

High Energy Resolved Fluorescence Detected X-ray Absorption Spectroscopy : a powerful structural tool in bio-environmental and bio-nanomaterial sciences

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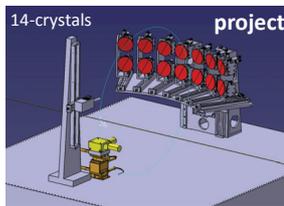
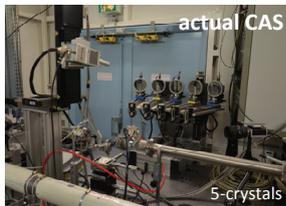
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WHY?

X-ray absorption spectroscopy (XAS) allows to probe the speciation of a target chemical element, i.e. its valence and the structure of the coordination shells. One of the specificities of XAS measurements in the biology and environmental sciences fields is that the probed element (e.g., pollutant or metal of the metalloprotein) is often diluted in the media, even in synthetic samples in order to be representative of realistic concentrations. In the case of nanoparticles as a sample, XAS spectra of good quality can only be obtained by carefully improving counting statistics and energy resolution. Indeed, the characteristics of the measured signals for this particular samples gather both bulk and surface contributions. The latter signal is the most meaningful (e.g. for toxicology studies), because the interactions between the nano-object and the external media occur mainly at its surface.

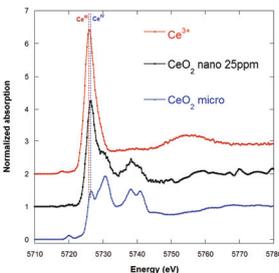
HOW ?

These points, importance of the detection limit and spectral resolution, lead us to improve the sensitivity of the fluorescence detection system. When the fluorescence signal is measured with a high energy resolution crystal analyzer ($\Delta E \sim 1-2\text{eV}$), the experimental broadening is greatly reduced and sharp features in the XAS edge can be resolved. Moreover, such high resolution allows to avoid any matrix contribution in the measured signal. Such measurements are already done on FAME beamline at ESRF and several examples of results will be given. In the future, the detection limit will be upgraded thanks to the development of a new multi crystal analyzers spectrometer.



NEW DETECTION LIMIT ?

Taking into account the capabilities of this new spectrometer under construction and the upgrade of the ESRF sources, the detection limit for XAS measurement will be decrease to the ppm.



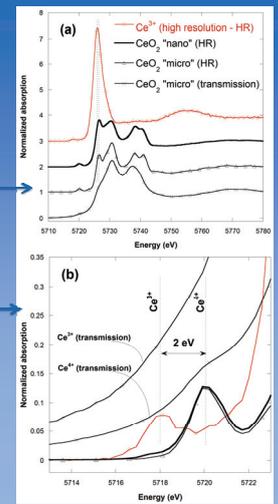
1 crystal / actual flux
 → XANES @ 25ppm (Ce)
 → XANES @ 48ppm (Ge)

14 crystals / flux x2 → ~1-2ppm

HIGH ENERGY RESOLUTION FLUORESCENCE DETECTED XANES

Measurement of fluorescence signals using crystal analyzer spectrometer instead of a solid state detector significantly improves X-ray Absorption Near Edge Structure (XANES) features. Measurements performed on CeO₂ micro- and nanoparticles, as well as Ce³⁺ reference, clearly showed the interest of high spectral resolution. All the XANES features of CeO₂ obtained classically just pop out using crystal analyzer.

For example, pre-edge peaks are not seen using classical measurement (transmission in this case) but clearly resolved in HR-XAS (Fig. b), which allows to clearly distinguish between 3+ and 4+ valence states. Spectral analysis is not only improved but simply made possible in many cases.

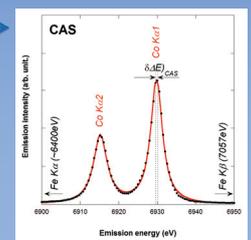
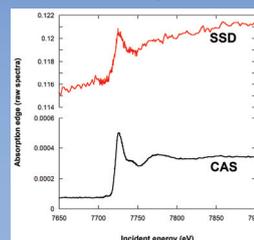
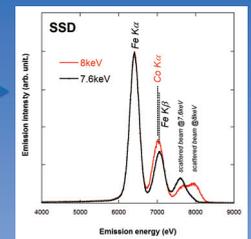


IMPROVED FLUORESCENCE SELECTIVITY

The use of a solid state detector (SSD) can find limitations when a high counting rate due to scattered beam and/or fluorescent signal from the matrix containing the diluted element does not allow to detect the signal of interest.

In the particular case of Co adsorbed on Fe oxide, the absorption spectrum at the Co K-edge is difficult to measure with a SSD detector because the Fe K_β fluorescence lines is superimposed to the Co K_α one ($\Delta E \sim 250\text{eV}$). With a CAS, the improved energy resolution ($\Delta E \sim 1\text{eV}$) allows to discriminate all the fluorescence lines.

Co K-edge XANES spectra have been then measured in total (SSD) and partial (CAS) fluorescence modes.



This project is financially supported by the french "grand emprunt" EquipEx (EcoX, ANR-10-EQPX-27-01), the CEA-CNRS CRG consortium and the INSU CNRS institute. Construction of the spectrometer prototype was financially supported by the INSU CNRS institute, ANR NANOSURF (coordinator: C. Chaneac, Laboratoire de Chimie de la Matière Condensée de Paris, France), ANR MESONNET (coordinator J.Y. Bottero, CEREGE), and CEREGE laboratory (Aix en Provence, France). Measurements at the Ge K-edge on Ge(48ppm) in ZnS were performed by J. Bonnet and J. Cauzié (Géoresources, Nancy).

References

- Hazemann et al., "High Resolution Spectroscopy on an X-ray Absorption Beamline", *J. Synchrotron Radiat.* **16** (2009) 283-292
- Llorens et al., "High energy resolution five-crystal spectrometer for high quality fluorescence and absorption measurements on an X-ray Absorption Spectroscopy beamline", *Review of Scientific Instruments* **83** (2012) 063104