# MERCURY SPECIATION ANALYSIS BY GAS CHROMATOGRAPHY/ELECTRON IMPACT/MASS SPECTROMETRY

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## ABSTRACT

Fast and reliable analytical methods for mercury speciation would aid in understanding mercury offgas chemistry. Presently, the U.S. Environmental Protection Agency (EPA) regulates only total mercury; however, many studies indicate that mercury toxicity is highly dependent on the mercury speciation. For example, amalgams and mercury sulfides have relatively low toxicities, while organomercury and halogenated organomercury compounds, apparently through the action of the methylmercury ion, $CH_3Hg^+$, have irreversible deleterious effects on the central nervous system. In addition, the distribution of mercury emissions (local versus global) is highly dependent on initial mercury speciation in the offgas.

Existing EPA methods for mercury analysis rely on capturing oxidized and elemental mercury in various solutions, and then analyzing the solutions for mercury by Cold Vapor Atomic Absorption (CVAA) or Cold Vapor Atomic Fluorescence (CVAF) techniques. Related procedures, for example the Ontario Hydro Method, give a measure of mercury speciation in offgases. Other methods based on carbon traps or direct AA or AF analysis of mercury vapor are applied as well, but give only limited information on mercury speciation. In addition to atomic adsorption and atomic fluorescence techniques, mass spectrometry (as part of inductively coupled plasma/mass spectrometry or ICP/MS) is often used to quantify mercury, but by itself does not provide information about mercury speciation.

Gas chromatography/mass spectrometry (GC/MS) is a well established technique for separating, identifying, and quantifying individual volatile and semi-volatile organic compounds contained in complex gaseous mixtures. Because elemental mercury and many inorganic and organic mercury compounds are similarly volatile, it appeared possible that gas chromatography would lend itself to separation of offgas mercury compounds, which could then be individually identified and quantified by mass spectrometry. Accordingly, MSE Technology Applications, Inc., under contract to the U.S. Department of Energy, conducted preliminary experiments to determine whether standard GC/MS equipment can be adapted to the measurement of mercury species in combustion offgases.

These developmental experiments focused on determining the behavior of organic and inorganic mercury species in a GC/MS system (1) by direct insertion of mercury compounds into an electron impact mass spectrometer (EI/MS), (2) by injection of liquid standards into a GC/EI/MS system, and (3) by head space sampling using solid phase microextraction (SPME).

From these experiments, we concluded that SPME coupled with GC/MS is a promising technique for sampling and analyzing speciated mercury compounds, but that unbiased sampling/preconcentration of all mercury compounds, and "freezing" the species distribution of mercury compounds during sampling and subsequent analysis may be problematic. Future work will include will include determining the rate and extent of redistribution of mercury species during SPME sampling and GC analysis and the retention efficiency of individual mercury compounds by various sampling adsorbents.

## INTRODUCTION

Trace substances referred to as air toxics or hazardous air pollutants (HAP) are emitted from power plants or waste incinerators and present a health risk. These substances are regulated by the U.S. Environmental Protection Agency (EPA). The facilities emitting these substances are obligated to measure the concentration of HAPs in their exhaust gases and to minimize these concentrations down to allowed levels.

Mercury, a toxic Resource Conservation and Recovery Act metal, exists in many of the hazardous and mixed waste streams being thermally treated throughout the U.S. Department of Energy (DOE) complex. The mercury contained in the waste streams is vaporized in the incineration process and is transferred almost entirely to the offgas. The Maximum Achievable Control Technology (MACT) standard requires that less than 130 µg/dscm of total mercury in the offgas can be released to the atmosphere. However, due to the complex chemistry of mercury in the incineration offgases, its speciation may vary widely depending on particular conditions of the incineration process.

Several recent studies of mercury species emissions by these processes became a matter of great concern for public and regulatory agencies. Mercury naturally occurs in fossil fuels and volatilizes during its combustion. Volatilized mercury introduced into the atmosphere can migrate over large distances. When different forms of mercury are introduced into aqueous matrixes, they can produce methylmercury ($HgCH_3^+$) and its complexes. The methylmercury moiety in these complexes is chemically inert and resists conversion to less complex species. Human consumption of aquatic life forms affected by methylmercury can cause irreversible damage to the nervous system and internal organs.

Fossil fuel combustion generates significant amounts of particulate matter that is typically removed from the flue gases by electrostatic precipitators (ESP). Mercury, naturally present in fossil fuels, is almost entirely volatilized during combustion. Incineration of wastes also volatilizes mercury compounds. Mercury in the combustion offgases may exist as gaseous elemental mercury and mercury compounds, or may be adsorbed onto offgas particulate solids. Adsorbed mercury is usually less than 10% of the total. To minimize the amount of mercury emitted by incineration and combustion processes, EPA established the MACT Standard restricting mercury emissions from existing hazardous waste incinerators (HWI) to 130 µg/dscm and from new ones to 45 µg/dscm (1). Typical concentration of mercury emitted from coal-fired utility boilers is 10 µg/dscm or less. However, the total amount of mercury emitted into the atmosphere by these sources is very large, and EPA is planning to regulate mercury emission from these sources in the near future. Most of the existing technologies used for flue gas cleaning are inefficient in mercury removal. Performance of these flue gas cleaning technologies can be affected by the speciation of mercury compounds present in the flue gas.

A fast analytical method capable of measuring individual mercury compounds is needed to monitor speciation (and corresponding toxicity) of mercury emissions and to enable better process control. The following discusses considerations and activities related to developing a gas chromatography (GC)-based mercury speciation monitoring system.

