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## Investigation of the local chemical interactions between Hg and self-assembled monolayers on mesoporous supports

K. M. Kemner

Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439, USA

X. Feng, J. Liu, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, M. Gong, and S. Mattigod

Pacific Northwest National Laboratory, Richland, WA 99352, USA

The synthesis of mesoporous silica has greatly expanded the possibilities for the design of open-pore structures. Because of their large surface area and well-defined pore size and pore shape, these materials have great potential in environmental and industrial processes, such as selective extraction of heavy metals from solutions. However, these applications require the materials to have specific attributes such as binding sites and charge density. Recently produced organic monolayers within ordered mesoporous silica have specific adsorption behavior for Hg and other heavy metals. This paper presents results of a study using Hg L<sub>III</sub> edge X-ray absorption fine structure (XAFS) to understand the adsorption of Hg to this material surface.

**Keywords:** environmental science; separations science

### Introduction

The synthesis of mesoporous silica has greatly expanded the possibilities for the design of open-pore structures (Beck *et al.*, 1992; Kresge *et al.*, 1992). Because of their large surface area and well-defined pore size and pore shape, these materials have great potential in environmental and industrial processes. However, many applications (e.g., adsorption, ion exchange, catalysis, sensing) require the materials to have specific attributes such as binding sites, stereochemical configuration, charge density, and acidity (Sayari, 1996). Functional groups (thiol groups in this particular material's case) have been introduced to the pore surface of mesoporous silica as the terminal groups of organic monolayers. The resulting material, called functionalized monolayers on mesoporous supports (FMMS), is a useful environmental remediation agent because it can efficiently remove mercury and other heavy metals (such as lead and silver) from contaminated aqueous and organic solutions. Mercury and heavy-metal contamination is a serious problem at waste-contaminated sites. Industrial and civilian sources deposit up to 10,000 tons of mercury into the environment every year (Mitra, 1986).

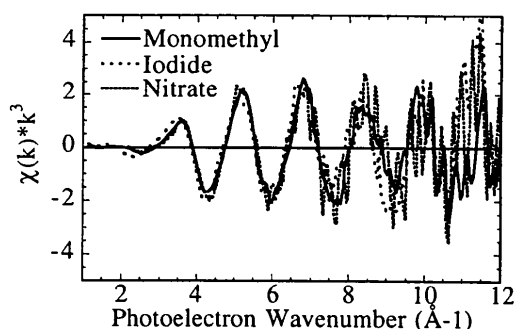
### XAS measurements of Hg in FMMS and discussion

To elucidate the specific chemical interactions between Hg and the FMMS material, X-ray absorption spectroscopy (XAS) measurements at the Hg L<sub>III</sub> absorption edge were made on three Hg-laden FMMS samples, as well as on HgS, HgO, and HgI<sub>2</sub> powder standards. Some of the solutions used to introduce the Hg to the FMMS material simulated radioactive wastes in holding tank L at the US Department of Energy's Savannah River Site (SRS) or nonradioactive vacuum pump oil waste from the SRS tritium facilities. Single-phase solutions of monomethyl mercury, mercury iodide, and mercury nitrate were also introduced to the FMMS material. More details of the sample preparation have been described elsewhere (Feng *et al.*, 1997).

The XAS experiments at the Hg L<sub>III</sub> absorption edge were performed on beamline X18B at the National Synchrotron Light Source and at the Materials Research Collaborative Access Team (MRCAT) insertion device beamline at the Advanced Photon Source. Measurements of tape mounts of HgS, HgI<sub>2</sub>, and HgO powder standards were made in the transmission mode. Measurements on the FMMS samples were made in the fluorescence mode by utilizing the Stern-Heald configuration (Stern & Heald, 1979), and in the transmission mode. The absorption signal of the HgS standard was monitored simultaneously with an additional ion chamber on the down side of the experiment to ensure consistent determination of incident X-ray energies, thus allowing investigation of the valence state of Hg in the FMMS. For the standards and the FMMS material, multiple sample thicknesses were measured to investigate the uniformity of the prepared samples. In all cases, the edge step height scaled linearly with the sample thickness. The linearity of the detector-sample experimental setup (Kemner, Kropf & Bunker, 1994) was tested when a new sample was mounted for an XAS measurement. These tests indicated less than 0.15% nonlinearity in response between ionization chambers, with 50% attenuation of the incoming X-ray beam. Data reduction and analysis were performed in adherence to recommended procedures (Sayers & Bunker, 1988).

