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International Journal of Mass Spectrometry 178 (1998) 31–41

International Journal of Mass Spectrometry

Development of a technique for the analysis of inorganic mercury salts in soils by gas chromatography/mass spectrometry

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Received 30 October 1997; accepted 26 March 1998

Abstract

A technique has been developed to analyze environmentally relevant samples for organic and inorganic mercury compounds. A solid phase microextraction (SPME) fiber was used as a sampling medium in both water and water/soil slurries. Quantification of inorganic mercury was accomplished through a chemical alkylation reaction designed to convert an inorganic mercury salt to an organomercury compound prior to GC/MS analysis; this was found to be the rate limiting step in the analysis. Two alkylating reagents were investigated: methylpentacyanocobaltate (III) ($K_3[Co(CN)_5CH_3]$) and methylbis(dimethylglyoximato)pyridinecobalt (III) ($CH_3Co(dmgH)_2Py$). Methylbis(dimethylglyoximato)pyridinecobalt (III) was found to be superior for this application because it produced a single reaction product, methylmercury iodide, with an efficiency of ~95%. Detection limits were ~7 ppb in water and ~2 ppm in soil. The poorer results in soil were due to an increase in background signal (~10 times compared to water) and a reduction in analyte signal (as much as 100 times). This reduction in signal intensity is believed to be caused by complex soil chemistry. Manipulation of the solution chemistry [e.g. oxidation of mercury (0) → mercury (II)], before or during the alkylation step, may improve the detection limits and increase the number of elements amenable to analysis. (Int J Mass Spectrom 178 (1998) 31–41) © 1998 Elsevier Science B.V.

Keywords: Gas chromatography/mass spectrometry; Inorganic analysis; Elemental; Mercury compounds; Chemical alkylation

1. Introduction

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 pollutant of concern to DOE is mercury because of its extensive use at the facilities in Oak Ridge, Tennessee from 1950 to 1963. Mercury contamination has been found in at least three bodies of water in the Oak Ridge reservation, and the long range effects of this pollution are still unknown.

Although both the inorganic and organometallic forms of mercury are toxic to humans, the organomercury compounds are often more toxic [1]. The reason for this enhanced toxicity lies in the existence of hydrophobic groups on species having a hydrophilic dipole. Because these compounds are often water soluble, they can be easily transported through the body after inhalation or ingestion; in addition,

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Dedicated to the memory of Al Nier.

PII S1387-3806(98)14091-5

many of these compounds are freely absorbed through the skin [2,3]. Inorganic mercury compounds can be absorbed through the lungs and gastrointestinal tract [4]; exposure to inorganic mercury salts, while rare, has been known to cause gastrointestinal, pulmonary, and respiratory ailments.

Because the toxicity of mercury is a function of its chemical form, an understanding of the interactions between commercially discharged mercury [5,6], naturally occurring mercury, and the environment in which they are present is vital. There are five major commercially discharged mercury species: metallic mercury, inorganic divalent mercury salts, phenylmercury, methylmercury, and methoxymethylmercury. The majority of mercury waste reaching open water consists of inorganic and phenylmercury [4]. Naturally occurring mercury can be found in its metallic form in rocks and minerals, or in soil in a variety of inorganic or humic complexes, including the relatively stable mercuric sulfide, HgS [5,6]. Under oxidizing conditions, HgS is converted to mercuric sulfate ($HgSO_4$), readily dissociating and releasing inorganic mercury into the environment [7].

Once in the environment, mercury compounds can undergo many changes. Those compounds that return to the soil usually degrade to metallic mercury and volatilize under the action of the sun [3,5]. Those compounds that are washed into river and lake bottoms are either converted into HgS in the presence of hydrogen sulfide under anaerobic conditions or become bound to lake sediment where microbes transform them into methylmercury derivatives [3,8]; these compounds are loosely bound to substrates, water soluble, and are accumulated by living organisms [5]. In this environment, the amount of organic matter, as opposed to other factors such as surface area, controls the concentration and identity of the mercury present.

To address the issue of toxicity, both the inorganic and organometallic forms of mercury need to be determined and quantified; this has driven trace elemental analysis into the area of chemical speciation. 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 [9] and to provide information about the organic ligand from 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 molecules, less has been done on the analysis of inorganic compounds [10–12]. In a previous publication [13], 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 mercury (II) nitrate into dimethylmercury; subsequent GC/MS analysis of this compound permitted quantification of the inorganic constituent.

