JAAS

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

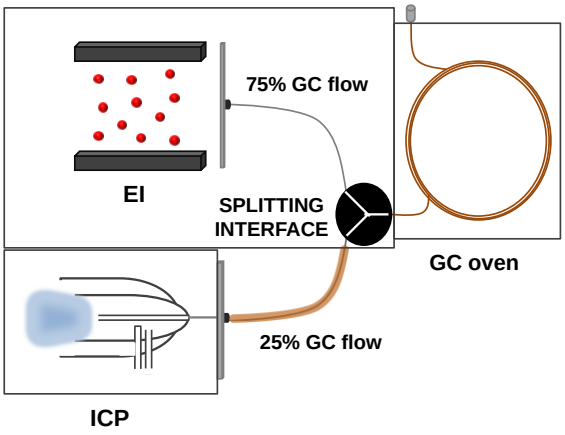
You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

Table of contents entry



Accurate quantitation and characterization of organometals is successfully achieved by splitting the GC flow to both an electron ionization mass spectrometer (EIMS) and an inductively coupled plasma mass spectrometer (ICPMS).

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

Lucia D'Ulivo[a,b], Lu Yang[b], Yong-Lai Feng[a*] John Murimboh[c] and Zoltán Mester[b*]

[a] Exposure and Biomonitoring Division, Environmental Health Science and Research Bureau, Environmental and Radiation Health Sciences Directorate, Health Canada, AL: 0800C, Ottawa, Ontario, K1A 0K9, Canada

[b] Chemical Metrology, National Research Council Canada, 1200 Montreal Rd., Ottawa, Ontario, K1A 0R6, Canada

[c] Chemistry Department, Acadia University, 6 University Avenue, Wolfville, Nova Scotia, B4P 2R6, Canada

**Corresponding authors: Zoltán Mester, Zoltan.Mester@nrc-cnrc.gc.ca; Yong-Lai Feng, yong-lai.feng@hc-sc.gc.ca*

Abstract

In analytical chemistry, improvement in instrument performances is always important for achieving better analytical results 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 are very important for identifying target analytes. A method is reported for the simultaneous determination of organometals including MeHg, dibutyltin (DBT), tributyltin (TBT) and SeMet using a unique interface with gas chromatography-electron ionization mass spectrometry (GC-EIMS) and GC-ICPMS systems synchronously. The method was validated with measurements of MeHg, DBT, TBT and SeMet in the certified reference materials (CRMs) including dogfish liver (DOLT-4), marine sediments (PACS-2) and selenium enriched yeast (SELM-1). Compared to EIMS, ICPMS achieved a remarkable gain in sensitivity for MeHg, DBT and SeMet (19-, 130- and 2850-fold S/N gain, respectively). The concentrations of MeHg (1.335±0.033 μg/g), DBT (1.171±0.005 μg/g) and TBT (0.834±0.003 μg/g) obtained with isotope dilution are in agreement with certified values of the corresponding CRMs. With the proposed method, ICPMS system can provide higher precision and sensitivity and the EIMS system can provide information on molecular structure which is essential for identification of target analytes.

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 for the quantitation of analytes but also structural information.[1,2] Compared to LC and CE separation techniques, GC provides a higher resolution for volatile analytes. Selection of 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 and provides high sensitivity. As a result, ICPMS has been frequently used for the determination of metals at trace levels. The hyphenated technique GC-ICPMS has been widely applied for speciation of organometallic compounds such as methylmercury (MeHg), butyltin (BuSn), and seleniomethionine (SeMet).[3-5] MeHg is a common contaminant that can provoke neurotoxic, nephrotoxic and hepatotoxic effects in both animals and humans.[6] Dibutyltin (DBT) and tributyltin (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.[7,8] SeMet has been widely employed as selenium supplement in yeast. Therefore, there is great interest in the quantitation and certification of SeMet in enriched foodstuffs.[9] Methods for such analyses, and in particular for the certification of MeHg, DBT, TBT and SeMet using GC-ICPMS have been reported by Yang *et al*.[10-12] Beyond providing high sensitivity, ICPMS can also convert a complex GC chromatogram into a simple "elementogram". However, despite numerous applications of GC-ICPMS in the last decade, the major drawback of this technique is the lacking molecular information of 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 was employed for the simultaneous determination of analytes in a synchronizing GC-EIMS and GC-ICPMS mode. This new and unique interface can split the GC eluent flow to EIMS and ICPMS detectors synchronously. Certified reference materials (CRMs), DOLT-4, PACS-2 and SELM-1, certified for MeHg, DBT and TBT, and SeMet, respectively, have been used to demonstrate the success of simultaneous determination of analytes in both EIMS and ICPMS. Isotope dilution (ID) was applied for the determination of

MeHg in DOLT-4, DBT and TBT in PACS-2. Due to the unavailability of a suitable enriched spike for specie-specific isotope dilution, just a qualitative investigation was carried out on SeMet in SELM-1.

