample positioner can hold up to eight solid or liquid samples for transmission or fluorescence measurements. The samples can be changed and positioned in the beam by remote control. The second sample positioner is designed to hold a closed-cycle He cryostat, which allows to cool the sample to 15 K. If a sample is brought into another position between two polyimide windows using a third sample positioner, it is possible to move two Ge fluorescence detectors very close to each side of the sample. This allows to collect the XAFS of an ultra-dilute sample in fluorescence mode. All detectors needed for the XAFS measurements, e.g., gas ionization chambers and solid state fluorescence detectors, are mounted on the optical bench outside the glove box, so that they can be easily accessed.

To calibrate the energy of the monochromatic beam, the XAFS spectrum of a non-radioactive reference sample positioned inside a Lytle detector can be recorded together with the sample spectrum in transmission or fluorescence mode. By moving the glove box in horizontal direction out of the beam, non-radioactive samples can easily be mounted on the optical bench and measured outside the glove box.

The current regulations agreed upon the ESRF and the French authorities make it possible to study the following actinides at ROBL: Th-nat, Pa-231, U-nat, Np-237, Pu-239, Pu-242, Am- 241, Am-243, as well as the radionuclides Ra-226, Po-208, Po-209, and Tc-99. The maximum equivalent activity of all samples present at ROBL at any given time is 185 MBq (5 mCi). The half live of these radionuclides and the amount of sample corresponding to 185 MBq are given in Table 1. Since the samples are safely contained inside the glove box, it is possible to modify the chemical conditions of liquid samples just before or during the XAFS measurement by adding non-radioactive substances like acid, base, or complexing agents. Additional possible sample manipulations include dissolution, dilution, sample cooling and heating, and electrochemical reactions.

Table 1. List of radionuclides which can be investigated at ROBL and the maximum amount of material to remain below the activity limit of 185 MBq (5 mCi).

Isotope	Half-Live (years)	Amount (g)	Isotope	Half-Live (years)	Amount (g)
Np 237	2.1×10^6	6.97	Pu 239	2.4×10^4	0.08
Am 241	433	1.4×10^{-3}	Pu 242	3.75×10^5	1.27
Am 243	7370	0.025	Ra 226	1600	0.005
Po 208	2.9	8×10^{-6}	Tc 99	2.1×10^5	29.1
Po 209	103	3.01×10^{-4}	U nat	4.47×10^9	1000
Pa 231	3.28×10^4	0.106	Th nat	1.4×10^{10}	1000

In addition to the glove box, the radiochemistry safety system of ROBL is complemented by separate ventilation, air filtering and air monitoring systems [6]. The ventilation system ensures negative pressure differences of about 10 Pa between the experimental hall and the RCH, and of about 200 Pa between RCH and the glove box. The in- and outgoing air is filtered using high-absorption absolute filters. The air inside RCH and the outgoing air are continuously monitored using various α-, β-, and γ-detectors. Deviations form standard values of any of the parameters of the radiochemistry safety system or any failure of one of its components is immediately reported optically and acoustically by an alarm system. This system is incorporated into the ESRF personnel safety system and closes beam shutter and vacuum valves automatically in case of an emergency.

4. Experimental

For XAFS measurements on liquid samples, 4 mL of the solution was filled in a polyethylene cuvette, which was sealed and put in a polyethylene bag. Multiple scans of the XAFS were collected at room temperature using the Si(111) DCM. The energy scale was calibrated using the first inflection point of the absorption spectra of various metal foils. The data were analyzed according to standard procedures [3] using the software EXAFSPAK [7]. Theoretical scattering phases and amplitudes were calculated using the scattering code FEFF6 [8].

To evaluate the feasibility of the radiochemistry station for future EXAFS studies on Tc samples, two solutions were prepared from $NaTcO_4$ for a first experiment with Tc-99 at ROBL. The amount of Tc in the concentrated sample with 127 mM $NaTcO_4$(aq) yielded an edge jump of ~ 1 across the Tc K edge at 21 keV. The second sample was with 1.3 mM 100 times more dilute and was measured in fluorescence mode using a quad-pixel Ge fluorescence detector [9].

A series of aqueous solutions containing 50 mM Np in three different oxidation states was prepared for measurements in transmission mode by dissolving solid 237-$NpO_2(NO_3)$ in 0.1 M HNO_3. Solution Np1 consisted of 50 mM Np(IV) in 0.1 M HNO_3 and 2 M H_2SO_4. The sulfuric acid was added to stabilize the Np(IV) oxidation state in the solution. The composition of solutions Np2 and Np3 was 50 mM Np(V) and Np(VI), respectively, in 0.1 M HNO_3. The different oxidation states of Np were obtained by electrochemical oxidation/reduction in a conventional H-formed electrolysis cell with a diaphragm between anode and cathode. The stability of the Np oxidation states was confirmed by UV/Vis spectroscopy.