A similar approach has been used by Cai and Bayona [14] to quantify mercury in fish and river water. In their work, a polydimethylsiloxane SPME fiber was used to sample CH_3Hg^+ and Hg^{2+} after they had been derivatized with sodium tetraethylborate to ethylmethylmercury and diethylmercury, respectively. Likewise, Gorecki and Pawliszyn [15] have used this approach to quantify tetraethyllead and inorganic lead in water. Both of these studies used sodium tetraethylborate to ethylate the element of interest into a highly volatile analyte prior to headspace sampling. In the work reported here, we demonstrate how a different alkylating reagent, methylpentacyanocobaltate (III) can be used to methylate not only Hg^{2+}, but Hg^+, and Hg^0 in soil. Several important refinements, not previously reported by these other groups, are demonstrated; these include the ability to sample the methylmercury salt directly, and the use of a second alkylation reagent that permits tailoring of the methylation reaction.

2. Experimental

2.1. Gas chromatography/ion trap mass spectrometry

The GC/MS instrument used in this investigation was a Finnigan MAT (San Jose, CA, U.S.) magnum ion trap mass spectrometer coupled with a Varian (Sunnyvale, CA, U.S.) gas chromatograph. Chromatographic separation was performed by using a 0.25 mm × 0.25 μm × 30 m DB-5MS column. The GC was temperature programmed from 35° to 250°C at a rate of 20°C/min. The injection port and transfer line temperatures were 250 and 260°C, respectively. The manifold temperature was 220°C. The carrier gas was research-grade helium. The column head pressure was 1.0 kg/cm^2. Mass spectral analysis was performed by using electron ionization under automatic gain control and a scan range of 45 to 500 Da. Selective ion monitoring was employed. Mass-to-charge ratios 202, 217, and 232 were monitored for Me_2Hg; mass-to-charge ratios 217, 329, and 344 were monitored for MeHgI.

Sampling involved the use of an SPME fiber (Supelco, Bellefonte, PA, U.S.) coated with either a 100 μm polydimethylsiloxane sorbent phase or a 65 μm partially crosslinked polydimethylsiloxane/divinylbenzene phase. A 10 μL aliquot of the analyte of interest was spiked into 50°C deionized water. The SPME fiber was placed directly into the solution. 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 [16]. Once the analytes were adsorbed onto the fiber, it was placed in the injection port of the GC where analytes were desorbed for 3 min prior to analysis by GC/MS.

2.2. Preparation of potassium methylpentacyanocobaltate (III), $K_3[Co(CN)_5CH_3]$

Methylpentacyanocobaltate (III) was prepared by the method of Kwiatek and Seyler [10,17] from cobaltous chloride ($CoCl_2$), potassium cyanide (CN/Co = 5:1), and methyl iodide in 0.075 M KOH under argon [18]. The product was isolated by precipitation as a brown oil in excess acetone. Addition of ethanol to the oil produced a tan powder that was filtered, washed with ethanol, diethyl ether, and dried under vacuum. The reaction product (10.58 g), isolated as a 1:1 mixture of methylpentacyanocobaltate (III) and iodopentacyanocobaltate (III), produced as a by product in the reaction, was dissolved in 0.018 M KOH (65 mL). The alkylpentacyanocobaltates are stable in dilute alkaline media for several days if protected from light [10].

2.3. Preparation of methylbis(dimethylglyoximato)pyridinecobalt (III) $[CH_3Co(dmgH)_2Py]$

Methylbis(dimethylglyoximato)pyridinecobalt (III) was prepared by the method of Schrauzer and Windgassen [19] by reduction of bis(dimethylglyoximato)pyridinecobalt (II) with sodium borohydride, followed by alkylation with dimethyl sulfate. The complex was recrystallized from a methanol—water mixture.

Caution! Organic and inorganic mercury compounds are highly toxic. Many of these compounds are readily absorbed through the skin and some protective gloves. These compounds are known to cause neurological damage and death [20,21] and must be handled in areas with adequate ventilation by using proper personal protection equipment. Anyone contemplating research with organometallic compounds is well advised to consult the material safety data sheets and the help of an industrial hygienist.

3. Results and discussion

The goal of this work is to develop an analytical method that accurately quantifies organometallic and inorganic mercury from the same soil sample. As we have been developing this technique, we have pointed to a method that will aid in environmental remediation. The method we are employing currently involves placing an aliquot of soil in a pH buffer with a dilute salt solution. This soil/water slurry is sampled with a solid phase microextraction fiber and analyzed by gas

chromatography/mass spectrometry to quantify the organometallic analytes present in the soil. Once this is complete, an aliquot of an alkylating reagent is added to the sample to transform the inorganic species into an organometallic compound not previously found in the sample. A second SPME extraction and GC/MS analysis then provides quantification of the inorganic species. To develop this technique, several parameters had to be evaluated and optimized including the choice of sorbent phase, sampling conditions, alkylation reagent, and reaction conditions. The results of these studies will be described as well as application of this method to environmental samples.

