Conceptual Design Report for the CRG-FAME-UHD beamline

The scientific case for the beamline(s) after the ESRF EBS phase

The FAME-UHD beamline is the French Absorption spectroscopy beamline for Material and Environmental Sciences for Ultra High Dilution at the ESRF. It is dedicated to X-ray Absorption Spectroscopy (XAS) measured in fluorescence mode with a high energy resolution using a Crystal Analyser Spectrometer. The beamline is actually under commissioning and will be opened to the users in November 2016. However, the beamline is based on a long development performed on FAME beamline since 2005 which allowed to make projections on the science which will be done on FAME-UHD.

Project history.

The first tests of using a crystal analyser spectrometer on FAME beamline have been done in 10 years ago. We developed a five crystals CAS prototype, opened to users in 2011. We showed then that it was possible to measure XAS spectra on highly diluted element on a BM beamline, the measured fluorescence signal of interest being free from any undesired background signals thanks to the energy resolution of the CAS (1-2eV instead of 200-300eV for a solid-state detector, SSD). Based on this experience and on a challenging scientific case, we presented the FAME-UHD project to the ESRF-SAC in May 2012, project which was approved by the ESRF-Council in July 2012.

Compare to the CAS prototype and to the FAME optic configuration, FAME-UHD main characteristics are:

- a 14 crystals CAS spectrometer (~ x 3)
- an increased flux on the sample (~ x 4)

Science case: in 2016 and after the ESRF EBS phase

The scientific case of FAME-UHD presented to the SAC in 2012 is the direct evolution of the FAME's one, in material, catalysis, biological, environmental and Earth sciences. Scientists of these communities aim to determine the local speciation of diluted elements in a given media of interest, now approaching a new challenge, a concentration barrier (few tenth of a part per million - ppm) intrinsic to the energy resolved fluorescence measurement with a SSD. There are strong scientific needs to overcome this limit and the use of a CAS allows it.[1]

- From a general point of view, the aim of the beamline is to offer to users the possibility of determining the local structure of elements down to 10 ppm in a first stage, and subsequently to ~1 ppm. Such objective is completely realistic as we already manage to obtain spectra at sub-ppm level with a 5 crystals CAS (Figure 1).
- The main parameter which limits the ability to perform XAS experiments on diluted elements in optimal conditions may arise from the signals delivered by the main constituents of the matrix (Compton, fluorescence lines), which can be discriminate by a CAS (Figure 2).
- The key point of a catalytic reaction, a toxicity impact, a biological or catalytic activity… can be driven by subtle structural variations between different states. The improvement of the spectral resolution of the XANES spectra (High Energy Resolution Fluorescence Detected) allows to perform such

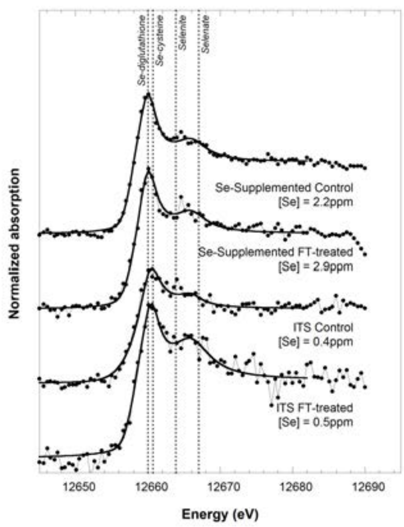

Figure 1. Selenium Spectra of "maturated" articular cartilage cultured in presence of Insulin-Transferrin-Selenium (ITS) and in presence of both ITS and sodium selenite

[1] The examples illustrating the science that will be done on FAME-UHD were obtained on FAME

acquisitions (Figure 3 & Figure 4).

