

Examination of the Speciation of Arsenic in Chemical Agent Simulant Using XAFS

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Introduction

The *Chemical Weapons Convention* [1] mandates that all stockpiled chemical weapons in the United States must be destroyed by the year 2007 [2]. Much of the stockpiled inventory has been destroyed. Analyses of containers housing agent, however, have shown that some agent destined for destruction contains elevated concentrations of metals [2]. High metal concentrations prevent agent from being thermally destroyed, as transfer of the metals to the atmosphere violates air pollution permits [3]. If the valence states of the metals are known, a waste treatment process, such as precipitation, could effectively sequester metals from the agent and allow treated agent to be destroyed.

The work presented here examines the state of arsenic in a mustard chemical warfare agent simulant, thiodiglycol. The research examines (1) arsenic in a water based solution and compares its speciation to that in thiodiglycol, (2) the effect that sodium hypochlorite (bleach) has on arsenic speciation, and (3) the effect that a caustic, sodium hydroxide, has on arsenic speciation. Arsenic characterizations were performed using extended x-ray absorption fine structure spectroscopy (EXAFS) and x-ray absorption near edge spectroscopy (XANES).

Methods and Materials

In the containers housing agent, high concentrations of other metals including cadmium, selenium, and iron can be present. Chemical reagents, including arsenic trioxide (As_2O_3), mercuric chloride ($HgCl_2$), cadmium chloride ($CdCl_2$), ferrous sulfate ($FeSO_4$), ferric oxide (Fe_2O_3), and selenious acid (H_2SeO_3), all from Aldrich, were added to the samples to simulate the chemical environment found in "real" containers. Two types of solutions were prepared: solutions in distilled water and solutions in the mustard chemical warfare agent simulant, thiodiglycol (Aldrich). The solutions were completely mixed, and allowed six months to equilibrate. The long equilibration period was intended to simulate the extended contact period (50 years) typically found in containers housing agent.

6mL of each solution were transferred to an XRF cup (Chemplex Industries, Inc.) and covered with Kapton film. The state of arsenic was determined using EXAFS and XANES (collectively, XAFS) at the GSECARS beam line 13. After

initial examination, the samples were opened, and sodium hypochlorite ($NaOCl$) was added to produce a resultant concentration of 0.04M $NaOCl$. Samples were re-analyzed with XAFS. Samples were again opened, and sodium hydroxide ($NaOH$) was added to produce a resultant concentration of 0.20M. Samples were analyzed with XAFS. During all XAFS analyses, samples were held at 45 degrees to the beam and the XAFS was recorded by measuring the fluorescent signal from Hg as a function of photon energy using a 16 element Ge detector placed along the polarization vector of the synchrotron radiation.

Table 1. Solutions prepared for XANES/EXAFS analyses

Sample Number	Solution constituents. Total volume of each solution is 6mL.
27	150 ppm As in distilled water
12	150 ppm As in thiodiglycol
32	150 ppm As, 1mg Fe_2O_3 in distilled water
18	150 ppm As, 1 mg Fe_2O_3 in thiodiglycol
35	150 ppm As, 100 ppm Cd in distilled water
33	150 ppm As, 100 ppm Cd in thiodiglycol
36	150 ppm As, 100 ppm Se in distilled water
34	150 ppm As, 100 ppm Se in thiodiglycol
28	150 ppm As, 1000 ppm Hg in distilled water
25	150 ppm As, 1000 ppm Hg in thiodiglycol

Results

XAFS was used to determine the state of arsenic in the samples. Analyses showed the following:

- The state of arsenic (from an As_2O_3 source) in thiodiglycol is different than its state in water (Figs. 1 and 2). The exact state of arsenic in simulant was not determined in this preliminary effort.
- The presence of mercury affects arsenic speciation in thiodiglycol; the presence of iron, selenium, and cadmium individually do not affect the state of arsenic in this medium.
- Regardless if other metals are present or absent, the speciation of arsenic in thiodiglycol is influenced by the addition of both sodium hypochlorite and sodium hydroxide.

Fig. 1. 150 ppm As in thiodiglycol. “s12b” denotes bleach is added, “s12bc” denotes that both bleach and sodium hydroxide are added. Fluorescence intensity in arbitrary units versus incident x-ray photon energy is shown.

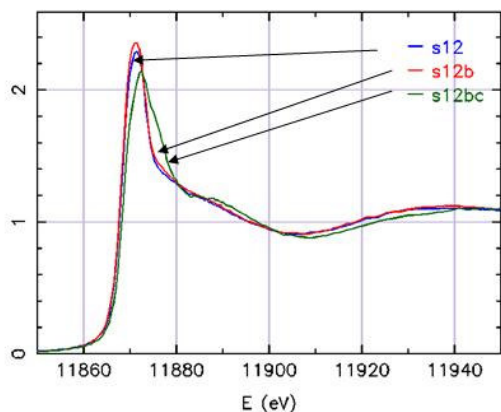


Fig. 2. 150 ppm As in distilled water. “s27b” denotes bleach is added, “s27bc” denotes that both bleach and sodium hydroxide are added. Fluorescence intensity in arbitrary units versus incident x-ray photon energy is shown.

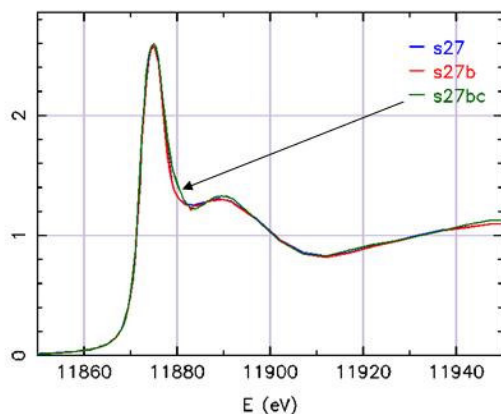
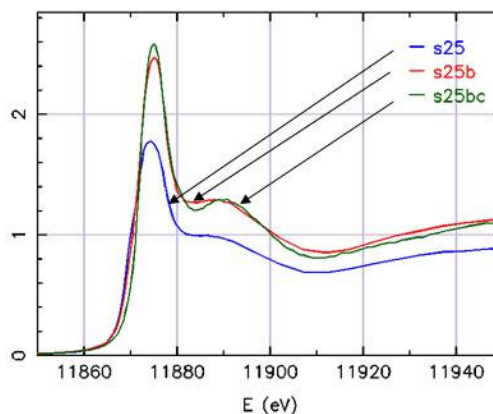


Fig. 3. 150 ppm As and 1000 ppm Hg in thiodiglycol. “s25b” denotes bleach is added, “s25bc” denotes that both bleach and sodium hydroxide are added. Fluorescence intensity in arbitrary units versus incident x-ray photon energy is shown.



Discussion

The speciation of arsenic in a distilled water matrix and in the mustard simulant, thiodiglycol, was evaluated. Results showed that the stable form of arsenic in thiodiglycol is different than the stable form of this ion in water. Addition of sodium hydroxide affects arsenic speciation both in the presence and absence of additional metal ions. Further investigations of arsenic speciation with combinations of metals present will ensue.

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References

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