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Trace-Level Automated Mercury Speciation Analysis

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Abstract

An automated system for methyl Hg analysis by purge and trap gas chromatography (GC) was evaluated, with comparison of several different instrument configurations including chromatography columns (packed column or capillary), detector (atomic fluorescence, AFS, or inductively coupled plasma mass spectrometry, ICP-MS, using quadrupole and sector field ICP-MS instruments). Method detection limits (MDL) of 0.042 pg and 0.030 pg for CH₃Hg⁺ were achieved with the automated Hg analysis system configured with AFS and ICPMS detection, respectively. Capillary GC with temperature programming was effective in improving resolution and decreasing retention times of heavier Hg species (in this case C₃H₇Hg⁺) although carryover between samples was increased. With capillary GC, the MDL for CH₃Hg⁺ was 0.25 pg for AFS detection and 0.060 pg for ICP-MS detection. The automated system was demonstrated to have high throughput (72 samples analyzed in 8 hours) requiring considerably less analyst time than the manual method for methyl mercury analysis described in EPA 1630.

Keywords

Mercury speciation; methyl mercury; purge and trap gas chromatography; atomic fluorescence spectroscopy; inductively coupled plasma mass spectrometry

Introduction

A robust and highly sensitive method for determining low levels of methyl Hg based on ethylation and purge and trap gas chromatography, first developed by Bloom,¹ has advanced the detection capabilities of CH₃Hg⁺ and enabled determination of low-level Hg species in different compartments of the environment. Due to its low detection limits, this method has successfully been applied to natural water samples, which play an important role in Hg cycling and bioaccumulation. Despite the very low detection limits of this technique, a drawback to the method is the long analysis time. For the EPA 1630 method each sample requires a 17 minute reaction time once the ethylating reagent has been added, a 17 minute purge time, a 7 minute drying time to remove moisture from the trap and 6 minute analysis time. Although the efficiency can be improved by reacting and purging several samples at once, each of these steps requires actions from the analyst, making the procedure highly labor intensive. This becomes problematic in environmental sampling because it limits the number of samples that can be analyzed in a single day, and Hg species are susceptible to transformation with storage.

In Bloom's method, which is the basis for EPA method 1630,² aqueous samples or diluted extracts of solid samples are derivatized with NaBEt₄ to convert CH₃Hg⁺ and Hg²⁺ into the volatile species (CH₃)(CH₃CH₂)Hg and (CH₃CH₂)₂Hg, respectively. The volatile species are then purged from solution onto a Tenax trap,³ thermally desorbed and transferred to a

packed gas chromatography (GC) column. After separation on the column, alkylated Hg species are pyrolyzed and detected by atomic fluorescence spectroscopy (AFS).

Several adaptations of this method have been reported, one of the most powerful being the use of inductively coupled plasma mass spectrometry (ICP-MS) to replace AFS as the detector.⁴ With ICP-MS detection, species-specific isotope dilution can be used for quantification,⁵ which allows correction for species transformation during analysis,⁶ matrix effects which affect ethylation efficiency,^{7,8} and changes in detector sensitivity over time. Isotope dilution also enables the quantification of Hg^{2+} , which is prohibited by external calibration due to decomposition of $(\text{CH}_3\text{CH}_2)_2\text{Hg}$ to Hg^0 during trap heating.³

Replacing NaBEt_4 in the original method with a propylating⁹⁻¹¹ or phenylating reagent^{9, 10, 12} has also been examined. A drawback of ethylation is that both Hg^{2+} and $\text{CH}_3\text{CH}_2\text{Hg}^+$ present in the sample are ethylated to form $(\text{CH}_3\text{CH}_2)_2\text{Hg}$, making these species indistinguishable.¹² The use of propylating or phenylating reagents allows determination of $\text{CH}_3\text{CH}_2\text{Hg}^+$ in the sample, and these reagents are robust over a larger range of pH, and form more stable derivatives than NaBEt_4 .^{9,13}

Substitution of the packed column GC with a capillary GC has been demonstrated to improve separation time and peak shape, particularly for heavier Hg species where the capillary GC offers much larger number of theoretical plates (N) thus providing higher resolution. Additionally, gradient heating can be used to decrease retention times of later eluting peaks and further improve peak shape. A major drawback to the capillary GC is a much lower column capacity than packed column GC, which limits the amount of sample that can be loaded and makes it incompatible with purge and trap preconcentration, and hinders achievement of low detection limits.