Materials and methods

Instrumentation

A centrifuge was from Damon/IEC Division (Needham HTS, MA, USA) and a microwave oven was 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 Technologies (Mississauga, ON, 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 the 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 custom designed and made by Agilent Technologies (Figure 1). A commercial heated GC transfer line (Agilent Technologies, Mississauga, ON, Canada) was used to connect the GC to ICPMS (Figure 1). The EIMS detector was used for the detection of fragment ions 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 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 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. ICPMS optimization was carried out by monitoring the signal of Xe contained in Ar sample gas for the tuning. Typical operational conditions for GC, EIMS and ICPMS are outlined in Table 1.

Chemicals

Deionized (DI) water was made in-house with a MilliQ 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 an 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 (95%), dibutyltin chloride (96%) and tributyltin chloride (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. The stock solution of SeMet (14.3 µg/g as Se) was prepared in DI water. ^{198}Hg-enriched MeHg ($Me^{198}Hg$) stock solution (~3.5 µg/g as Hg) in methanol was prepared using commercially available inorganic ^{198}Hg.[13] ^{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.). 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 spikes. Four MeHg RID samples were prepared by mixing 0.23 g of MeHg (2.0515 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 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

The procedure for DOLT-4 digestion was similar to that reported by D'Ulivo *et al.*[14] Briefly, each 0.5 g of DOLT-4 was weighed into a glass flask followed by addition of 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 h.

Procedure for PACS-2 digestion was similar to that reported by Yang *et al.*[15,16] 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), respectively. 6 mL of glacial acetic acid was then added, the vial was capped and the sample was digested in a CEM microwave for 10 min (100 ^{o}C, pressure 250, power max, medium stirring). The digested samples were then centrifuged for 10 min at 2000 rpm and stored at +4 ˚C till analysis.

Preparation of SELM-1 samples for qualitative investigation

The procedure for SELM-1 digestion was carried out according to the previous study[17]. Briefly, 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 ^{o}C, pressure 250, power max, medium stirring).

SPME sampling of DOLT-4 and MeHg samples

Procedures for derivatization of MeHg and SPME sampling were optimized by Yang *et al.*[10] Briefly, 0.5 mL of methylmercury standards (MeHg and RID solutions) or 2 mL DOLT-4 extract (pH adjusted to 5-6 with 1 mL ammonium hydroxide) and 10 mL of 1 M acetate buffer (pH 5) were added in a glass vial. After addition of 1 mL of 1% $NaBPr_4$, the vial was capped with a cap fitted with a PFTE-silicon septum. The derivatized analyte was head space sampled by SPME for 10 min and then injected to GC column for analysis.

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

Similarly, prior to GC injection, derivatization of DBT and TBT in samples was performed as previously reported.[11] Briefly, 0.5 mL of DBT and TBT standards (DBT, TBT and corresponding RID solutions) or 2 mL PACS-2 extract (pH adjusted to 5-6 with 2 mL ammonium hydroxide) were added in a glass vial first and then 10 mL acetate buffer (pH 5), 1 mL $NaBEt_4$ 2% and 2 mL hexane were added. The vial was shaken manually for 5 min. After the derivatization, the vials were centrifuged at 2000 rpm for 10 min to help the separation of the organic and aqueous phases. 1 mL of the organic phase was transferred to GC vials for GC-EIMS and GC-ICPMS analysis.

Preparation of SELM-1 and SeMet samples for liquid sampling

Derivatization of SeMet in samples was performed as previously described.[18,19] Briefly, 1 mL SeMet standard solution or SELM-1 extract were added in a 10 mL glass vial. The SELM-1 extract was neutralized with 0.48 mL of ammonium hydroxide solution. After addition of 0.75 mL pyridine/MeOH mixture solution (1:3), 0.25 mL of methyl chloroformate was slowly added. The vial was shaken manually for 1 min and 1 mL chloroform was then added in the mixture. The vial was capped and shaken manually for 1 min. 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 GC-EIMS and GC-ICPMS analysis.