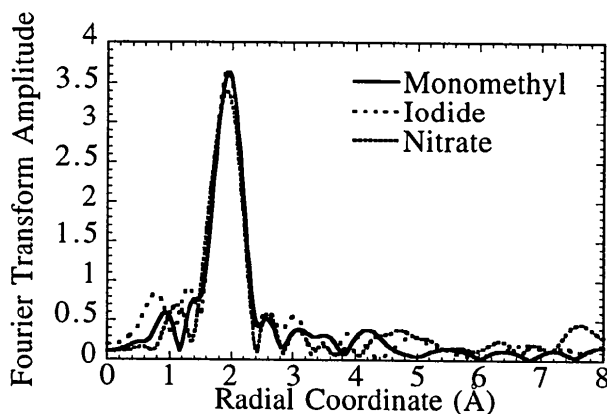
Comparison of the Hg XANES region for the FMMS samples and the HgS and HgO standards (valence II) indicated that Hg was in the same valence state in all samples. Fig. 1a illustrates the single-scan quality of the  $\chi(k) \cdot k^3$  data for the FMMS samples investigated. Fig. 1b shows the Fourier transform (1.2–11.5 Å<sup>-1</sup> with Hanning windows of 0.25 Å<sup>-1</sup>) of the  $k^3$ -weighted data in Fig. 1a.

The HgS and HgO standards used in these experiments were characterized with X-ray diffraction. Results from these measurements indicated that the HgS standard was a mixture of two phases (15% cinnabar [Wyckoff, 1963] and 85% metacinnabar [Wyckoff, 1963]), while the HgO standard was single-phase montroydite (Wyckoff, 1963; Aurivillius, 1956). The local environments about the Hg atoms in cinnabar and metacinnabar are drastically different. Cinnabar has two Hg-S bonds at 2.03 Å, while metacinnabar has four Hg-S bonds at 2.53 Å (Wyckoff, 1963). Therefore, the use of the data from this HgS standard to simulate a well-characterized Hg-S correlation could result in erroneous



**Figure 1a**

$\chi(k)*k^3$  data for dried FMMS material after introduction to  $HgI_2$ ,  $CH_3Hg$ , and  $HgNO_3$  solutions.



**Figure 1b**

Fourier transform of  $\chi(k)*k^3$  data ( $1.2-11.5 \text{ \AA}^{-1}$ ) shown in Fig. 1a.

values of Hg-S coordination number and radial distance for the FMMS. To reduce these errors, the FEFF7 theoretical codes were used to simulate the first-shell Hg-S correlations expected for a sample consisting of 15% cinnabar and 85% metacinnabar. The parameters (specifically  $S_0^2$  and  $E_0$ ) used as inputs to the FEFF7 codes to reproduce the multiphase HgS standard accurately were used to create a Hg-S single shell standard with four Hg-S correlations at 2.53 Å. Similarly, the parameters used as inputs to the FEFF7 codes to reproduce the HgO (montroydite) standard accurately were used to create an Hg-O single-shell standard representing two Hg-O correlations with a radial distance of 2.03 Å.

Investigation of the  $\chi(k)*k^3$  data in Fig. 1a or the Fourier transform of the  $\chi(k)*k^3$  data in Fig. 1b indicates that the average local chemical environment surrounding the Hg in each of the FMMS samples studied is very similar. Had the counterion in solution with the Hg somehow remained in contact with the Hg after it had reacted with the FMMS material, the local chemical environment of the Hg would have changed noticeably, because the backscattering amplitudes of  $CH_3$ , I, and  $NO_3$  ions are very different. This result indicates that the presence of these counterions in

solution has very little effect on the final binding configuration of the Hg to the FMMS surface.