While numerous approaches for analyzing methylmercury in various sample types have been demonstrated, only a few of these methods have been fully automated, as well as having achieved detection limits sufficient for determining Hg species in natural waters (sub ng L^{-1}). Solid phase microextraction (SPME) has been shown to provide an effective preconcentration method that can be coupled with capillary GC with full automation.²¹ Most of these methods have not achieved detection limits in water sufficient to analyze environmental samples, however, Geerdink et al. reported an LOD of 0.016 ng L^{-1} using headspace SPME-GC with atomic emission detection and Bravo-Sanchez et al. achieved detection limits of 0.011 ng L^{-1} in seawater by SPME-GC-ICP-MS. Also, a novel automated method using thiourea complexation and separation by liquid chromatography followed by cold vapor AFS detection has been demonstrated to achieve absolute detection limits of 0.59 pg in 5 mL or greater.²²

Recently, an automated methylmercury analyzer with ultra-trace detection capabilities have become commercially available. In this study, the MERX-M automated system was assessed for high throughput determination of low-level Hg species by EPA method 1630. The system consists of an autosampler for 40 mL vials, an automated purge and trap unit, a packed column isothermal GC and pyrolysis unit, and an AFS detector. Samples in this study were ethylated according to the EPA method, which allows for faster elution than the heavier derivatization products produced by propylation or phenylation. An aliquot of *n*-propyl Hg was also added to samples, to examine the behavior of a heavier Hg species. The system was modified to operate in several different configurations, including AFS and ICP-MS for Hg detection and packed column and capillary GC for species separation. Method detection limit (MDL), sensitivity and precision for three Hg species were assessed with each configuration, along with consideration of analysis time and application to real samples.

Experimental Section

Reagents

All solutions were made up using ultrapure water ($>18 \text{ M}\Omega \text{ cm}^{-1}$) produced by a Purelab Pluswater purifier (US Filter, MA, USA). Acetic acid, HCl, and HNO_3 were Fisher Optima Grade (Pittsburgh, PA, USA). Stocks of CH_3HgCl and n-propyl Hg ($\text{C}_3\text{H}_7\text{Hg}$) were obtained from Brooks Rand Labs (Seattle, WA). Enriched ^{199}HgO and ^{201}HgO were purchased from Cambridge Isotope Laboratories (Andover, MA.) A single isotope $^{199}\text{Hg}^{2+}$ spike was prepared by dissolution in 0.5% acetic acid and 0.2% HCl. A solution of $\text{CH}_3^{201}\text{HgCl}$ was synthesized by conversion of ^{201}HgO to $^{201}\text{HgCl}_2$ followed by reaction with methylcobalamin, as described by Bancon- Montigny.²³

Ethylating reagent was prepared by dissolution of 1 g sodium tetraethylborate ($>98\%$, Strem Chemical, Newburyport, MA) in 100 mL 2% KOH (Fisher) under argon, divided into 2 mL vials and frozen immediately in a -80°C freezer. Once frozen, the reagent was transferred to a -18°C freezer for long-term storage (up to 6 months). Vials were thawed immediately prior to usage. Citrate buffer (pH 4.5) was prepared from 10.7 g citric acid monohydrate (Fisher), 14.7 g sodium citrate (Fisher) and 12 μL antifoaming reagent A (Sigma-Aldrich, St. Louis, MO, USA) in 100 mL water.

Derivatization of blanks, standards and samples

Calibration standards and spikes were weighed into 40 mL amber glass sample vials with Teflon-lined septa lids (Brooks Rand Labs), and diluted to near the rim with water. Aliquots of 0.3 mL of citrate buffer and 40 μL of ethylating reagent were added to each sample. The vials were then filled completely until a slight convex meniscus was formed, then capped and shaken, ensuring no air bubbles were present.

Instrumentation

MERX-M System—A MERX-M automated methylmercury system from Brooks Rand Labs (Seattle, WA), consisting of an autosampler, a purge and trap unit, a packed column GC/pyrolysis unit, and a Model III atomic fluorescence spectrophotometer (AFS), was used in this work. High purity Ar and N_2 gas (99.99%, Air Gas, Salem, NH, USA) were attached to gas ports of the purge and trap unit via 1/8" Teflon tubing with in-line gold sand traps to remove Hg impurities in the gas. The autosampler consists of 3 sample racks, each holding up to 24 40 mL amber glass vials.

