

Laboratory-scale X-ray absorption spectroscopy approach for actinide research: Experiment at the uranium L3-edge

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X-ray absorption spectroscopy without a synchrotron for actinide research: an example for uranium L₃-edge near edge study.

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Abstract

We report the first proof of principle of an efficient and cost-effective benchtop alternatives to synchrotron radiation beamlines to perform at laboratory scale X-ray Absorption Spectroscopy (XAS) at the U L₃-edge in transmission mode. We find excellent agreement with synchrotron-based studies for concentrated samples, in reasonable acquisition time, for UO₂, KUO₃ and β-UO₃ samples. The approach described here already constitutes an inexpensive answer to the XAS beamline over-subscription in the field of actinide's research for state of the art experiments. Moreover, our results opens the door to many future applications in the field of actinide's research, including f-electron chemistry, environmental chemistry and nuclear energy physico-chemistry such as advanced nuclear fuel and long term nuclear waste disposal.

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1. Introduction

X-ray Absorption Spectroscopy (XAS) is a well established non destructive method to determine both the oxidation state of and the local environment around one given element of the studied compound. One major strength of this technique is that no special sample preparation is usually required, and that it is a bulk sensitive method due to the long range penetration length of X-rays in matter. Its sensitivity to the very local order makes such experimental approach to be useful not only for crystalline materials but also for liquids, gases, or amorphous matter. For example, XAS is regularly reported in literature in the field of actinide's research such as, among many others, actinide's molten salts [1], nuclear fuels [2, 3], nuclear waste [4] and environmental [5] studies. Indeed, by taking advantage of X-ray high penetration depth, XAS allows to perform measurements despite the necessary but highly constraining confinement barrier arising from safety considerations when studying radioactive matter, and especially actinide's bearing materials.

XAS experiments need a monochromatic, tunable over a wide range of energy and high flux photon beam. These needs have strongly limited its development to only synchrotron radiation facilities. In addition, the finite and low success rate of synchrotron beamtime access strictly restricts the number of possible studies, and subsequently excludes a large amount of potentially important scientific research to be considered, especially because of the absence of any alternative. The case of actinide's research is even worst due to the demand of radioactive material dedicated beamlines, and specific authorizations from radioprotection safety agencies to bring radioactive samples to the synchrotron. Associated to the high costs of radioactive sample shipment, the low number of dedicated beamline strongly limits the experimental opportunities. For example, in Europe, only few beamlines are clearly dedicated to actinides research: the MARS beamline [6] at the French

synchrotron radiation facility SOLEIL (Saint Aubin, France), the ROBL beamline [7] at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), and the INE [8] and CAT-ACT beamlines [9] at the ANKA synchrotron radiation facility of the Karlsruhe Institute of Technology (KIT, Karlsruhe, Germany). Consequently, the development of alternatives are mandatory to compensate the currently lacking beamtime availability. Approaches for XAS using laboratory-based sources and crystal optics have been reported since the early 1980's [10–20]. Typical geometries are Von Hamos, Johansson and Johann geometries using cylindrically [10–17, 19] and spherically [18, 20] bent analyzer crystals (CBCA and SBCA respectively). Compared to CBCA, SBCA's offer a relatively higher collection solid angle and a higher resolution in the hard x-ray regime depending on the considered configuration and energy range [18]. However, the reported laboratory scale XAS devices have been mainly used on energies situated between 5 and 12 keV, which does not include the actinide M and L-edges. This paper aims to demonstrate the proof of principle of an efficient and cost-effective alternatives to synchrotron at the uranium L_3 -edge energy range, i.e. between 17 and 18 keV.

2. Material and experimental methods

2.1. Sample preparation

All samples were prepared from depleted nuclear grade UO_{2+x} , supplied by FBFC International (Dessel, Belgium). An assessment of the impurity content of this powder has been reported elsewhere [21]. Conditions for preparation of the various samples were evaluated via simultaneous thermal analysis (Netzsch STA 449 F1 Jupiter).

