



Low-cost vacuum compatible liquid cell for hard X-ray absorption spectroscopy

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ABSTRACT

We present the design, fabrication, and commissioning of a new liquid cell for X-ray absorption spectroscopy, compatible with measurement in both transmission and fluorescence modes. The design consists of easily demountable and replaceable parts: body, windows, elastomer spacer, washers and a holding screw. The pathlength of the liquid chamber can be adjusted by simply selecting the appropriate thickness of the spacer, making the cell extremely customizable to overcome experimental constraints. The cell has probed to be leak tight under low vacuum conditions. The compact and simple design makes the cell compatible with cryogenic applications. Finally, the possibility of manufacturing the cell by 3D printing makes it readily available and very competitive from a cost point of view (each unit is estimated less to be than 10 €).

1. Introduction

X-ray absorption spectroscopy (XAS) is a versatile structural technique for characterization and investigation of materials [1]. In contrast with diffraction methods or other optical spectroscopies (Raman, Infrared, Auger), XAS is an element specific probe which provides quantitative information about the local structure and electronic properties around an absorbing atom. Since it is based on the photoelectric effect, and on the consequential back-scattering of the ejected photoelectron waves from the neighboring atoms of the absorber, XAS only provides information about short-range order. No assumption of periodicity or symmetry is done in its theoretical formulation [2], which means that XAS is equally applicable to condensed matter in all forms (solid crystalline or amorphous, liquid, and gas). The data are interpreted in terms of pseudo radial distribution functions and the projected electron density of states, i.e. the type, number and distances of the surrounding atoms.

Liquid samples are investigated in several different fields of research. Chemical and biological reactions/processes mainly occur in condensed phases, i.e. solids and liquids. Indeed, many precursors for specific reactions are in liquid form [3] and, it is worth mentioning that some catalysts can show higher activity in liquid form [4]. Additionally, the high mobility of liquids has implications in electrochemistry, analytics, environmental science and pharmaceuticals [5–7]. Hence, it is imperative to have the possibility to probe local dynamics and geometry

in liquids, since they directly determine their physical and chemical properties.

The potentiality of XAS in providing information on disordered matter (and in particular on liquids) has been widely demonstrated in the past years (a review is given in Ref. [8]). XAS can be measured in transmission and fluorescence modes. To measure in transmission mode with a reasonable signal-to-noise ratio, the absorption jump of the sample must be ≥ 0.1 . At the same time, in order to avoid compression of the spectral features, the total absorption of the sample needs to be controlled and limited [9]. In the case of a liquid, these two factors lead to severe limitations in terms of the X-ray pathlength. Apart from the energy limitations due to specific beamline settings, the material and thickness of the windows determine the accessibility to the desired edges especially at low energy. The most common materials used are: Kapton, Mylar, poly (vinyl chloride), glassy carbon.

Several technical solutions to measure liquids have been proposed for both hard and soft X-ray beamlines in order to overcome the different experimental difficulties and constraints. In 1993, Villain and co-authors reported about the modification and use of a commercial infrared cell from Specac [10]. The cell (consisting of a sample holder, windows, and sealing o-rings) allowed the investigation of only one sample at the time and only in transmission mode [10]. Subsequently Sanchez-Marcos et al., presented a transmission/fluorescence-compatible cell [11,12], in which the sample (located into a hollow cylinder of variable thickness)

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had a minimum path-length of 1.2 mm with its sealing assured by a fixing system with seven screws. Also in this case, only one sample could be measured. In 1998, Weber et al. designed a cell for fluorescence measurements as a function of temperature. The liquid was injected in a properly machined Teflon spacer (i.e. fixed thickness) and sealed between two windows by four screws and bolts. An U-shaped copper cooling block permitted to vary the temperature of the sample [13]. In 1999, a polycarbonate flow cell for transmission measurements with a fixed path-length of 3 mm was designed by Villinski and co-authors for investigating geochemical reactions [14]. In 2005, an in-situ cell based on a thermostated carbon-reinforced Teflon chamber was constructed by D. Lützenkirchen-Hecht et al. [15] for transmission measurements from room temperature up to about 133 °C. Also in this case, only one sample could be investigated and the presence of the two quartz windows made impossible to measure liquids at low energy. Over the last decades, few models of flow cells have been developed for transmission mode soft X-ray absorption on liquids. Nagasaka et al. studied oxygen K-edge spectra of water trapped between two 100 nm-thick SiN_x membranes. Artifacts of the higher order X-rays at the O K-edge region were evaluated and successfully removed by varying the sample thickness between 100–800 nm [16]. Meibohm et al. described a control system for soft X-ray temperature dependent absorption studies in the range –10 °C to 50 °C [17]. Schreck et al. co-authors extended the investigation from water to 3d metal ions aqueous solutions and alcohol–water mixtures with a similar cell [18]. More recently, X-ray microscopy transmission images have been recorded during electro-deposition of zinc oxide with a multi-technique compatible “wet” cell [19].

All the cells mentioned above have some common limitations: (i) the number of investigated samples (only one), (ii) complex and multi-element tightening system for the sealing (consisting in several screws and bolts, squeezing o-rings and windows); (iii) the manufacturing procedure (often involving the use of milling and/or lathe machines), (iv) cost of components, production of not commercially available ones, and assembly of the device.