3.1. Solid phase microextraction

Sampling by solid-phase microextraction involves two distinct steps: partitioning of the analytes between the fiber coating and the solution, and thermal desorption of concentrated analytes into the injection port of a gas chromatograph [16]. As a consequence of the volatility of the mercury compounds in this study, an injector temperature of 250°C should desorb all of the analytes rapidly and completely. We have observed that subsequent desorption from the same fiber (i.e., no additional extraction) produced no detectable analyte signal. Under equilibrium conditions, a linear relationship exists between the amount of analyte absorbed by the coating and the concentration in the sample [16]. Because the partition coefficient between the coating and the sample is large, the fiber produces a concentrating effect that helps improve sensitivity [16].

The choice of sorbent phase used for SPME sampling will directly affect the selectivity of the analysis. For example, Me_2Hg is efficiently extracted from aqueous solutions with the polydimethylsiloxane (PDMS) SPME fiber, however, control experiments have shown that MeHgCl and MeHgI are not extracted. If the same analytes are sampled with the partially crosslinked polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber, both Me_2Hg and MeHgX (where X is Cl^- or I^- are observed in the spectrum. In this manner, fiber selectivity can be used to ones advantage by employing a phase that extracts many analytes (like PDMS/DVB) or conversely by selecting a phase that targets only certain analytes (like PDMS). We have used both in these studies.

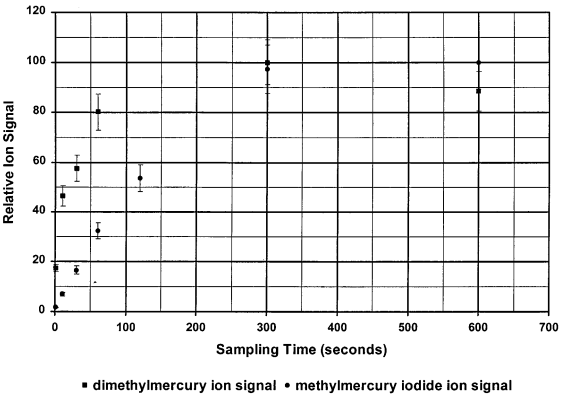

Fig. 1. (Filled square) Relative dimethylmercury ion signal vs. SPME sampling time for a 20 ppb Me_2Hg solution in 50°C NaCl (*aq*). A 100 μM polydimethylsiloxane fiber was used to sample this solution. (Filled circle) Relative methylmercury iodide ion signal vs. SPME sampling time for a 20 ppb MeHgI solution in 50°C KI (*aq*). A 65 μM partially cross-linked polydimethylsiloxane/divinylbenzene fiber was used to sample this solution.

3.2. Sampling time

Several factors can be used to enhance the rate of analyte extraction from an aqueous solution, including sample agitation and heating [16,22]. Reports in the literature indicate that stirring with a magnetic stirrer typically produces equilibrium times of between 2 and 60 min [16,22]; however, inconsistent stirring can be worse than no stirring at all. Because equilibration times vary depending upon the partition coefficient of the analyte, sampling time must be determined for each analyte. The SPME sampling time for the two fibers was optimized by spiking one series of solutions with dimethylmercury and sampling it with the PDMS fiber, and a second series of solutions with methylmercury iodide, and sampling it with the PDMS/DVB fiber. Figure 1 illustrates our results for a 50°C aqueous solution of saturated sodium chloride containing 20 ppb of dimethylmercury, stirred rapidly and consistently with a magnetic stirrer, and sampled with the PDMS fiber. Three replicate measurements were taken for each data point. Equilibration seems to be complete after 2 min;

however, a 5 min sampling time was used for all subsequent analyses to provide better precision, as this time occurs well away from the steeply rising portion of the curve. Figure 1 also illustrates the results obtained when a PDMS/DVB fiber was used to sample 20 ppb of methylmercury iodide from a 50°C aqueous solution of 10% KI. Although the signal was observed to rise more slowly than in the previous case, after a 5 min sampling time the maximum intensity was reached and maintained. At room temperature a substantially reduced signal was observed.