## Analytical Approaches to Mercury Analysis

Quantification of mercury is usually performed by atomic absorption, atomic emission or atomic fluorescence, mass spectrometry (MS), x-ray fluorescence, and gold-film resistance measurements. Cold-vapor atomic fluorescence spectroscopy (CVAAF) and cold-vapor atomic absorption spectroscopy (CVAAS) are the most popular approaches for mercury analysis. Most of these detection techniques are well developed as final steps in determining total mercury in solid or aqueous matrices or ambient air. Mercury analysis in combustion gases is undeveloped, especially speciation analysis of mercury compounds. The development of mercury continuous emission monitors (CEMs) relies primarily on CVAAF and CVAAS. Most of these monitors require an additional preconcentration step (usually amalgamation) and cannot work directly with the target analyzed gas. However, mercury amalgamation and recovery from the amalgam may be affected by some flue gas constituents, such as nitrosyl chloride (NOCl).

One of the evolving field-operable, continuous mercury analyzers is under development by ADA Technologies, Inc. (ADA). The analyzer was field tested at MSE Technology Applications, Inc. (MSE) during 1998 and 1999 (2, 3, 4, 5). The analyzer was designed and developed by ADA in cooperation with Sandia National Laboratory. The mercury concentration in the offgas is monitored by transferring the gas through two heated cells illuminated with ultraviolet (UV) light at 253.7 nm. The attenuation (based on absorption) of this UV light by vapor-phase mercury is the basic measurement for determining the mercury concentration of the offgas. One of the cells is maintained at a temperature of 200 °C and detects only elemental mercury in the offgas, while the other cell is held at a temperature of 800 °C. At the higher temperature, oxidized forms of mercury are decomposed to elemental mercury, so this cell indicates the total mercury concentrations.

In real offgases, interference from certain gas components, primarily sulfur dioxide ($SO_2$), makes it necessary to split the UV light into two polarized components so the UV absorbency by the interferents can be taken into account. This light-splitting process is called the Zeeman Effect and is accomplished by placing the UV lamp in a strong magnetic field. The light emitted from the magnetic field zone is then passed through a rotating polarizing lens that produces alternate pulses of in-phase and out-of-phase light. A computer algorithm determines the light attenuation due to elemental mercury only and calculates the mercury concentrations in the offgas.

Examples of gas-phase, elemental mercury atomic fluorescence analyzers are Sir Galahad of PS Analytical, LTD and Tekran 2537 of Tekran, Inc. In these analyzers, the gas, containing mercury vapor (typically air), passes through a gold-impregnated sorbent trap. Gold extracts mercury from the air, creating an amalgam. At the end of the trapping cycle, argon or another inert gas is flashed through the trap at a low temperature to remove any remaining sample gas. Then the heating cycle is activated when the trap is flashed with inert gas and heated to approximately 500 °C or above—the temperature at which amalgam releases elemental mercury and the oxidized mercury compounds are decomposed releasing elemental mercury as well. In the analyzer, mercury vapor entrained in a carrier gas (usually argon) passes through an optical cavity illuminated with a high-intensity mercury lamp. The resulting fluorescence at a wavelength of 253.7 nm is measured with a conventional photomultiplier tube (PMT). Using argon as the carrier gas ensures maximum sensitivity due to minimization of the quenching effect on the fluorescence signal. Quenching reactions depopulate the excited states of mercury (Hg*) in collisions with other gas molecules (M):

$$Hg^* + M \rightarrow Hg + M \qquad \text{(Eq. 1)}$$

The quenching effect increases in the row argon, nitrogen, oxygen, and the reduction of signal in air is approximately 30 times higher than in argon.

Another technique for mercury analysis is x-ray fluorescence (XRF) spectrometry. A practical example of the XRF-based analyzer is the CEM of stack metal emissions developed by Cooper Environmental Services. The XRF CEM operates by extracting an isokinetic sample from a gas stream and transporting the sample through an approximately 18-inch long, 1/2-inch diameter, heat-traced, stainless steel pipe to the main sampling and analysis compartment. The extracted sample is drawn through a resin-impregnated filter tape. The filter tape collects both the particulate and vapor-phase metals. The resulting deposit is then moved into analysis position where the metals are quantified by energy-dispersive x-ray fluorescence (EDXRF) analysis while another sample is being collected. The stack gas elemental concentrations are calculated from the EDXRF results, mass flow meter data, and oxygen concentration.

An example of the gold-film sensor is the Jerome 431-X mercury vapor analyzer from Arizona Instruments®. The response time of the 431-X is 13 seconds with a range of 0.003 to 0.999 $mg/m^3$ $Hg^0$. The analyzer works by measuring the resistance of the gold filament. The resistance of the filament depends on the amount of elemental mercury reversibly amalgamated in gold. The analyzer, however, is used almost exclusively for environmental analysis of air due to strong matrix effects from ozone, nitrogen dioxide, and some other compounds, which are usually present in the incineration offgases.

## Practical Analysis

Practical analysis includes procedures for extracting mercury compounds from the incineration offgases and preparing extracted analyte for quantitative analysis. Analysis is typically performed by atomic absorption or atomic fluorescence after transformation of mercury into an elemental vapor form in the balance of the inert gas or air.

EPA Methods 101A and 29 are wet preconcentration methods which rely on capturing elemental and oxidized mercury in aqueous solutions (6, 7). Method 101A contains one set of impingers with acidic permanganate solution and is designed to analyze the incineration offgas for total mercury content. In Method 29, two sets of impingers are installed within the sampling train. The first impinger set is filled with 10% hydrogen peroxide in a 5% nitric acid solution, and the second impinger set is filled with 4% potassium permanganate in a 10% sulfuric acid solution. The first solution is intended to capture oxidized mercury, while the second solution is intended to capture elemental mercury. The spent solutions can be analyzed based on EPA's Method 245.2 using a CETAC M6000A atomic absorption mercury analyzer. The Ontario-Hydro method is a modification of Method 29. This method is applicable to elemental, oxidized, particle-bound, and total mercury concentrations ranging from approximately 0.5 to 100 µg/dscm. In this method, the two acidified peroxide solutions of Method 29 are replaced by a solution of 1M potassium chloride dissolved in deionized water. The advantage of this method relative to Method 29 is that it better measures the oxidized-to-elemental mercury ratio, which is biased in Method 29 due to partial oxidation of elemental mercury in hydrogen peroxide impinger solution. Also, possible $SO_2$ effects on mercury speciation are avoided. Another modification is the acetate buffer method where the first empty impinger of Method 29 is replaced by a sodium acetate/acetic acid buffer solution. The purpose of the buffer is to remove the $SO_2$ and oxidized mercury without capturing the elemental mercury.