(upper spectra)[2]

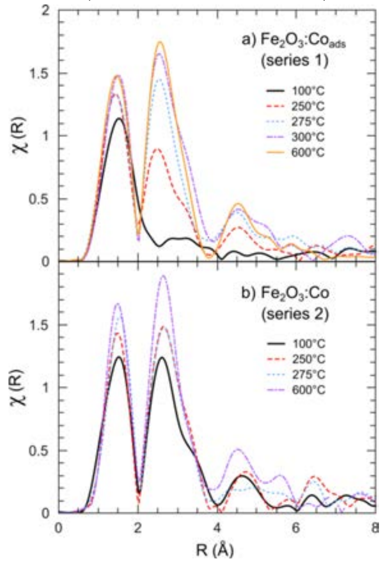

Figure 2. Fourier transforms moduli of k^2-weighted Co K-edge EXAFS oscillations for (a) Fe_2O_3:Co_{ads} and for (b) coprecipitated Fe_2O_3:Co samples annealed between 100 and 600 °C.[3]

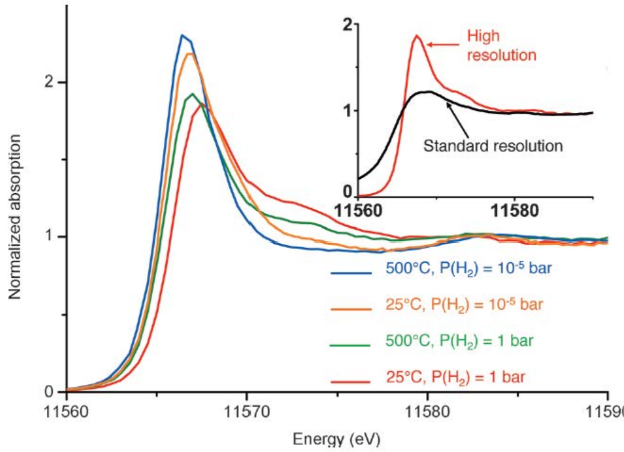

Figure 3. Pt-L_3 edge HERFD–XANES of Pt/Al_2O_3 catalysts recorded at different operating conditions. Inset: spectra recorded at 25°C and 1 bar of H_2, in HERFD mode (High resolution) and in standard fluorescence mode (Standard resolution). The influence of the H atoms on the shape of the Pt clusters is only visible with the shoulders at 11573eV on HERFD measurements.[4]

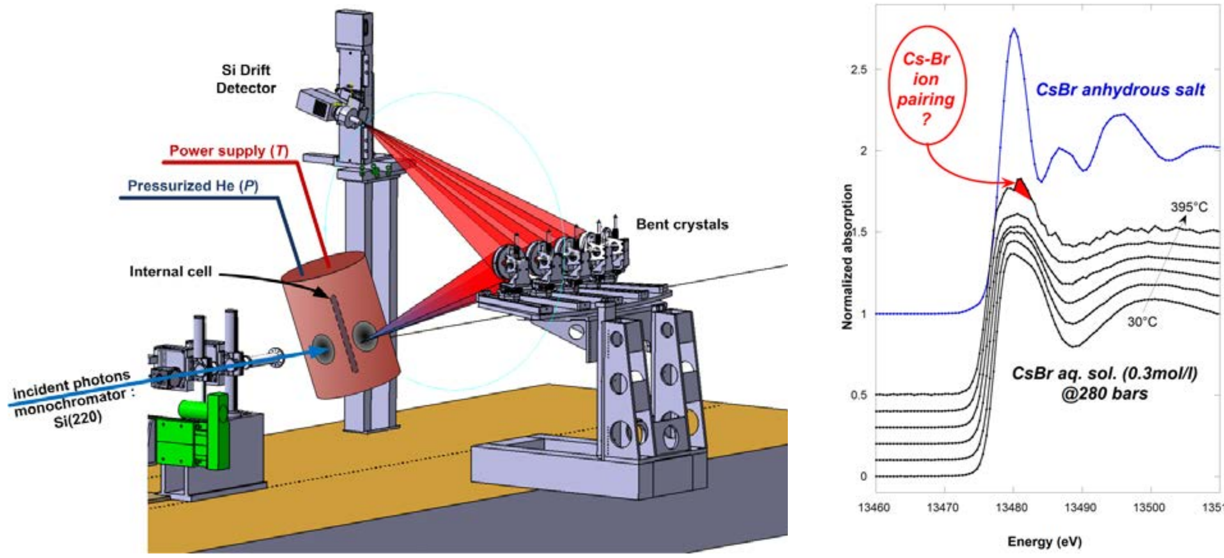

Figure 4. Left. Schematic view of the HP/HT vessel in operation with the CAS. Right. HERFD-XANES obtained at the Br K-edge from ambient to supercritical conditions for CsBr aqueous solution and CsBr anhydrous salt in order to put in evidence the existence of ion pairing[5]

Our scientific case can be summarized by the three main possibilities we can offer to the users:

- study of **highly diluted elements (sub-ppm)** typical of the concentration of metals in metalloproteins, in biological systems or ecosystems (Figure 1), in natural soils…,
- **high spectral resolution** measurements for very sensitive structural studies (Figure 3 & Figure 4),
- ***in situ* and *in operando* studies**, typical of chemistry, chemical physics , material, Earth science… studies (Figure 3 & Figure 4).

