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A specimen chamber for soft X-ray spectromicroscopy on aqueous and liquid samples

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A specimen chamber is described for soft X-ray spectromicroscopy of hydrated specimens and solutions. Applications include imaging and carbon edge spectroscopy of hydrated clay/polymer suspensions.

Keywords: X-ray microscopy; spectromicroscopy; wet specimen chambers; wet cells; colloidal systems.

1. Introduction

In colloid chemistry, biology, materials and environmental science, moist samples very often need to be investigated in their natural hydrated state. The aqueous environment is crucial for the measurements as the structure and properties of the sample are affected by the water surrounding it.

Soft X-ray microscopes offer especially favorable contrast mechanisms for studies of hydrated specimens when they are operated in the 'water window' spectral region between the C and O *K*-absorption edges, where water is relatively transparent and organics (and dense inorganics) can be viewed with good contrast. To exploit this capability, wet specimen chambers of different design have already been used with transmission X-ray microscopes (TXM) (Niemann *et al.*, 1994; Medenwaldt *et al.*, 1994; Meyer-Ilse *et al.*, 1998) and with the X1-A scanning transmission X-ray microscope (STXM) (Goncz *et al.*, 1992; Pine & Gilbert, 1992). Compared with TXM, the STXM is better coupled to the optics of high-resolution monochromators, and thus better suited to spectromicroscopy applications. However, in STXMs today it is the specimen (not the optics) which is scanned, and this places restrictions on wet chamber dimensions and mass.

In the STXM, one type of wet sample chamber has used rapidly interchangeable windows for easy exchange of different cell culture samples and periodic flow of fresh culture medium (Pine & Gilbert, 1992). This chamber cannot be used for the present studies because, owing to its ~1 mm internal air gap, it does not provide a fully hydrated sealed environment.

Other wet cells have used glued-on windows in a configuration that is good for interchange of sub-micrometer samples, but not for the type of specimen studied here. In addition, the sample windows used require more effort in window fabrication than for the wet cell described here (Goncz *et al.*, 1992).

For work at the C *K*-absorption edge one requires a chamber able to handle the few hundred micrometer working distance that is typical for high-resolution zone plates. Some wet cell designs [*e.g.* from the Göttingen X-ray microscopy group (Niemann *et al.*, 1994)] use polymer films to support the sample. For spectroscopy near the C edge it is favorable to use SiN or Si windows, that do not contain carbon (unlike polymer films).

We have therefore developed a wet specimen chamber which uses a clamp and O-ring system to permit rapid exchange of samples that are held between SiN windows, and which is able to be used with working distances as small as 350 μm. We demonstrate the use of this chamber for imaging clay/polymer aggregates at 60 nm resolution, and for obtaining C near-edge spectra of hydrated organic materials for the first time.

2. Design of the wet specimen chamber

Our wet specimen chamber (see Fig. 1) was designed to be used with the X1-A scanning transmission X-ray microscope at the National Synchrotron Light Source [described, for example, by Jacobsen *et al.* (1991)]. Its features are as follows:

(i) As a sample support, two 100 nm-thick SiN windows, 3 × 3 mm in size, are used, as they are thin, uniform, flexible and have a high transmission for soft X-rays. The windows sit in the center of a 9 × 9 mm Si wafer, of thickness 200 μm.

(ii) The thickness of the liquid sample layer between the two SiN windows has to be in the range of a few micrometers in order to be able to detect photons of the energy range of the water window between 284 and 543 eV in transmission.

(iii) The sample must be placed a few hundred micrometers away from a pinhole (order-sorting aperture); this works by using a thin shim metal as a support for one SiN window. The distance between the sample and the flat upstream side of the wet cell is presently 250 μm.

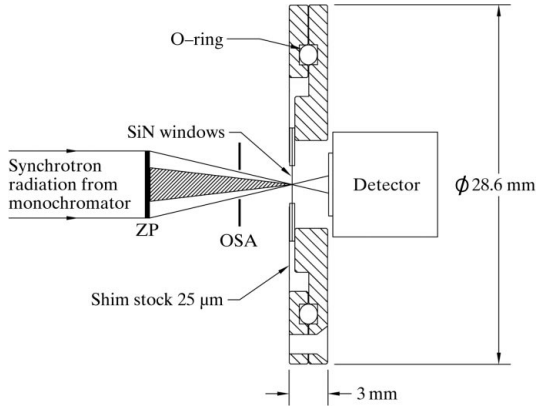

Figure 1
Cross section overview of the wet specimen chamber. Note that the wet cell dimensions are not to scale with respect to the zone plate (ZP), order-sorting aperture (OSA) and detector.

(iv) The wet cell is sealed by O-rings to prevent the sample from drying out; it can be kept hydrated and stable for up to 8 h. Exposure times may vary depending on the incident photon flux and image size, but a typical STXM image with good photon statistics takes between 10 and 30 min.

(v) The chamber has to be low in mass because it is scanned in the microscope and it must be thin in the beam direction to minimize absorption in the atmospheric-pressure air or helium path leading to the detector.