5. Results and discussion

The raw Tc K-edge k^3-weighted EXAFS spectra of two model solutions containing 127 mM and 1.3 mM TcO_4^- are shown in Fig. 1. The spectrum of the 127 mM Tc solution was recorded in a single sweep up to $k = 21$ Å^{-1}. During this sweep the counting time per data point was gradually increased from 2 to 20 sec. It follows from the best theoretical fit to the data (Table 2) that Tc is surrounded by 4 oxygen atoms at a distance of 1.72 Å. The EXAFS

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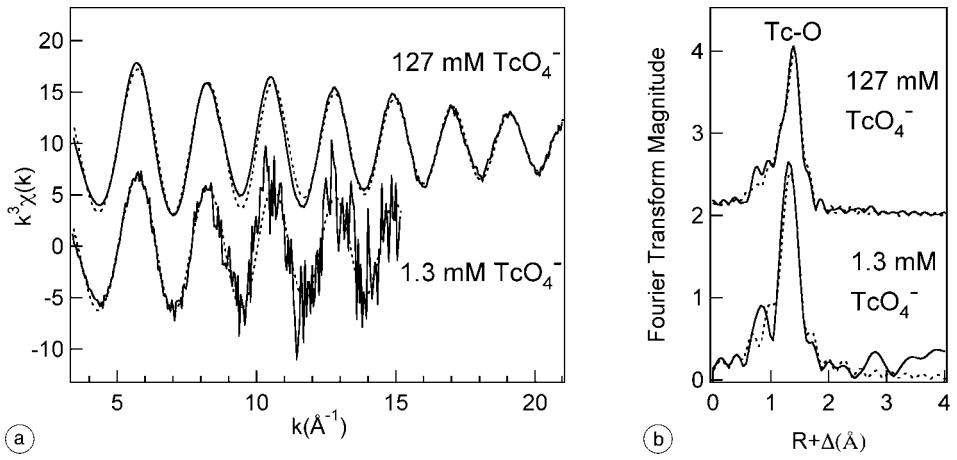


Fig. 1. Raw Tc K-edge k^3-weighted EXAFS spectra (**a**) and corresponding Fourier transforms (**b**) of experimental data (solid line) and theoretical fits (dots) for 127 mM (top) and 1.3 mM (bottom) $NaTcO_4$(aq).

Table 2. EXAFS structural parameters for TcO_4^- solutions. The 95% confidence limits were estimated by EXAFSPAK.

Sample	Shell	R(Å)	N	σ^2 (10^{-2} Å^2)
127 mM Tc	Tc–O	1.72 ± 0.01	4.1 ± 0.2	0.1 ± 0.1
1.3 mM Tc	Tc–O	1.72 ± 0.01	3.9 ± 0.6	0.2 ± 0.1
200 mM Tc [10]	Tc–O	1.72	4.2	0.15

spectrum of the 100 times more dilute $NaTcO_4$(aq) sample is also shown in Fig. 1 and represents an average of four sweeps measured in fluorescence mode. The intensity of the Tc K_α-fluorescence line was 1.2×10^5 counts/sec. The total count rate processed by the fluorescence detector was 6.4×10^5 counts/sec. Under these conditions, it was possible to analyze the Tc K-edge k^3-weighted EXAFS spectrum of the 1.3 mM Tc solution up to $k = 15$ Å^{-1}. As can be seen from Table 2, the structural parameters obtained are the same as for the TcO_4^- ion in the concentrated solution and agree with a previous Tc K-edge EXAFS measurement of a 200 mM NH_4TcO_4(aq) solution [10].

These measurements on two Tc model solutions show the capability of ROBL to record EXAFS spectra over a large energy range covering at least two orders of magnitude in metal concentration due to the high degree of beam stability, which was achieved using an additional monochromator feed-back system. The possibility to record an EXAFS spectrum over 21 Å^{-1} as in the case of the 127 mM Tc solution, which is a record in itself, is of great practical importance. The ability to resolve neighboring atoms as individual coordination shells, i.e., the expected smallest interatomic distance known as resolution ΔR, is given by the ratio $\Delta R = \pi/2\partial k$, where ∂k is the k-range of the data. For the two spectra given in Fig. 1, the expected resolution ΔR is 0.09 and 0.13 Å, respectively.

