

## 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.



	<b>Experiment title:</b> EXAFS study on the complexation of CH <sub>3</sub> Hg <sup>+</sup> and Hg <sup>2+</sup> to functional groups in organic substances from soils and streams	<b>Experiment number:</b> ME-64
<b>Beamline:</b> ID 26	<b>Date of experiment:</b> from: 28/03/01 to: 03/04/01	<b>Date of report:</b> 09/01/02
<b>Shifts:</b> 18	<b>Local contact(s):</b> Pierre-Emmanuel Petit	<i>Received at ESRF:</i>

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**Report:** (Experiment ME-64 was originally allotted 18 shifts 26/04/00 – 02/05/00. However, a serious incident with the monochromator put the beamline out of operation, and we received 18 new shifts in 2001)

**Introduction:** Atmospheric deposition of anthropogenic mercury is a large-scale environmental problem at northern latitudes. In areas dominated by wetlands, organic soils and humic surface waters, high concentrations of the very toxic form of Hg, methyl mercury, is formed. Limited knowledge about the coordination chemistry of Hg<sup>2+</sup> and CH<sub>3</sub>Hg<sup>+</sup> in natural organic matter (NOM) of soils and streams has hampered mechanistic research about central biochemical processes in soils and surface waters such as methylation of Hg<sup>2+</sup> to CH<sub>3</sub>Hg<sup>+</sup>, demethylation of CH<sub>3</sub>Hg<sup>+</sup> and reduction of Hg<sup>2+</sup> to Hg<sup>0</sup>.

The main aim of this EXAFS study was to determine the coordination chemistry of methyl mercury (CH<sub>3</sub>Hg<sup>+</sup>) and the inorganic ion Hg<sup>2+</sup> in soil and stream organic matter. Taking advantage of the high brilliance of Beamline ID26 this could be done at very low concentrations of metal, making EXAFS results as relevant as currently possible for natural situations in soils and streams. Our hypothesis was that Hg in CH<sub>3</sub>Hg<sup>+</sup> is two-coordinated with one carbon (the methyl group) and one sulfur atom (RSH, thiols in NOM) and in Hg<sup>2+</sup> with at least one sulfur atom (RSH in NOM). Data on the concentration of RSH in soil and stream organics were obtained from earlier sulphur K-edge XANES determinations on the samples used.

**Methods:** EXAFS data at the Hg L<sub>III</sub>-edge (12 284 eV) were collected for pelleted organic samples in fluorescence mode using Si photodiodes. A Ga filter was used to reduce scattering radiation. No radiation damage was detected, except for a model compound consisting of a carboxyl resin added CH<sub>3</sub>Hg. We performed EXAFS experiments at molar CH<sub>3</sub>Hg / RSH ratios in the range 0.01 - 1.62 (corresponding to 100-15000 ppm CH<sub>3</sub>Hg) and at molar Hg / RSH ratios in the range 0.01 – 0.85.

**Results:** Our hypothesis was confirmed. At low CH<sub>3</sub>Hg / RSH ratios, Hg was associated to one C atom (the methyl-group) at an average distance of 2.03 ± 0.02 Å and to one S atom (the RS<sup>-</sup> group) at an average

distance of  $2.34 \pm 0.03 \text{ \AA}$ , in the first coordination shell. In Fig. 1 stacked  $k^3$  data are presented together with fitted spectra (using FEFF-7) and in Fig. 2 corresponding Fourier transforms are shown. Experimental data were satisfactorily fitted by one C and one S atom in the first coordination shell for samples with a  $\text{CH}_3\text{Hg} / \text{RSH}$  ratio of 0.01 – 0.30. At higher ratios O and / or N atoms (which are not possible to separate) also were included in the first shell. In Fig. 2 the RSF peak at approximately  $1.55 - 1.60 \text{ \AA}$  (not corrected for phase-shift), most obvious in FP sample, represents the Hg-C bond within the methyl mercury molecule, whereas the peak / shoulder at  $1.95-2.00 \text{ \AA}$  represents a Hg – S bond with the thiol group. At calculated  $\text{CH}_3\text{Hg} / \text{RSH}$  ratios above 0.37 in organic soils, 0.32 in gently extracted organics from soil and 0.24 in stream organics, the organic  $\text{RS}^-$  sites were completely saturated by  $\text{CH}_3\text{Hg}^+$  and therefore O and / or N atoms were found in the first coordination shell of Hg at an average distance of  $2.09 \pm 0.01 \text{ \AA}$ . This Hg – O/N bond is reflected by a peak around  $1.60 \text{ \AA}$  in samples in Fig. 2 with  $\text{CH}_3\text{Hg} / \text{RSH}$  ratios of 0.95 and 1.08. Based on the assumption that RSH and RSSH groups take part in the complexation of  $\text{CH}_3\text{Hg}^+$ , whereas RSSR and RSR groups do not, our results suggest that approximately 17 % of total organic S consisted of RSH + RSSH functionalities in the organic soil. Corresponding figures for gently extracted soil organics and stream organics were 14 and 9 %, respectively. Also  $\text{Hg}^{2+}$  was found to be two-coordinated in soil and stream NOM, with at least one S atom at low Hg / RSH ratios (data not shown). Overall the EXAFS experiment was very successful and the unique data generated will lay a basis for further in-depth biogeochemical research about Hg in the environment. Similar studies with other trace metals, using beamline ID 26, will produce results with an unique quality at a very low metal concentration as compared with existing EXAFS studies on metal-NOM associations.

