

Development of a Technique for Mercury Speciation and Quantification Using Gas Chromatography/Mass Spectrometry

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Introduction

While most pollutants that make the news headlines are complex organic molecules like polychlorinated biphenyls, a small group of inorganic compounds contributes to a significant portion of the pollution problem; included among these compounds are the salts of tin, lead, arsenic, and mercury. Although these metals occur naturally, it is through their re-introduction into the environment by man that most problems have arisen. Chlor-alkali producing industrial plants, mining operations, pulp and paper mills, paint production, and some agricultural practices are just some of the sources of inorganic pollution (1). Recently, environmental remediation efforts at the U.S. Department of Energy's (DOE) national laboratories have been instrumental in identifying some of the biggest contributing factors to environmental pollution, as well as some of the toxic effects specific pollutants have on humans.

One element of concern to DOE is mercury. Mercury was used extensively at the DOE facilities in Oak Ridge, Tennessee from 1950 to 1963 in the process of making lithium deuteride, a component of nuclear weapons. Although both the inorganic and organometallic forms of mercury are toxic to humans, the organic compounds are often more toxic (2). Since the toxicity of mercury is a function of its chemical form, an understanding of the interactions between commercially discharged mercury, naturally occurring mercury, and the environment in which they are present is vital.

To address the issue of toxicity, both the inorganic and organometallic forms of mercury need to be determined and quantified; this has driven chemical speciation into the area of trace elemental analysis. Conventional elemental analysis techniques like inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AA), and glow discharge mass spectrometry (GDMS) suffer from the limitation that virtually no information about the chemical form of the element can be obtained due to the energy imparted to the molecule during the atomization step. High-performance liquid chromatography (HPLC) has been interfaced with the ICP to separate different charge states of the element (3) and information about the organic ligand can be obtained from the LC retention times. However, the technique relies heavily on standards, and the analysis of unknown samples is problematic.

As an alternative to these conventional techniques, we have been investigating gas chromatography/mass spectrometry (GC/MS) for the analysis of both the organometallic and inorganic forms of mercury in the same environmental sample (e.g., solutions, soils, and sludges). Although gas chromatography is the classical technique for analyzing organic

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molecules, (e.g., organometallic compounds) little has been done on the analysis of inorganic compounds (4-6). In a previous publication (7), we described how a solid phase microextraction (SPME) fiber could be used to sample organomercurials from aqueous samples. An alkylation reaction was then carried-out to transform chemically mercury (II) nitrate into dimethylmercury; subsequent GC/MS analysis of this compound permitted quantification of the inorganic constituent. Subsequently, several different alkylation reagents have been synthesized that methylate any inorganic mercury compound to methylmercury iodide. Here, we report results on alkylation reaction time and the effect of pH on the population of the product.

Experimental

Gas Chromatography/Ion Trap Mass Spectrometry

The GC/MS instrument used in this investigation was a Finnigan MAT (San Jose, CA, USA) Magnum ion trap coupled with a Varian (Sunnyvale, CA, USA) gas chromatograph. Chromatographic separation was performed using a 0.25 mm x 0.25 μ m DB-5MS column of either 10 m or 30 m length, depending on the amount of chromatographic separation needed. The GC was run under either isothermal conditions or temperature-programmed from 35° to 250° C at a rate of 20° C/min. The injection port and transfer line temperatures were 250° C and 260° C respectively. The carrier gas was research-grade helium. The column head pressure was 1.0 kg/cm². Mass spectral analysis was performed using 70 eV electron ionization and a scan range of 45 to 500 *m/z*.

Solid Phase Microextraction

Sampling involved the use of an SPME fiber (Supelco, Bellefonte, PA, USA) coated with a 65 μ M polydimethylsiloxane/divinylbenzene cross-linked sorbent phase. A 10 μ L aliquot of the analyte of interest was spiked into 50° C aqueous buffer saturated with potassium iodide. It is recommended that a salt solution be used to increase the ionic strength and reduce the solubility of some analytes; this, in turn, enhances analyte extraction (8). Once the analytes were adsorbed onto the fiber, it was placed in the injection port of the GC where analytes were desorbed prior to analysis by GC/MS.

Chemical Alkylation

Since inorganic mercury salts can't be sampled directly using the SPME fiber, they must first be transformed into organomercury compounds. This is accomplished by one of two alkylating reagents: methylpentacyanocobaltate (4) or methylpyridinacobaloxime (9). Depending upon the reaction conditions, one or several products may result. Under ideal conditions (namely in the presence of an excess of potassium iodide, and in a 50° C aqueous solution), only methylmercury iodide is formed.

Caution!

Organic and inorganic mercury compounds are highly toxic. Many of these compounds are readily absorbed through the skin and are known to cause neurological damage. These compounds must be handled in areas with adequate ventilation. Anyone contemplating research with organometallic compounds is well advised to consult the material safety data sheets and the help of an industrial hygienist.

Results and Discussion

Both alkylating reagents we have been investigating show a strong pH dependence (increasing analyte signal with increasing pH), as well as a dependence on the counter ion in solution (e.g., Cl⁻, I⁻, etc.). In addition, there is a minimum time for the reaction to go to completion. Figure 1 illustrates the pH dependence, and Figure 2 illustrates the dependence of product ion formation on the total reaction time.

