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Speciation of organometals using a synchronizing GC-MS and GC-ICPMS system for simultaneous detection

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Abstract

In analytical chemistry, improvement in instruments is always important for achieving better analytical performances and/or obtaining more information on the target analytes. A combination of the powerful separation and high sensitivity, gas chromatography-inductively-coupled plasma mass spectrometry (GC-ICPMS) has found broad applications in sensitive speciation of organometals such as methylmercury (MeHg), butyltin (BuSn), and seleniomethionine (SeMet). Unfortunately, GC-ICPMS is unable to provide molecular information of the analytes such as molecular fragmentations or isotopic patterns, which is very important for identifying target analytes. This study is to develop a method using an unique interface to allow simultaneous detection of organometals including MeHg, dibutyltin (DBT), tributyltin (TBT) and SeMet in both gas chromatography- mass spectrometry (GC-MS) and GC-ICPMS systems synchronously. The method was validated with measurements of MeHg, dibutyltin (DBT), tributyltin (TBT), and SeMet in the certified reference materials (CRMs) including dogfish liver (DOLT-4), marine sediments (PACS-2) and selenium enriched yeast (SELM-1). While isotope dilution calibration was used for the quantitation of MeHg in DOLT-4 and DBT and TBT in PACS-2, qualitative analysis of SeMet in SELM-1 was used for comparison on sensitivity of GC-MS and GC-ICPMS systems. Our results demonstrated that quantitation of organometals can be successfully performed with synchronizing GC--MS/GC-ICPMS by splitting the GC eluent flow to both an electron ionization mass spectrometer (EIMS) and an ICPMS. While the ICPMS system can provide higher precision and sensitivity, the GC-MS system can provide information on molecular structure which is essential for identification of target analytes.

Keywords

Synchronizing GC-MS/ICPMS system, Isotope dilution, Organometals, Sensitive speciation.

Abbreviations

Butyltin (BuSn), Certified reference material (CRM), Dibutyltin (DBT), Dogfish liver (DOLT-4), Gas chromatography-inductively coupledplasma mass spectrometry (GC-ICPMS), Gas chromatography- mass spectrometry (GC-MS) Methylmercury (MeHg), Reverse isotope dilution (RID), Selenium enriched yeast (SELM-1), Selenomethionine (SeMet), Tributyltin (TBT).

Introduction.

Gas chromatography (GC), liquid chromatography (LC) and capillary electrophoresis (CE) have shown great potential for separation of analytes. All these techniques can be hyphenated to mass spectrometry (MS) that can provide not only high sensitivity measurements of analytes but also selectivity for the structural information (1,2). Compared to LC and CE separation techniques, , GC can provide a higher resolution for volatile analytes. However, selection of the ionization source is very important in the development of hyphenated methods using GC coupled to mass spectrometers because it can significantly influence the limit of detection (LOD). Inductively coupled plasma (ICP) is a strong ionization source that can completely ionize target analytes to provide high sensitivity. As a result, ICPMS has been frequently used for the determination of metals at trace levels. The hyphenated technique between GC and ICPMS has been widely applied for speciation of organometallic compounds such as methylmercury (MeHg), butyltin (BuSn), and seleniomethionine (SeMet) analyses (3,4,5). DBT and TBT are two significant environmental contaminants from organotin-based antifouling paints, which have been widely used on commercial ships, and have been proven to be toxic (6,7). On the other hand, SeMet has been widely employed as selenium supplement in yeast. Therefore, there is great interest in quantitation and certification of SeMet level in enriched foodstuffs (8). Methods for such

analyses, and in particular for the certification of MeHg, DBT, TBT and SeMet using GC-ICP-MS have been reported by Yang *et al* (9,10,11). Beyond providing high sensitivity, the ICPMS system can also convert a complex GC chromatogram into a simple "elementogram". However, despite numerous applications of GC-ICPMS which have been published in the last decade, the major drawback of this technique is the incapability of providing molecular information of the analytes compared to electron ionization mass spectrometry (EIMS). Consequently, information on fragmentations or isotopic patterns of analytes is completely missed with ICPMS.

In this study, a special interface has been designed to allow simultaneous detection of analytes in a synchronizing GC-MS and GC-ICPMS. The new unique interface can split the GC eluent flow to EIMS and ICPMS detectors synchronously. The instrument software is able to record chromatogram and data for both GC-MS/GC-ICPMS detections. The certified reference materials (CRMs), DOLT-4, PACS-2 and SELM-1, containing MeHg, dibutyltin (DBT) and tributyltin (TBT), and SeMet have been used to demonstrate the success of simultaneous detection in both EIMS and ICPMS. Isotope dilution was used for the determination of MeHg in DOLT-4, DBT and TBT in PACS-2. The information on both sensitive and quantitative detection and molecular identification has been achieved through comparable results from both GC-MS/GC-ICPMS systems.

Materials and methods.