Examples of dry preconcentration methods include the mercury speciation adsorption (MESA) or Sorbent Ontario Hydro (SOH) method and the sorbent total mercury (STM) method of Frontier Geoscience, Inc. (FGS). The STM method is attractive because of the simplicity in sample preparation and collection and short turnaround time for analysis. The FGS STM method has been compared with Method 101A, Method 29, and the aqueous Ontario-Hydro method. Analysis of real samples has shown the STM method to agree well with Method 101A and Method 29, for total mercury analysis (8, 9).

The STM method employs iodine-impregnated activated carbon traps. The carbon traps adsorb both the oxidized ($Hg^{2+}$) and elemental ($Hg^0$) forms of mercury, resulting in a total mercury determination. The carbon trap is divided into two zones. The first functions as the sample collection trap and the second serves as a field blank or breakthrough indicator.

The SOH method is similar to the STM Method, the main difference being that four traps are used in this method. The first two traps contain sand coated with potassium chloride (KCl) and are intended to adsorb speciated mercury (i.e., mercuric $Hg^{2+}$ and mercurous $Hg_2^{2+}$ compounds). The last two traps contain iodine-impregnated activated carbon that is intended to adsorb elemental mercury.

During sampling, offgas is drawn from the center of the offgas pipe through the activated carbon traps, which adsorb the mercury species from the offgas. The sampling train is comprised of a quartz sampling probe, the activated carbon traps, a desiccant moisture trap, a flow meter with a volume totalizer, a throttling valve, and a sampling pump. The components of the sampling train are connected via Teflon tubing. The flow rate, measured at standard conditions (101 kPa and 300 K), through the trap is approximately 0.5 slpm, and the duration of each sampling event is approximately 15 minutes.

After completing each sampling event, the activated carbon traps are removed from the sampling train, sealed, and sent to the laboratory. At the laboratory, the solid sorbent undergoes an oxidizing acid reflux followed by tin chloride reduction and preconcentration via dual gold amalgamation. The mercury content of the samples is quantified using cold vapor atomic fluorescence analysis with a minimum detection limit of 0.05 µg/dscm. In addition to analyzing the offgas samples, the laboratory prepares spiked test samples to determine the percent recovery for the analyzer.

### Mercury Speciation Analytical Methods

The application of GC/MS is not currently a widespread technique for mercury analysis; however, there are several investigations involving both techniques for analysis of mercury compounds, primarily organic. Many metals, particularly mercury, are more toxic in organometallic form than when present as the element or as inorganic compounds. At the same time, organometallic compounds are more volatile than corresponding inorganic compounds or metals. In natural conditions, mercury transforms between its different forms, such as elemental mercury ($Hg^0$), oxidized mercury ($Hg^{2+}$), methylmercury ($MeHg^+$), dimethylmercury ($Me_2Hg$), and other organomercury species. Many properties of mercury, such as its transport in the environment, biological activity and availability, and physical chemistry and toxicology are highly dependent on the chemical forms it presents. Therefore, development of accurate and selective analytical methods for mercury speciation analysis is of great importance.

The speciation analysis of mercury in sediments is often performed by derivatization of such forms of mercury as $MeHg^+$ or $Hg^{2+}$ into more volatile compounds by hydride generation or ethylation (10, 11). Sometimes, Grignard derivatization is applied to convert inorganic mercury into more volatile forms, for example (12):

$$HgCl_2 + BuMgCl \rightarrow BuHgCl + MgCl_2 \quad \text{(Eq. 2)}$$

For hydride generation, treatment of the sample by sodium tetrahydroborate ($NaBH_4$) is applied in the following scheme:

$$MeHg^+ + NaBH_4 + 3H_2O \rightarrow MeHgH + Na^+ + H_3BO_3 + 3H_2 \quad \text{(Eq. 3)}$$
$$Hg^{2+} + 2NaBH_4 + 6H_2O \rightarrow Hg^0 + 2Na^+ + 2H_3BO_3 + 7H_2 \quad \text{(Eq. 4)}$$

where the second reaction illustrates the transformation of $Hg^{2+}$ to elemental mercury vapor, which can then be accumulated in the head space of the reactor and measured directly by one of the mercury-sensitive detectors. Potassium tetrahydroborate can also be applied for conversion of methylmercury chloride into its hydride form (13).

Ethylation is performed by sodium tetraethylborate ($NaBEt_4$) (Et-ethyl radical) treatment in the following scheme:

$$Hg^{2+} + 2NaBEt_4 \rightarrow HgEt_2 + 2Na^+ + 2BEt_3 \quad \text{(Eq. 5)}$$
$$MeHg^+ + NaBEt_4 \rightarrow MeHgEt + Na^+ + BEt_3 \quad \text{(Eq. 6)}$$

After derivatization, methylmercury hydride and $Hg^0$ are preconcentrated by cryotrapping, separated chromatographically, and detected by quartz furnace atomic absorption spectroscopy. Some other variations of this approach are applied for determining $MeHg^+$ and $Hg^{2+}$ in biological samples (14). A shortcoming of this approach is that is usually involves several complicated manual steps, and the cost of equipment is relatively high.
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Mass spectrometry is also applied to mercury analysis. A GC/inductively coupled plasma (ICP)/MS method for mercury speciation analysis in natural gas condensate was developed by Hiroaki Tao *et al.*(15). The investigators used a hydrogen bromide pretreated polar DB-1701 column to obtain sharp peaks for monoalkylmercury species and also other species without derivatization. Six organomercury species, $Me_2Hg$, methylethylmercury, diethylmercury ($Et_2Hg$), methylmercury chloride, dibutylmercury, and ethylmercury chloride were baseline separated from $Hg^0$ and mercuric chloride. Separating $Hg^0$ from mercuric chloride was performed using the on-column injection mode. Subpicogram detection limits were obtained on a Hewlett Packard® (HP) 4500 ICP/MS.