The preparation of UO_2 is detailed in [22]. KUO_3 was prepared by mixing stoichiometric amounts of U_3O_8 and K_2CO_3 (Sigma-Aldrich, Belgium) powders and

annealing at 800 °C for 10 h under reducing conditions. A wet-chemical route was employed to produce β -UO₃. As-received UO_{2+x} powder was first dissolved in nitric acid and subsequently titrated with an excess of ammonia aqueous solution, which results in precipitation of ammonium diuranate (ADU). β -UO₃ was then obtained by calcining the ADU powder at 550 °C for 30 min.

Phase purity of all samples was confirmed via X-ray diffraction. About 30-50 mg of compound powders were intimately mixed with boron nitride powder and compacted into thin pellets. These pellets were then doubly confined in kapton and polyethylene.

2.2. Synchrotron radiation experiments

X-ray Absorption Near Edge Structure (XANES) were first measured at the Rossendorf Beamline (ROBL, BM20) [7] situated at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The storage ring operating conditions were 6.0 GeV and 170-200 mA. A double-crystal monochromator mounted with a Si(111) crystal coupled to collimating and focusing Rh-coated mirrors was used. U L₃-edge (17.166 keV) XANES spectra of all samples were recorded in transmission mode between 17 and 17.3 keV. The energy calibration was carried out measuring a Y foil (K-edge, 17.038 keV) in transmission mode simultaneously with each sample. A step size of 0.75 eV was used in the edge region. The energy E₀ of the edge absorption threshold position was taken at the first inflection point of each spectrum by using the first node of the second derivative. Several acquisitions were performed on the same sample and summed up to improve the signal to noise ratio. However, the spectra presented here are for comparison purpose only, and so, one scan of approximately 30 min is shown. The ATHENA software (Version 0.9.18) [23] was used to remove the background and to normalize the spectra.

2.3. Laboratory-scale experiments

The benchtop instrumentation developed at University of Helsinki is based on the use of SBCA which allows simultaneous monochromatization and focus of the X-ray beam to the sample. The main interest of using SBCA instead of other wavelength dispersive systems comes from their ability to achieve spectrometers with a very good energy resolution while having large collection solid angle [24, 25]. They have recently become very attractive at synchrotron radiation and X-ray Free Electron Laser beamlines through the design of high-resolution X-ray emission spectrometers [8, 9, 26–35]. The general principles of the used set-up [36] is schematically shown in Figure 1.

Sample, X-ray source and SBCA are positioned in a Rowland circle. When scanning the energy, both crystal and sample move synchronously to track the corresponding Rowland circle. The broadband x-ray radiation from the laboratory X-ray source directly illuminates the SBCA which monochromatizes and focuses the corresponding wavelength onto the sample. Slits reduce the ambient X-ray background arising from elastic scattering and limit the undesired wavelengths to hit the sample. The detector collects the photon transmitted through the sample.

U L_3 -edge XANES spectra of some samples as measured at ROBL were collected using the laboratory scale XAS setup at the University of Helsinki [36]. The X-ray source was a fine-focus Ag anode X-ray tube (Seifert/XRD Eigenmann) with $0.4 \times 0.8 \text{ mm}^2$ effective source size (Horizontal \times Vertical). The accelerating potential and electron current was fixed to 30 kV and 10 mA respectively. The detector was a CdTe detector (Amptek XR-100T) with an active area of approx. 3 mm of diameter. Coupled to an integrated signal processing electronic including Multi-Channel Analyser (Amptek, Inc.), its good energy resolution allowed to reject elastic and inelastic scattering background and harmonics. The incident beam was "monochromatized" by a Ge(111) SBCA. The U L_3 -edge (17.166 keV)

XANES spectra of all samples were recorded in transmission mode between 17 and 17.3 keV. This energy range corresponds to the (999) reflection of the Ge(111) SBCA with Bragg angle between 81° and 86° .