Instrumentation

The centrifuge was from Damon/IEC Division (Needham HTS, MA, USA) and the microwave from CEM (Matthews, NC, USA). A GC-MS (5975C, equipped with triple-axis detector) and

ICPMS (7500 series, equipped with a collision cell), were from Agilent (Canada). A manual solid-phase microextraction (SPME) device, equipped with a fused-silica fiber coated with a 100-μm film of polydimethylsiloxane (PDMS) (Supelco, Bellefonte, PA) was used for sampling of the derivatized MeHg in headspace. A DB-5MS GC column (30 m length x 0.25 mm i.d. × 0.25 μm film thickness, Iso-Mass Scientific Inc., Calgary, Alberta, Canada) was used for the separation of MeHg, DBT, TBT and SeMet. The interface for splitting the GC eluent to ICPMS and EIMS detectors was customer designed and made by Agilent (**Figure 1**). Agilent commercial transfer line (Agilent, Canada) was used to connect the GC to ICPMS (**Figure 1**). The EIMS detector was used for detection of derivatized MeHg (MeHgPr), DBT (Bu_2Et_2Sn), TBT (Bu_3EtSn) and SeMet ($C_8H_{15}O_4NSe$). The EIMS detection was performed in both the SIM mode (m/z ions 256 and 260, 232 and 235, and 266, 267, 269, and 271 for MeHg, DBT and TBT, and SeMet derivatives, respectively) and the SCAN mode (m/z range 100-300). For the ICPMS detection, ^{198}Hg and ^{202}Hg, ^{117}Sn, and ^{118}Sn, and ^{77}Se, ^{78}Se, ^{80}Se and ^{82}Se were monitored. ICP-MS optimization was carried out using Xenon in Ar sample gas for the tuning. All operational conditions for both GC-MS and ICP-MS are outlined in **Table 1**.

Materials.

Deionized (DI) water was made in-house with a MiliQ Nanopure mixed bed ion exchange system (Thermo Scientific, Canada). Sodium acetate (≥99%) and acetic acid (≥99.7%) were from Fisher Scientific (Canada). 1M acetate buffer was prepared by dissolving the appropriate amount of sodium acetate in DI water and adjusting the pH to 5 with acetic acid. Ammonium hydroxide (20%) was from Anachemia Science (Montreal, Quebec, Canada). Methanesulfonic acid (≥99.5%) and methyl chloroformate (99%) were purchased from Sigma (Canada). Sodium tetrapropylborate ($NaBPr_4$) (99%) was from 3B Scientific Corporation (Libertyville, IL, USA).

Sodium tetraethylborate ($NaBEt_4$) (98%) was obtained from Strem Chemicals (Newburyport, MA, USA). Methanol (99.9%), chloroform (99.8%) and pyridine (≥99%) were from Fisher Scientific (NJ, USA). Hexane (99%) was from Caledon Laboratories LTD (Georgetown, Canada). DOLT-4, PACS-2 and SELM-1 were provided by National Research Council (Ottawa, ON, Canada). Methylmercury chloride (MeHgCl, 95%) and dibutyltin chloride (DBT, 96%) were from Alfa Aesar (Word Hill, MA, USA). SeMet (99%) was from Acros Organics (NJ, USA).

Preparation of solutions

Individual stock solutions of MeHg (46.3 μg/g as Hg), DBT (542.2 μg/g as Sn) and TBT (540.1 μg/g as Sn) were gravimetrically prepared in methanol, respectively. The stock solution of SeMet (14.3 μg/g as Se) was prepared in DI water. The working standard solutions of MeHg (2.0515 μg/g as Hg), DBT (2.4355 μg/g as Sn) and TBT (2.4355 μg/g as Sn) were prepared by gravimetrically diluting the corresponding stock solutions in methanol. Working standard solution of SeMet (1.4535 μg/g as Se) was prepared by gravimetrically diluting the corresponding stock solution in water. ^{198}Hg-enriched MeHg stock solution (~3.5 μg/g as Hg) in methanol was prepared using commercially available inorganic ^{198}Hg (12). ^{117}Sn-enriched DBT and TBT stock solutions (90.5 μg/g as Sn) were obtained from the Laboratory of Government Chemistry (LGC, Teddington, U.K.). Working enriched standard solutions of $Me^{198}Hg$ (~0.73 μg/g as Hg), ^{117}DBT (~0.46 μg/g as Sn) and ^{117}TBT (~0.46 μg/g as Sn) were prepared by gravimetrically diluting the corresponding stock solutions in methanol. All solutions were kept in refrigerator till use. The $NaBPr_4$ (1% w/v) and $NaBEt_4$ (2% w/v) solutions were prepared by dissolving the corresponding salts in DI water. The $NaBPr_4$ solution was then divided into

Eppendorf tubes and stored in a freezer (-80 °C) till use. Due to the lower stability, $NaBEt_4$ solution was freshly prepared.

Preparation of MeHg, DBT and TBT reverse isotope dilution (RID) samples.

Reverse isotope dilution (RID) analysis was carried out to accurately determine the concentration of enriched $Me^{198}Hg$, ^{117}DBT and ^{117}TBT standards. Four MeHg RID samples were prepared by mixing 0.23 g of MeHg (2.0514 μg/g) and 0.14 g of enriched $Me^{198}Hg$ (~0.73 μg/g) in 10 mL methanol. Other four RID samples were prepared by mixing 0.41 g of DBT (2.4355 0.46 μg/g) and 0.38 g of enriched ^{117}DBT (~0.46 μg/g) in 10 mL methanol. Similarly, four TBT RID samples were prepared by mixing 0.41 g of TBT (2.4355 μg/g) and 0.38 g of enriched ^{117}TBT (~0.46 μg/g) in 10 mL methanol.

Preparation of DOLT-4 and PACS-2 samples using ID calibration.

Each 0.5 g of DOLT-4 was weighed into a glass flask followed by adding 0.21 g of enriched $Me^{198}Hg$ spike (~0.73 μg/g), 8 mL of methanesulfonic acid and 16 mL of DI water in the flask. The samples were then digested under reflux for 16 hours. Blanks consisted of only methanesulfonic acid, water and an amount of 0.3674 g of an enriched spike (~0.069 μg/g).