3.3. Potassium methylpentacyanocobaltate (III) alkylating reagent

In a previous study, we demonstrated how the reaction of a 1:1 mixture of potassium methylpentacyanocobaltate (III) and iodopentacyanocobaltate (III) with inorganic mercury produces a small amount of dimethylmercury (Me_2Hg), in addition to the known reaction product, $MeHg^+$ (isolated as a mixture of methylmercury chloride and methylmercury iodide in excess sodium chloride or as methylmercury iodide in excess potassium iodide) [13]. Although the original work by Zarnegar and Mushak [10] reported only monomethylation, their analysis was done by using a packed GC column. Under these conditions, Me_2Hg may have coeluted with the solvent peak [10]. It has been reported in the literature that methylcobaltamin methylates MeHgCl to Me_2Hg, although the rate of methylation is approximately 25–40 times slower than methylation of mercury chloride to MeHgCl [23]. The following reaction schemes are proposed:

$$Hg^{2+} + [Co(III)(CN)_5CH_3]^{3-} + X^- + OH^- \rightarrow CH_3HgX + [Co(III)(CN)_5OH]^{3-}$$

$$OH^- + CH3HgX + [Co(III)(CN)_5CH_3]^{3-} \rightleftarrows (CH_3)_2Hg + [Co(III)(CN)_5OH]^{3-} + X$$

The rate constants for methyl transfer from cobalt to mercury (II) have been shown to be strongly dependent on the counter ion, with the reactivities being acetate > chloride > bromide [24]. This order is opposite to that observed for the stabilities of the mercury (II) complexes and supports a mechanism involving the electrophilic attack by a cationic mercury species. Therefore, we would predict that alkylation of CH_3HgCl to be faster than CH_3HgI, and experimentally, we do not observe the formation of Me_2Hg in the presence of KI.

3.4. Alkylation reaction time

Because the alkylation reaction is the rate limiting step in the analysis, we have strived to maximize the reaction rate while minimizing sampling time. Figure 2 shows the results of a study done to assess the rate of reaction of $[Co(CN)_5CH_3]^{3-}$ with Hg^{2+}. In Fig. 2(a), a series of solutions, 20 ppm in mercury (NIST SRM 3133), was sampled for 5 min with the PDMS fiber after reacting with an excess of the methylpentacyanocobaltate (III) reagent for the indicated time. In Fig. 2(b), a second series of 20 ppm solutions was sampled for 5 min with the PDMS/DVB fiber after reacting with an excess of the methylpentacyanocobaltate (III) reagent. Each data point is the average of three replicate measurements. The dimethylmercury signal [Fig. 2(a)] was observed to rise for the first 30 min of the reaction, after which it leveled off. Not shown on this curve is a data point taken for a reaction time of 4500 min (3.125 days). This value is statistically the same as that obtained at both 30 and 60 min, indicating that after ~30 min the reaction has proceeded to completion. The methylmercury iodide signal [Fig. 2(b)] exhibited a similar but somewhat unusual behavior rising to a maximum at 30 min and then decreasing slightly before it levels off. Because the signal at 30 min is statistically the same as that beyond 30 min, this minimum value was used for all subsequent studies.

To determine the yield of the methylation reaction, we spiked an aqueous solution with enough NIST SRM 3133 solution to make it 20 ppm in mercury. After reacting with $K_3[Co(CN)_5CH_3]$ for 30 min, we sampled the solution with a PDMS fiber and quanti-

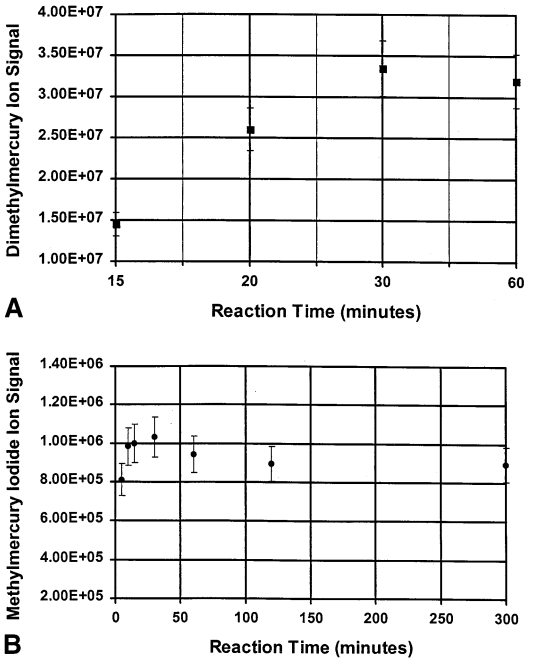

Fig. 2. (A) Dimethylmercury ion signal vs. reaction time. 10 μL 10 000 ppm NIST SRM 3133 in 4.5 mL of 50°C NaCl (*aq*) plus 0.5 mL methylpentacyanocobaltate (III) reagent; 5 min sampling time; 100 μM polydimethylsiloxane SPME fiber. (B) Methylmercury iodide ion signal vs. reaction time. 10 μL 10 000 ppm NIST SRM 3133 in 4.5 mL of 50°C, KI (*aq*) plus 0.5 mL methylpentacyanocobaltate (III) reagent; 5 min sampling time; 65 μM partially cross-linked polydimethylsiloxane/divinylbenzene SPME fiber.