Another investigation, more directly related to the offgas analysis of mercury species by the GC/MS, was performed by Christopher Pécheyran *et al.*(16). The objective of the investigation was to develop a sensitive method for multielemental speciation analysis of volatile metal and metalloid compounds in environmental air samples. The analytes were sampled simultaneously in the field by cryofocusing on a small, glass wool packed column (trap tube) at -175 °C. Detection was by low-temperature GC interfaced to an ICP/MS. This GC/ICP/MS system provided subpicogram detection limits, in particular, 0.8 pg (as $Hg^0$) for mercury species ($Hg^0$, $Me_2Hg$, and $Et_2Hg$).

## PROCESS AND EQUIPMENT DESCRIPTION

Mass spectrometry experiments were performed using two mass spectrometry systems located in the Department of Chemistry, Montana State University, Bozeman, MT. One system consisted of a HP 5890 Plus GC coupled to a VG TRIO-2 Quadrupole low-resolution MS. The second GC/MS system utilized a similar GC, interfaced to a medium-resolution MS VG 70E-HF dual (electric/magnetic)-sector mass spectrometer. The second system was also equipped with a direct insertion probe (DIP) for the mass spectrometer, discussed in the following.

In the GCs, 30-meter capillary columns with three different stationary phases were used [DB-5, 5% diphenyl/ 95% dimethylsiloxane, low polarity stationary phase; ZB-WAX, polyethyleneglycol (PEG), high polarity stationary phase; and RTX-1701, 14% cyanopropylphenyl/86% dimethylsiloxane, intermediate polarity stationary phase]. GC separations were followed by MS analysis, with the MS operated in selected ion monitoring (SIM) mode or scanning mode. SIM mode gave better detection limits, and would probably be required for environmental monitoring applications.

In general, samples can be injected into the GC section of a GC/MS either as gases through a gas sampling loop or as liquids through a liquid injection port. The liquid injection port can also be used for thermal desorption, e.g., solid-phase microextraction (SPME), analysis.

As noted, the VG 70E-HF dual (electric/magnetic)-sector MS was equipped with a direct insertion probe. The DIP system allows for inserting a small vial containing a target analyte into the immediate vicinity of the ion source of the MS. The target component evaporates into a vacuum (approximately $10^{-6}$ Torr) at ambient temperature or some elevated temperature achieved by heating the probe. The compound of interest is ionized in the ionization source, and the mass spectra of the compound is obtained. This technique is used for generating the library spectra of different compounds.

## MERCURY SPECIATION ANALYSIS USING GC/ELECTRON IMPACT (EI)/MS

Analysis of elemental mercury was performed through headspace adsorption of elemental mercury onto a polymer-coated fused silica SPME fiber. Carboxen-coated fibers were selective for elemental mercury; the detection limit was ~60 $\mu g/m^3$ using the GC/EI/MS VG TRIO-2 and SPME exposure times of 2 minutes and 10 minutes. The detection limit could be improved by using longer exposure times, by using a more sensitive detector, or by other modifications to the system.

SPME extraction and analysis of other mercury species was done qualitatively. Further experiments will be done to determine the SPME stability and recoveries of speciated mercury compounds.

In order to investigate within-the-mass spectrometer effects, the mass spectra of several mercury compounds were examined using the direct injection probe. Mass-spectra of methylmercury chloride, dimethylmercury, mercuric chloride, methylmercury bromide, methylmercury iodide, and mercuric nitrate monohydrate were generated.

In addition, GC/MS calibration curves for methylmercury chloride, mercuric chloride and dimethylmercury were obtained. The observed detection limits of about 100 ng per injection (1 $\mu$L) were significantly higher than typical 100 pg or lower detection limits observed for other compounds. The higher detection limits may have been due to loss of analyte in the GC/MS system.

### Elemental Mercury Analysis

Elemental mercury in offgases can be analyzed by atomic absorption or atomic fluorescence techniques directly or indirectly with the application of ICP/MS, XRF, and some miscellaneous methods. Direct analysis of elemental mercury with GC/EI/MS is possible with direct gas injection or by applying traps, such as SPME fibers. The advantage of GC/EI/MS in analysis of elemental mercury is a relatively high stability against strong matrix effects, while atomic absorption and atomic fluorescence methods seriously suffer from these interferences. The interferences are primarily due to the presence of compounds absorbing light at a wavelength of 253.7 nm in the offgases at concentrations several orders of magnitude higher than the concentration of elemental mercury.

Attempts to run air samples (250 $\mu$L and 100 $\mu$L) on a GC HP 5890 Plus/MS VG TRIO-2 Quadrupole were performed with an SP-5 column, operated isothermally at 25 and 40 °C. No separation from the air peak was obtained, and the quality of the mercury mass spectra was poor (with the MSE HP 6890/5972A system quality of mercury mass spectra was very good even without separation). High-volume air injections (up to 1 mL) produce some additional (ghost) peaks. This seems to be reasonable taking into account that the helium carrier gas flow rate (approximately 1 sccm) was low compared to the injection volume and reasonable peak width of several seconds.

Due to difficulties with direct air injection, and to avoid column degradation, most of the elemental mercury data was collected using the SPME technique. Mercury vapor was prepared by injecting saturated mercury vapor (typically at 30 °C) into the 125- or 250-mL analyte bulb. The concentration of mercury vapor in the bulb was calculated based on a known dilution ratio and a known partial pressure of mercury at a given temperature.