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2 Bissardon et al., "High resolution X-ray spectroscopy of selenium in articular cartilage at ppb level", submitted

3 Vichery et al., "Introduction of cobalt ions in γ-Fe_2O_3 nanoparticles by direct coprecipitation or post-synthesis adsorption: dopant localization and magnetic anisotropy", *J. Phys. Chem. C* **117** (2013) 19672–19683

4 Gorczyca et al., "Monitoring morphology and hydrogen coverage of subnanometric Pt/γ-Al_2O_3 particles by in situ HERFD-XANES and quantum simulations", *Angewandte Chemie* **53** (2014) 12426 –12429

5 Irar M., Hazemann J.-L., Testemale D., Proux O., preliminary results (M. Irar PhD)

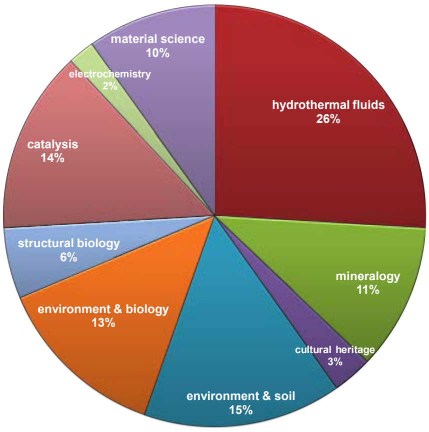

Figure 5. Repartition of the beamtime using CAS on FAME as a function of the scientific fields (IHR, CRG and ESRF review committees). Total = ~900 shifts / ~50 experiments.

The repartition of the scientific activities on FAME-UHD can be extrapolated from the use of the CAS prototype on FAME (Figure 5). The ratio of the beamtime performed on hydrothermal fluids is quite high due to the large number of IHR experiments performed by the team. The other scientific fields are quite homogeneously distributed.

FAME and FAME-UHD are complementary. As mentioned in FAME's CDR, the two beamlines benefit from **our partnership with an International Consortium for Environmental Implications of Nano Technology (ICEINT)** and a **national consortium (equipex PLANEX)** which includes 8 French laboratories on the studies of HP-HT fluids in Earth Sciences. The scientific topics addressed fit in with the priority area “Environmental urgency and eco-technology” laid down by the National strategy for research and innovation (SNRI), in particular by its focus on natural resources and issues related to climate change, and in the need for greater energy independence.
The beamline also benefited from the increased support of the CNRS Earth Sciences Institute (INSU) in particular with the recruitment of a new research engineer in October 2016 for the operation of the beamline.
A federative tool between both beamlines will be also the annual training course we propose since 2004, with the help of the CNRS permanent training, for actual or potential users of XAS beamlines (FAME+). Based on lecturers (XAS theory, X-ray optics basis…), tutorials (EXAFS, XANES, multiplets calculations) and practicals on beamline, FAME+ was the perfect place to prepare the users to the possibilities offered by CAS, on FAME in a first time, on FAME-UHD now. We will continue and developed this course involving all the beamline staff.

The choice of the new source

Ray tracing calculations were carried out with the Oasys interface. They show that, among the 4 proposed wiggler configurations (3-pole, 2-pole A and B, 1-pole “SBM”), it is possible to separate the wiggler contribution from the surrounding bending magnets at the sample position in the 3:1 geometry only with the SBM configuration (Figure 6). In the other configurations, the bending magnets will generate a less intense but wider spot centered near the wiggler spot. **Our experience shows that it is very important to have the spot as clean as possible, even with less photons**. Indeed, a background coming from a wider diffuse zone of the sample will generate at best noise (photons scattered by an area that does not contain the element of interest) and at worst spurious signal giving artifacts on the data (variation of probed concentration on non homogeneous samples, which is often the case in natural samples).
Besides, with the SBM, the source size will be of the same order of magnitude or slightly smaller than with the 2-pole or 3-pole wigglers while the flux will be less than two times weaker.