fied the dimethylmercury. This was compared with the signal obtained for an aqueous solution containing 20 ppm of dimethylmercury. The SPME fiber extraction efficiencies should be identical for the two solutions, and any difference should be indicative of the reaction efficiency. The efficiency of the methylation reaction was 10.3% $\pm$ 0.8%. In a similar manner, a 20 ppm mercury sample (NIST SRM 3133) was reacted with $K_3[Co(CN_5CH_3]$ for 30 min and sampled with a PDMS/DVB fiber. This time the methylmercury iodide signal was compared with a 20 ppm standard of methylmercury iodide. An efficiency of 13.8% $\pm$ 1.1% was measured.

The limit of detection (LOD) was calculated by taking three times the standard deviation of the blank, plus the blank, divided by the slope of a linear calibration curve. Results indicated that the LOD for inorganic mercury in water (post-alkylation, by using Me_2Hg for quantification) was on the order of 41 ppb. Similarly, an LOD of 32 ppb was calculated when the methylmercury iodide signal was quantified after alkylation. When standards of Me_2Hg and MeHgI were spiked into water, a detection limit of 4 ppb was calculated for both, confirming the ~10% reaction efficiency reported above (i.e., 41 ppb versus 4 ppb).

3.4. Methylbis(dimethylglyoximato)pyridinecobalt (III) alkylating reagent

In the reaction of $CH_3Co(CN)_5^{3-}$ with mercury salts, CH_3Hg^+ has a rich coordination chemistry, forming complexes with a variety of ligands. The dominant mercury complex in solution will depend on the ligands in solution and the stabilities of the complexes. For example, in the reaction of $CH_3Co(CN)_5^{3-}$ with Hg^{2+} in saturated sodium chloride, CH_3HgCl and CH_3HgI were detected by GC/MS because $Co(CN)_5I^{3-}$ hydrolyzes to $Co(CN)_5OH^{3-}$ and I^-; the formation constant for formation of CH_3HgI is 10^3 greater than that for CH_3HgCl [25]. Subsequent reactions were run in 10% KI to simplify the reaction mixtures. However, in these reactions an unexpected product, CH_3I, was observed. Although the origin of the CH_3I has not been completely defined, it most likely arises from air oxidation of I^- to form I_2, followed by electrophilic attack on $CH_3Co(CN)_5^{3-}$ to form CH_3I and $Co(CN)_5^{3-}$. The reaction of organocobalt (III) compounds with halogens has been previously described [24] and in view of the weak oxidizing power of I_2, oxidative dealkylation of organocobalt (III) complexes is probably unlikely. The reaction of I_2 with cobaloximes proceeds via a two step reaction involving a preequilibrium followed by a bimolecular rate determining step in which the intermediate $[Co(dmgH)_2(H_2O)I_2]$ acts as an electrophile [24]. All of these things considered, we concluded that methylpentacyanocobaltate (III), while an "effective" alkylating reagent, is not an "ideal" alkylating reagent. Therefore, we have recently been investigating the methylation of alkylation salts with cobaloximes.

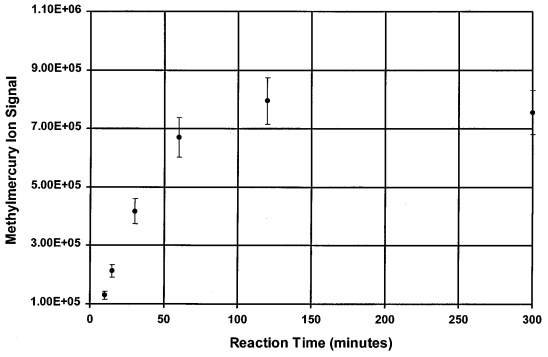

Fig. 3. Methylmercury iodide ion signal vs. reaction time, 10 μL 10 000 ppm NIST SRM 3133 in 4.0 mL of a pH 10 buffer, 0.5 mL of 50°C KI (*aq*), and 0.5 mL methylbis(dimethylglyoximato-)pyridinecobalt (III) reagent; 5 min sampling time; 65 μM partially cross-linked polydimethylsiloxane/divinylbenzene SPME fiber.