Procedure for PACS-2 digestion was similar to that reported by Yang *et al* (13,14). Each 0.10 g of PACS-2 was weighed into a glass vial followed by spiking with 0.12 and 0.091 g of enriched ^{117}TBT and ^{117}DBT spike (~0.15 μg/g). 6 mL of glacial acetic acid was then added, the vial was capped and the sample was digested in CEM microwave for 10 min (100 °C, pressure 250, power max, medium stirring). Nitrogen gas was used to cool down the sample after digestion. Blanks

consisted only of glacial acetic acid and 0.09 g of the enriched spike (~0.088 μg/g). The digested samples were then centrifuged for 10 minutes at 2000 rpm and stored at +4 °C till analysis.

Preparation of SELM-1 samples for qualitative investigation.

Each 0.10 g of SELM-1 was weighed into a glass vial and 1.5 mL of methanesulfonic acid and 4.5 mL of DI water were then added. The vial was capped and the sample was digested in CEM microwave for 25 min (165 °C, pressure 250, power max, medium stirring). The microwave was equipped with nitrogen gas stream for cooling down the sample. Blanks consisted only of the methanesulfonic acid-water mixture.

Preparation of DOLT-4 and MeHg samples for SPME sampling.

Prior to GC injection, MeHg alkylation was performed with $NaBPr_4$ and $NaBEt_4$. Procedures for derivatization of MeHg standards and SPME sampling of DOLT-4 were optimized by Yang *et al.* (9). Briefly, 0.5 mL of methylmercury standards (MeHg and RID solutions) and 10 mL of 1 M acetate buffer (pH = 5) were added in a glass vial. The vial was vortexed and 1 mL of 1% $NaBPr_4$ was then added. The vial was capped with a cap fitted with a PFTE-silicon septum. The mixture was kept under stirring with a magnetic stir bar. Then, a SPME needle of PDMS fiber was punched through the silicon septum and the fiber was placed in the middle of the headspace to extract the derivatized methylmercury species for 10 minutes. After that, the fiber was retracted in the holder, inserted into the GC injection port and held 1 minute at 220 °C for complete thermal desorption of the analytes. To evaluate the mass bias drift, the MeHg mass bias standard solution was injected at the beginning of the analysis and every four runs. DOLT-4 sampling procedure was similar to that used for the standards. However, due to the lower concentration of MeHg in the extracts, 2 mL supernatant from the above digested sample was

diluted in 4 mL 1 M acetate buffer (pH 5). In order to obtain optimum conditions for the derivatization, the pH was adjusted to 5-6 with 1 mL ammonium hydroxide.

Preparation of PACS-2, DBT and TBT samples for liquid sampling.

Similarly, prior to GC injection, derivatization of DBT and TBT in standards and sampling of PACS-2 was performed as previously reported (10). Briefly, 0.5 mL of DBT and TBT standards (DBT, TBT and corresponding RID solutions) were added in a glass vial first and then 10 mL acetate buffer (pH 5), 1 mL $NaBEt_4$ 1% and 2 mL hexane were added. The vial was shaken manually for 5 minutes. Derivatization of digested PACS-2 samples was similar to the procedure of derivatization of DBT and TBT. Instead using 0.5 mL standard solution and 10 mL acetate buffer, 2 mL supernatant from the above digested sample and 2 mL ammonium hydroxide for adjusting the pH were used. After the derivatization, the vials were centrifuged at 2000 rpm for 10 minutes to help the separation of the organic and aqueous phases. 1 mL of the organic phase was transferred to GC vials for GCMS and GC-ICPMS analysis.

Preparation of SELM-1 and SeMet samples for liquid sampling.

Derivatization of SeMet in standards and sampling of SELM-1 were performed as previously described (15,16). Briefly, 1 mL SeMet standard solution and 0.75 mL pyridine/MeOH mixture solution (1:3) were added in a 10-mL glass vial. Then 0.25 mL of methyl chloroformate was slowly added in the mixture. The vial was shaken manually for 1 min and 1 mL chloroform was then added in the mixture. The vial was then shaken again for 1 min to extract the derivatized SeMet. The vial was centrifuged at 2000 rpm for 10 min to help the separation of the organic and aqueous phases, and the chloroform layer was transferred to a 1-mL GC vial for GCMS and GC-ICPMS analysis.

Safety consideration.

MeHg, DBT, TBT and methyl chloroformate are toxic compounds. Moreover, methyl chloroformate, $NaBEt_4$ and $NaBPr_4$ are inflammable. Material Safety Data Sheet must be consulted and safety precaution taken for all manipulations.

Results and discussion.

The Interface of the GC-MS/ICPMS system

Inductively coupled plasma (ICP) is a strong ionization source that can completely ionize target analytes to provide high sensitivity and ICPMS has been frequently used for the determination of metals at trace levels. However, the major drawback of ICPMS is to the lacking of providing molecular information of the analytes compared to electron ionization mass spectrometry (EIMS). Consequently, information on fragmentations or isotopic patterns of analytes is completely missed. In order to achieve both sensitivity and structure information, a specific interface is needed to bridge the EIMS detector and ICPMS detector together after GC elution. In this study, a split interface was custom designed and made by Agilent according to the needs of our study to meet this goal (**Figure 1**). The interface is a "Y" shape of split and is placed inside the oven of GC. The input **A** of the "Y" split is connected to the end of the GC column. The outlet **B** is connected to EIMS transfer line directly and the outlet **C** is connected the transfer line to ICPMS. The transfer line to ICPMS is surrounded with a heater which provided a temperature at 280 °C to keep the GC eluent being completely transferred to the ICP torch injector of the ICPMS. The "Y" split is specifically designed to synchronously and seamlessly split 25% of the GC flow to ICPMS and 75% of the GC flow to EIMS (The technique has been patented by