3. First experimental results

The wet specimen chamber allows imaging with high spatial resolution (sub-100 nm) and XANES spectroscopy with an energy resolution down to 0.1 eV of fully hydrated and liquid samples. When preparing the sample the two SiN windows are pulled together by surface tension and a thin liquid layer forms. This shows in interference fringes of different colors which appear when looking at the SiN windows. For suspensions the layer thickness depends on the size of the particles in suspension, and the windows flex over the particles. For particles of several micrometers in diameter the liquid layer is in the range 1–2 µm. The intention of this publication is to describe the instrumental details of this technique and to illustrate it by showing examples from clay science. In Fig. 2 we show a demonstration of flocculation when polyacrylamide is added to irrigation water to prevent soil erosion and promote water uptake. Fig. 2 shows a fully hydrated clay polymer aggregate. Fig. 3 shows the first C-XANES absorption spectra of hydrated polymers (polyacrylamide, for image see Fig. 4) and paraffin oil, as an example of applying this technique also to non-aqueous liquid systems. Further applications have been found in colloid chemistry in imaging and spectroscopically analyzing oil–water emulsions stabilized by solid colloids both near the C *K* and Ca *L* X-ray absorption edges (Neuhäusler *et al.*, 1999).

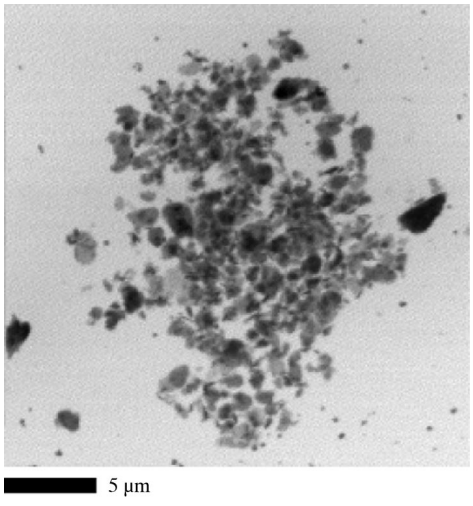

Figure 2
Image of a fully hydrated aggregate consisting of 2–0.2 µm kaolinite clay particles and polyacrylamide (PAM), an organic flocculant, suspended in an aqueous solution of 0.01 *M* $CaCl_2$ taken with the scanning transmission X-ray microscope at a wavelength of 42 Å. Clay content is 10 mg ml^{-1}, PAM content is 0.025 mg ml^{-1}.

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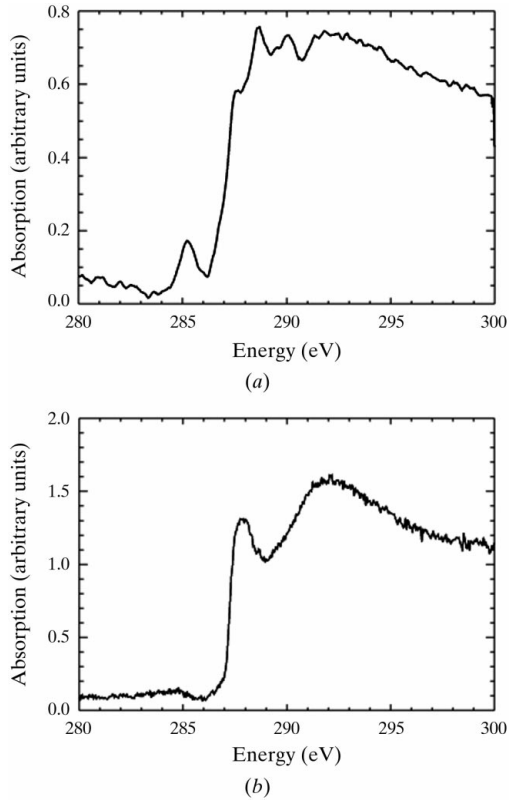

Figure 3
C *K*-XANES absorption spectra of (*a*) hydrated polyacrylamide macromolecules (see Fig. 4) and (*b*) paraffin oil (bulk sample).

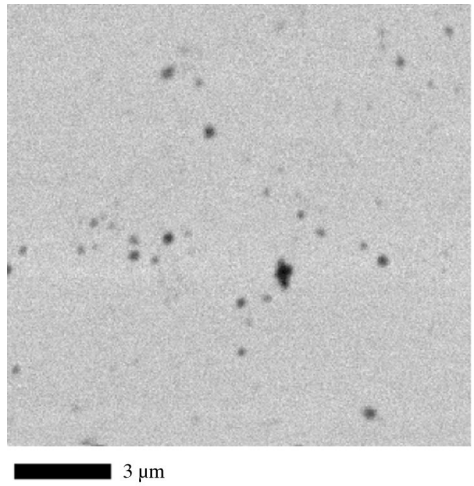

Figure 4
Image of hydrated polyacrylamide dissolved in water taken with the X1-A STXM at a wavelength of 4.2 nm (strong absorption for C). The macromolecules with a molecular weight of 18×10^6 u appear to be spheres.

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