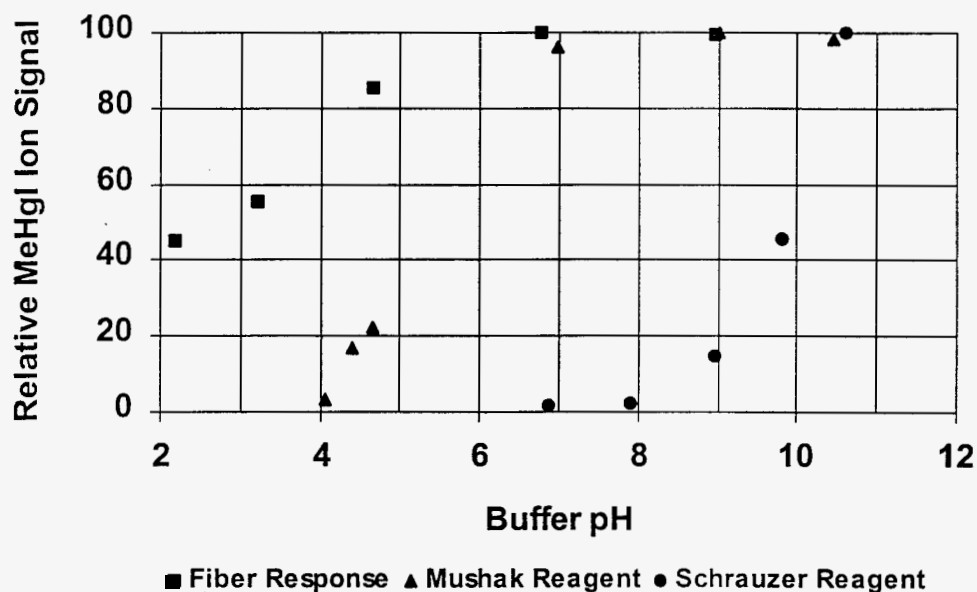


Figure 1. Methylmercury iodide ion signal versus solution pH for inorganic mercury in each of two different alkylating reagents.
• methylpyridinatocobaloxime; ▲ methylpentacyanocobaltate

Although results to date have been encouraging, our goal remains one of finding a reagent that reacts quickly (<30 minutes) and has a high alkylation efficiency. We have already demonstrated an effective scheme for quantification that possesses good accuracy (better than 10% relative error) and a relatively short sampling time (< 5 minutes), as well as the ability to speciate a wide range of organometallic compounds. Detection limits are 2 ppb for organomercury compounds

in water and 10 ppb in soil. LOD's for inorganic mercury compounds are 100 times poorer in both media.

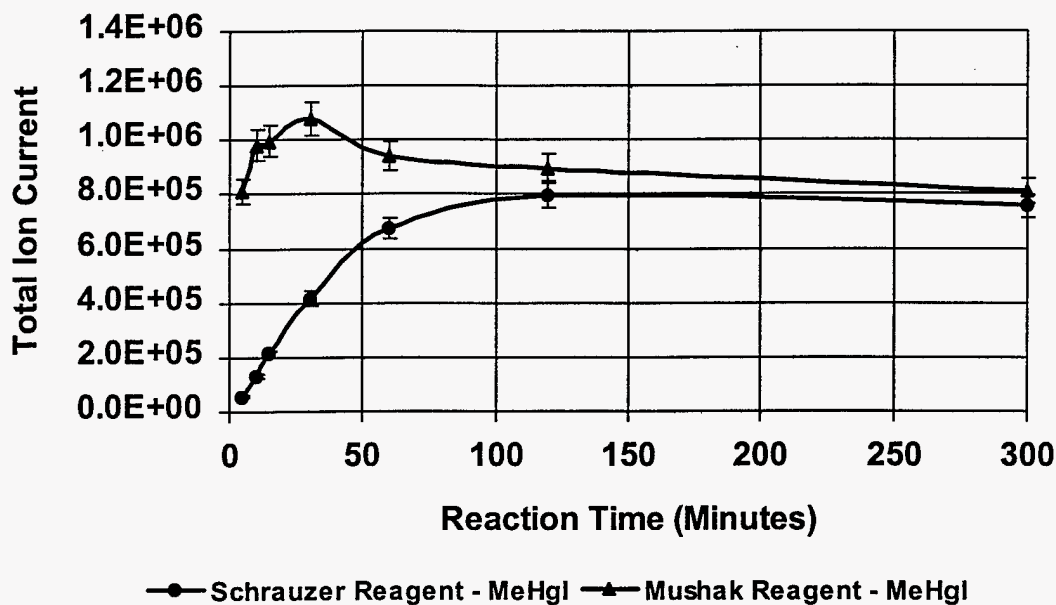


Figure 2. The dependence of product ion formation on total reaction time.

References

1. Wallace, R.A.; Fulkerson, W.; Shults, W.D.; Lyon, W.S. "Mercury in the Environment: The Human Element", *Oak Ridge National Laboratory Report ORNL NSF-EP-1*.
2. Adriano, D.C., Ed. *Biogeochemistry of Trace Metals*; Lewis Publishers: Boca Raton, FL, 1993.
3. Byrde, F.A.; Caruso, J.A. *Environ. Health Persp.* **1995**, *103*, 21.
4. Zarnegar, P.; Mushak, P. *Anal. Chim. Acta* **1974**, *69*, 389.
5. Jones, P.; Nickles, G. *J. Chromatogr.* **1973**, *76*, 285.
6. Chau, Y.K. *Analyst* **1992**, *117*, 571.
7. Barshick, C.M.; Barshick, S.A.; Mohill, M.L.; Britt, P.F.; Smith, D.H. *Rapid Communications in Mass Spectrometry* **1996**, *10*, 341.
8. Zhang, Z.; Yang, M.J.; Pawliszyn, J. *Anal. Chem.* **1994**, *66*, 844A.

9. Schrauzer, G.N.; Windgassen, R.J. *J. Am. Chem. Soc.* **1966**, *88*, 3738.

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