High Energy Resolution Fluorescence Detection X-ray Absorption Spectroscopy in Environmental and Earth Sciences on CRG-FAME beamline at ESRF

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The FAME beamline (French Absorption spectroscopy beamline in Material and Environmental sciences) at the ESRF (Grenoble, France) is devoted to X-ray absorption spectroscopy and particularly for the study of highly diluted chemical element. An upgrade of the FAME instrument has been realized to overcome some limitation of Solid State Detector (SSD) and also to increase the sensitivity and selectivity with the design and installation of a crystal analyser spectrometer (CAS). A five crystals focusing spectrometer has been built for this purpose and is open to users since 2012. The advantages of measuring fluorescence-XAS with a CAS are illustrated from results obtained by our users on the beamline, especially in the environmental, geochemical and Earth science fields using different spectroscopic techniques :

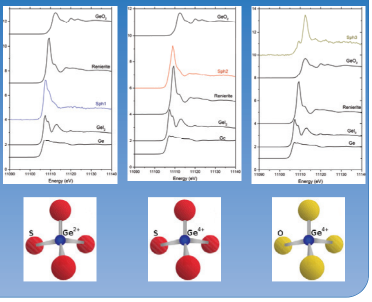
- High Energy Resolution Fluorescence Detected XANES
- Conventional XAS with an improved fluorescence selectivity
- X-ray Emission Spectroscopy & spin selective measurement

IMPROVED FLUORESCENCE SELECTIVITY

The main parameter that limits the ability to perform XAS experiments on diluted elements in optimal conditions may arise from the nature of the bearing phase. When the probed element is diluted in a soil (which can contain clays, silicate, Fe or Mn oxides...) the fluorescence signals delivered by this soil can :

- saturate the detectors,
- overlap with the fluorescence peak of the probed element.

CAS enables to get rid of that difficulties

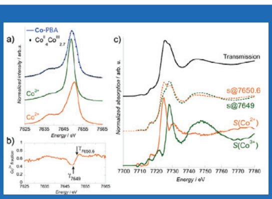


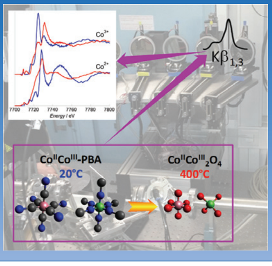
***Example** : speciation of Ge in sphalerite* (ZnS : Ge Kα overlaps with Zn Kβ). ([Ge]=800ppm). XAS spectra were recorded through the CAS aligned at the maximum of the Ge Kα1 line, which enabled to filter out the Zn fluorescence. 3 configurations of Ge incorporation in sphalerite were thus identified. The two most abundant show Ge^{II} and Ge^{IV} surrounded by S atoms in tetrahedral coordination suggesting the replacement of Zn by Ge. In the 3rd configuration Ge^{IV} is surrounded by O atoms, a configuration also observed in argutite (GeO_2).

XES & SPIN SELECTIVE MEASUREMENT

The energy position of the Kβ fluorescence lines is known to be sensitive to the spin-state ($K\beta_{1,3}$) and to the ligands ($K\beta_{2,5}$ & Kβ") of the probed element. X-ray Emission Spectroscopy (XES) and XAS spectra obtained by measuring such lines are then spin-, redox- or ligand- sensitive.

***Example** : in situ study of the calcination of a Co^{II}Co^{III} Prussian Blue Analog (PBA) into Co_3O_4.* In this PBA, Co^{II} and Co^{III} cations are both present in an *Oh* site but with different neighbors, while in Co_3O_4, the Co^{II}(HS) (resp. Co^{III}) cations occupy the *Td* (resp. *Oh*) site of the spinel structure. Redox-selective $K\beta_{1,3}$ XAS enabled to singly monitor the change of each site during calcination.

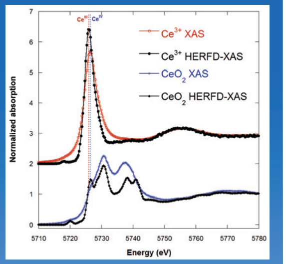




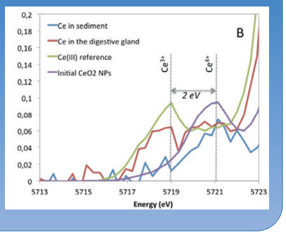
HIGH ENERGY RESOLUTION FLUORESCENCE DETECTED XANES

CAS measurement allows also to obtain HERFD-XANES signal with a spectral resolution much sharper than what could be classically achieved. This possibility is of great interest for the scientists because :

i) difference between spectra are often subtle
ii) improved resolution enables a precise determination of the local structure around the absorbing atom.



***Example** : distribution of CeO_2-based nanomaterials (NMs) within a pond ecosystem at low concentration.* The transfer, redox change and impacts of 1 mg.L^{-1} of bare and citrate coated CeO_2 NMS were followed toward an ecologically relevant organism exposed in a system mimicking a pond ecosystem. After 4 weeks, Ce was observed in the digestive gland of benthic organisms ([Ce]=280ppm) and associated with 65−80% of Ce^{IV} reduction into Ce^{III} for both bare and coated CeO_2 NMs. HERFD-XANES enabled to thoroughly study this redox change in the organisms and to attribute it to the digestive activity of the snails, and not to an interaction with the biofilm present on the surface sediments.



CURRENTLY

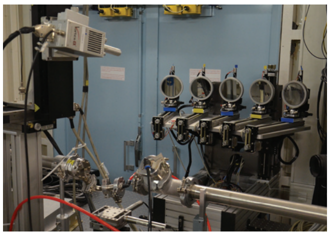
- **photon flux** : typically 5.10^{11} ph/s (monochromator : Si220)
- **beamsize** : 300x100 µm² (HxV, FWHM)
- **30 element** Ge SSD
- **5 crystals** spectrometer (Johann-type, 1m radius of curvature)
- **detection limit** : 25ppm with SSD, ~1-2 ppm with CAS (XANES)

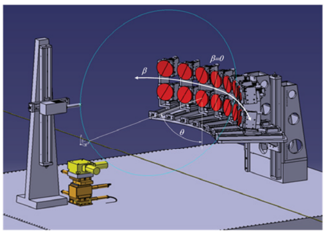
NEAR FUTURE &

The FAME-UHD (for Ultra High Dilution) beamline will be complementary to the FAME one, dedicated to CAS detection, and therefore optimized for this technique. Two parameters will be optimized :

- The **photon flux** on the sample will be increased (**x3**), with optical elements allowing a collection over a large solid angle
- A new CAS will include **14 crystals**.

→ **detection limit** : below 1ppm for XANES on FAME-UHD





FAME-UHD will be installed on BM16 at the ESRF. FAME & FAME-UHD will operate simultaneously with a common staff in order to optimize the complementarities between these two X-ray absorption spectroscopy instruments. FAME-UHD will be then the 5th French Collaborating Research Group beamline at the ESRF.

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