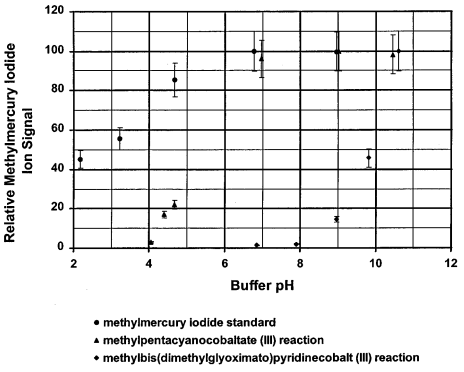

Fig. 4. Relative methylmercury iodide ion signal as a function of sample pH (see text).

3.5. Alkylation reaction time

As with methylpentacyanocobaltate (III) reagent, it was necessary to measure the time required for the methylbis(dimethylglyoximato)pyridinecobalt (III) reagent to react to completion with inorganic mercury. Figure 3 shows these results. Paralleling the earlier investigation, a 20 ppm mercury solution (NIST 3133) was allowed to react with an excess of methylbis(dimethylglyoximato)pyridinecobalt (III) reagent prior to being sampled with a PDMS/DVB fiber for 5 min. Because the reaction is pH dependent [26], all reactions were carried out in a pH 10 buffer. As was the case for the methylpentacyanocobaltate (III) reagent, the signal increases quickly, leveling off after about 60 min. Although this is slightly longer than what we found for the methylpentacyanocobaltate (III) reagent, the formation of a single product (MeHgI, when the reaction is performed in KI) provides enough of an analytical advantage that this extra reaction time can be tolerated.

As in the case of the methylpentacyanocobaltate (III) reagent, we were able to evaluate the reaction efficiency of the methylbis(dimethylglyoximato)pyridinecobalt (III) reagent by comparing the signal obtained for a known concentration of mercury after alkylation with the signal for the same concentration of a MeHgI standard. To an aqueous solution 2 ppm in mercury (NIST SRM 3133), we added an excess of methylbis(dimethylglyoximato)pyridinecobalt (III) reagent (0.1 M in ethanol). We found that the solubility of the methylbis(dimethylglyoximato)pyridinecobalt (III) reagent was greater in ethanol than water. A reagent solution prepared in ethanol produced a factor of two times the MeHgI ion signal after alkylation as one prepared in water. The reaction was allowed to proceed for 1 h; a reaction efficiency on the order of 95% was measured. By using this reagent, the limit of detection for elemental mercury in water was 7 ppb, a factor of five improvement over the methylpentacyanocobaltate reagent.

3.6. pH effects on alkylation reaction

Results in the literature indicate that pH plays a significant role in the alkylation of mercury [26]. To gauge the effect of pH on the alkylation reaction, a 20 ppm inorganic mercury standard was reacted for 30 min with the two alkylating reagents, methylpentacyanocobaltate (III) and methylbis(dimethylglyoximato)pyridinecobalt (III), in buffers ranging from pH 4 to pH 10.5 [27]. The SPME fiber manufacturer recommends maintaining a pH between 2 and 11 [28]. Figure 4 illustrates our results. Below pH 7, the MeHgI signal from the methylpentacyanocobaltate (III) reaction responded similarly to the signal from the standard (displaying a linearly increasing signal with increasing pH). Although this behavior is be-

lieved to be due mostly to the poor response of the fiber at pH <7, the difference between the maximum and minimum signals for the MeHgI standard (i.e., no methylation) is smaller than the difference between the maximum and minimum signals after alkylation; this implies that reactivity is pH dependent. Above pH 7, no increase in MeHgI is observed. Contrast this with the solutions containing the methylbis(dimethylglyoximato)pyridinecobalt (III) reagent. Below pH 7 no signal was observed. Above pH 7, a strong pH dependence is observed (increasing with increasing pH). In aqueous solution, a pyridine ligand dissociates from methylbis(dimethylglyoximato)pyridinecobalt (III) ($CH_3CO(dmgH_2Py)$ to form the aquo complex with an equilibrium constant of 4.9×10^{-4} as shown in the reaction below:

$$[CH_3Co(dmgH)_2Py] + (H_2O) \rightleftarrows [CH_3Co(dmgH)_2\ H_2O] + Py$$

(see [26]).