The SPME was used for elemental mercury introduction into the inlet of the GC. Only one material showed reversible sorption of mercury and was suitable for mercury analysis—carboxin (CAR). Two types of fibers with this material produced quantifiable peaks of elemental mercury—Supelco StableFlex divinilbenzene (DVB)/CAR/polydimethylsiloxane (PDMS) fiber and CAR/PDMS fiber. Other fibers, such as PDMS, PDMS/DVB, polyacrilate, CW (Carbowax®)/DVB showed no adsorption of mercury and produced no signal.

More polar GC columns produced better results with elemental mercury, namely, sharper peaks with a higher retention time. The best resolution and peak quality was obtained with a 30m x 0.25mm i.d. x 0.50um film thickness ZB-WAX column [equivalent to Supelcowax-10 i.e., a poly(ethylene glycol) stationary phase]. The $Hg^0$ peak appeared at 1.80 minutes at a 40 °C column temperature. At 25 °C, the retention time increased to 1.90 minutes. Carrier gas conditions were 50 kPa head pressure, 1.10 mL/min flow rate, and 37.5 cm/s linear velocity. The inlet temperature was 200 to 220 °C, and the MS conditions were ion source at 180 °C, 70 eV EI mode, scan 185 to 210 amu.

An example of an elemental mercury GC peak with a corresponding mass spectrogram for the peak is shown in Figures 1a and 1b. The mass spectrogram reveals an easily recognizable and unique pattern reflecting the natural abundance of mercury isotopes. The most abundant isotopes are at 202 amu and 200 amu. Figure 1c shows the calibration curve obtained with the extraction of mercury vapor from the analyte bulb by SPME followed by GC/MS analysis. The extraction was performed with various exposure limits. The line corresponding to 2 min of exposure crosses the abscissa axis at some nonzero value, indicating underexposure. Yet, even with this short exposure time, the calibration curve is fairly linear within at least an order of magnitude of concentration. Points obtained with 10 min of exposure produced a linear calibration curve that projects well through a zero point, which indicates that a saturation limit was reached; therefore, 10 min of exposure is sufficient, even for low concentrations.

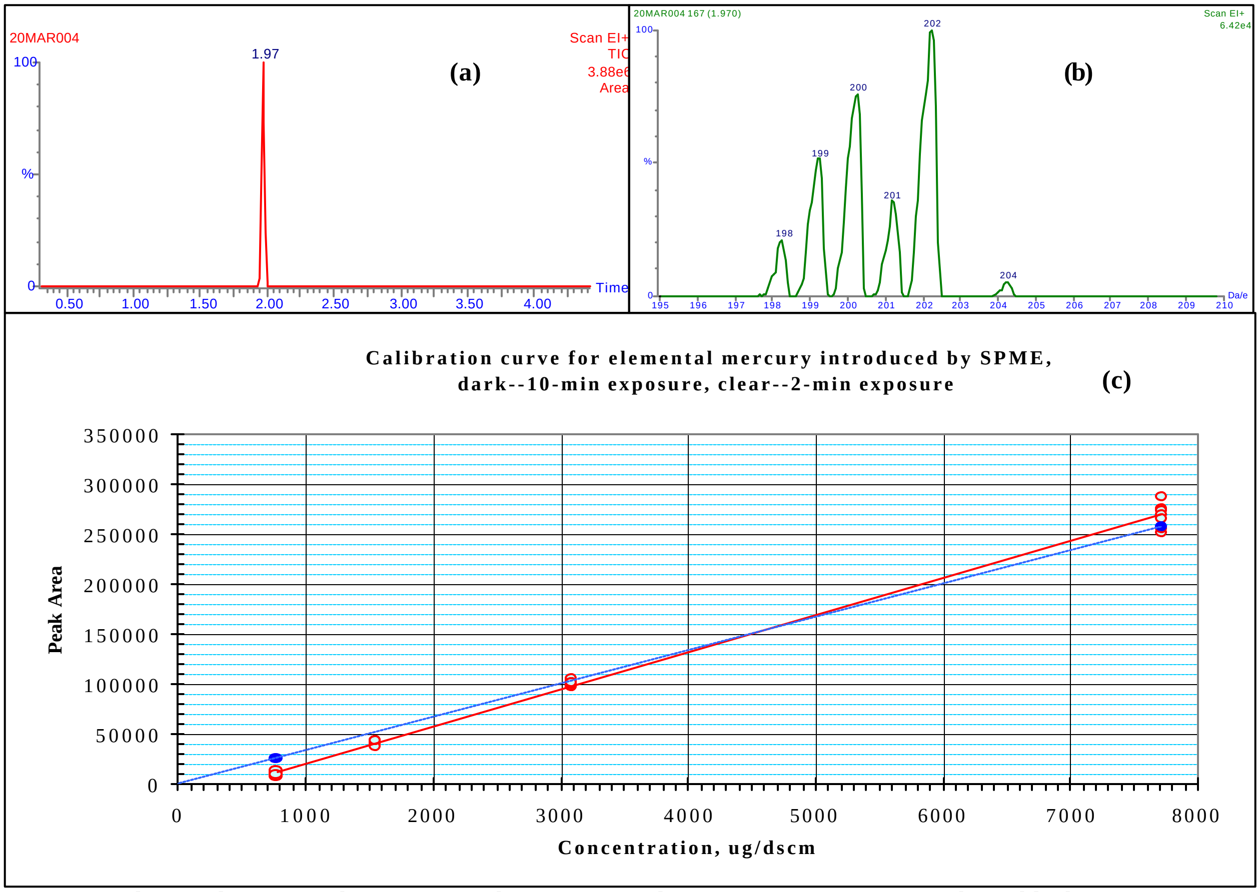

Fig. 1. a) Elemental mercury chromatogram; b) SPME sampling (CAR/PDMS, 75 μm, phase, black), 60-sec exposure, column ZB-WAX, isothermal run at 25 °C; a corresponding mass spectrum; and c) calibration curves

An important factor in analysis of mercury compounds by GC is volatility. At the same time, highly volatile mercury compounds are the compounds of environmental concern. Mercuric chloride has a relatively high vapor pressure—its pressure is only slightly lower than that of mercury vapor itself at room temperature; however, at temperatures exceeding approximately 150 °C, the vapor pressure of mercuric chloride is higher than the vapor pressure of elemental mercury.