Agilent) according to the sensitivity of two ionization sources. The ICP source can provide much higher ionization efficiency and therefore much higher sensitivity than the EI source does. 25% to ICPMS and 75% to EIMS enable good signals in the synchronizing analysis. Figure 2 is a typical example for synchronous monitoring MeHg with the new GC-MS/GC-ICPMS system. Compared to the chromatogram of EIMS result (**Figure 2a**), the ICPMS provided a simple, clean and sensitive signal (**Figure 2b**), while the EIMS provided a clear mass spectrum of MeHg in scan mode (**Figure 2a insert**). In the study, MeHg, DBT and TBT in DOLT-4 and PACS-2 were quantitatively measured with the synchronizing GC-EIMS/GC-ICPMS system, while SeMet in SELM-1 was just qualitatively determined with the EIMS detector.

Quantitation of enriched standards with RID samples.

Prior to validating the synchronizing system, it is crucial to evaluate isobaric interferences in ICPMS to avoid biased results. The DOLT-4 and PACS-2 samples without spiking any enriched target analytes were injected to measure the intensities of ^{202}Hg and ^{198}Hg, and ^{118}Sn and ^{117}Sn isotopes. Values of 2.934±0.015 and 3.1673±0.050 (mean, 1 SD, n=3) for $^{202}Hg/^{198}Hg$ and $^{118}Sn/^{117}Sn$ were obtained, close to the theoretical values of 2.9950 and 3.1536, respectively, indicating no isobaric interference to the measurement.

Reverse isotope dilution (RID) technique has been commonly used to determine the exact concentrations of the $Me^{198}Hg$, ^{117}DBT and ^{117}TBT (17) and it was recommended to analyze both RID and isotope dilution (ID) samples within the same day to achieve the most accurate results. It is not usually easy to analyze both RID and ID samples in the same day for most laboratories. Therefore, it is better to evaluate the variation of measurements between different days. In this study, the RID standards were measured the first day and DOLT-4 and PACS-2 ID

samples and blank samples were analyzed in the second day. Concentrations of the enriched $Me^{198}Hg$ and ^{117}DBT standards were found 0.2112±0.0178 μg/g and 0.1842±0.0034 μg/g, respectively. A mass bias solution was injected between each RID standard to evaluate the mass bias drift. Mass bias drift factor (*f*) was calculated with the following equation:

$$f = \frac{r_t}{r_0}$$

where r_t and r_0 are the isotope ratios measured at number t time and at the beginning of the sequence, respectively. The results showed that mass bias drift factor for MeHg and DBT were 0.9995±0.0148 and 0.9990±0.0050, respectively, indicating that mass bias drift is negligible and will not affect the measurement results.

Quantitation of MeHg in DOLT-4, and DBT and TBT in PACS-2.

ID-MS technique is capable of generating high accuracy and precision results, provided the isotopic equilibrium is achieved between the added spike and the endogenous analyte in the sample, and two interference free isotopes are available.In a double-phase system, isotope equilibration is usually achieved after sample digestion. In order to avoid contamination, the sample pretreatment and the standard preparation were all conducted in a class 10 clean room. Blank control samples were used for monitoring any possible contamination from the reagents (18).

The following equation was then used to calculate MeHg, DBT and TBT concentrations in DOLT-4 and PACS-2, respectively:

$$C_x = C_z \frac{m_y}{m_x} \cdot \frac{m_z}{m'_y} \cdot \frac{A_y - B_y \cdot R_n}{B_{xz} \cdot R_n - A_{xz}} \cdot \frac{B_{xz} \cdot R'_n - A_{xz}}{A_y - B_y \cdot R'_n} - C_b \cdot f_b$$

where C_x is the concentration of the analyte in DOLT-4 or PACS-2 given for dried mass, C_z is the concentration of the natural abundance standard in the spike, C_b is the concentration of the blank normalized for the sample weight, m'_y is the weight of the enriched spike used to prepare the blend solution of both enriched and natural abundance standards, m_y is the weight of enriched spike used to prepare the blend solution of enriched standard and sample, m_x is the mass of sample used, w is the dry weight correction factor, A_y is the abundance of the reference isotope (^{202}Hg or ^{118}Sn) in the enriched standard, B_y is the abundance of the spike isotope (^{198}Hg or ^{117}Sn) in the enriched standard, A_{xz} is the abundance of the reference isotopes in the sample or in the natural abundance standard, B_{xz} is the abundance of the spike isotopes in the sample or in the natural abundance standard, R_n is the measured and mass bias corrected reference/spike isotopic ratio in the blend solution of the spike and the sample, R'_n is the measured and mass bias corrected reference/spike isotopic ratio in the blend solution of the spike and the natural abundance standard, and the factor f_b is given by the following equation:

$$f_b = 1 - \frac{m_y}{m'_y} \cdot \frac{A_y - B_y \cdot R_n}{B_{xz} \cdot R_n - A_{xz}} \cdot \frac{B_{xz} \cdot R'_n - A_{xz}}{A_y - B_y \cdot R'_n}$$

All concentrations are given in µg/g and calculated as mercury or tin.

