



	Experiment title: Mercury binding to natural organic matter	Experiment number: EC-665
Beamline:	Date of experiment: from: 30/06/2010 to: 06/07/2010	Date of report: 14/02/2011
Shifts: 18	Local contact(s): Olivier Proux	<i>Received at ESRF:</i>

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Report:

Context

The objectives of this proposal were to investigate mercury(II) coordination environment in sulfur-rich compounds using Hg-EXAFS spectroscopy. We have focused our analyses on model mercury-thiolate compounds, which have a defined speciation and favour sulfur-only coordination of mercury. Indeed, peptides and pseudopeptides bearing several cysteines have been developed in our laboratory (CEA/INAC/SCIB) to obtain efficient chelating agents for soft metal ions like Cu(I) to obtain intracellular copper lowering agents to treat metal overload.¹⁻⁵ This type of chelators exhibit also a high affinity for mercury and may be of great interest for mercury detoxication. Besides, the corresponding complexes are good models for sulfur-based coordination environment for mercury, i.e. HgS₂ and HgS₃, which will be useful model systems to interpret mercury coordination in NOM (Natural Organic Matter) in which the sulfur content is high.

Samples investigated

- 2 solid compounds, which X-ray structures are known to get reference EXAFS spectra for linear HgS₂ and trigonal HgS₃ coordination environments.
- 2 samples of NOM
- 12 liquid samples with cysteine-containing peptides or pseudopeptides. The speciation of mercury complexes and the coordination of the metal ion as a function of the experimental conditions had been fully investigated prior to the EXAFS experiments, so as to be able to choose adequate experimental conditions (concentration, pH, Hg to ligand ratio) that favour one type of metal species and one type of coordination. These informations were mainly obtained by analytical and spectroscopic technics like UV-visible spectroscopy, mass spectrometry, ¹H NMR and ¹⁹⁹Hg NMR. The mercury concentration was around 4 mM to get enough sensitivity in the EXAFS experiment.

The EXAFS spectra were collected on frozen solutions at mercury L₃-edge and 5-15 K to avoid any structural transformations, especially those caused by beam damage.

Results

The EXAFS data collected on the mercury complexes of cysteine-containing peptides or pseudopeptides afford the direct and final proof of mercury coordination in sulfur-only chemical environments. These measurements allowed us to evidence the change of mercury coordination with pH, which is HgS₂ at low pH and HgS₃ at high pH (see Figure 1). These results confirm unambiguously what was concluded from other spectroscopic data, specifically from the NMR chemical shift of ¹⁹⁹Hg which is sensitive to the metal ion coordination. In addition, new information has been obtained on the geometry of the HgS₃ complexes in the peptides and pseudopeptides and on the medium-range order of Hg up to 4.1 Å.

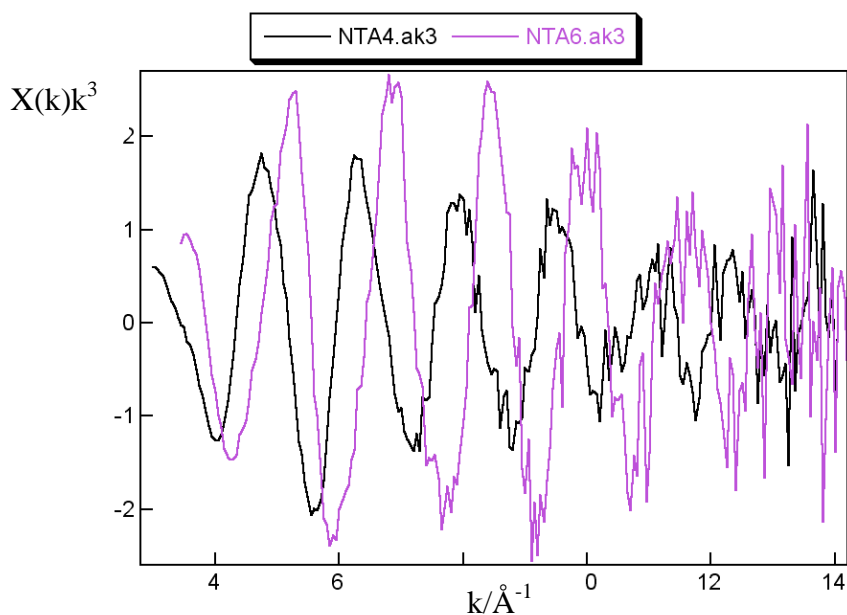


Figure 1. Hg L₃-edge EXAFS spectra of a HgL complex at pH 3.5 (in pink) characteristic of a HgS₂ coordination and at pH 8.5 (in black) characteristic of a HgS₃ coordination.

A first article is in preparation and will be submitted soon.

- (1) Seneque, O.; Crouzy, S.; Boturn, D.; Dumy, P.; Ferrand, M.; Delangle, P. *Chem. Commun.* **2004**, 770-771.
- (2) Rousselot-Pailley, P.; Seneque, O.; Lebrun, C.; Crouzy, S.; Boturn, D.; Dumy, P.; Ferrand, M.; Delangle, P. *Inorg. Chem.* **2006**, *45*, 5510-5520.
- (3) Pujol, A. M.; Gateau, C.; Lebrun, C.; Delangle, P. *J. Am. Chem. Soc.* **2009**, *131*, 6928-6929.
- (4) Pujol, A. M.; Cuillel, M.; Renaudet, O.; Lebrun, C.; Charbonnier, P.; Cassio, D.; Gateau, C.; Dumy, P.; Mintz, E.; Delangle, P. *J. Am. Chem. Soc.* **2011**, *133*, 286-296.
- (5) Pujol, A. M.; Gateau, C.; Lebrun, C.; Delangle, P. *Chem. Eur. J.* **2011**, in press DOI: 10.1002/chem.201003613.