

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: A combined XAS and UV/VIS spectroscopy set-up for studying radiation damage in solution	Experiment number: 26-01-1081
Beamline:	Date of experiment: from: 12-12-2016 to: 15-12-2016	Date of report: 18-01-2017
Shifts:	Local contact(s): Dipanjan Banerjee	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Tom Vander Hoogerstraete, Jeroen Sniekers, Bieke Onghena, Simona Sobekova Foltova Name of institute : Katholieke Universiteit Leuven Laboratory/Department : Laboratory of Coordination Chemistry Address : Molecular Design and Synthesis Department of Chemistry Celestijnenlaan 200F 3000 LEUVEN BELGIUM		

We have succeeded in combining the EXAFS and UV/VIS set up for studying the stability of different copper complexes in solution. The following samples were measured $[\text{Cu}(\text{II})\text{Cl}_3][\text{C}_{32}\text{H}_{68}\text{P}]$, $[\text{Cu}(\text{II})\text{Cl}_4][\text{C}_{32}\text{H}_{68}\text{P}]_2$, $[\text{Cu}(\text{II})\text{Br}_3][\text{C}_{32}\text{H}_{68}\text{P}]$, $[\text{Cu}(\text{II})\text{Br}_4][\text{C}_{32}\text{H}_{68}\text{P}]_2$ and $[\text{Cu}(\text{II})\text{Cl}_4][\text{C}_{32}\text{H}_{68}\text{N}]_2$. The samples were also measured in different solvents (ionic liquids and toluene), different temperatures and different X-ray energies. The data are currently analysed, processed and published.

As an example, the results obtained for a solution of 500 ppm $[\text{Cu}(\text{II})\text{Cl}_3][\text{C}_{32}\text{H}_{68}\text{P}]$ in $[\text{C}_{32}\text{H}_{68}\text{P}][\text{Cl}]$ are given. Two new peaks appear in the UV/VIS spectrum at 295 nm and 420 nm when $[\text{Cu}(\text{II})\text{Cl}_3]$ is irradiated with X-rays with an energy just above the Cu-edge (9000 eV) (Figure 1). As a comparison, we have also measured $\text{Cu}(\text{I})\text{Cl}_2$ dissolved in 12 M HCl. The spectrum is also shown in Figure 1 and proves that the decomposition product after radiation is $\text{Cu}(\text{I})\text{Cl}_2$. Cu(II) is thus reduced by X-rays to Cu(I). In fact, the whole spectrum of $\text{Cu}(\text{II})\text{Cl}_2$ is shifted 28 nm to lower wavelengths because of the different solvent (ionic liquid versus water). We have manually shifted the spectrum 28 nm for a good comparison with the data obtained for the ionic liquid phase $[\text{C}_{32}\text{H}_{68}\text{P}][\text{Cl}]$.