Safety consideration

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

Results and discussion

The interface of the GC-EIMS/GC-ICPMS system

Inductively coupled plasma (ICP) is a strong ionization source that can efficiently ionize target analytes to provide high sensitivity. However, information on fragmentations or isotopic patterns of the analytes is completely missed with ICPMS. 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 Technologies for this purpose (Figure 1). The interface is a "Y" shape of split made from fused-silica capillary, which is connected to the end of a GC column (input **A**). The outlet **B** is connected to EIMS transfer line directly and the outlet **C** to the ICPMS transfer line. Depending on the length and the diameter of each side of the capillary, the splitting ratio between the ICPMS and EIMS varies. The split using 0.25 mm i.d. fused-silica capillary seamlessly results in 25% of the GC flow to ICPMS and 75% of the GC flow to EIMS, since ICPMS has much higher sensitivity than that of the EIMS. As shown in Figure 2, good signals for MeHg were obtained on both GC-EIMS and GC-ICPMS. Compared to the chromatogram of EIMS (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 in DOLT-4, and DBT and TBT in PACS-2 were quantitatively measured with this synchronizing GC-EIMS/GC-ICPMS system, while SeMet in SELM-1 was just qualitatively determined.

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

Prior to validate 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 $^{202}Hg/^{198}Hg$ and $^{118}Sn/^{117}Sn$ ratios. 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, not significantly different to the theoretical values of 2.9950 and 3.1536, respectively, confirming no significant isobaric interferences.

Reverse isotope dilution (RID) technique has been commonly used to determine the exact concentrations of the $Me^{198}Hg$, ^{117}DBT and ^{117}TBT.[20] The RID standards were measured the first day, while DOLT-4 and PACS-2 ID samples and blank samples were analyzed on the second day. A mass bias solution was injected between every four 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, DBT and TBT were 0.9995±0.0148, 1.002±0.005 and 0.9995±0.0178, respectively, indicating that the mass bias drift is negligible and will not affect the measurements.

ID-MS technique is capable of generating accurate and precise 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.[21]

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 analyte in the natural abundance standard, C_b is the concentration of the blank normalized to the sample weight, m_z is the weight of the natural abundance standard used, m'_y is the weight of the enriched spike used to prepare the blend solution of enriched spike and natural abundance standard, m_y is the weight of enriched spike used to prepare the blend solution of enriched spike and sample, m_x is the mass of sample used, A_y is the abundance of the reference isotope (^{202}Hg or ^{118}Sn) in the enriched spike, B_y is the abundance of the spike isotope (^{198}Hg or ^{117}Sn) in the enriched spike, 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 Hg or Sn.

Table 2 summaries the measured concentrations of MeHg in DOLT-4, and DBT and TBT in PACS-2 and good agreement between the measured values and the certified values is evident. Moreover, the results from EIMS detector and ICPMS detector are in good agreement, demonstrating that both detectors can provide reliable quantitation. However, the standard deviations of the EIMS results were slightly higher than those 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 for the analysis of organometallic compounds. 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. However, not all elements respond in the same way in ICPMS due to their various ionization energies. In general, an element with high ionization energy would have low sensitivity in ICPMS. For instance, the element Se has high ionization energy of 9.75 eV and therefore has much lower sensitivity than elements with low ionization energies such as Hg or Sn.[22] In this study, the sensitivity of two mass spectrometers, 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). The intensity gain is given by the ratio of ICPMS and EIMS intensities. For ICPMS detector, since the signal was recorded as total counts, it was thus corrected to counts/s (cps) by considering the dwell time of 0.05 s for comparison purposes. As shown in Figures 2, 3 and 4, a significant gain in sensitivity was observed with the ICPMS detector. This is clearly evident in Figure 4, where the EIMS and ICPMS chromatograms of SeMet in SELM-1 are compared. The chromatogram in Figure 4a