Figure 3 is another typical example for the simultaneous detection of derivatized BuSn compounds with the synchronous GC-MS/GC-ICPMS system. **Table 2** summarized the concentrations of MeHg in DOLT-4, and of DBT and TBT in PACS-2, which indicated a good

agreement between the measured values and the certified values. Moreover, the results from EIMS detector and ICPMS detector are close, demonstrating that both detectors can provide good quantitative detection. However, the deviation of the EIMS results was slightly higher than that of the ICPMS results. This can be explained by the higher sensitivity of ICPMS detector which allows better and more precise integration of the peaks compared to the EIMS detector. This observation confirms that ICPMS detector achieves more accurate and precise results than EIMS although both can be employed for quantification purposes.

Sensitivity of EIMS and ICPMS detectors

It is well-known that ICPMS has much higher sensitivity than EIMS in analysis of elements. As a hard ionization technique, ICP can provide more complete ionization than other ionization sources commonly used in organic mass spectrometry such as the electron ionization source in GC-MS devices. As such, ICPMS is element-specific and can transfer GC chromatogram to a simple and clean "elementogram". However, not all elements respond in the same way to ICPMS due to their various ionization energies. In general, an element with high ionization energy will have low sensitivity in ICPMS. On the other hand, an element with low ionization energy will have high sensitivity in ICPMS detection. For instance, the element Se has high ionization energy as 9.75 eV and therefore has much lower sensitivity than those elements with low ionization energies such as Hg or Sn (19). In this study, the sensitivity of two MS detectors, EIMS and ICPMS, was evaluated by comparing the peaks of MeHg, DBT and SeMet in the same samples of reference materials, DOLT-4, PACS-2 and SELM-1. Sensitivity was compared in two ways, i.e. absolute value and signal to noise ratio (S/N), and is listed in Table 3. For ICPMS detector, as the signal was recorded as total counts, the ICPMS signal was corrected to counts/seconds (cps) by considering the dwell time of 0.05 seconds for comparison purposes. As

shown in **Figures 2, 3** and **4**, a significant gain in sensitivity was observed for the ICPMS detector. **Table 3** also shows that the ICPMS detector significantly improved the sensitivity for all the target species (MeHg, DBT, and SeMet) in terms of both absolute signal intensity and S/N. In particular, SeMet showed the highest gain in sensitivity (3 orders of magnitude S/N ratio). Although ICPMS has the advantage of high sensitivity, the EIMS can provide useful identification information that the ICPMS detector cannot provide. **Figure 5** is a typical example of the isotopic pattern of the SeMet species obtained by EIMS. The target species can be identified through the mass spectra of EIMS, while the ICP-MS side can simultaneously provide the high sensitivity for quantification purposes.

Conclusions.

GC-ICPMS has been used for a long time as a valuable tool for the detection of organometallic species. The main drawback of this technique is that it is not able to provide the information of analytes on isotopic patterns or fragmentations for structure identification purposes. In this paper, a unique interface has been designed to split the GC eluent flow to both EIMS and ICPMS detectors synchronously for simultaneous speciation of four organometals, MeHg, DBT, TBT and SeMet. The measured results of three reference materials containing the four organometals, DOLT-4 CRM, and PACS-2 CRM, and SELM-1 are in agreement with the certified values, demonstrating the success of the developed method in quantitation. This unique setup allows the identification of target analyte structure through EIMS chromatogram and more sensitive, accurate and precise measurements on ICPMS side simultaneously. To the best of our

knowledge this is the first report of speciation of organometals in biological and sediment samples using a synchronized GC-MS and GC-ICPMS system.

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Table 1. GC-ICPMS operating conditions for MeHg, DBT, TBT and SeMet determination in DOLT-4, PACS-2 and SELM-1, respectively.

GC			
	MeHg	**DBT/TBT**	**SeMet**
Column	DB-5MS (30 m x 0.25 mm i.d. x 0.25 μm□m_f)	DB-5MS (30 m x 0.25 mm i.d. x 0.25 μm□m_f)	DB-5MS (30 m x 0.25 mm i.d. x 0.25 μm□m_f)
Injection mode	Splitless	Splitless, 1 μL□	Splitless, 1 μL□
Injection temperature	220 °C	220 °C	280 °C
Oven program	50 °C (2 min) to 250 °C (20 °C/min), 1 min post run	50 °C (2 min) to 250 °C (25 °C/min), 1 min post run	120 °C (2 min) to 260 °C (20 °C/min), 1 min post run
Carrier gas, flow rate	He, 1.5 mL/min	He, 1.5 mL/min	He, 1.5 mL/min
Detector temperature	250 °C	250 °C	250 °C
ICP-MS			
RF power	900 W		
RF matching	1.8 V		
Sample depth	5.0 mm		
Torch-H	1.7 mm		
Torch-V	-0.4 mm		
Carrier gas (He)	1.02 L/min		

Table 2. Results for MeHg, DBT and TBT in DOLT-4 and PACS-2, respectively. Each number is an averaged value (n=3).

MeHg quantification in DOLT-4	
EIMS	**ICPMS**
1.288±0.058 μg/g[a]	1.335±0.033 μg/g[a]
DBT quantification in PACS-2	
EIMS	**ICPMS**
1.124±0.065 μg/g[b]	1.171±0.005 μg/g[b]
TBT quantification in PACS-2	
EIMS	**ICPMS**
0.830±0.015 μg/g[b]	0.834±0.003 μg/g[b]

a) certified MeHg value: 1.33±0.12 μg/g; b) certified TBT and DBT values: 0.832±0.095 μg/g and 1.100±0.135 μg/g, respectively.