Analysis of mercuric chloride was successfully performed for aqueous or solid-state matrixes by derivatization of this and other inorganic mercuric compounds into volatile alkyl mercuric organics that were analyzed by GC/ICP/MS or GC/atomic emission spectrophotometry systems. It appears that the current project was the first successful attempt to directly analyze inorganic mercury compounds such as mercuric chloride. The obtained fragment mass spectra of mercuric chloride allowed unambiguous identification of gas chromatographic peak locations of the compound and to evaluate some decomposition processes during sampling and analysis of the compound.

Introduction of mercuric chloride into the GC was performed by SPME or acetone solution injection; also, the direct probe introduction of the compound into MS was tested. Acetone solutions of $HgCl_2$ were used for calibration experiments. A mercuric chloride signal was not produced at 40 °C on the PEG (ZB-WAX) column with both headspace sample and SPME sample introduction. It was found that the very polar ZB-WAX column retained mercuric chloride virtually irreversibly—the area of the peaks at different amounts of analyte injected into the GC/MS was about the same, and some extended zones with relatively high background levels appeared on chromatograms. Thermal programming of the GC allowed obtaining elemental mercury bleed together with other column bleed at oven temperatures exceeding 220 °C. Perfect mercury mass spectra was observed. The injection was performed at a 200 °C inlet temperature with an acetone solution of $HgCl_2$. The results suggest that mercuric chloride was irreversibly adsorbed on this column, and it started to thermally decompose at approximately 220 °C, producing elemental mercury.

Intermediate and low polarity columns (such as DB-5) allowed for obtaining good chromatographic peaks of mercuric chloride with readily recognizable mass spectra. Ion fragment groups of $Hg^+$, $HgCl^+$ and $HgCl_2^+$ can be seen on the experimental mass-spectrogram. The theoretical isotope distribution within the $HgCl_2^+$ group is shown for comparison. Table I shows the results of the $HgCl_2$ acetone solution analysis with GC/MS System 1 (quadrupole MS).

Table I. Analysis of $HgCl_2$ acetone solution, RTX-1701 column

| **Analyte** | **$HgCl_2$** | **$HgCl_2$** | **$HgCl_2$** | **$HgCl_2$** | **$HgCl_2$** | **$HgCl_2$** | **$HgCl_2$** |
|---|---|---|---|---|---|---|---|
| Concentration, mg/mL | 1 | 1 | 1 | 1 | 0.2 | 0.2 | 0.2 |
| Injection amount, ng | 1,000 | 1,000 | 1,000 | 1,000 | 200 | 200 | 200 |
| Retention time, minutes | 7.82 | 7.82 | 7.83 | 7.81 | 7.84 | 7.82 | 7.82 |
| Peak area, counts | 9,892 | 10,931 | 8,167 | 5,420 | 1,259 | 993 | 1,213 |

The data suggests that some of the analyte was decomposed or otherwise lost during analysis. While typical detection limits for these types of instruments are better than 100 pg for most of the compounds, the data suggests the experiment detection limit of approximately 100 ng for $HgCl_2$ is 3 orders of magnitude higher. Also, high deviations of the peak area and poor GC peak quality suggests that the conditions of the GC run were not optimum. At the same time, the fact that the GC signal of $HgCl_2$ can be obtained is very encouraging.

Figure 2 shows an example of the direct insertion probe mass spectra of the acetone solution of mercuric nitrate monohydrate obtained on the VG 70E-HF mass spectrometer. The main groups of ions containing one $^{202}Hg$ were 329 *amu*, 371 *amu*, 386 *amu*, and 456 *amu*. Based on the mass defects between these groups of ions, it is possible that 456, 329, and 202 *amu* groups are formed by consecutive fragmenting of 127 *amu* from 456 *amu* and 329 amu ions. This mass defect corresponds to $N_2O_6H_3$ group ($2HNO_3$ + H). However, these groups of ions were not observed in the direct insertion probe mass spectra of the pure mercuric nitrate monohydrate. In the DIP measurements performed on the VG TRIO-2 instrument, groups of ions 326, 264, 218 *amu* with one $^{202}Hg$ atom were observed. These masses apparently corresponded to $Hg(NO_3)_2^+$, $HgNO_3^+$, and $HgO^+$ ions. A group 234 amu may correspond to the $HgO_2^+$ ion; however, some higher mass ions within this group are hard to interpret.

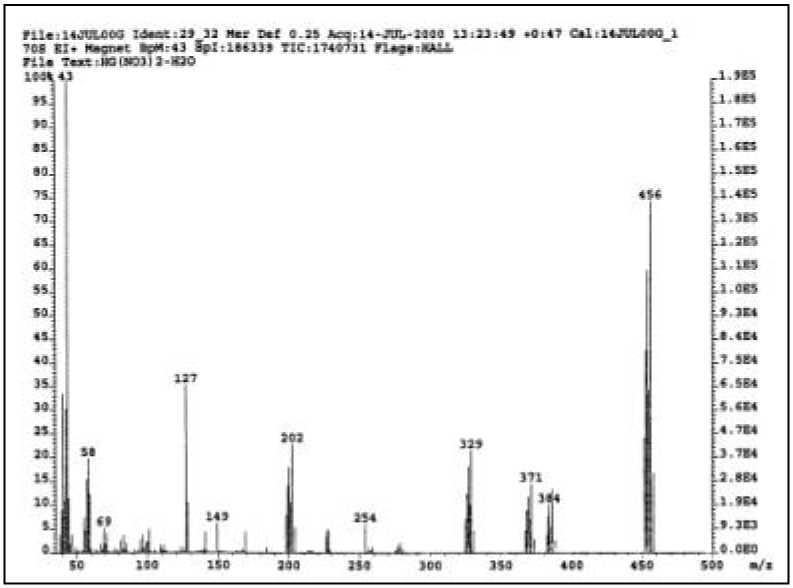

Fig. 2. DIP mass spectrum of mercuric nitrate monohydrate

The experiments on GC/MS analysis of organo-mercury (dimethylmercury and methylmercury chloride) were performed on both a GC HP 5890 Plus/MS VG TRIO-2 quadrupole system and the GC HP 5890 Plus/MS VG 70E-HF dual (electric/magnetic)-sector system. Nonpolar (DB-5) and polar (ZB-WAX, RTX-1701) columns separated available organo-mercury compounds well, and the preference to the nonpolar (weakly polar) DB-5 column was primarily given due to the shorter analysis time.