(EIMS detection in scan mode) is complicated, but ICPMS provides a clear detection of SeMet (Figure 4b). The ICPMS detector significantly improved the sensitivities of all the target species (MeHg, DBT, and SeMet) in terms of both absolute signal intensity and S/N. For example, the gains in absolute intensity were 94-, 117- and 30-folds for MeHg, DBT and SeMet, respectively. The gain in S/N was 19-folds for MeHg and 132-folds for DBT. Surprisingly, SeMet showed the highest gain in sensitivity (2850-folds) in term of S/N ratio. The limits of detection (LODs) for MeHg in DOLT-4, DBT and TBT in PACS-2 were 0.51, 0.52 and 0.39 µg/g with EIMS, respectively. Much better LODs of 0.037, 0.004 and 0.001 µg/g for MeHg, DBT and TBT, respectively, were obtained with ICPMS detector. Although ICPMS has the advantage of high sensitivity, the EIMS can provide useful identification information that ICPMS cannot. The insert in Figure 4a is a typical example of the isotopic pattern of the SeMet species obtained by EIMS. Figure 5 shows the fragmentation pattern of the ionized MeHg derivative ($MeHgPr^+$). The specificity of both fragmentation and isotopic patterns plays a pivotal role in the characterization of the organometals. The target species can be identified through the mass spectra of EIMS, while the ICPMS side can simultaneously provide the high sensitivity for the quantification purpose.

Conclusions

In this study, a unique interface is employed to split the GC eluent flow to both EIMS and ICPMS detectors synchronously for the speciation of four organometals: MeHg, DBT, TBT and SeMet. Accurate quantitation of organometals can be achieved with both EIMS and ICPMS detectors. The results obtained for MeHg in DOLT-4 and DBT and TBT in PACS-2 CRMs are in agreement with the certified values, demonstrating the success of the developed method in quantitation. This technical improvement allows the sensitive and specific determination of organometals (ICPMS) without sacrificing important structural information (EIMS) that might be helpful for the identification of the species. To the best of our knowledge this is the first report on the speciation of organometals in biological and sediment samples using a synchronized GC-EIMS and GC-ICPMS system.

Acknowledgements

Lucia D'Ulivo is grateful to NSERC Canada and Health Canada for financial support in the form of post-doctoral fellowship. This project was financially supported by the Canadian Government under the Chemicals Management Plan (CMP).

References

1. W.M.A. Niessen, in *Liquid chromatography-mass spectrometry*, Ed. CRC Press Taylor and Francis Group, Boca Raton FL, 3rd edn., 2006, vol. 97., ch. 3, pp 55-67.
2. J. Abian, *J. Mass Spectrom*, 1999, **34**, 157-168.
3. J.R. Ashby and P.J. Craig, *Appl. Organomet. Chem.*, 1991, **5**, 173-181.
4. G. Centineo, E. B. González and A. Sanz-Medel, *J. Chrom. A*, 2004, **1034**, 191-197.
5. M.V. Peláez, M.M. Bayón, J.I.G. Alonso and A. Sanz-Medel, *J. Anal. At. Spectrom.*, 2000, **15**, 1217-1222.
6. T. W. Clarkson, L. Magos, *Crit. Rev. Toxicol.*, 2006, **36**, 609-662.
7. F. Zahir, S.J. Rizwi, S.K. Haq and R.H. Khan, *Environ. Toxicol. Pharmacol.*, 2005, **20**, 351-360.
8. M. Hoch, *Appl. Geochem.*, 2001, **16**, 719-743.
9. Z. Pedrero and Y. Madrid, *Anal. Chim. Acta*, 2009, **634**, 135-152.
10. L. Yang, V. Colombini, P. Maxwell, Z. Mester and R.E. Sturgeon, *J. Chrom. A.*, 2003, **1011**, 135-142.
11. C. Bacon-Montigny, P. Maxwell, L. Yang, Z. Mester and R.E. Sturgeon, *Anal. Chem.*, 2002, **74**, 5606-5613.
12. L. Yang, R.E. Sturgeon, W.R. Wolf, R.J. Goldschmidt and Z. Mester, *J. Anal. At. Spectrom.*, 2004, **19**, 1448-1453.
13. C. Bancon-Montigny, L. Yang, R. E. Sturgeon, V. Colombini and Z. Mester, *Appl. Organometal. Chem.*, 2004, **18**, 57-64.
14. L. D'Ulivo, L. Yang, Y.-L. Feng and Z. Mester, *Anal. Methods*, 2013, **5**, 7127-7131.
15. L. Yang, Z. Mester and R. E. Sturgeon, *Anal. Chem.*, 2002, **74**, 2968-2976.
16. L. Yang and J.W.H. Lam, *J. Anal. At. Spectrom.*, 2001, **16**, 724-731.
17. L. Yang, P. Maxwell and Z. Mester, *Anal. Methods*, 2013, **5**, 525-529.
18. L. Yang, Z. Mester and R.E. Sturgeon, *Anal. Chem.*, 2004, **76**, 5149-5156.
19. C. Haberhauer-Troyer, G. Álvarez-Llamas, E. Zitting, P. Rodríguez-González, E. Rosenberg and A. Sanz-Medel, *J. Chromatogr. A*, 2003, **1015**, 1-10.