Table 3. Gain comparison in absolute intensity and S/N ratio between ICPMS and EIMS detections.

DOLT-4 (MeHg)	
Absolute intensity gain	**S/N gain**
9.39*E01	1.86*E01
PACS-2 (DBT)	
Absolute intensity gain	**S/N gain**
1.17*E02	1.32*E02
SELM-1 (SeMet)	
Absolute intensity gain	**S/N gain**
2.99*E01	2.85*E03

Figures and Captions

Figure 1. Schematic of GC-EIMS/GC-ICPMS synchronous system. Inlet A is connected to GC column. Outlets B and C are connected to EIMS transfer line and ICPMS transfer line, respectively.

Figure 2. Typical example of simultaneous detection of MeHg in DOLT-4 with the GC-EIMS/GC-ICPMS synchronous system. (a) EIMS chromatogram in SIM mode with m/z 256 and m/z 260, (b) ICPMS chromatogram with isotopes of ^{198}Hg and ^{202}Hg.

Figure 3. Simultaneous determination of MBT, DBT and TBT in PACS-2 with the GC-EIMS/GC-ICPMS synchronous system. (a) EIMS chromatogram in SIM mode with m/z 232 and m/z 235), (b) ICPMS chromatogram with isotopes of ^{117}Sn and ^{118}Sn.

Figure 4. Simultaneous determination of SeMet in SELM-1 with the GC-EIMS/GC-ICPMS synchronous system. (a) EIMS chromatogram in scan mode with a range of m/z 100 to m/z 300, (b) ICPMS with isotopes of ^{77}Se, ^{78}Se, ^{80}Se and ^{82}Se.

Figure 5. The typical GC-EIMS spectrum of SeMet in SELM-1 in scan mode (m/z range: 100-300).

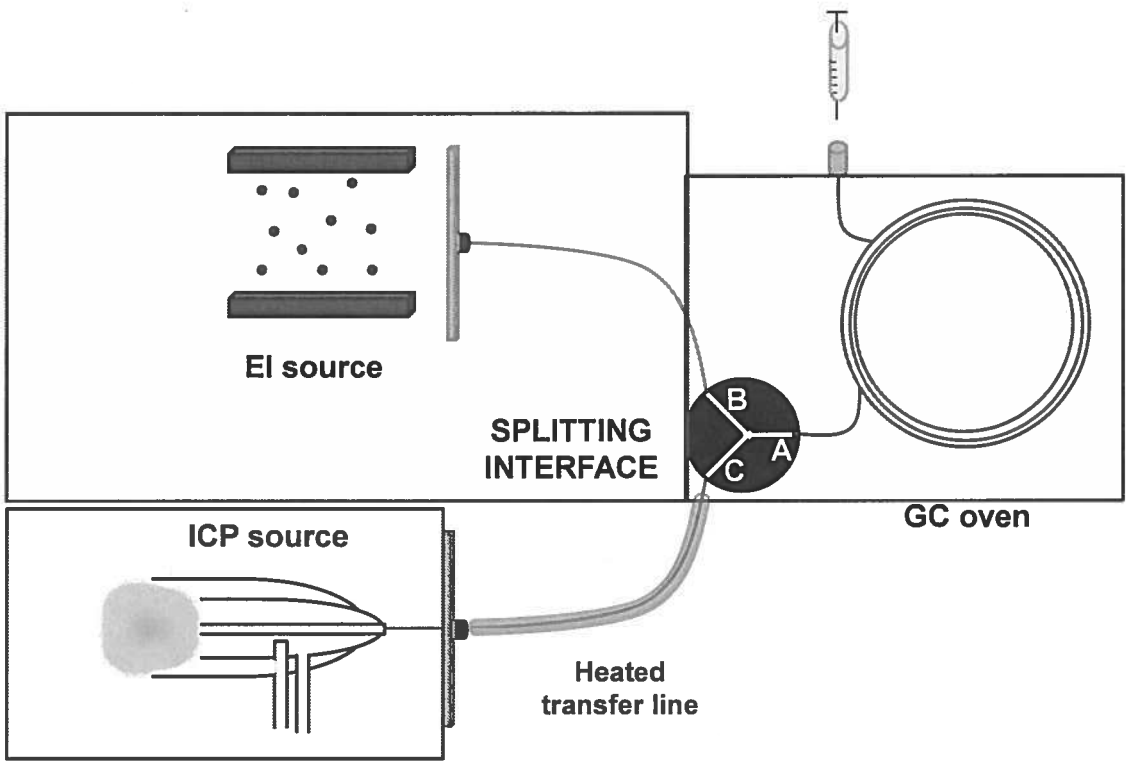
EI source
SPLITTING
INTERFACE
B
A
C
GC oven
ICP source
Heated
transfer line

Figure 1.