Interesting results were obtained while analyzing methylmercury chloride. The direct probe mass spectrum of this compound is shown in Figure 3. Heavy mass ion fragments of methylmercury bromide and methylmercury chloride, containing mercury, were observed in the mass spectra of the compound, in addition to the expected $Hg^+$, $HgCH_3^+$, $HgCl^+$, and $HgCH_3Cl^+$ ions. Interestingly, similar high-mass ions were present in some of the MeHgCl spectra from the mass spectra library. High-resolution mass-spectrometric measurements suggested these heavy fragments were derivatives of methylmercury bromide and methylmercury iodide, apparent impurities in the methylmercury chloride used in the experiments. This finding suggests the potential for use of the GC/EI/MS technique for mercury speciation analysis and study of mercury chemistry.

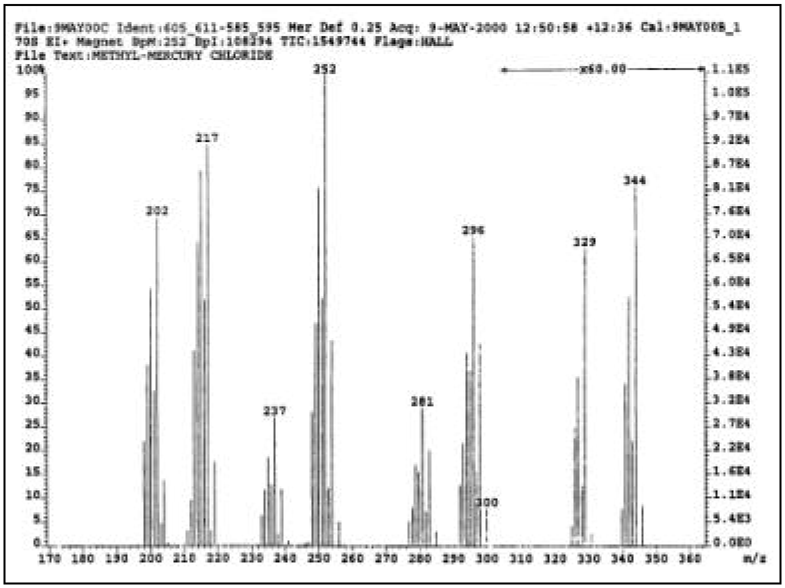

Fig. 3. Direct probe mass spectrum of methylmercury chloride

Quantifiable GC/MS signals were also obtained for two of the most common organic mercury compounds, $Hg(CH_3)_2$ and $CH_3HgCl$ dissolved in acetone or other organic solvents. In addition to the previously described (elemental mercury section) procedure for the detection limits identification based on the standard deviation of the consecutive measurements of the similar samples, the detection limits were determined based on the noise levels during the GC/MS measurements.

There are two types of noises that play an important role in the GC/MS measurements—chemical noise ($N_{chem}$) and instrumental noise ($N_{in}$). The chemical noise for the second GC/MS system (electric/magnetic-sector MS) was more than an order of magnitude higher than the instrumental noise. The detection limit at 10:1 signal-to-noise (S/N) ratio (chemical) for dimethylmercury was 1 ng in nonoptimized EI-SCAN mode. This detection limit can be improved dramatically (two orders of magnitude or more) by optimizing the gas chromatographic parameters and by using EI-SIM mode.

Table II shows the results of the analysis of methylmercury chloride. Although the peak quality was good, the detection limits were high (on the order of nanogram per injection), yet saturation did not occur even at 4,000 ng injections. This implies that the analyte was lost on its way through the GC/MS system.

Table II. Analysis of MeHgCl acetone solution, RTX-1701 column

| **Analyte** | **MeHgCl** | **MeHgCl** | **MeHgCl** | **MeHgCl** | **MeHgCl** | **MeHgCl** |
|---|---|---|---|---|---|---|
| Concentration, mg/mL | 1 | 1 | 1 | 0.2 | 0.2 | 0.2 |
| Injection amount, ng | 1,000 | 1,000 | 1,000 | 200 | 200 | 200 |
| Retention time, minutes | 5.10 | 5.09 | 5.10 | 5.07 | 5.06 | 5.06 |
| Peak area, counts | 26,529 | 24,909 | 28,697 | 6,102 | 6,589 | 6,822 |
| **Analyte** | **MeHgCl** | **MeHgCl** | **MeHgCl** | **MeHgCl** | **MeHgCl** | **MeHgCl** |
| Concentration, mg/mL | 0.2 | 4 | 4 | 4 | | |
| Injection amount, ng | 200 | 4,000 | 4,000 | 4,000 | | |
| Retention time, minutes | 5.06 | 5.17 | 5.15 | 5.16 | | |
| Peak area, counts | 6,122 | 98,731 | 80,872 | 93,976 | | |

As part of the present work, analysis of mixed mercury samples in air was attempted with the SPME technique as a sampling procedure; acetone solutions were also analyzed. An example of a chromatogram and the corresponding mass spectrograms of dimethylmercury, methylmercury chloride, and mercuric chloride are presented in Figure 4. The compounds were successfully separated, and their specific mass spectra were obtained.