Derivatized standards were sealed into 40 mL vials with no headspace; under these conditions, the ethylated derivatives decompose at a rate of 2% in 24 hrs, which is within analytical uncertainty. The samples can therefore be derivatized up to 24 hrs prior to analysis. Samples are placed on the autosampler, and are individually transferred to the purge vessel where volatile Hg species are transported to one of three Tenax traps in the purge and trap unit by a stream of N_2 . The three traps are alternately loaded, dried, and thermally desorbed by IR radiation. Hg species are then passed to the GC/pyrolysis unit and separated on an isothermally heated packed GC column. Finally, Hg species are reduced to Hg^0 by heating in the pyrolysis unit, passed to the AFS for detection, and the data recorded in the MERX software. Operating conditions for the MERX-M are given in Table 1, and a detailed schematic of the MERX-M can be found at <http://www.brooksrand.com/default.asp?contentID=615>. Concentrations and absolute masses of Hg species were measured and reported as Hg (not CH_3Hg) by both AFS and ICP-MS.

Connection of the MERX-M to ICP-MS

The MERX-M was connected to both a magnetic sector ICP-MS (Element 2, Thermo, Bremen, Germany) and a quadrupole Agilent 7500ce ICP-MS (Agilent Technologies, Santa Clara, USA). For this configuration, the Ar gas was replaced with a gas mixture of 1000 ppm Xe in Ar, for optimizing the ICP-MS torch position. A length of 1/8" Teflon tubing was attached to the outlet of the GC/pyrolytic unit, then connected to a 1/8" Y-connector; the other arm of the Y-connector was attached to the carrier gas line from the ICP-MS. The outlet branch of the Y-connector was attached to a glass ball joint, which was clipped to the injector/torch of the ICP-MS. For a short length of transfer tubing used in this configuration (~0.5 m), no difference in sensitivity was observed when heating the transfer line; as such an unheated transfer line was used. The trigger from the autosampler of the MERX-M was attached to a contact closure trigger on the ICP-MS such that data acquisition by the ICP-MS was triggered by the MERX-M as each trap was heated. Connection of the MERX-M to the ICP-MS is depicted in Figure 1. For ICP-MS detection using the magnetic sector instrument (Element 2), data was exported into Excel and peaks were integrated manually. For detection by the quadrupole ICP-MS, peaks were integrated in the ICP-MS software (Mass Hunter, Agilent).

Connection of the MERX-M to capillary GC and AFS—In a third instrument configuration, the open column GC of the MERX-M was replaced with a capillary GC (Agilent 6890N) equipped with an HP-1 megabore column (0.53 mm ID, 15 m length; Agilent), a split/splitless inlet and direct inlet liner. Prior to connecting the capillary GC, the open column inside the GC-pyrolysis unit was bypassed with a length of 1/16" ID Teflon tubing. The Ar gas was disconnected from the MERX-M and attached to the gas inlet on the capillary GC. The carrier gas line leading to the split/splitless inlet was cut and the outlet of the MERX-M purge and trap unit was attached to the inlet side of the GC carrier gas line while the outlet side was connected to the Ar gas inlet on the back of the MERX-M purge and trap unit. The outlet of the column was connected via an adapter to the AFS unit. The trigger cable from the autosampler of the MERX-M was connected to a remote start/stop cable on the capillary GC unit. A schematic of the connection of the MERX-M to the capillary GC is given in Figure 2.

Operating conditions for the MERX coupled with capillary GC and AFS are given in Table 1. The GC heating program was developed as a compromise between maximum peak height for a CH_3Hg^+ standard, and complete resolution between Hg^0 and CH_3Hg^+ . The carrier gas flowrate in this configuration was limited by the pressure in the capillary column, and as such the widest available column was used (0.53 mm ID) was used, which allowed a flowrate of 15 mL/min, still lower than the optimal flowrate through the traps and AFS detector (32 mL/min). The addition of a makeup gas of 15 mL/min, which was heated inside the GC oven and mixed with the carrier gas after the column, was investigated, to increase the flow rate through the detector, and improve flow from the capillary column to the much wider (1/8") flow path through the detector cell. The makeup gas caused a significant decrease in sensitivity (as peak height of a CH_3Hg^+ standard) and was not implemented.