Taking into account these general findings and trying to overcome these restrictions, here we propose a new versatile liquid cell in polycarbonate, which has selectable path-length and is compatible with low vacuum (pressure 10^{–2} bars) for use in the hard X-ray range. Its extremely compact design, together with the use of common commercially available components and its vacuum compatibility, facilitates the adaptation of the design to cryogenic applications.

Finally, taking advantage of recent developments in 3D printing, the proposed design results in extremely low production cost (0.60 €/pc in polycarbonate and 8.30 €/pc in PEEK), making it very competitive from an economical point of view. Moreover, since the sealing of the sample is done between the elastomer o-ring and the windows (not in the 3D printed body — see below), the cell does not require a high printing layer precision (as occurring for the electrochemical cell described in Ref. [20]), it can be manufactured via economic 3D printing technologies currently available in the market. The STL file of the cell is included as supplementary material (SM).

First commissioning results on chromium and selenium solutions are presented at room temperature and low temperature.

2. Technical design

A technical drawing of the cell is shown in Fig. 1. The cell is composed of three parts: body, sample enclosure (made of a succession of o-rings and windows), and a holding screw (M8 screw with a 4 mm hole in the center). The body of the cell is made in polycarbonate, but the design can be adapted to Polyetheretherketone (PEEK). This materials choice makes use of the mechanical/corrosion resistance of these two plastics combined with their rather good thermal properties [21].

The cell has been designed for transmission measurements but it is also compatible with fluorescence measurements. An example of spectrum collected in fluorescence mode is reported in the SM. Special

care has been taken in designing the cell with an angular aperture of 45° (chamfered) to avoid shadows from the body when collecting spectra in fluorescence mode. Due to their chemical composition, the use of polycarbonate or PEEK minimizes the contribution of additional lines to the fluorescence spectra of the liquid sample. The body of the cell contains three liquid compartments (which fits inside the cryostat set-up of CLÆSS beamline [22]), permitting the simultaneous loading of three liquid samples, thus reducing the beamtime lost during sample changes. The cell assembly consists of an aluminum washer followed by a first window (upstream) and an elastomer o-ring, whose thickness can be chosen according to the required X-ray path. The liquid sample is loaded by dropping the liquid into the o-ring. The compartment is then sealed with another window (downstream), followed by another metallic washer. For the measurements reported in this work, we used a 50 μm thick Kapton windows, but other materials such as Mylar, poly (vinyl chloride) or glassy carbon can be used for the windows if different performance is required for certain applications. The washer in aluminum, instead of in stainless steel or other alloys, minimizes X-ray fluorescence background since Al emission line (1486 eV) is completely screened by the body of the cell. Finally, the holding screw seals the assembly by pressing the Al washer against the window film squeezing slightly the spacer. The extremely simplicity of the sealing system lies on the fact that there is only one tightening element. In addition, this element does not interfere significantly with the fluorescence detection since the screw is not on the same plane as the sample (the Multi-Channel-Analyzer spectra of the fluorescence detector shows the background contribution of other elements when measuring a 5 mM solution of Se(IV), see SM). O-rings of several thicknesses are commercially available but, in order to customize the cell to specific experimental constraints, it is possible to replace the elastomer o-ring with a piece of commercial silicone tube (#16 from Watson Marlow [23]) cut to the desired thickness up to a maximum of 5 mm liquid path. For commissioning purposes, the sample thickness has been changed from 1 mm to 4 mm. We have tested the resistance of the Kapton window to stress after loading the liquid by performing several pumping/venting cycles. No leakage and/or degradation of vacuum performance of the cell have been observed. To overcome the poor leakage detection due to the low vacuum working conditions (10^{–2} bars), the leakage was monitored by weighting the cell before and after each pumping/venting cycle that was repeated 10 times. In addition, the leakage ratio of the cell has been tested by keeping the cell under vacuum for 12 h (see dedicated section in SM). In both cases, a small difference in weight (less than 5%) is observed. The loss can be considered negligible considering the time scale of the XAS measurements of liquid samples carried out in CLÆSS (around 10 min in transmission; 1 or 2 h in fluorescence mode).

A correct determination of sample temperature is a key parameter for temperature dependent studies (Ref. [13]), which depends on the thermal conductivity of both, sample and cell (body and components), and on the efficiency of the cryostat used for the experiment. To monitor the temperature during the measurements, the cell has three additional slots for mounting thermocouples close to the liquid samples. In the SM, an off-line temperature calibration curve for water solutions using CLÆSS cryostat is provided as a possible indication of temperature gradients.

3. Data and discussion

Here we report the results obtained from the commissioning of the cell. We have performed XAS measurements on Cr and Se salts dissolved in water at Cr K-edge (5989 eV) and Se K-edge (12 658 eV) respectively. The choice of Cr and Se is based on their role in biological metabolism as well as environmental pollution.

Cr is recognized as an essential nutritional element for human health due to its role in glucose metabolism [24]. However, ingested Cr above 0.05 mg L^{–1} may have serious consequences including tumors, ulcers, and cancer [25,26]. In addition, Cr(VI), has been found to be more

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