

## 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 using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

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

Reports can now 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:** Speciation changes of colloidal and solid-phase Hg during flooding of a contaminated floodplain soil

**Experiment number:**  
EC572

**Beamline:**

**Date of experiment:**

from: 9.12.2009 to: 15.12.2009

**Date of report:**

25.2.2010

**Shifts:**

9

**Local contact(s):**

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*Received at ESRF:*

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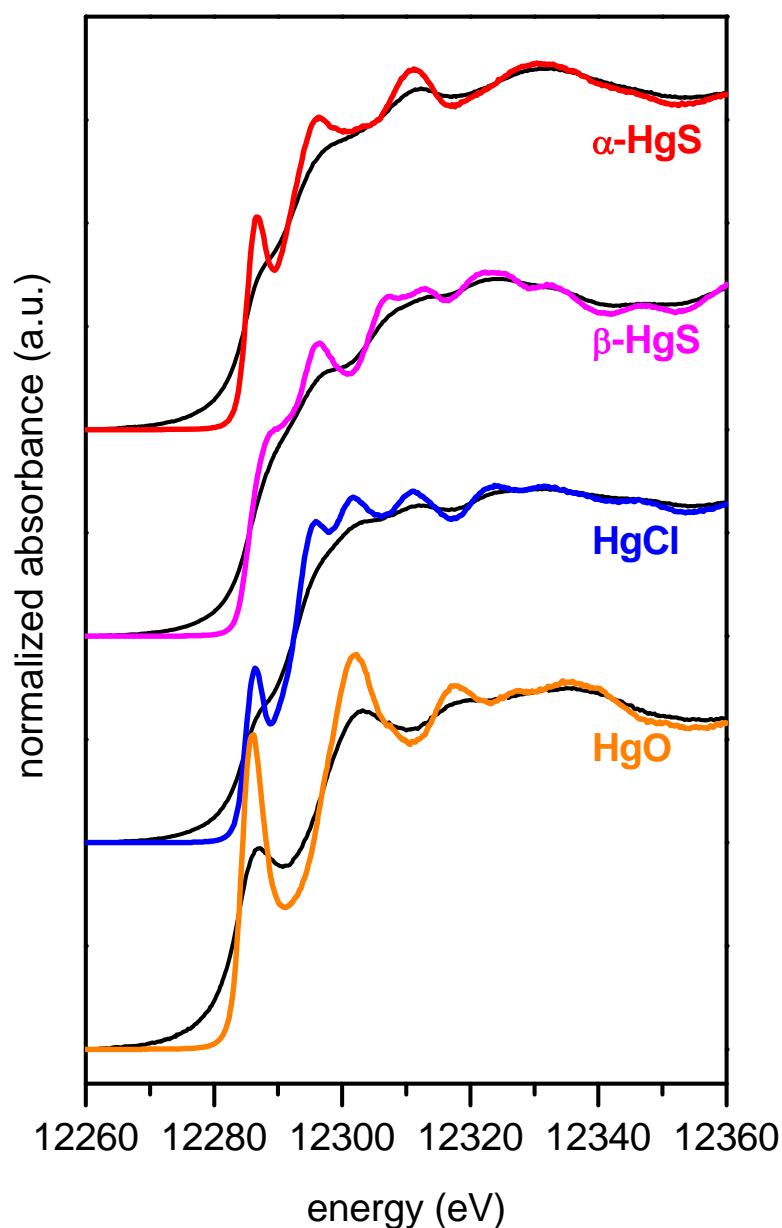
## **Report: HERFD-XANES analysis of Hg speciation in environmental samples**

We performed a laboratory microcosm incubation experiments to study the speciation of Hg in a contaminated floodplain soil during a periodic flooding event. Special emphasis was placed on the speciation of Hg in colloids forming in the porewater during soil flooding and reduction. Even though Hg concentrations in these samples are high from the perspective of environmental quality (1.4 mg/kg Hg in the soil matrix), they are very low with respect to their analysis by XAS. We proposed to analyze these samples by Hg L3-edge XAS at ID26 to take advantage of the beamline's high photon flux combined with the possibility to eliminate unwanted fluorescence radiation via the use of the emission spectrometer. However, we were not able to collect spectra on the respective soil and colloid samples because of two reasons: Firstly, even though the emission spectrometer effectively filtered the Hg L3-edge fluorescence signal, the limited solid angle covered by the spectrometer crystals resulted in a detection limit that was too high to analyze our samples. Secondly, despite sample cooling to 77K, the high flux of the photon beam was observed to cause damage to some organic Hg reference phases, namely Hg bound to carboxylic groups, and likely also affected soil and colloidal Hg, whereas thiol-bound Hg and Hg minerals seemed not to be affected.

Therefore, instead of the intended soil and colloid samples, we analyzed a series of samples collected near a former Hg mine (New Idria, California, USA). These samples comprised untreated and calcined mine wastes with Hg contents of 100-1000 mg/kg. HERFD-XANES

spectra measured with the emission spectrometer revealed much more spectral details than conventional fluorescence spectra (Figure 1). The measured crystalline Hg compounds exhibited distinct structural features allowing for their distinction in sample spectra. Analysis of the spectra of New Idria waste samples by linear combination fitting suggested that most Hg in the untreated mine wastes was present as cinnabar. In addition to cinnabar, metacinnabar and calomel were important Hg species in the calcined waste samples, suggesting Hg transformation during calcination.

Speciation results on Hg-bearing mine waste samples demonstrate the suitability of Hg L3-edge HERFD-XANES for distinction of different environmentally relevant Hg species, especially for dilute samples where the collection of EXAFS spectra with a signal-to-noise ratio allowing for a similarly detailed analysis may take considerably longer. In continuing work, we plan to evaluate the experimental HERFD-XANES (and corresponding EXAFS) spectra by comparison with FEFF-based simulations.



**Figure 1.** HERFD-XANES spectra of cinnabar ( $\alpha$ -HgS), metacinnabar ( $\beta$ -HgS), calomel (HgCl), and montroydite (HgO) (in color). Corresponding conventional fluorescence spectra are shown in black and reveal much less spectral detail.

