

## 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.



	<b>Experiment title:</b> Speciation of indium and germanium for the design of bioleaching and extraction processes.	<b>Experiment number:</b> CH 4358
<b>Beamline:</b> BM25A	<b>Date of experiment:</b> from: 24.06.2015 to: 29.06.2015	<b>Date of report:</b> 28.08.2016
<b>Shifts:</b> 15	<b>Local contact(s):</b> Alvaro Munoz-noval	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): G. Frisch* (Institut für Anorganische Chemie, TU Bergakademie Freiberg) J. Hartley* (Institut für Anorganische Chemie, TU Bergakademie Freiberg) C. Ashworth* (Institut für Anorganische Chemie, TU Bergakademie Freiberg)		

### Report:

EXAFS spectra were acquired for indium and germanium salts dissolved in either sulphuric acid, MSA or hydrochloric acid at varying pH (0 – 3) and chloride content. Spectra of solid indium chloride and germanium powder were obtained for reference purposes.

The fluorescence data quality for the germanium samples was excellent, even down to a concentration of 1 mM. Transmission data for the indium data was generally good, except for samples of < 10 mM, at which point it was necessary to switch to fluorescence mode. Fluorescence data for the indium samples exhibited high noise levels, even with multiple scans and extended data acquisition times. The same fluorescence detector (13-element Si(Li) detector) was used for both edges.

Liquid samples were measured in both transmission and fluorescence mode, with the solid samples being measured in transmission mode and diluted in a cellulose matrix. Precipitation was observed in some of the indium samples with higher pH and these were filtered prior to the experiment. However this does not seem to have unduly affected the data quality. Solubility of the germanium salt was low in all solvents, however sufficient sample had dissolved in order to be measurable via EXAFS.

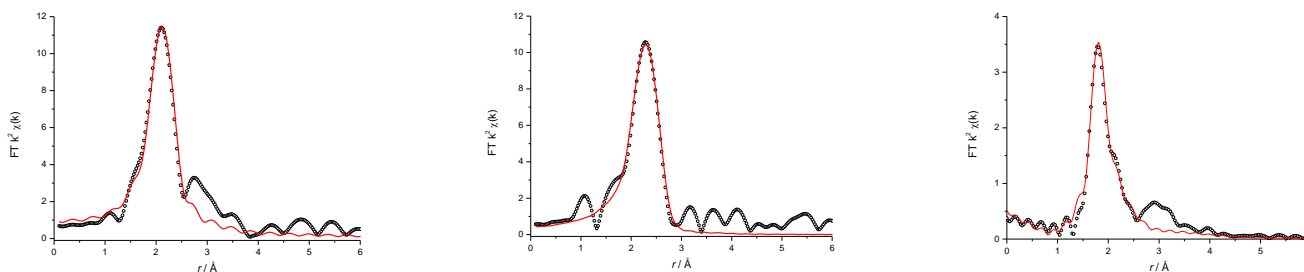
Metal-ligand distances were calculated to be around 1.75 Å for Ge-O, 2.0 to 2.2 Å for In-O and around 2.4 Å for In-Cl, which is consistent with both the solid reference samples and

previous experimental data. Generally, as the amount of chloride in the bulk sulphuric acid samples was increased via addition of NaCl, a corresponding change in the speciation was observed, up to a maximum of 4xCl per In atom – the same speciation as that of indium chloride in 1 M hydrochloric acid. The pH of the sample did not have an obvious effect on the speciation of the sample. This suggests that any changes seen in our electrochemical experiments are due to changes in speciation due to chloride ligands and not hydrolytic effects. Changes in EXAFS speciation coincides with changes in the UV-vis spectroscopic results and this may help us to analyse solution using laboratory techniques in the future.

For all the germanium samples, a 4xO coordination was calculated. This did not vary, even in hydrochloric acid. A signal at approx. 3 Å in the FT was observed and could be fitted using a multiple scattering model of tetrahedrally coordinated germanium with oxygen-donor ligands.

For the indium samples in sulphuric acid or MSA, two peaks were observed, the first of which could be fitted to 6xO coordination. The second peak is anticipated to be a mixture of secondary hydration shells and signal from the S-atom in the sulphate/MSA ligand. At this time, we cannot resolve the exact composition of this peak due to the overlapping signals, however any S-coordination contributions are expected to be quite low due to it generally being a weakly coordinating ligand in these solutions.

Indium samples in chloride-containing media displayed a broader first peak which could be fitted to a mixture of Cl and O ligands. After a ratio of 5 chlorides per indium, the fit converged for 4xCl and 2xO ligands.



*Fourier transforms of the EXAFS data (black circles) and fits (red line) for In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> (left), InCl<sub>3</sub> in HCl (middle) and GeO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> (right).*

These results have allowed us to understand the connection between anion concentration and speciation of the target elements. Results correlate with electrochemical and UV-Vis spectroscopic experiments. pH had no significant effect on speciation up to pH3, at which point hydrolysis of In(III) and precipitation takes place.