RECENT ACHIEVEMENT AND PERSPECTIVES IN SYNCHROTRON RADIATION X-RAY ABSORPTION SPECTROSCOPY

JURIS PURANS[1,3], SIMONE BENAZETH[2], AND CHARLES SOULEAU[3]

1 *Institute of Solid State Physic, University of Latvia-Kengaraga 8, 1063 Riga*
2 *L.U.R.E.-Bat 209D-Université Paris XI, 91405 Orsay*
3 *Laboratoire de Chimie Inorganique-UFR Pharmacie-Université ParisXI, 92296 Paris*

During the last 20 years, x-ray absorption spectroscopy (XAS) has found extensive application in the materials science [1-3], solution chemistry [4], biology [5], therapeutic chemistry [6] and geochemistry. However, it is relatively recently XAS methods have been utilized for measurements on archaeological materials [7,8].

Rapid advance in the XAS method is caused by appearance of synchrotron radiation (SR) sources [9], as well as by considerable achievement in the theory and its practical realization in convenient and easily available software packages [1,2]. The third-generation SR sources of a continuous spectrum from infrared light to hard X-ray are many orders of magnitude brighter than x-ray tubes and ensure quick (as short as several milliseconds) XAS-spectrum measurement for low concentration of an element and access most of the elements in the periodic table.

Note, that a wide range of techniques is employed at SR centres to study the composition and structure of a wide range of solid materials and solutions [9]. Techniques include X-ray diffraction, X-ray fluorescence, X-ray absorption spectroscopy and infrared spectroscopy which can provide, often non-destructively, information about mineralogical and elemental composition, crystallographic structure and oxidation state determination with excellent spatial resolution and rapid data collection [8,9]. Recently XRD method using SR has also been applied for identification of archaeological cosmetic chemicals [10].

Several review books and papers [1,2] have been written about XAS and its applications. Here, a brief survey of the XAS spectroscopy and its analysis techniques suitable for the investigation of the archaeological materials and cosmetic (therapeutic) chemicals. When x-rays of energies close to the electron binding energies are absorbed, features known as absorption edges are observed. XAS spectroscopy refers to the measurement of the x-ray absorption coefficient near and above the threshold of an absorption edge of a specific element in a given compound. The success of XAS is due to its chemical element sensitivity and independence on the aggregation state. As a matter of fact, XAS spectroscopy probes the electronic and geometrical structure of matter in gaseous, liquid or condensed state providing information about local structure and dynamics.

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The principal scheme of XAS measurements is shown in Fig. 1 and the typical x-ray absorption spectrum is shown in Fig. 2. Generally, a XAS spectrum is considered and analyzed as composed of three parts:

1) X-ray absorption edge region extending a few eV below and above the edge is determined by the local density of vacant states in an absorbing atom; the region is very sensitive to the valence state of the an absorbing atom (Cr^{3+}/ Cr^{6+}; V^{4+}/ V^{5+}; Fe^{2+}/ Fe^{3+}; Pb^{2+}/Pb^{4+} etc.)

2) X-ray absorption near edge structure (XANES) region extending from the edge up to about 30-50 eV above it is determined by multiple-scattering effects (scattering of an excited photoelectron on several atoms); the region is very sensitive to the symmetry of polyhedra (first and second coordination shells); for crystalline materials the region contain information about the atomic structural organization over distances up to about 6-8 Å;

3) extended x-ray absorption fine structure (EXAFS), extending from about 30-50 eV up to 1000 eV and more, above the edge; Fourier transform of the EXAFS oscillations gives a pattern close to the radial atomic distribution for crystalline materials; the region contain information about the atomic structural organisation over distances up to about 4-6 Å. This circumstance testified to the crystallographic origin of information contained in the EXAFS oscillations.

