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://wwws.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.

ESRF	**Experiment title:** **XAS at low analyte concentrations at beamline BM31**	**Experiment number**: 31-01-82
Beamline: BM31	**Date of experiment**: from: 19.2.2018 to: 23.2.2018	**Date of report**: 26. April 2018
Shifts: 6	**Local contact(s)**: Hermann Emerich	*Received at ESRF:*

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Report:

The aim of this experiment was to analyse environmental samples containing Ce or Tl at different concentratins in different matrices by Ce K-edge (40'443 eV) and Tl L_{III}-edge (12'658 eV) X-ray absorption spectroscopy (XAS) to gain information on the possibilities at BM31 with respect to the study of trace elements in dilute environmental samples.

Measurements at the Ce K-edge were performed first, using the 12-element Ge solid state detector available at SNBL for fluorescence detection. From a study on the transformation of engineered CeO_2 nanoparticles in sewage sludge before and after incineration, digested sewage sludge and incinerated sewage sludge ash with Ce contents of 2000 and 4000 mg/kg, respectively, were analyzed; as well as a series of reference materials. A second set of samples consisted of solutions containing humic acids at different pH values that were spiked with 500 mg/L Ce(III) to assess the extent of Ce(III) complexation or Ce(III)-to-Ce(IV) oxidation by the humic acid. By adjusting the sample length accordingly (4-5 cm tubes in the case of the sewage sludge and sewage sludge ash; 12-cm tubes in the case of the humic acid samples), even the extended X-ray absorption fine structure (EXAFS) spectra of the dilute samples could be measured in transmission mode. Comparison with the corresponding fluorescence spectra showed that measurements in transmission mode were of superior quality even at the lowest analyzed Ce concentrations, thanks to data integration over relatively large sample thicknessess at the high energy of the Ce K-edge (40'443 eV). For lower concentrations than the ones tested here, however, fluorescence detection would have become mandatory. The results from these test measurements are planned to be included in two publications.

After switching to the Tl L_{III}-edge, the 12-element Ge detector stopped working after one sample due to vacuum problems, and further tests had to be performed with the 1-element silicon drift detector (SDD). For testing, we collected data on 3 layered Mn-oxides spiked with Tl at loadings of 30'000 mg/kg, 10'000 mg/kg and 3'000 mg/kg; and on two waste materials from a Zn smelter with Tl contents of 10'000 and 3'000 mg/kg Tl. At the lowest concentrations of 3'000 mg/kg Tl, the X-ray absorption near-edge structure (XANES) spectra measured in transmission mode were still interpretable, whereas the EXAFS signal became too noisy. However, the transmission data were were less noisy than the fluorescence data recorded with the 1-element SDD. Thus, for analyses at the Tl L_{III}-edge at lower concentrations in fluorescence mode, a sensitive multielement fluorescence detector would be needed. The results obtained at the Tl L_{III}-edge served to refine experiments on the interaction of Tl with Mn-oxides that involve synchrotron analyses.

In conclusion, the test experiments revealed the very high potential of BM31 for environmental XAS analyses at high energies, where even relatively low trace element contents can be analyzed in transmission mode. However, for experiments at lower concentrations (as often encountered in environmental samples), XAS measurements must be performed in fluorescence mode using a sensitive multielement fluorescence detector.