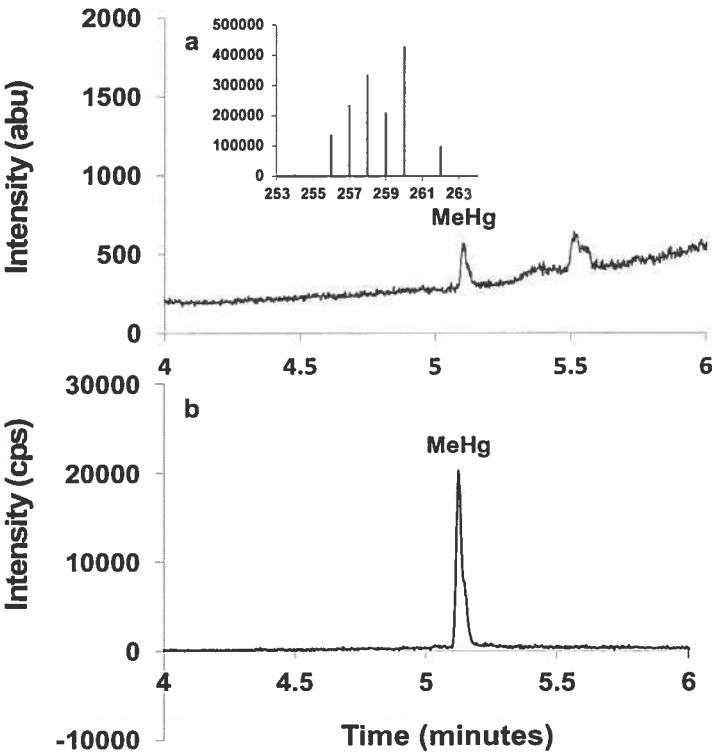
a
MeHg
Intensity (abu)
2000
1500
1000
500
0
4
4.5
5
5.5
6
500000
400000
300000
200000
100000
0
253 255 257 259 261 263
b
MeHg
Intensity (cps)
30000
20000
10000
0
-10000
Time (minutes)

Figure 2.

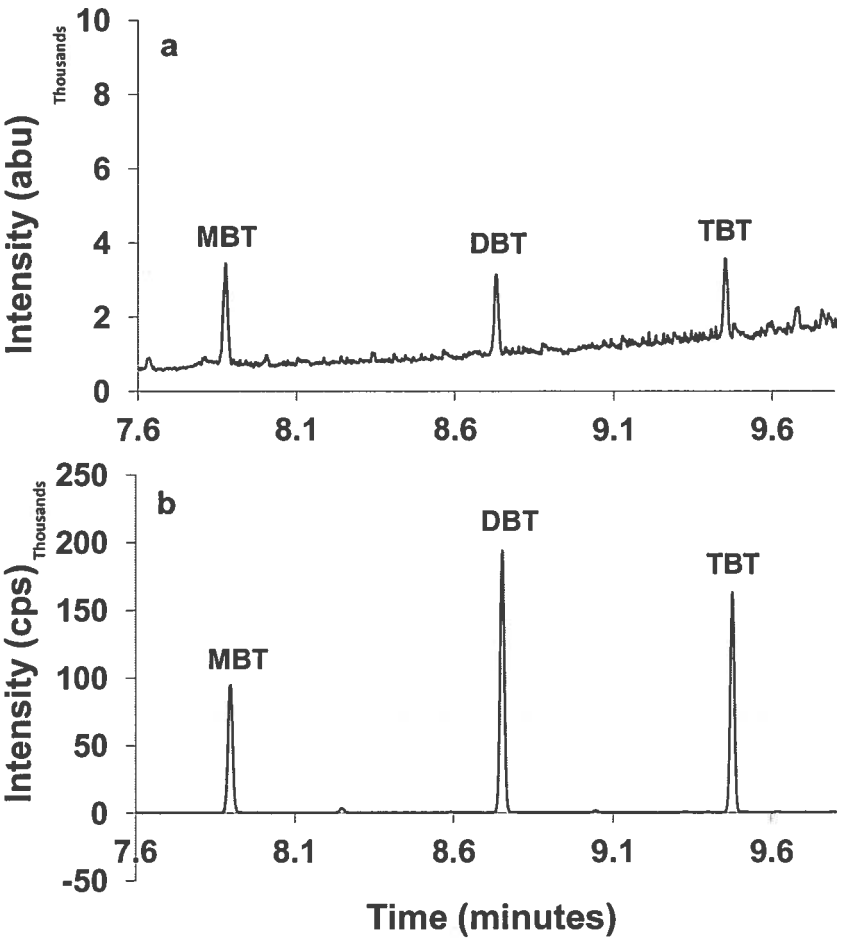
a
Thousands
Intensity (abu)
10
8
6
4
2
0
MBT
DBT
TBT
7.6
8.1
8.6
9.1
9.6
b
Thousands
Intensity (cps)
250
200
150
100
50
0
-50
MBT
DBT
TBT
7.6
8.1
8.6
9.1
9.6
Time (minutes)

Figure 3.