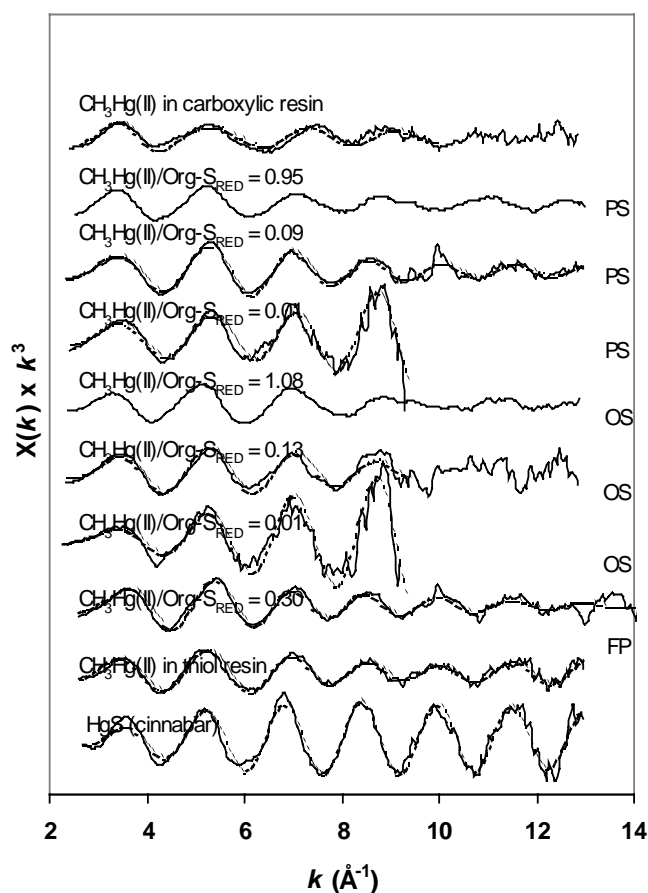


Figure 1.  $k^3$ -weighted Hg EXAFS data for model compounds, organic soil (OS) and gently extracted organics from soil (PS) and fen peat (FP) at varying  $\text{CH}_3\text{Hg} / \text{RSH}$  ratios. Experimental spectra (solid lines) are overlaid by spectra derived from fitting parameters (dashed lines) for models with C, S and O/N atoms in the first coordination shell.

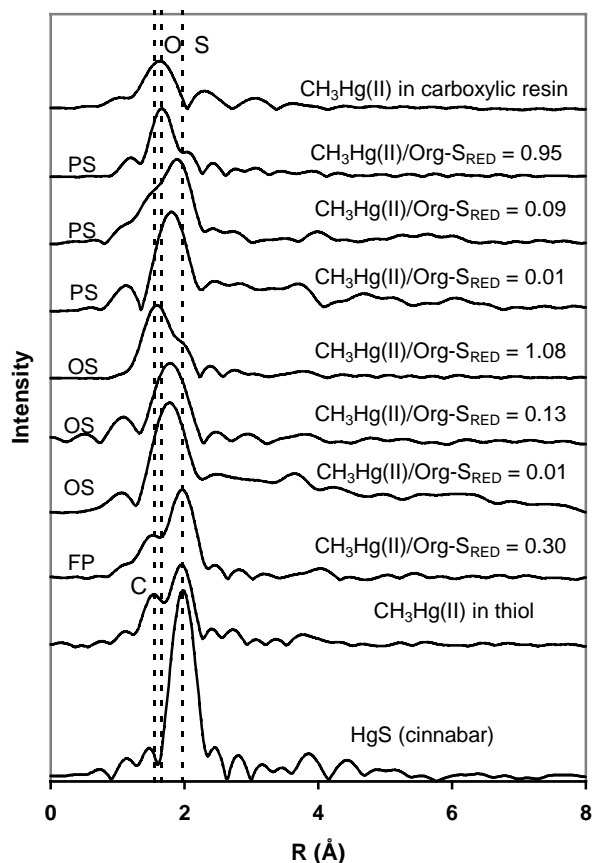


Figure 2. Fourier transformed EXAFS spectra (RSF) for the same samples as in Fig. 1. Spectra are not corrected for phase shift.