The energy dependence of the incident flux is usually characterized by removing the sample and repeating the energy scan [18]. Unfortunately, strange spectral behaviour, probably caused by elastic and inelastic scattering on the doubly confined sample holder, were observed following this method. To overcome this difficulty, we took advantage of the presence of harmonics in the incoming beam as shown in Figure 2.

Assuming that in the absence of sample, both Ge(888) and Ge(999) behave similarly upon the Bragg angle probed range, one can simultaneously measure the incoming beam intensity and the U L₃-edge absorption spectra. In the absence of any edge or X-ray source features within the energy range covered by the chosen harmonics, absorption decreases linearly with energy increase which justifies the validity of such approach, given the fact that there is no additional feature from the X-ray source. Then, the acquisition duration is no longer limited by the needs to repeat the experiment without sample to collect the incident flux.

3. Experimental results and discussion

Uranium L₃-edge XANES spectra for UO₂, KUO₃ and β -UO₃ and collected using both the laboratory-scale set-up and the ROBL beamline at ESRF are compared in Figure 3.

In this figure, the two datasets are in excellent agreement for both synchrotron and laboratory data. All the spectral features are well reproduced whatever the considered sample. Statistical noise is clearly visible on laboratory scale spectra. It comes from that the several order of magnitude photon flux differences between

synchrotron radiation and standard X-ray tube sources, which is not completely compensated by longer integration time per spectra which is here 24 hours at laboratory and 2 hours at synchrotron. However, 24 hours is not a limiting factor for experiments performed at laboratory and further improvements are expected in the near future. One can also note that slight discrepancy is observed below the edge. This phenomenon is due to imperfect background removal on laboratory spectra. Improvements are currently under progress to eliminate such undesirable feature, which comes from the static integration range on fluorescence spectra instead of dynamic ones. Indeed, the integration energy range must follow the incoming beam energy which is scanned along the XAS spectrum. But, the short energy range presented here is not so much affected by this effect, and the results are good enough in first approximation to comparison and proof of principle purpose.

4. Conclusion

We have demonstrated the effectiveness of the laboratory scale XAS set-up to measure U L_3 -edge in transmission mode. We find excellent agreement with synchrotron-based studies for concentrated samples, in reasonable acquisition time. Improvement and optimization of such experimental device are on-going to ensure faster acquisition and fluorescence mode to be performed in the near future. By avoiding the high costs associated to radioactive materials shipments from dedicated laboratories to synchrotron radiation facilities, the laboratory scale XAS device constitutes, as demonstrated in this paper, an efficient and non expensive alternative to synchrotron radiation state of the art XAS studies that strongly suffer beamline over-subscription in the field of actinide's research. Consequently, this versatile device, by providing a easy to access complement to synchrotron radiation facility, opens the door to many applications in the field of actinide's

research, including f-electron chemistry, environmental chemistry and nuclear energy physico-chemistry such as advanced nuclear fuel and long term nuclear waste disposal.