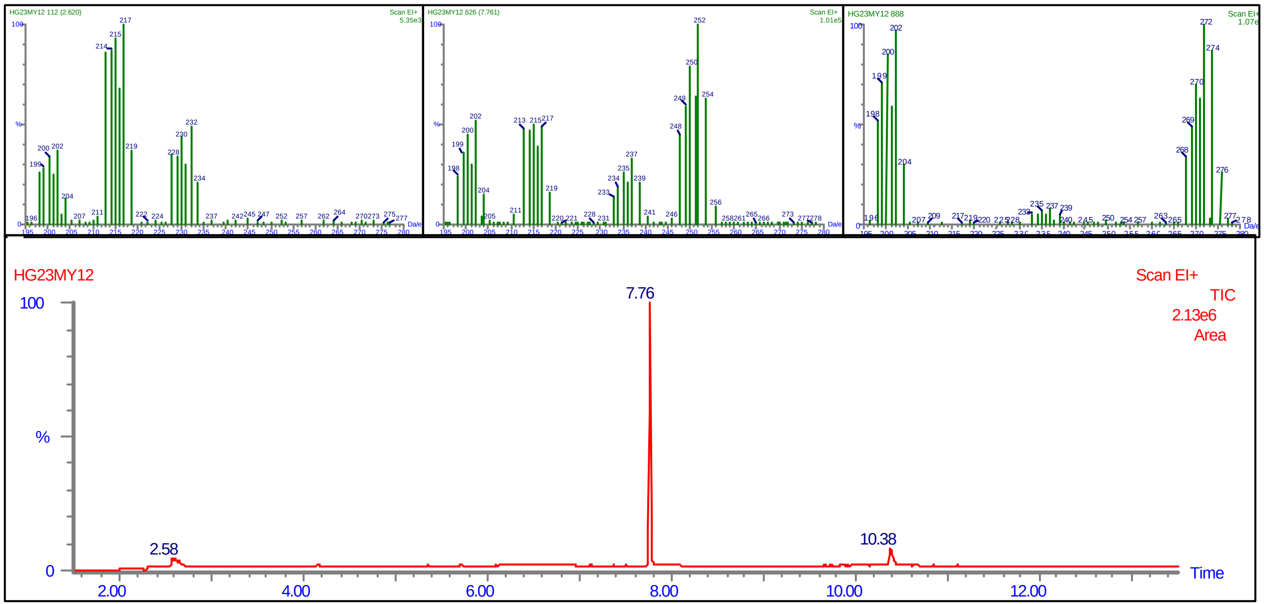

Fig. 4. Chromatogram and correspondent mass-spectrograms of dimethylmercury, methylmercury chloride, and mercuric chloride mixture

## CONCLUSIONS

This experimental data supports the feasibility of using standard GC/MS with an EI ion source for mercury speciation analysis. Several mercury compounds (mercuric chloride, dimethylmercury, methylmercury chloride, and elemental mercury) were quantitatively analyzed by this instrument; however, at present the detection limits were not low enough for regulatory compliance offgas analysis.

Analyte extraction/preconcentration techniques were investigated. SPME is one of these techniques; however, the SPME technique does not allow for collecting particulate that also contains mercury species. Therefore, the SPME technique is intrinsically incomplete and can be applied to the analysis of a limited set of mercury compounds. As an alternative, standard thermal desorption can be applied. The collection of a sample is provided by passing a known amount of offgas through the sampling tube containing adsorbent/filtration material selective to mercury species. The analytes collected in a sampling tube can then be thermally desorbed into the GC/MS. The problem with this approach is the potential of chemical transformations of mercury species during the adsorption/desorption cycle. To avoid these complications, cryotrapping of mercury compounds on inert materials can be attempted. One of the most attractive options with cryotrapping is the collection of the offgas sample into the sampling bulb (up to 15 liters) followed by injection of this sample through the GC inlet in a cryotrapping/cryofocusing mode with further GC/MS analysis of the extracted mercury compounds.

Detection limits obtained during the present experiments were relatively high, and additional work is required to improve them. Yet the detection limits for analysis of elemental mercury with SPME injection were reasonable for practical applications. The detection limit calculated as a standard deviation with a 95% confidence level based on eight consecutive measurements at 3,000 µg/dscm concentration was 58 µg/dscm. The detection limit obtained for elemental mercury was in the range of the MACT standard of 130 µg/dscm (45 µg/dscm for new sources). For compliance testing, the detection limit would have to be a fraction of the regulatory limit. In our experiments on microextraction of elemental mercury from air, only the Carboxen® sorption phase was suitable for elemental mercury analysis. Yet, this SPME/GC/MS analysis was characterized by a repeatable linear response within a wide range of concentrations. Organo-mercury was also readily extracted and detected using this technique; however, inorganic mercury compounds were practically undetectable. One of the problems associated with mercuric chloride, for example, was that it under some conditions it apparently decomposed on of the SPME and GC column phases. This decomposition process was indicated by the appearance of wide peak of elemental mercury. Normally, the GC peak for mercuric chloride was sharp and contained ions of three molecular fragments—$Hg^+$, $HgCl^+$, and $HgCl_2^+$.

Application of the enlarged SPME syringes and utilization of more sensitive MS systems may allow significant improvement of the observed detection limits, as may application of other preconcentration techniques.

The present experiments suggested that GC/EI/MS will be a useful tool for mercury speciation analysis. The preconcentration step was, as expected, more problematic. The SPME techniques investigated appeared to be feasible for analysis of elemental and dimethylmercury; other variants of SPME, or other sampling techniques, may be necessary for analysis of other mercury species. Planned work includes investigation of GC inlet cryotrapping, followed by thermal desorption, as a means for analyte concentration and introduction into the GC. This approach should minimize the potential for chemical transformation during the adsorption/desorption cycle.

## ACKNOWLEDGEMENT

This work was conducted through the DOE National Energy Technology Laboratory at the Western Environmental Technology Office under DOE Contract Number DE-AC22-96EW96405.

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