20. R.L. Watters Jr., K.R. Eberhardt, E.S. Beary and J.D. Fassett, *Metrologia*, 1997, **34**, 87-96.

21. L. Yang and R.E. Sturgeon, *J. Anal. At. Spectrom.*, 2005, **20**, 724-729.

22. E.H Larsen and S. Stürup, *J. Anal. At. Spectrom.*, 1994, **9**, 1099-1105.

Figure captions

Figure 1. Schematic representation 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 ^{198}Hg and ^{202}Hg. The insert in part (a) shows the typical isotopic pattern of mercury obtained by analyzing DOLT-4 in scan mode (m/z range: 100-300).

Figure 3. Simultaneous determination of monobutyltin (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 ^{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 (m/z range: 100-300), (b) ICPMS with isotopes ^{77}Se, ^{78}Se, ^{80}Se and ^{82}Se. The insert in part (a) shows the typical isotopic pattern of selenium by analyzing SELM-1 in scan mode (m/z range: 100-300).

Figure 5. Typical fragmentation pattern of the ionized MeHg derivative ($MeHgPr^+$, $[M+H^+]$) obtained by analyzing DOLT-4 in scan mode (m/z range: 100-300).

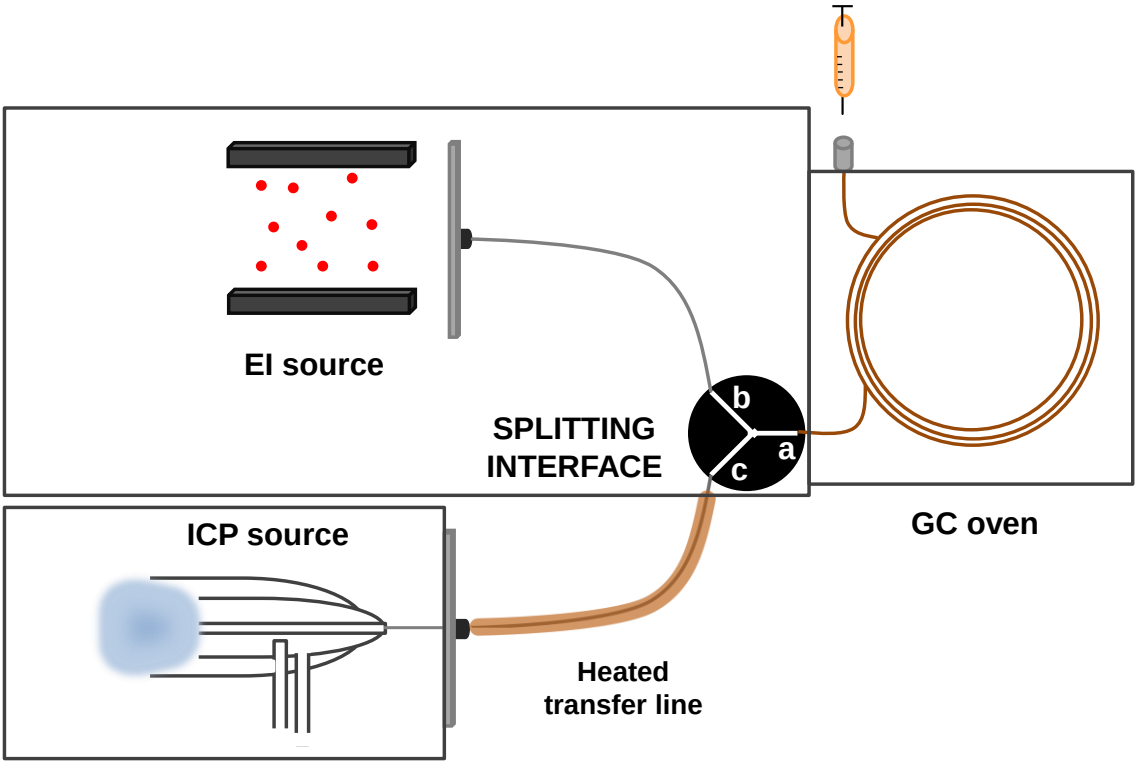


Figure 1.