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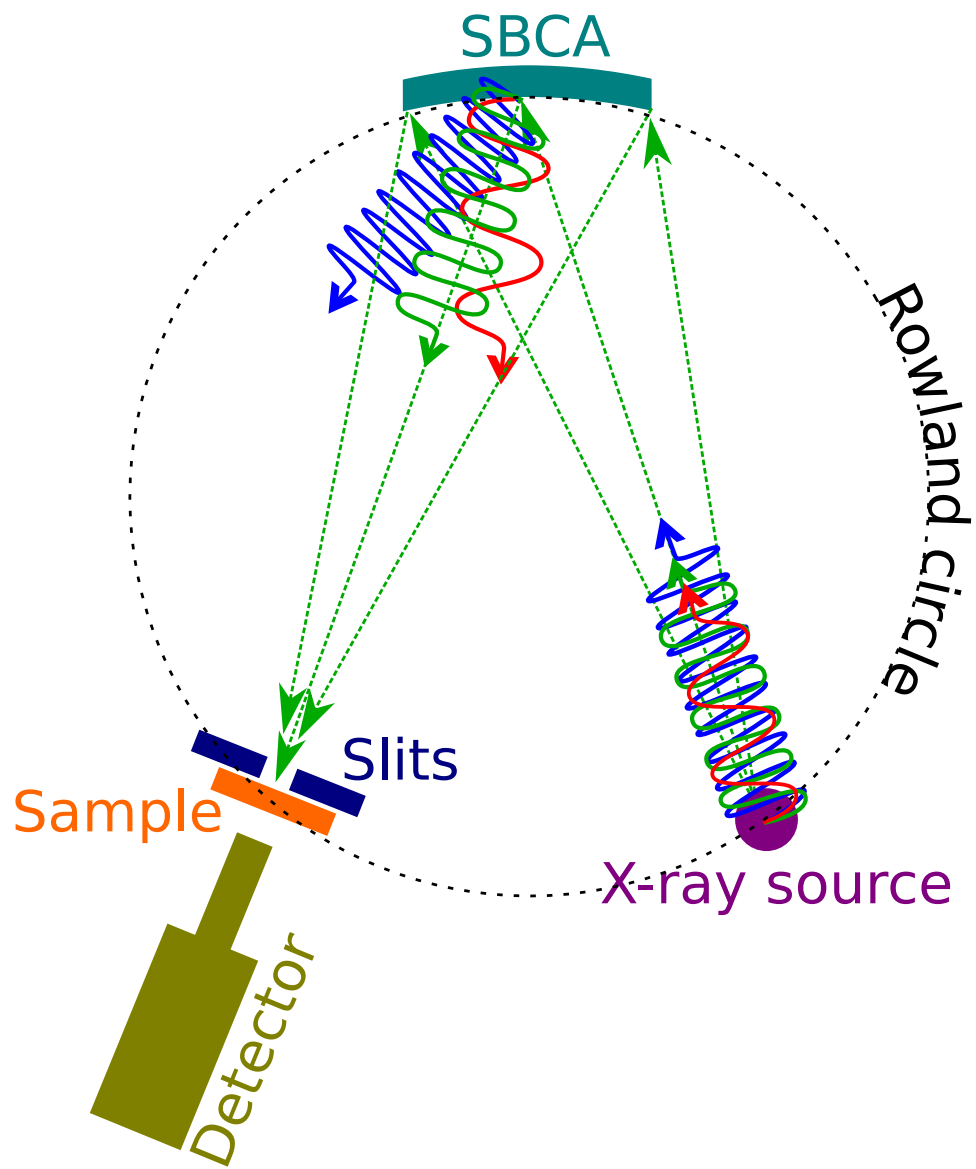


Figure 1: Laboratory scale instrument principles and configuration as for X-ray Absorption Spectroscopy.