XAS can provide information that substantially complements the results of other experimental methods, such as the diffraction (scattering) of x-rays and neutrons, photoelectron, and emission x-ray spectroscopy. The basic XAS advantages are (i) selectivity in the chemical-element type (in some cases, also in the location of an element in a material), which enables one to acquire information on pair and multiatomic distribution functions for the local environment of each elements of the material under investigation; (ii) sensitivity to the partial densities of vacant states near the Fermi level; (iii) high density sensitivity (10–100 particles per mole) and relatively short times (from milliseconds to tens of minutes) of detecting experimental spectra when the synchrotron radiation is used; and (iv) a small required sample volume (usually, an amount less than 30 mg/cm^2 is enough). Due to these advantages, the employment of XAS is especially attractive for studying the micro- and nanocrystalline [2] and disordered multicomponent materials (ceramics [7,8], clays [11] and glasses [2,3]), as well as complex fluids and solutions [4,5].

For example, recently were made the first combined *in situ* diffraction and XAFS measurements on the H10 beam line (LURE, Orsay) on Lu- and Eu-montmorillonite at high temperatures [12]. Such measurements exploit fully the novel capabilities of the H10 beam line and are the most certain method of correlating the changes in the Ln^{3+} coordination with structural changes in the clay. That is complimentary study to our previous papers on the structural transformations of interlamellar Ce^{3+} ions complexes in the montmorillonite clay at different temperatures (RT-245 °C) presenting various dehydration state of clay [11].

The high penetration of hard X-ray at high photon energies also enables the non-destructive analysis at the K-absorption edges of the interior (mm) of archaeomaterials

[8]. At the other hand, the low penetration of soft X-ray at low photon energies enable the non-destructive analysis of the *surface* of materials (10^{-6}-10^{-9}m).

At present, the third-generation SR sources ESRF (CE, France); ALS and APS (USA); ELETTRA (Italy); and SPRING8 (Japan) with radiation brightness up to ~10^{19} photons are in operation. More than 50 sources are now in operation and more than 10 are being designed [9]. Having high brightness and distinct linear or circular polarization, SR provides unique research possibilities.

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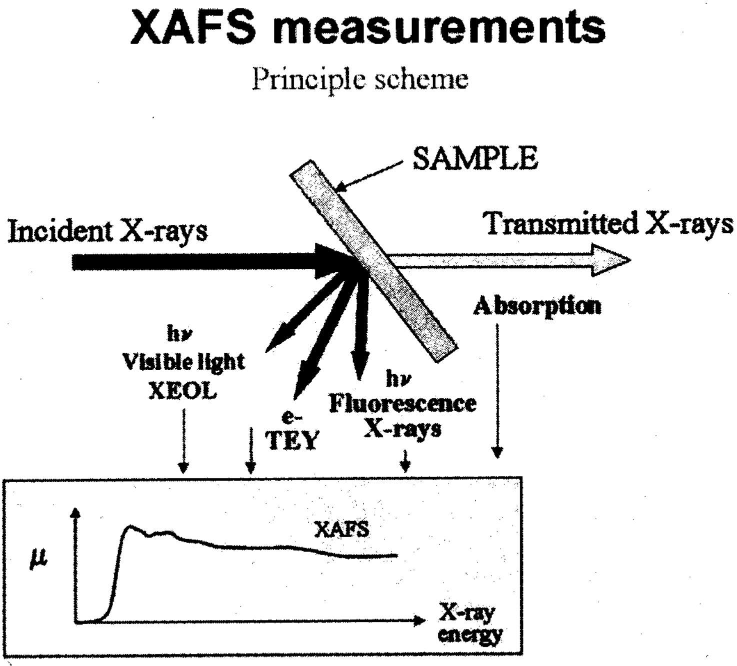

Figure 1. Principal sheme of X-ray absorbtion fine structure (XAFS) measurement.

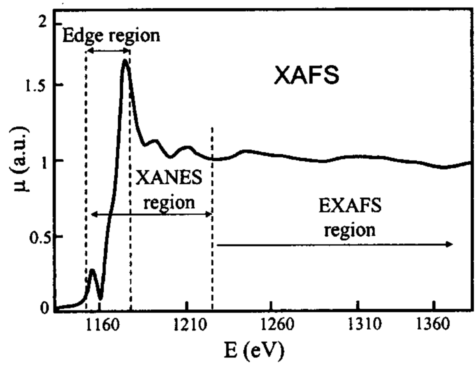

Figure 2. XAFS spectrum subdivided in its characteristic regions.