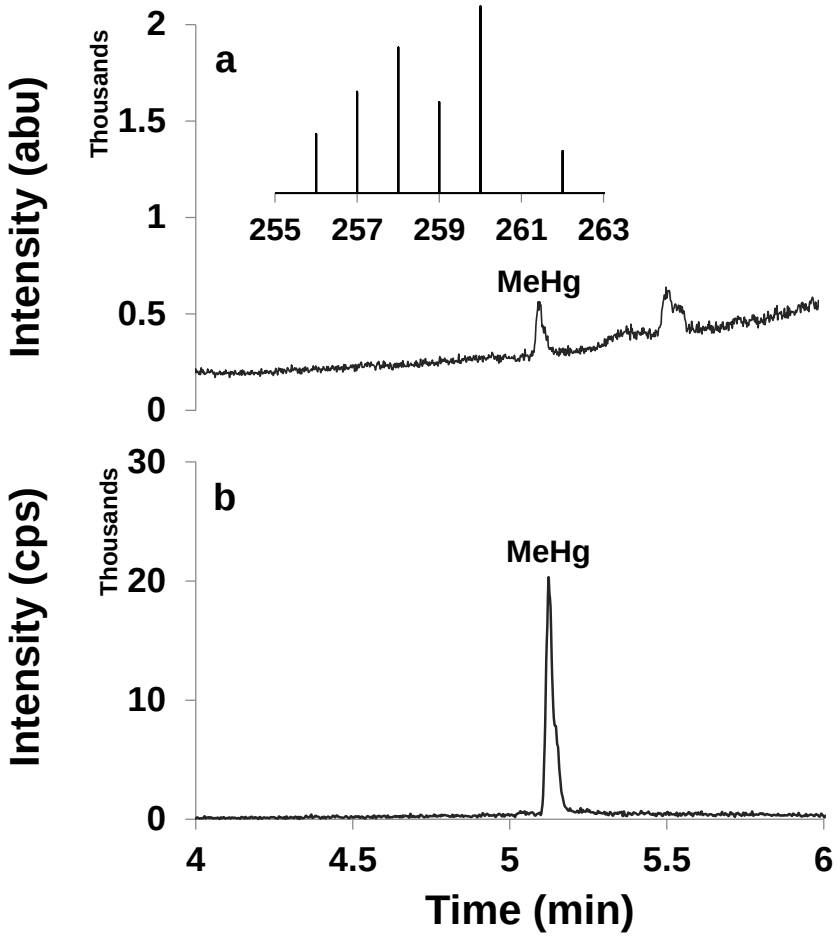


Figure 2.