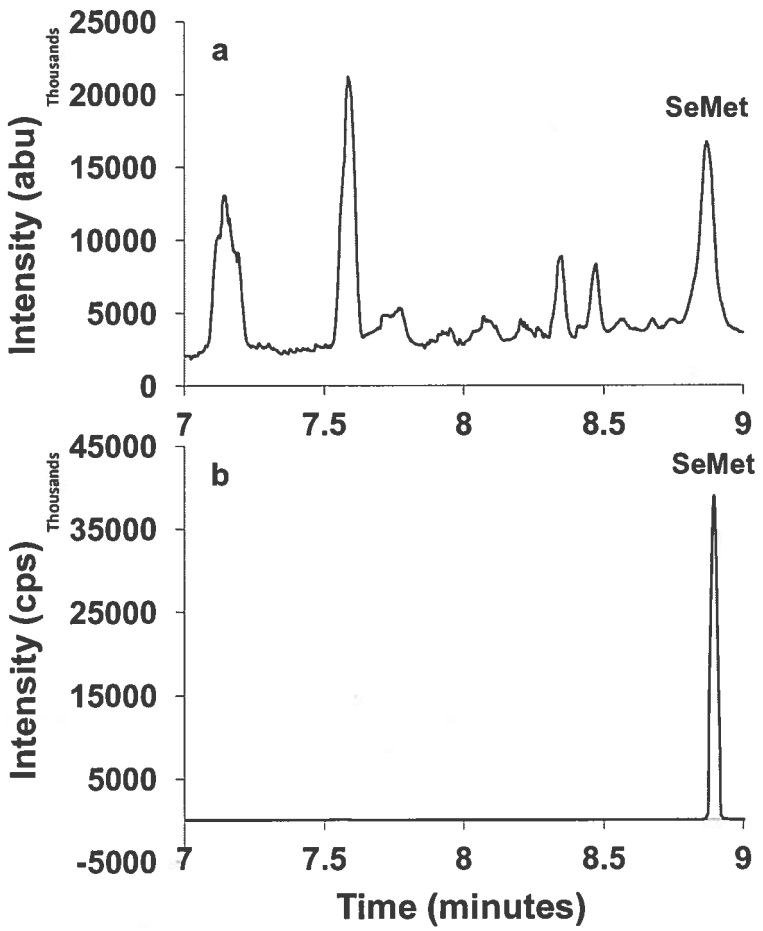
a
SeMet
Intensity (abu)
Thousands
25000
20000
15000
10000
5000
0
7
7.5
8
8.5
9
b
SeMet
Intensity (cps)
Thousands
45000
35000
25000
15000
5000
-5000
7
7.5
8
8.5
9
Time (minutes)

Figure 4.

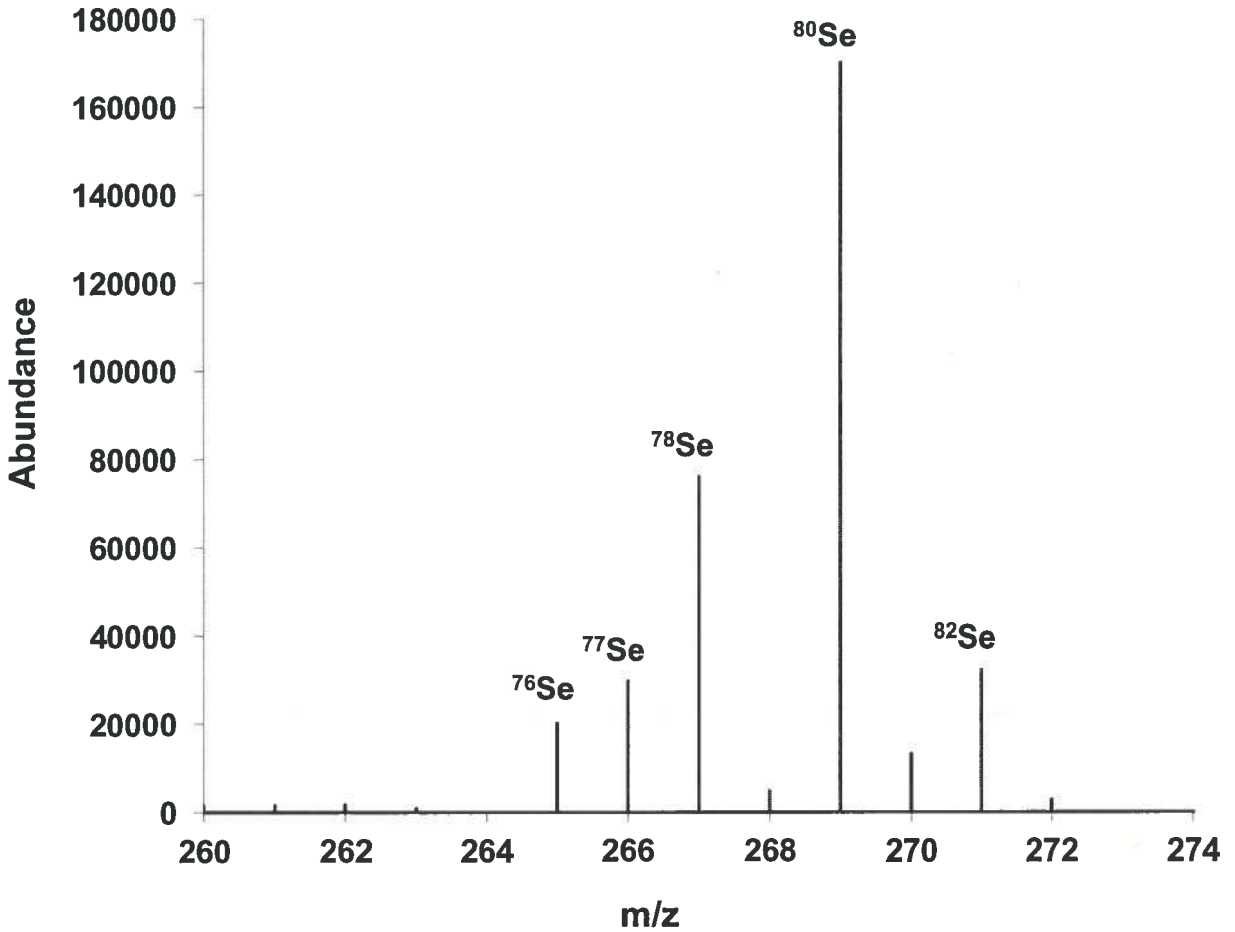
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
Abundance
260
262
264
266
268
270
272
274
m/z
80Se
78Se
77Se
76Se
82Se

Figure 5.