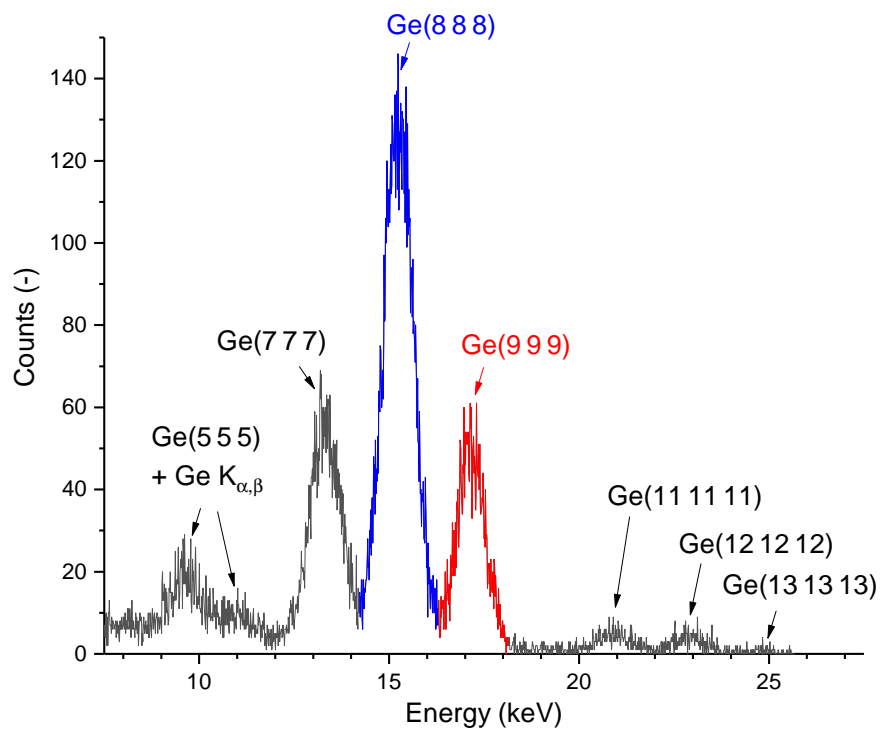


Figure 2: X-ray spectra of the incoming beam collected through the slits, without any sample. The different harmonics due to the Ge crystal as well as the resulting Ge fluorescences are also indicated. Note that lower harmonics were intentionally suppressed using Al filter, in order to not saturate the detector. The Ge(888) reflection (in blue) was used as a measure of the incoming beam intensity while the Ge(999) reflection (in red) was the interesting signal.

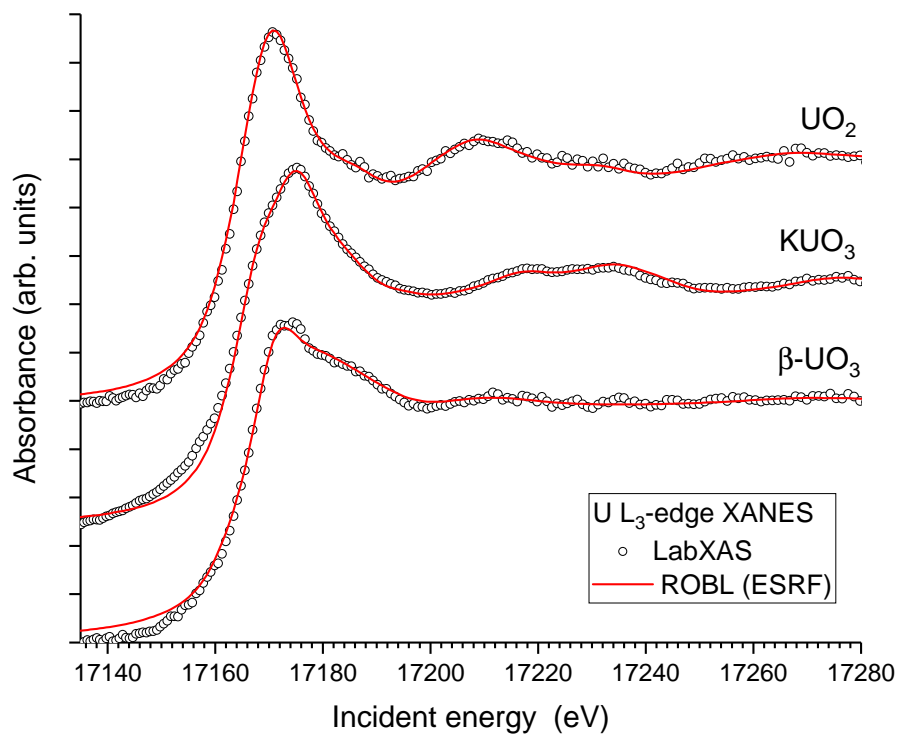


Figure 3: Uranium L₃-edge XANES spectra obtained for UO₂, KUO₃ and β-UO₃ and collected in transmission mode using both the laboratory-scale set-up (open symbols) and the ROBL beamline at ESRF (full lines). The spectra are vertically shifted for clarity.