Fig. 2 shows the normalized Np L(III)-edge XANES spectra of 50 mM Np solutions of the different Np oxidation states IV, V, and VI. In contrast to Np(IV), Np in its oxidation states V and VI is known to form trans dioxo cations. This is the reason why the Np L(III)-edge XANES spectra of Np(V) and Np(VI) have a similar shape, which significantly differs from that of Np(IV). As can be seen from Fig. 2, the increase in the formal oxidation state from V to VI leads to a small shift of the absorption edge by 2.5 eV toward higher energy. The observed spectral features allow to distinguish between these three different Np oxidation states by Np L(III)-edge XANES spectroscopy.

In addition to the Np XANES spectra, information on the molecular structure is also contained in the EXAFS where it can be extracted in a quantitative way as several structural parameters. The raw EXAFS data and the best theoretical fit for solutions Np1–Np3 are shown in Fig. 3. The obtained structural parameters are given in Table 3. In solution Np1,

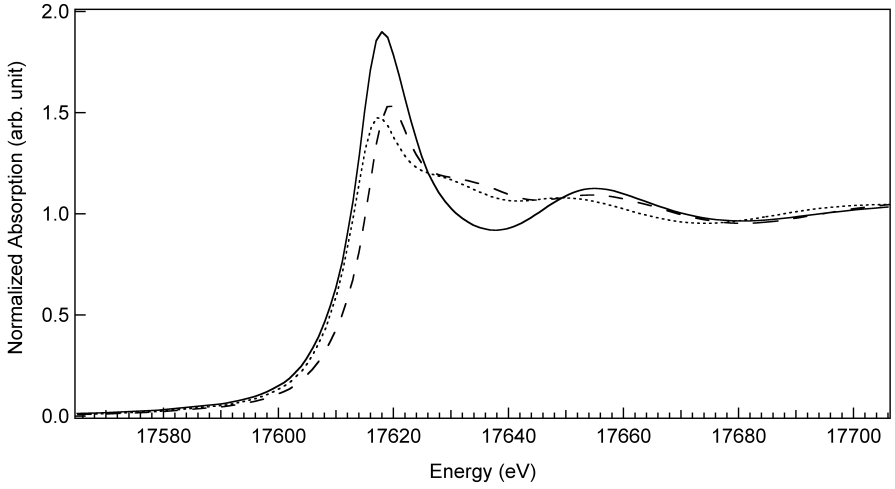


Fig. 2. Normalized Np L(III)-edge XANES spectra of 50 mM Np solutions. Solid line – Np(IV); short dashed line – Np(V); long dashed line – Np(VI).

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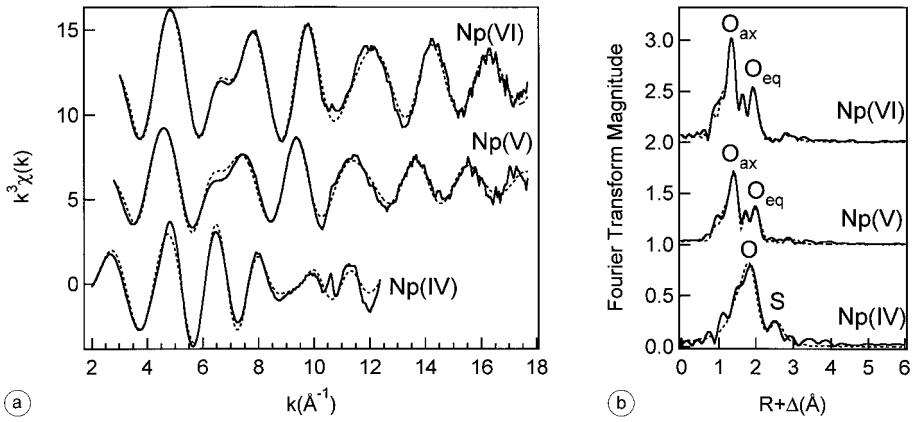


Fig. 3. Raw Np L(III)-edge k^3-weighted EXAFS spectra (**a**) and corresponding Fourier transforms (**b**) of 50 mM Np solutions. Solid line – experiment; dots – theoretical fit.

Np(IV) is surrounded by 11 oxygen atoms at a distance of 2.39 Å. The same number of oxygen atoms at a distance of 2.40 Å was found for a 5 mM Np(IV) solution in 1 M HCl [11]. In the second Np coordination sphere of solution Np1, we observed two sulfur atoms with a Np−S distance of 3.07 Å. This distance corresponds to a bidentate coordination of the SO_4^{2-} ion to the Np. Using the measured Np−O distance of 2.39 Å and the structural parameters of the SO_4^{2-} unit (S−O = 1.51 Å, angle O−S−O = 109° [12]), the calculated Np−S distance of 2.93 Å agrees within error limits with the measured value of 3.07 Å.