Connection of the MERX-M to capillary GC and ICP-MS

The MERX-M was connected to capillary GC as described above, except the outlet end of the capillary column was attached via a carrier gas line to the ICP-MS instead of to the AFS. A trigger cable with a relay circuit was required to electrically isolate the GC and ICP-MS instruments from each other, while both receive the trigger signal from the MERX-M. In this configuration, a makeup gas of 1 L/min, controlled by the ICP-MS, was passed through the GC oven, and mixed with the carrier gas after the column. In this configuration, a higher initial temperature and ramp rate were found optimal than with the AFS detector (Table 1),

presumably due to a decrease in peak broadening by the addition of a makeup gas after the capillary column, such that peak width of Hg^0 and CH_3Hg^+ were narrower and more easily resolved.

Preparation of calibration standards

Sub-stocks of Hg species and enriched isotope spikes were prepared in 0.5% acetic acid and 0.2% HCl. Instrumental performance was evaluated for both CH_3Hg^+ and $\text{C}_3\text{H}_7\text{Hg}^+$; CH_3Hg^+ is the analyte of interest in most Hg speciation studies, and $\text{C}_3\text{H}_7\text{Hg}^+$ can be added as an internal standard to correct for matrix effects or ethylation efficiency. Resolution and detection of $\text{C}_3\text{H}_7\text{Hg}^+$ may also be used as an approximation for other large Hg species produced when alternate derivatizing agents (ie. propyl or phenyl borate) are applied to separate Hg^{2+} and $\text{CH}_3\text{CH}_2\text{Hg}^+$.

A standard containing 1 ng each of CH_3Hg^+ , Hg^{2+} and $\text{C}_3\text{H}_7\text{Hg}^+$ was prepared to optimize resolution on the GC. Inorganic Hg^{2+} , which after ethylation elutes as $(\text{CH}_3\text{CH}_2)_2\text{Hg}^+$, between $(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{Hg}^+$ and $(\text{C}_3\text{H}_7)(\text{CH}_3\text{CH}_2)\text{Hg}^+$, was not assessed in this work. Unlike for CH_3Hg^+ and $\text{C}_3\text{H}_7\text{Hg}^+$, a significant Hg^{2+} peak can be present in the blank, due to contamination in reagents and vessels, as well as an ambient atmospheric concentration in the laboratory, so resolution of the analyte species from this peak is required. The derivatized species, $(\text{CH}_3\text{CH}_2)_2\text{Hg}^+$, has been shown to degrade to Hg^0 during trap heating, so resolution from Hg^0 from CH_3Hg^+ is also required.

Calibration curves of 9 blanks followed by 7 standards (0.5 pg, 1 pg, 2 pg, 10 pg, 50 pg, 250 pg, 1000 pg) of both analyte species were prepared. All intensities (as peak height or peak area) were blank corrected and sensitivity was calculated as the linear correlation coefficient of intensity to pg Hg species. Carryover between samples was also tested by running a blank on the same trap following a high (1000 pg) standard; carryover was then defined as the intensity of the blank divided by the intensity of the standard.

Limit of detection (LOD) and limit of quantitation (LOQ) were estimated as three and ten times the standard deviation of the nine blanks, respectively. The LOD was tested by analyzing 8 standards at the estimated LOD for each Hg species, which was 0.2 pg for CH_3Hg^+ and 0.6 pg for $\text{C}_3\text{H}_7\text{Hg}^+$. Method detection limit (MDL) was then determined as 3 times the standard deviation of 8 replicates of a standard at the estimated LOQ, which was 0.5 pg for CH_3Hg^+ and 1.5 pg for $\text{C}_3\text{H}_7\text{Hg}^+$.

Preparation of Standard Reference Materials

Three biological standard reference materials (TORT-2, DOLT-4, and DORM-2, all obtained from NRC Institute for National Measurement Standards, Ottawa, Canada) were extracted according to the procedure in Reyes, 2009.²⁴ Briefly, 0.05 g portions of each reference material were weighed into 60 mL polypropylene tubes, and 10 mL of 5 mol L⁻¹ HCl with 0.25 mol L⁻¹ NaCl added to each tube. Samples were heated to 60°C for 10 minutes in a Mars Xpress microwave digestion system (CEM Corps, Matthews, NC, USA). Aliquots of 0.03 to 0.05 g were weighed into 40 mL glass vial, along with 0.1 g of a 1 ng propyl-Hg standard. Vials were then filled with ultrapure water pH buffered and derivatized (as described above). Propyl Hg was used as an internal standard in these samples.