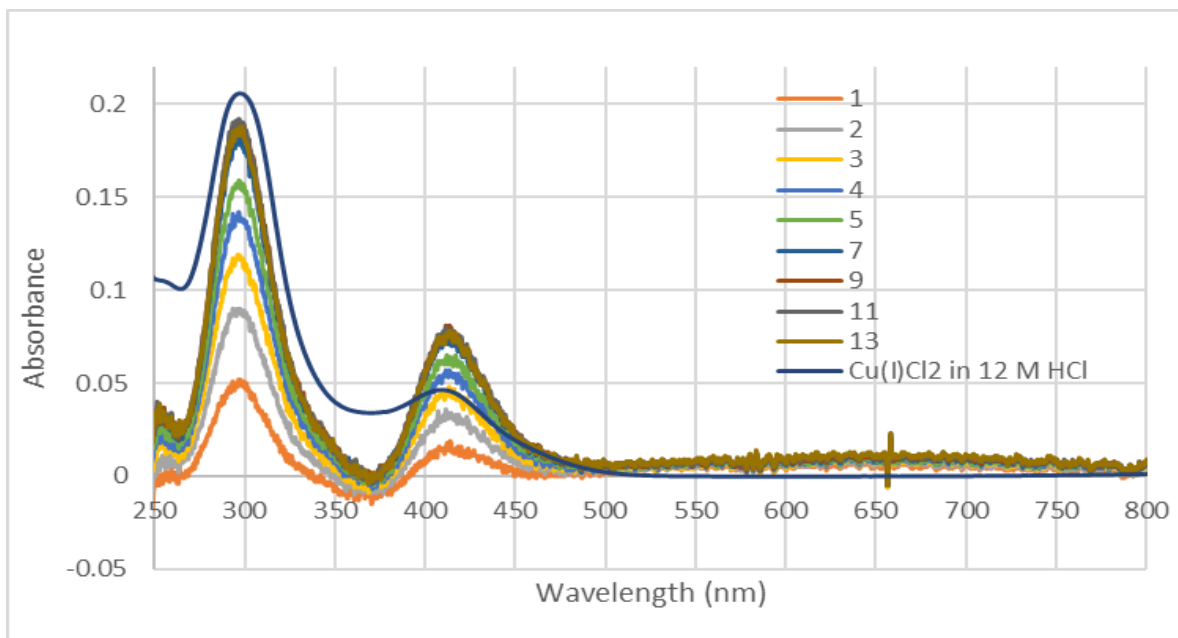


Figure 1. Background corrected UV/VIS spectra of 500 ppm $[Cu(II)Cl_3][C_{32}H_{68}P]$ in $[C_{32}H_{68}P][Cl]$ as function of the X-ray radiation time (9000 eV).

The peak intensity at 296 and 421 nm have been plotted against time in Figure 2. The peak intensities do not further increase after 9 minutes. Both peaks prove that all $Cu(II)Cl_3$ is reduced and transformed into $Cu(I)Cl_2$ after about 9 minutes of radiation. This is a very important finding and shows that care should be taken with analysing this kind of samples with all kind of different techniques using X-rays.

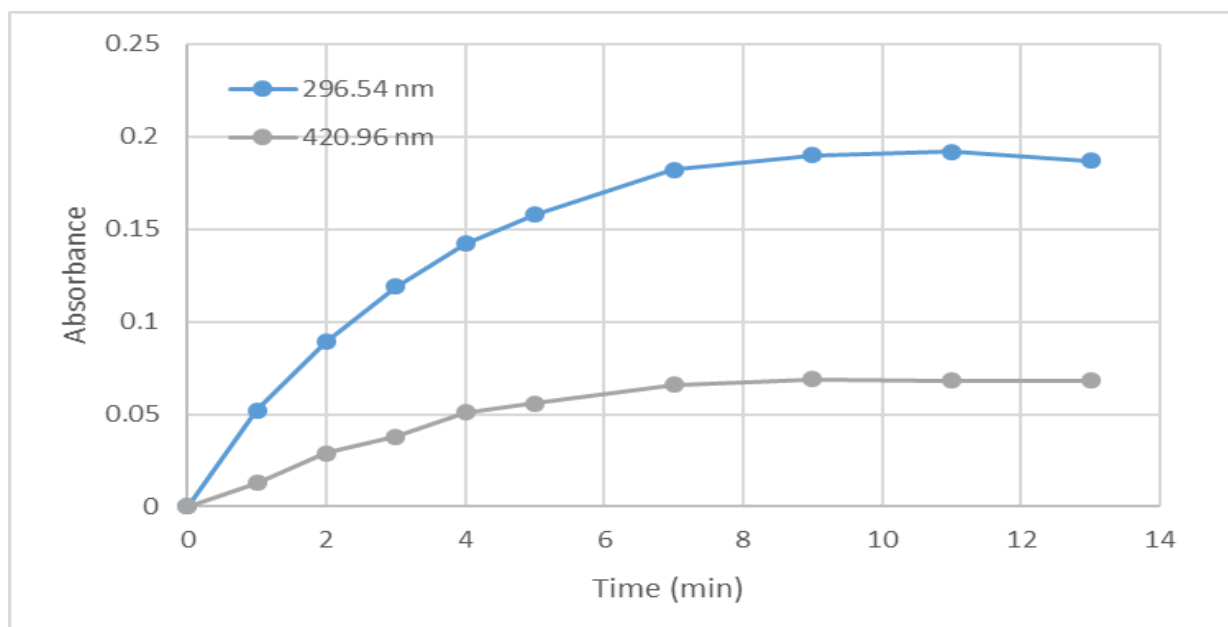


Figure 2. Intensity at 296 and 420 nm as function of the radiation time.

Within the next months, the data will be processed with care. Questions and difficulties that might appear are (1) a proper background subtraction because some of the copper species (e.g. $CuCl_4$, $CuBr_4$) are giving also signals in the UV/VIS region and their intensities decrease while the intensity of the decomposition product $Cu(I)Cl_2$ increases. Probably, we have to do some linear combination analysis on the data. (2) How to compare X-ray fluxes and intensities at different energies and (3) how to deal with path length effects (e.g. Cu

present at the beginning of the X-ray path length through the sample will suffer from more X-ray than Cu at the end of the sample path).