At pH < 7, pyridine will react with the acid to form the pyridinium salt that cannot complex with the cobalt complex. Therefore, the equilibrium will be driven to the right (i.e. $[CH_3Co(dmgH)_2Py]$ will completely hydrolyze in acidic solutions to $[CH_3CO(dmgH)_2H_2O]$). At pH ~8.5 (i.e. >95% free base), only 5–10% of $[CH_3Co(dmgH)_2Py]$ will hydrolyze to $[CH_3Co(dmgH)_2H_2O]$. It has been shown that the rate coefficient for the reaction of Hg^{2+} with organo(dimethylglyoximato)cobalt reagents is slower with the aquo complex than with those having a more basic ligand such as a pyridine or 5,6-dimethylbenzimidazole [26]. Therefore, the observed increase in reactivity at high pH is probably a result of a change from $[CH_3Co(dmgH)_2H_2O]$ as the major species in solution to $[CH_3Co(dmgH)_2Py]$ as the major species.

3.7. Monovalent, univalent, and divalent mercury analysis

Because mercury can exist in a number of different forms in soil, it was necessary to study several different salts to determine what levels of product would be formed for each. Mercury forms compounds

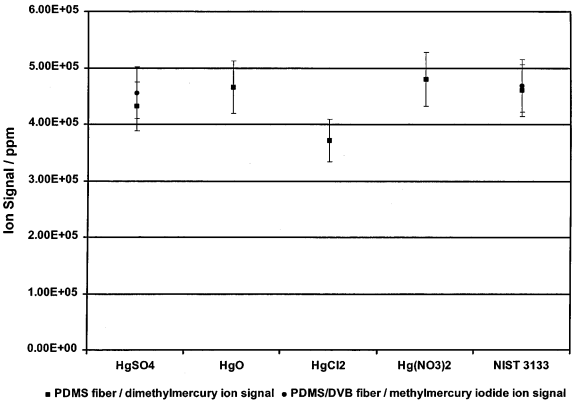

Fig. 5. Total ion signal measured after reaction with methylpentacyanocobaltate (III) reagent for 30 min. Each solution contained 20 ppm of a mercury salt; the data has been corrected for the amount of mercury in each sample (see text).

in both the 1+ and 2+ oxidation states. In the 1+ state, two mercury (I) ions are joined by a covalent bond to give Hg_2^{2+}. In an ideal situation, 0, 1+, and 2+ oxidation states would produce the same amount of dimethylmercury or methylmercury iodide. Figure 5 shows the results for several 2+ salts (five different samples—$HgSO_4$, HgO, $HgCl_2$, $Hg(NO_3)_2$, and NIST SRM 3133, incorporating four different divalent salts). NIST SRM 3133 is a solution of elemental mercury prepared in 10% HNO_3; under these conditions mercury will exist as the divalent mercury nitrate. Each solution contained 20 ppm of the mercury salt, and the data has been corrected for the amount of elemental mercury in each. The sulfate, oxide, and nitrate all produced similar amounts of dimethylmercury iodide per ppm. Mercury chloride produced a slightly lower dimethylmercury signal, although it overlaps with the oxide and the nitrate salts if the 1 α relative standard deviation error bars are incorporated.

Although in nature, one is most likely to find mercury in the +2 state, under conditions in which environmental remediation is being pursued, both elemental and univalent mercury may need to be measured. Univalent mercury salts have a more complex chemistry than the divalent salts. Mercurous ion (Hg_2^{2+}) disproportionates into elemental mercury (Hg^0) and the mercuric ion (Hg^{2+}) in a one-to-one

ratio with an equilibration constant of 1.1×10^{-2} in aqueous solutions [24]. In addition, if the mercury salt is present in an oxidizing environment or a ligand can selectively complex with Hg^{2+}, the reaction will be driven toward the formation of Hg^{2+}. For this study, all mercury salts were stabilized in a weakly oxidizing medium, 10% nitric acid. When a solution of mercurous sulfate (20 ppm in mercury) was reacted with an excess of the methylpentacyanocobaltate reagent, the methylmercury signal intensity was comparable to that observed for mercuric sulfate (~493 000 counts/ppm versus ~455 000 counts/ppm). The ten percent uncertainty associated with these results makes them identical. Other salts in the 1+ state have shown a comparable intensity per ppm, when the same ions were monitored.

In our previous work, we were unable to detect any dimethylmercury ion signal when we reacted an aliquot of elemental mercury with the methylpentacyanocobaltate reagent; this solution was sampled with the PDMS fiber. Here we performed a similar experiment by using the PDMS/DVB fiber. The smallest amount of elemental mercury that could be accurately weighted was 0.7 mg (in the 5 mL sampling volume this corresponded to a concentration of 140 ppm). When this solution was allowed to react with an excess of the methylating reagent, we observed a methylmercury iodide signal of ~1800 counts/ppm. Although this value is significantly lower than the signal observed for either the divalent or univalent mercury salts, we are encouraged. Results in the literature indicate that a solution of tris (1,10-phenanthraline) Fe (III) hexaflurophosphate can be used to oxidize Hg_2^{2+} to the 2+ state [27]. When 1.0 mL of a 1×10^{-3} M solution of this reagent was added to a mercury aliquot prior to methylation, a factor of 3.5 improvement in the signal was observed. Further investigations are underway.

