

XAS Spectroscopy and Molecular Environmental Science

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Synchrotron-based X-ray absorption spectroscopy (XAS) is a powerful technique that gives information on the coordination around atoms of type **A** for all elements except the lightest. For an **AB_n** complex where **A** is the absorbing atom, the extended fine structure part of the X-ray absorption spectrum (EXAFS) gives information on the average interatomic distance **A-B**, and the number *n* of the bonded atoms, **B**. The structural features near the absorption edge of the spectrum (XANES) are connected to the oxidation state and bonding of the absorbing element **A**. Some examples of environmental interest are given below.

The flexible coordination of the calcium ion is an important feature for its many biochemical roles, but also makes its hydration in solution notoriously difficult to study. EXAFS and large angle X-ray scattering (LAXS) techniques showed a hydration number of eight waters asymmetrically distributed around the Ca²⁺(aq) ion. We reached this conclusion by comparing the mean Ca-O distance in solution, 2.46(1) Å, with the Ca-O distances from Ca²⁺-hydrates in crystals. Molecular dynamics (MD) simulations of the EXAFS spectra gave information on vibrational amplitudes and water exchange in the hydration sphere.

Synchrotron-based X-ray absorption spectroscopy (XAS) is used in actinide research to predict the fate of nuclear waste products in the environment. Convenient model elements for the coordination chemistry of tetravalent actinides are Th(IV) and U(IV). We determined the mean metal-oxygen bond distance and hydration numbers of the U⁴⁺ and Th⁴⁺ ions and their fluoride complexes in acidic solutions from their L_{III} edge EXAFS spectra.

We applied sulfur XANES spectra on wooden core samples of the 17th century Swedish warship *Vasa*, and found high concentration of sulfur in reduced forms within the moist wood of the artefact. This explained its recently discovered, severe problems of high acidity and salt precipitation (*Nature* **2002**, 415, 893-897). Sulfate, SO₄²⁻, is the major form on the surface but inside the wood reduced forms of sulfur dominates. Our analyses indicates that hydrogen sulfide, produced by sulfate-reducing bacteria in anoxic polluted sea-water around the submerged artefacts, has penetrated the wood and then transformed and accumulated as elemental sulfur. We used Fe-K edge EXAFS to show that for other marine-archaeological shipwrecks, e.g. the *Batavia* in Australia, iron sulfides and pyrite (FeS₂), also have formed due to the availability of corroded iron from nails, iron bolts, cannons, etc. In the museum, a catalyzed stepwise oxidation of the reduced sulfur compounds takes place in the moist wood, finally giving sulfuric acid with ancillary salt formation and wood degradation. Analyses of total sulfur show surprisingly high sulfur concentrations, for the *Vasa* sometimes exceeding 10 mass% S in the surface layer. This indicates that totally about 6 tonnes sulfuric acid could form in the wood of the *Vasa*. The XANES spectra show systematic variations of the intermediate sulfur species with depth in the core samples. By revealing the oxidation mechanism and rate we can propose more efficient conservation procedures.

Sulfur XANES spectroscopy can also be used to study on a molecular basis, the effects of atmospheric sulfur dioxide (SO₂) and hydrogen sulfide (H₂S) exposure on plants. Examples will be given on how speciation of the sulfur compounds in the wood can be made through comparison with a XANES library of standard compounds. The results can be used to test different proposed pathways for sulfur metabolism in plants and leaves, and when and how too high exposure causes detrimental effects.