In addition to the combined UV/VIS EXAFS set up, we have measured EXAFS function of different elements extracted to $[\text{C}_{32}\text{H}_{68}\text{P}]_2[\text{SO}_4]$ (In, REs, Fe, Y). The data are of good quality and will be published soon. A remarkable finding is that Fe(III) for instance is present as a dimer or oligomeric structure in the ionic liquid $[\text{C}_{32}\text{H}_{68}\text{P}]_2[\text{SO}_4]$ (Figure 3 and 4, Table 1)

Table 1: Fitting results of the ionic liquid phase of Fe(III) extraction with Cyphos SO_4 .

Scattering path	N	r (\AA)	σ^2 (\AA^2)
Fe-O ₁	5.9(3)	2.010(4)	0.010(1)
Fe-S _{bi}	0.5(2)	2.689(19)	0.008(3)
Fe-S _{mono}	1.1(3)	3.237(7)	0.003(1)
Fe-Fe	1*	3.516(11)	0.008(1)

The data were Fourier transformed between $k = 2.5$ and 13.86 \AA^{-1} without window function and fitted to the model between $R = 0$ and 3.41 \AA^{-1} .

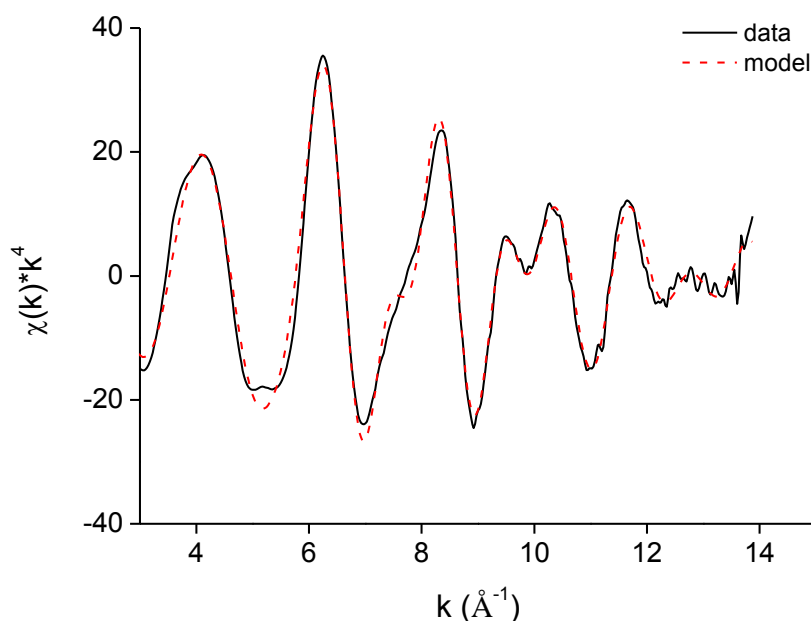


Figure 3: EXAFS function $\chi(k)*k^4$ and model of the Fe(III) sulfate complex in the ionic liquid phase for extraction of Fe(III) with Cyphos SO_4 from a 1 M $\text{Fe}_2(\text{SO}_4)_3$ solution.

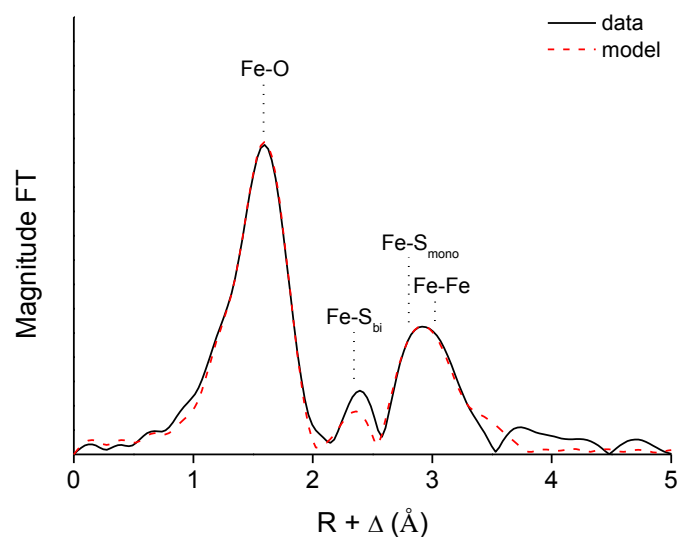


Figure 4: Fourier-transform of the Fe(III) sulfate complex in the ionic liquid phase for extraction of Fe(III) with Cyphos SO_4 from a 1 M $Fe_2(SO_4)_3$ solution. The data were Fourier transformed between $k = 2.5$ and 13.86 \AA^{-1} and fitted to the model between $R = 0$ and 3.41 \AA .

We are satisfied with the beamline performance, the help of the beamline scientist and the help of the ESRF regarding the safety issues related to the experiments (UV radiation).