Both Np(V) and Np(VI) solutions Np2 and Np3 show the typical structural parameters of an actinyl ion. The distance to the axial oxygen atoms, O_{ax}, is 1.82 Å for Np(V). The Np is surrounded in the equatorial plane by four water molecules with a Np−O_{eq} distance of 2.49 Å. The number of water molecules is lower than previously observed by EXAFS on 5 mM and 1.3 mM Np(V) solutions in Cl^- and ClO_4^- media [11, 13], respectively (see Table 3). The reason for this is not yet understood. However, a low number of four water molecues was also oberserved by EXAFS for an aqueous species of Pu(V) [2]. The increase of the Np oxidation state from Np(V) to Np(VI) leads to a shortening of the axial and equatorial oxygen bonds by 0.07 Å and an increase of the number of water molecules attached to the neptunyl from four to five. The bond distances Np−O_{ax} and Np−O_{eq} of the Np(VI) solution are 1.75 Å and 2.41 Å, respectively.

The observed Np−O bond distances of Np(IV) and Np(V) are in good agreement with the values reported for 5 mM Np in chlorine solution [11]. The structural parameters for Np(IV) sulfate and Np(VI) hydrate, given in Table 3, are reported for the first time.

6. Conclusions

The following conclusions can be drawn from the XAFS studies on Tc and Np solutions at ROBL:

1) All EXAFS spectra measured in transmission mode in the energy range of 17–21 keV, which have a high signal-to-noise ratio, demonstrate the excellent performance of all beamline components including the synchrotron source, the monochromator and mirrors, sample positioners, and detectors. Based on our experience from radionuclide experiments on second- generation synchrotron light sources, we conclude that the large k-range and data quality that can be achieved at ROBL are superior.
2) The examples of Tc and Np EXAFS spectroscopy show that it is a powerful technique to obtain structural information on radionuclide species in solutions.
3) The actinide L(III)-edge XANES spectra are sensitive to the electronic and molecular structure of the actinide complexes and can be used to determine the oxidation state of the element under study [14]. XANES spectroscopy is especially valuable in cases where other analytical techniques, like UV/Vis spectroscopy, are limited due to matrix effects.
4) One disadvantage of performing experiments at a synchrotron light source is that the samples are usually prepared at the home institute and shipped to the experimental station, which may occasionally introduce undesirable changes of the sample composition during transport. This may be important for experiments with actinides. It is possible to overcome this disadvantage at ROBL by preparing/modifying the radioactive samples in the glove box. For example, it is difficult to stabi-

Table 3. EXAFS structural parameters for Np solutions. The 95% confidence limits were estimated by EXAFSPAK.

Sample	Shell	R(Å)	N	σ^2 (10^{-2} Å^2)
Np1, Np(IV)	Np−O	2.39 ± 0.01	11 ± 1	1.2 ± 0.2
	Np−S	3.07 ± 0.02	2.2 ± 0.9	0.7 ± 0.3
Np2, Np(V)	Np−O_{ax}	1.822 ± 0.003	1.9 ± 0.2	0.23 ± 0.03
	Np−O_{eq}	2.488 ± 0.009	3.6 ± 0.6	0.6 ± 0.1
$NpO_2(H_2O)_x^+$ [13]	Np−O_{ax}	1.83	1.6	0.002
	Np−O_{eq}	2.52	5.2	0.008
$NpO_2(H_2O)_x^+$ [11]	Np−O_{ax}	1.85	2	0.18
	Np−O_{eq}	2.50	5.0	0.70
Np3, Np(VI)	Np−O_{ax}	1.754 ± 0.003	2.0 ± 0.1	0.15 ± 0.03
	Np−O_{eq}	2.414 ± 0.006	4.6 ± 0.6	0.56 ± 0.09

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lize the Np(III) hydrate in solution. But with an electrochemical cell positioned in the synchrotron beam, one can prepare the Np(III) oxidation state and measure the XANES and EXAFS spectra in situ. Additional experimental conditions will be available at ROBL for time-dependent and spatially-resolved XAFS studies using the monochromator in quick-EXAFS mode and by focusing the synchrotron beam [5]. In conclusion, the radiochemistry station at ROBL provides many unique features, which will contribute significantly to a better understanding of processes that are currently of great interest in nuclear coordination chemistry and environmental radiochemistry.

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