



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**

Valence-to-Core Detected EXAFS: A Site-Selective Probe of Geometric Structure

**Experiment number:**

C-4595

**Beamline:**

ID26

**Date of experiment:**

from: 25.08.2015 to: 01.09.2015

**Date of report:**

13.09.15

**Shifts:**

21

**Local contact(s):**

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*Received at ESRF:***Names and affiliations of applicants (\* indicates experimentalists):**

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**Report:**

There are many examples in natural and material systems such as proteins and catalysts where several metal atoms of the same identity exist in different chemical environments. The goal of this experiment was to use the ligand selectivity of valence-to-core (VtC) X-ray emission spectroscopy (XES) to provide a site selective probe of geometric structure. This was to be achieved by collecting extended X-ray absorption fine structure (EXAFS) spectra by monitoring the energy resolved fluorescence from iron complexes with the XES instrument at ID26.

The samples chosen for this experiment were simple Fe complexes and mixtures of these complexes. The complexes chosen for this study were FeO, Fe<sub>2</sub>O<sub>3</sub>, and FeF<sub>3</sub>. Additionally, the following mixtures were prepared: 2FeO:Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>:2FeF<sub>3</sub>, and FeF<sub>3</sub>:FeO. For each of these systems we have collected EXAFS from the K $\beta$ <sub>1,3</sub>, K $\beta$ <sub>2,5</sub>, and K $\beta$ '' features. Figure 1 shows the VtC spectra Fe<sub>2</sub>O<sub>3</sub> and FeF<sub>3</sub>. Vertical lines in the spectrum indicate energies at which EXAFS spectra were measured in a mixture of the complexes. Fe<sub>2</sub>O<sub>3</sub> has a single K $\beta$ '' feature located at 7.0913 keV while FeF<sub>3</sub> contains two K $\beta$ '' features at 7.0845 and 7.0889 keV. Meanwhile, the more intense K $\beta$ <sub>2,5</sub> exhibits a single feature for Fe<sub>2</sub>O<sub>3</sub> but multiple features for FeF<sub>3</sub>.

The EXAFS spectra of a mixture of Fe<sub>2</sub>O<sub>3</sub> and FeF<sub>3</sub> are shown in Figure 2. Spectra collected from the VtC region of the K $\beta$  XES are compared with the EXAFS from the K $\beta$ <sub>1,3</sub> and the total fluorescence yield (TFY) data. All EXAFS scans collected in this beamtime were collected out of an

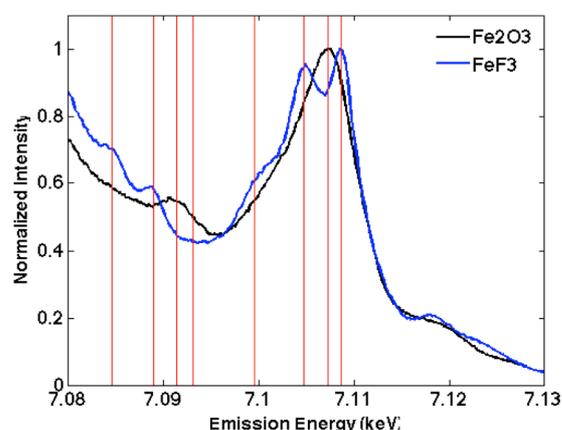


Figure 1. Fe K $\beta$  XES of Fe<sub>2</sub>O<sub>3</sub> and FeF<sub>3</sub>. Red lines indicate energies at which VtC EXAFS data were collected.