To balance the charge between the  $Hg(II)$  and the thiol group of the FMMS surface, the Hg probably binds to the FMMS in one of two ways. The Hg atom can bind to two S atoms at the surface of the FMMS, or the Hg atom can bind to a single S atom at the FMMS surface and be linked to an adjacent Hg atom by a common oxygen atom. These two possibilities were investigated in an attempt to fit the FMMS data with the Hg-S and Hg-O standards.

For the Fourier-filtered data range ( $1.1-2.5$ , uncorrected for electron phase shift), and for the fitting range ( $2.8-11.5 \text{ \AA}^{-1}$ ) used here, the maximum number of fit parameters that may vary at one time is more than seven. (See Ellis Horwood, [1991]). A two-shell fit to the data (one Hg-S shell and one Hg-O shell), with the coordination numbers, radial distances, and XAFS Debye-Waller factors allowed to vary during the fit, resulted in a six-variable fit. Therefore, a two-shell approach may be used to fit the data. The most realistic, best fit to the experimental data was identified by monitoring the  $\chi^2$  value for all realistic fitting scenarios. Realistic fitting scenarios were restricted to positive values for coordination number, radial distances, and XAFS Debye-Waller factors.

The results of the best two-shell fits to data for FMMS material loaded with monomethyl Hg or  $HgNO_3$  indicate Hg-O coordination numbers of 0-0.06. The results of the best two-shell fit to the data for FMMS material loaded with  $HgI_2$  indicate an Hg-O coordination number of 0.4. If the Hg in the FMMS material had bonded to a single S atom and a bridging O atom, the average coordination number for Hg in the samples would have been 1 S and 1 O. Our XAS results indicate that the majority of the Hg in the FMMS materials studied did not have the local chemical environment of 1 S and a bridging O atom. Further, these results indicate that the majority of the Hg in the all the FMMS material investigated was bonded to 2 S atoms. To investigate this question further, a single Hg-S shell fit to the Fourier-filtered data was attempted. In all cases, fitting the single Hg-S shell to the data resulted in an increase in the normalized  $\chi^2$  parameter of less than 0.1. This indicates that a fitting scenario to the data that incorporates the possibility of an Hg-O correlation might not be statistically significant. Minimum  $\chi^2$  values for best fits to the data with either a two-shell or one-shell approach were 0.8-1.4.

To illustrate the statistical significance of the Hg-O correlation for a two-shell fit to the data, a two-shell fit with two separate Hg-S shells was attempted. This comparison removed any dependence of the normalized minimum  $\chi^2$  value on the number of floating variables used during a fit. For this scenario, the best fits to the data for all FMMS material samples resulted with one coordination shell of 1.8-2.2 Hg-S correlations and a radial distance of 2.39-2.41 Å plus another coordination shell of 0-0.2 Hg-S correlations and a radial distance of 2.1 Å. More importantly, however, the normalized  $\chi^2$  parameter for these fits, relative to the normalized  $\chi^2$  parameter for the Hg-S and Hg-O two shell fit attempt, decreased by 0.1. Stated more simply, the presence of an additional coordination shell of less than 0.2 Hg-S correlations resulted in a better fit to the Fourier filtered data than the presence of any Hg-O correlations. Thus, the use of

any Hg-O correlations to fit the Hg L<sub>III</sub> absorption edge XAS data did not result in a statistically significant increase in the goodness of the fit.

The best single-shell fits to the Fourier-filtered first-shell peak, for all Hg-loaded FMMS materials investigated, resulted in 1.85-2.2 Hg-S correlations at a distance of 2.39-2.41 Å and XAFS Debye-Waller factors of 0.0067-0.0091 Å<sup>2</sup>. These values represent the differences in the best-fit results among the three FMMS material samples measured. The variance due to correlations of the fitting variables, (i.e., an increase of +1 in the  $\chi^2$  parameter) for all samples, was less than 0.4 for coordination number, 0.01 Å for radial distance, and 0.0018 Å<sup>2</sup> for XAFS Debye-Waller factor.

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