Results and discussion

Performance of the MERX-M system

MERX-M with packed column GC and AFS detection—With the MERX-M in its initial configuration, using a packed column GC and detection by AFS, complete resolution

of 1 ng each of the two analytes CH_3Hg^+ and $\text{C}_3\text{H}_7\text{Hg}^+$, and the ubiquitous species Hg^0 and Hg^{2+} , was achieved in 10 min (Fig. 2a). In this configuration, the peak height for 1 ng CH_3Hg is more than 2X greater than for 1 ng $\text{C}_3\text{H}_7\text{Hg}^+$, whereas peak area is approximately the same (Table 2). This is due to band broadening for the later eluted species, and caused a significantly higher MDL for $\text{C}_3\text{H}_7\text{Hg}^+$ than CH_3Hg^+ . The MDL of 0.042 pg (0.001 ng/L) for CH_3Hg^+ was significantly lower than the MDL defined by EPA 1630² (0.02 ng/L). The carryover on each trap was slightly higher for $\text{C}_3\text{H}_7\text{Hg}^+$ than CH_3Hg^+ , and to analyze standards or samples with a concentration range of greater than a factor of 500, a washout sample should be run on each trap between samples.

MERX-M with packed column GC and ICP-MS detection—Operating conditions of the MERX-M with the packed column and ICP-MS detection were the same as for the AFS detection, and similar resolution of the four Hg species was achieved, with band broadening for the later eluted species (Fig 2b). In this configuration, the pyrolysis unit was left online, so no difference in sensitivity of the different species can be attributed to transport or ionization in the ICP. With ICP-MS detection, peak heights for 1 ng CH_3Hg^+ and $\text{C}_3\text{H}_7\text{Hg}^+$ were slightly higher than with AFS detection, whereas peak area was lower than by AFS detection. The higher peak height can be explained by slight differences in gas flow rates between runs, which are also reflected in the slightly earlier retention times by ICP-MS.

The magnetic sector ICP-MS (Element 2) was replaced with a quadrupole ICP-MS (Agilent 7500ce) having lower sensitivity, and peak height and peak area for 1 ng CH_3Hg^+ were reduced by about an order of magnitude. With detection by the Element 2, MDL was slightly lower than by AFS, whereas with the quadrupole instrument, MDL was 5 times higher. With the Element 2, an MDL of 0.06 pg (0.0015 ng/L) for CH_3Hg^+ was also achieved by isotope dilution, similar to value for external calibration, and in good agreement with the MDL of 0.003 ng/L achieved using the same ICP-MS instrument but with the manual EPA 1630 method.⁸ Carryover, which occurs on the traps of the MERX-M system, was the similar to the prior configuration.

MERX-M with capillary GC and AFS detection—A chromatogram of the four Hg species (Hg^0 , CH_3Hg^+ , Hg^{2+} , $\text{C}_3\text{H}_7\text{Hg}^+$) shows resolution was accomplished in 6 minutes (Fig. 2c). With the capillary GC, retention time and band broadening of the larger Hg species was diminished by gradient heating of the column. In this configuration, peak height and peak area for 1 ng CH_3Hg^+ are twice as high as with the packed column GC, however the MDL was significantly higher than with the packed column GC for both species (5X for CH_3Hg^+ and 3X for $\text{C}_3\text{H}_7\text{Hg}^+$). Carryover was also significantly (10x) higher by the capillary GC configuration, due to the lower carrier gas flowrate causing a slower rinsing of the traps. This limits the range of concentrations of samples and standards that can be analyzed in this configuration. The higher MDL associated with the capillary GC configuration is caused partly by carryover on the traps, as well as greater instability of the baseline, which may be due to the lower gas flow rate and memory effects in the analyte path.

MERX-M with capillary GC and ICP-MS detection—With the MERX configured with a capillary GC and ICP-MS detection, resolution of the four Hg species was accomplished in 4 minutes (Fig. 2d). In this configuration, band broadening of the larger Hg species was effectively eliminated, and peak height was equal for CH_3Hg^+ and $\text{C}_3\text{H}_7\text{Hg}^+$. Peak height for 1 ng Hg species was also greater than with packed column GC and ICP-MS detection, but peak area was slightly diminished. The MDL for $\text{C}_3\text{H}_7\text{Hg}^+$ achieved by this configuration was lower than by any other configuration, due to the elimination of peak broadening, and was similar to the MDL for CH_3Hg^+ . Carryover in this configuration was 3 times worse than by packed column GC. The lower carrier gas flow rate necessitated by the

capillary GC caused incomplete washout of the traps, which is a limitation to this configuration.