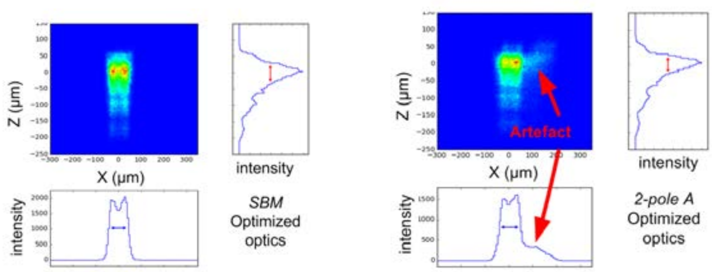

Figure 6. ***Examples of Ray tracing calculations performed with two sources using state-of-the-art optics elements. The "optimized optics" are defined in the § "Highly desirable modifications"***

We will thus choose the SBM configuration. Compared to current situation, the flux will be equivalent, but the source size will be decreased by 6 in horizontal and almost 10 in vertical: i.e. **a gain of 60 in term of brilliance**.

The necessary measures needed to adapt the beamline(s) to the new source

- *Modification of the beamline's optics and experimental equipment*

Mandatory modifications

Present BM16 beamline is installed on the 9 mrad axis. With the SBM, the beamline will have to move of less than 5 mm away from the ring at front-end and of 35 mm away from the ring at sample position. The actual hutches allow such motions. It will be possible to carry out experiments without other major changes.

Highly desirable modifications

The main gain brought by the EBS should be the spot size. In the frame of the construction of the FAME-UHD beamline, we carried out a study on the optimisation of the cooling of the 1st mirror to fully benefit from the state-of-the-art polishing capabilities of the manufacturers.[6] With an SBM source, we could gain a factor 2 on the vertical spot size (Figure 7 left and middle).
To gain in the horizontal direction, it will be necessary to optimize the geometry of the 2nd crystal of the monochromator. Indeed, it is a bent crystal designed with ribs to avoid the anticlastic deformation. These ribs induce focalisation defaults and were optimized for the current source size. It will be necessary to optimize them for the new source size. Consequently, this will imply a new design and a change of the 2nd crystal. The study has been already carried out at Neel Institute in Grenoble. Given those changes, the FAME-UHD beamline will be able to take advantage of the new source size in the full flux configuration (Figure 7 right).

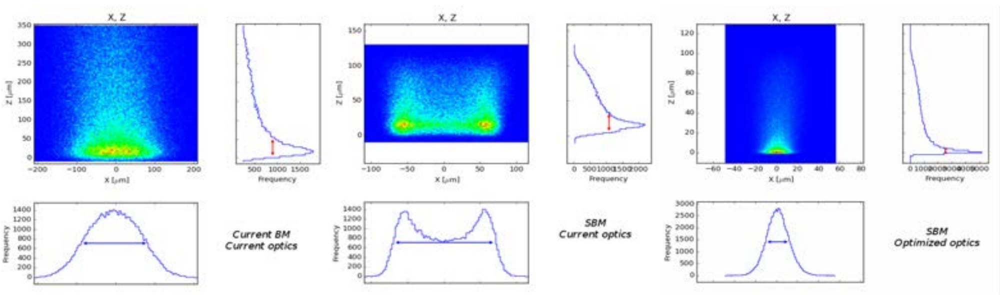

Figure 7. ***Ray tracing calculations performed for the current source with the actual optics elements (left), the new source with the actual optics elements (middle) and the new source with the optimized optics elements (right)***

- *Modification of the beamline's general infrastructure (Hutches, networks,…)*

Apart from the slight displacement of the optics, no major modification is mandatory.

Support requested from ESRF services for these measures

In order to be able in operation in 2020, from ESRF, FAME-UHD will require the support of alignment, modification of shielding.

A timeline and list of milestones

to avoid any interruption of FAME-UHD, all the minors works on the beamline will be done during the ESRF shutdown in 2019, mostly by CRG staff.

6 Bertrand et al., Optimisation of a first x-ray beamline optical element by coupling thermo-mechanical calculations and ray-tracing to accommodate high heat load: the case of ESRF BM16 M1 mirror, to be published.