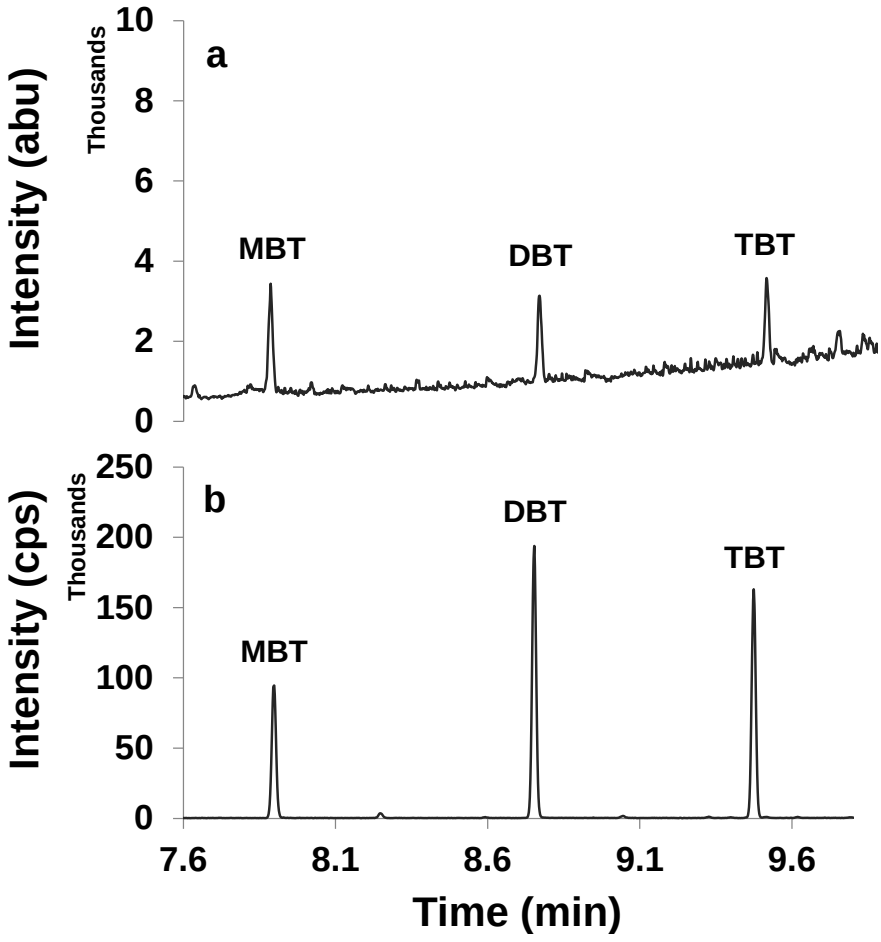


Figure 3.

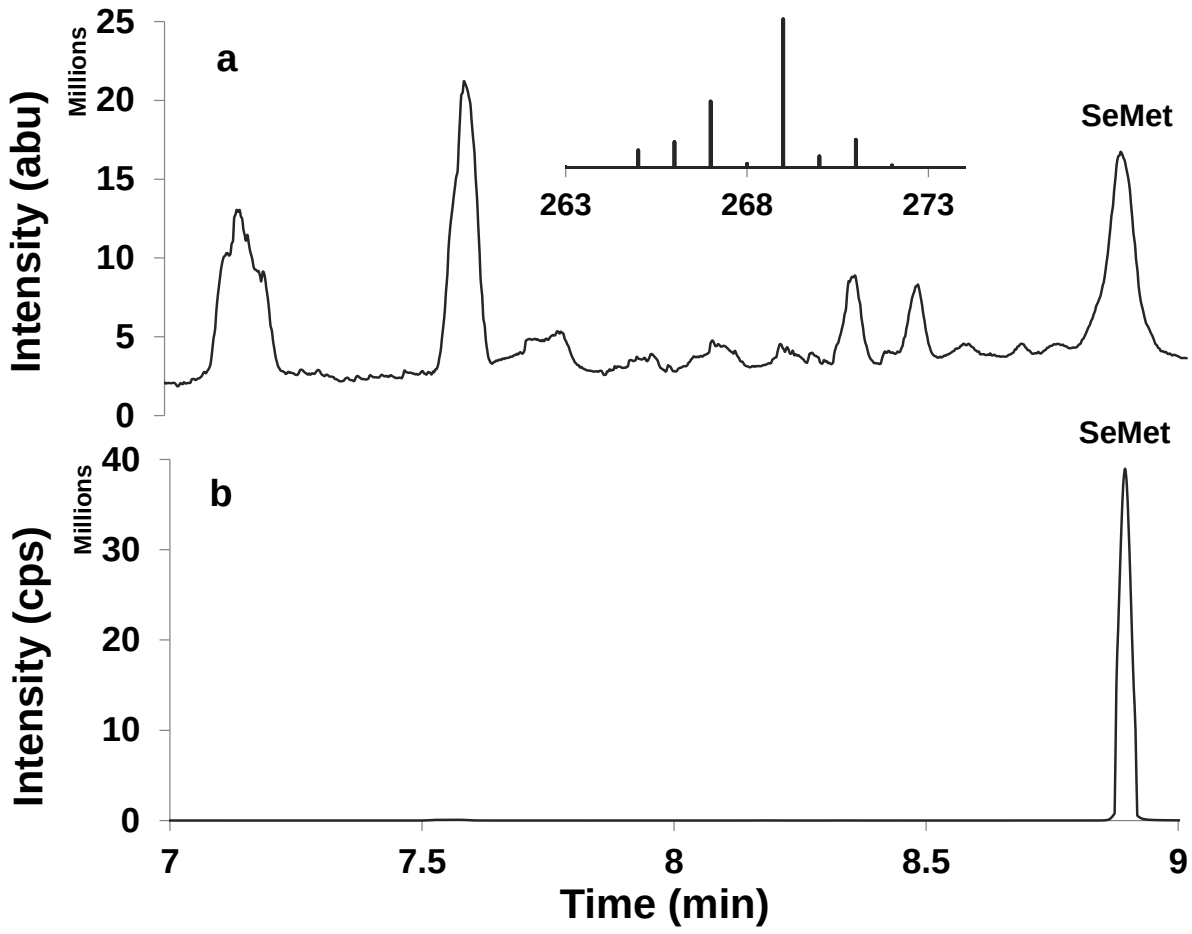


Figure 4.