3.8. Inorganic mercury salts sampled from soils

Soil is a difficult medium to analyze. Not only does it have a complex chemical matrix comprised of oxides, nitrates, sulfates, and silicates, but because it is a solid, it presents a sample introduction challenge for many analytical techniques. Often, chemical digestion (e.g., on a hot plate or in a microwave by using several aliquots of HNO_3, HF, and HCl) is used to get the soil into an aqueous medium. This is a time-consuming step that may result in the loss of volatile material. To analyze soils by solid phase microextraction, it is not necessary to transform the sample into a different chemical form, but it is necessary to modify the sampling protocol slightly to prevent damage to the fiber. To approximately one gram of soil, we add 4 mL of pH 11 buffer, 0.5 mL of 10% KI, and 0.5 mL of 0.1 M alkylating reagent. During the alkylation reaction we stir the sample, but then stop during sampling; although this certainly reduced the analyte signal by an unknown amount, it was a necessary step to prevent the soil particles from damaging the fiber. Two approaches have been taken to preparing soil standards: spiking with mercury solutions and spiking with mercury oxide solids.

For the first approach, 10 μL of five different mercury nitrate solutions (NIST SRM 3133 solutions with concentrations ranging from 0.1 to 1000 ppm) were spiked into 1 g of blank soil, previously analyzed by ICP-MS and found to contain only trace levels of mercury (<0.1 ppb). These samples were allowed to air dry for 12–18 h prior to sampling. A linear calibration curve was generated with an r^2 value of 0.9998. From these results a detection limit of 1.9 ppm was calculated. This result is considerably poorer than that obtained for elemental mercury in water, a none too surprising result. We have observed that the background signal intensity in a clean water sample is ~ten times better than in soil; we believe this to be due to the complexity of the matrix (i.e. all soils have a certain amount of organic material adsorbed on the individual particles). In addition, analyte signal intensity has been shown to be reduced by as much as 100 times. We believe this to be attributable to a complexing of the mercury salt with the soil matrix. Data has been taken to confirm that when an aliquot of solution is added to a soil/buffer slurry (i.e. no drying of the sample), no signal reduction occurs. No mercury loss is believed to have occurred during air drying. For the second approach, mercury (II) oxide was mixed directly with the soil to

generate standards. The resulting calibration curve was linear over three orders of magnitude (from a low of 8 ppm to a high of 8000 ppm) with an r^2 value of 0.9991. The calculated detection limit for this scheme was 1.0 ppm, slightly better than the previous approach. A series of blind samples prepared under each of the two approaches were analyzed and found to agree to within 10% of their true value.

Although we are encouraged by the accuracy of these preliminary results, we are more encouraged that these results were obtained without the need for dissolution. We are also encouraged by the fact that the waste generated for the analysis was substantially less than conventional techniques involving dissolution. Work continues on different quantification schemes, methods to improve accuracy and detection limits, and the analysis of a variety of environmental samples.

4. Conclusions

Improvements have been demonstrated to a technique for determining the total elemental concentration of mercury in soils and solutions. The concept is based on converting the inorganic mercury species into an organometallic compound prior to GC/MS analysis. Solid phase microextraction was used for sampling, providing a simple way of reducing waste associated with conventional solvent extraction and dissolution techniques. Reaction and sampling times are short enough that the technique provides a considerable time savings over conventional methods for inorganic mercury analysis. When combined with a sampling step prior to alkylation, a single sample can be analyzed for both the organometallic and inorganic compounds, minimizing disturbance of the sample and eliminating possible contamination. Manipulation of the chemistry [e.g. oxidation of mercury (0) $\rightarrow$ mercury (II)], prior to or during the alkylation step, may improve the detection limits, as well as increase the number of compounds amenable to analysis. This methodology has as yet untapped applicability to other environmentally important inorganic species (e.g. tin and lead).

Acknowledgements

Research was sponsored by the Laboratory Directed Research and Development Program, under contract no. DE-AC05-96-OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation. We would like to acknowledge the help of R.R. Turner and M. Morris, previously of ORNL's Environmental Sciences Division. D.A.L. and E.B.W. would like to acknowledge the U.S. Department of Energy's Science and Engineering Research Semester Program for funding. M.A.V. would like to acknowledge the Great Lakes College Association/Associated Colleges of the Midwest Oak Ridge Science Semester Program for funding.

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