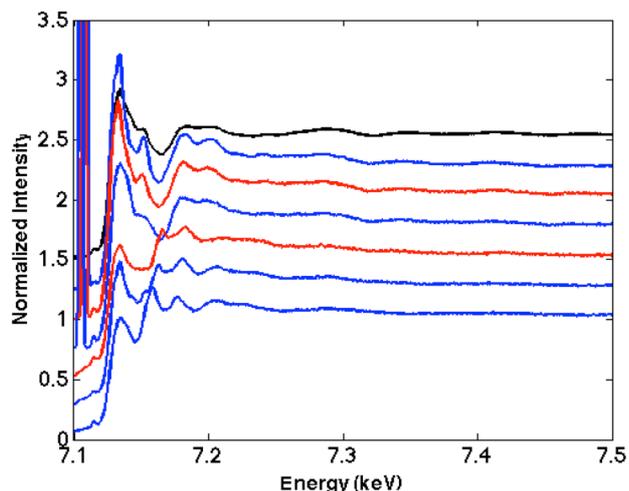


Figure 2. EXAFS spectra taken from a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{FeF}_3$ . From top to bottom the curves are TFY followed by fluorescence detected spectra at 7.1086, 7.1072, 7.1047, 7.0913, 7.08889, and 7.08845 keV. Blue and red curves indicate detection energies that are more heavily weighted with  $\text{FeF}_3$  and  $\text{Fe}_2\text{O}_3$  contributions, respectively. All data were collected to 7.8 keV.

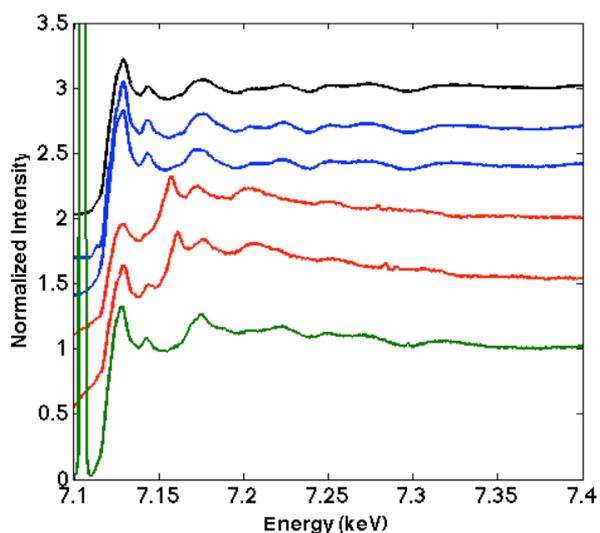


Figure 3. EXAFS spectra from pure  $\text{FeO}$  from different detection energies. The curves are color-coded according to the region of the  $\text{K}\beta$  emission spectrum chosen for detection. From the top the curves are TFY (black),  $\text{K}\beta_{1,3}$  (blue),  $\text{K}\beta'$  (blue),  $\text{K}\beta''$  (red),  $\text{K}\beta''$  (red),  $\text{K}\beta_{2,5}$  (green).

energy of 7.8 keV. It can be seen in the spectrum that there are significant differences in spectra collected at different energies. Not all curves mimic the TFY closely. While it is not evident there are differences between the  $\text{Fe}_2\text{O}_3$  (red) and  $\text{FeF}_3$  (blue) spectra. Each spectrum sits on a significant background from the  $\text{K}\beta_{1,3}$ . Data analysis to subtract the  $\text{K}\beta_{1,3}$  collected EXAFS from the VtC EXAFS is ongoing.

Finally, Figure 3 presents EXAFS spectra measured from pure  $\text{FeO}$ . The first  $\sim 300$  eV of the EXAFS spectrum is presented for different regions of the  $\text{K}\beta$  emission spectrum. It can be seen that the TFY spectrum (black curve) is well reproduced by the  $\text{Fe K}\beta$  mainline (blue curves) detected EXAFS. The spectrum of from the  $\text{K}\beta_{2,5}$  (green curve) feature also resembles the TFY spectrum quite closely, but the spectra from the  $\text{K}\beta''$  (red curves) are quite different from the rest of the spectra. There is a maxima at  $\sim 7.16$  keV that is out of phase with the maxima in the other spectra. This is surprising since the  $\text{K}\beta''$  emission lies between the other emission features that resemble the TFY spectrum. Moreover, we would expect all spectra to be very similar since  $\text{FeO}$  is a pure substance, and it was expected that XAS spectra sufficiently far above the absorption edge would be the same regardless of choice of detection energy. The difference in the  $\text{K}\beta''$  from the other features was similarly present in  $\text{Fe}_2\text{O}_3$  and  $\text{FeF}_3$  suggesting that we have identified a fundamental feature of fluorescence detected XAS. Analysis of this effect is ongoing.

In summary, we were able to collect EXAFS spectra from  $\text{Fe K}\beta$  emission features of three chemicals and each mixture of these totalling six systems. Multiple energies were chosen in each case collecting 3 – 8 EXAFS spectra for each system from the VtC region. The spectra exhibit differences at different fluorescence energies. Analysis is being performed to establish VtC detected as a viable technique.