Evaluation of MERX-M for the analysis of standard reference materials—

Certified values and concentrations of CH_3Hg^+ determined by the MERX-M with AFS and ICP-MS detection are given in Table 2. All determined concentrations were within ranges of certified values, demonstrating the system has a similar response to samples as to standards. The use of a propyl Hg internal standard was useful for correcting drift which occurred over the course of the run by ICP-MS detection.

Conclusions

Coupling the MERX-M automated methyl mercury system to both ICP-MS and AFS detection achieved MDLs applicable to ultra-trace Hg speciation, enabling analysis of natural waters and samples of limited size. The use of species-specific isotope dilution at low concentrations was also demonstrated by coupling the MERX-M with ICP-MS, which gives the ability to correct for species transformation and matrix effects. The automated system significantly reduced both the analysis time to 5 min per sample, and the analyst's time to 2 hours for a 72 sample run compared with 8 hours for a 24 sample run by the manual EPA 1630 method.

For analysis of later eluting species from the GC column, such as $\text{C}_3\text{H}_7\text{Hg}$, coupling the MERX-M to capillary GC significantly reduced band broadening and analysis times compared to the open column method, although carryover was higher in this configuration. The automated MERX-M system greatly improved sample throughput for low-level Hg speciation, enabling more efficient analysis of environmental samples.

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Fig. 1. Schematic of MERX-M connected to capillary and packed column GC, and AFS and ICP-MS detectors.

Figure 2. Chromatograms for 1ng CH_3Hg^+ , Hg^{2+} , $\text{C}_3\text{H}_7\text{Hg}^+$ by packed column GC with detection by a) AFS b) ^{202}Hg by ICP-MS; and capillary GC with detection by c) AFS and d) ^{202}Hg by ICP-MS.

Table 1**Instrument operating conditions**

MERX-M parameters		
Purge gas flowrate (N ₂) (ml/min)	45	
Drying gas flowrate (N ₂) (ml/min)	30	
GC gas flowrate (Ar) (ml/min)	32	
ICP-MS plasma parameters		
Make-up gas	1 L/min	
Auxiliary gas	0.9 L/min	
Plasma gas	16 L/min	
z-position	4.0 mm	
Rf power	1000 W	
ICP-MS acquisition parameter		
Isotopes measured	¹⁹⁹ Hg, ²⁰⁰ Hg, ²⁰¹ Hg, ²⁰² Hg	
Sample time	0.25	
Samples per peak	50	
Integration window	20	
Scan type	E-scan	
Operating conditions of capillary GC		
Inlet mode	Splitless	
Column flowrate	15 ml/min	
Temperature program	AFS detection	ICP-MS detection
Initial temperature	60°C	80°C
Initial time	60 sec	60 sec
Ramp	30°C per min	40°C per min
Final Temp	190°C	220°C

Table 2

Peak height and peak area for 1 ng Hg species determined by the MERX-M using packed column and capillary column GC, and with detection by AFS and ICP-MS; retention time and method detection limit (3 times the standard deviation of 8 samples containing 0.5 pg CH₃Hg⁺ and 1.5 pg (C₃H₇)Hg⁺ and carryover (intensity of blank analyzed immediately after 1 ng standard divided by intensity of standard) in each instrument configuration.

	Packed Column GC				Capillary GC			
	CH ₃ Hg ⁺		C ₃ H ₇ Hg ⁺		CH ₃ Hg ⁺		C ₃ H ₇ Hg ⁺	
	AFS	ICP-MS Element 2	ICP-MS Agilent	AFS	ICP-MS Element 2	AFS	ICP-MS Element 2	AFS
Peak height (1 ng Hg)	5.3×10 ⁵	3.0×10 ⁶	6.2×10 ⁵	1.2×10 ⁵	7.6×10 ⁵	1×10 ⁶	1.2×10 ⁶	3.9×10 ⁵
Peak area (1 ng Hg)	1.1×10 ⁸	2.6×10 ⁷	8.5×10 ⁶	9.8×10 ⁷	3.1×10 ⁷	2.1×10 ⁸	9.2×10 ⁶	1.2×10 ⁸
Retention time (min)	1.56	1.45	1.50	8.20	8.14	2.40	1.11	4.80
MDL (pg)	0.042	0.030	0.15	0.27	0.25	0.25	0.06	0.53
Carryover	0.17%	0.18%	N/A	0.54%	0.60%	1.70%	0.56%	4.8%
								1.6%