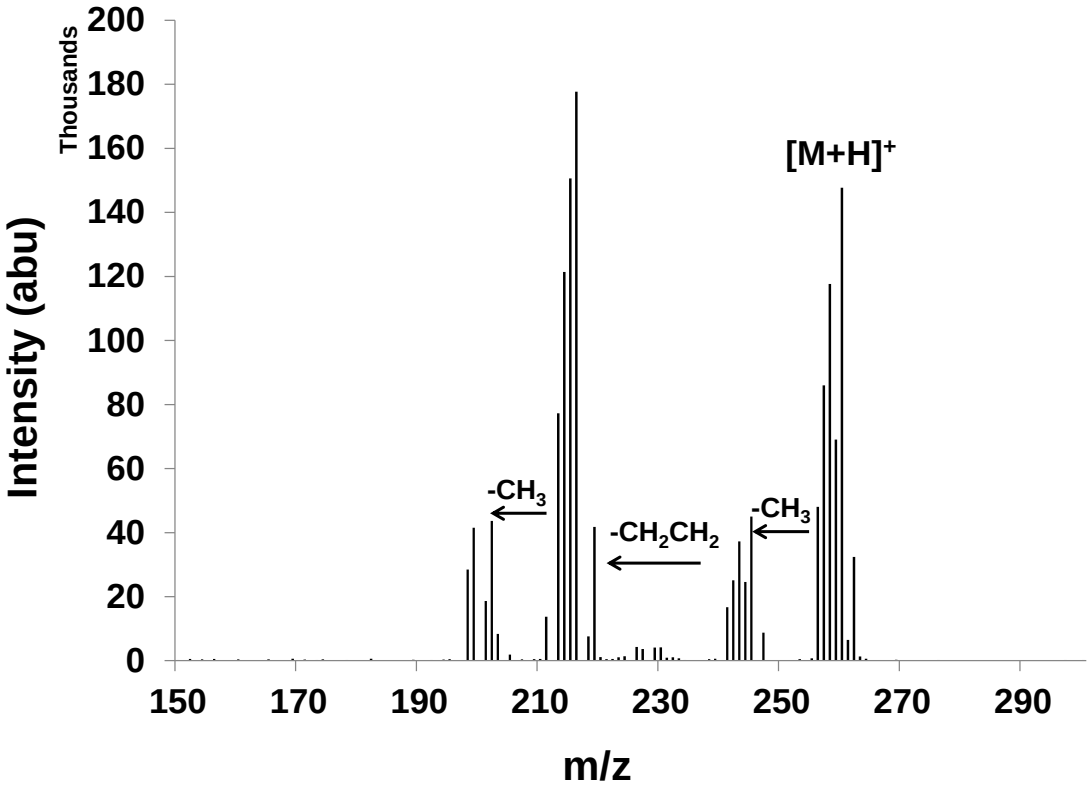


Figure 5.

Table 1. GC-ICPMS operating conditions for determination of MeHg, DBT and TBT, and SeMet 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 μmm_f)	DB-5MS (30 m x 0.25 mm i.d. x 0.25 μmm_f)
Injection mode	Splitless, 1 μL	Splitless, 1 μL
Injection temperature	220 ^oC	280 ^oC
Oven program	50 ^oC (2 min) to 250 ^oC (20 ^oC/min), 1 min post run	120 ^oC (2 min) to 260 ^oC (20 ^oC/min), 1 min post run
Carrier gas, flow rate	He, 1.5 mL/min	He, 1.5 mL/min
ICPMS		
RF power	900 W	
RF matching	1.8 V	
Sample depth	5.0 mm	
Torch-H	1.7 mm	
Torch-V	-0.4 mm	
EIMS		
Source temperature	250 ^oC	
EM Volts	1847 V	
Electron energy	69.9 eV	
Ion polarity	positive	
Detector temperature	250 ^oC	

Table 2. Results for quantitation of MeHg, and 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**	**Certified value**
1.288±0.058 μg/g	1.335±0.033 μg/g	1.33±0.12 μg/g
DBT quantification in PACS-2		
EIMS	**ICPMS**	**Certified value**
1.124±0.065 μg/g	1.171±0.005 μg/g	1.100±0.135 μg/g
TBT quantification in PACS-2		
EIMS	**ICPMS**	**Certified value**
0.830±0.015 μg/g	0.834±0.003 μg/g	0.832±0.095 μg/g