Rapid and direct speciation of methyltins in seawater by an on-line coupled high performance liquid chromatography–hydride generation–ICP/MS system

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ARTICLE INFO

Article history:

Received 26 June 2008

Received in revised form 29 August 2008

Accepted 30 August 2008

Available online 9 September 2008

Keywords:

Speciation

Methyltin

Seawater

High performance liquid chromatography

Hydride generation

ICP/MS

ABSTRACT

A novel on-line coupled HPLC–hydride generation (HG)–ICP/MS system was developed for rapid, direct and sensitive speciation of methyltins in seawater without any pretreatment step. Methyltin compounds were separated by reversed phase HPLC, and then on-line reacted with potassium borohydride and acetic acid to generate volatile hydride products. The volatile derivatization products were separated in the spray chamber of ICP/MS and then introduced into ICP/MS by argon gas for detection. Monomethyltin (MMT), dimethyltin (DMT) and trimethyltin (TMT) were baseline separated in less than 15 min by reversed phase HPLC. The influence of KBH_4 concentration and type of acid on the system performance was investigated and optimized. Calibration curves, based on peak heights against concentration, were linear in the range of 0.5–50 ng (Sn) mL^{-1} of methyltins with correlation coefficients of 0.9990, 0.9990 and 0.9996 for MMT, DMT and TMT, respectively. The relative standard deviations measured at 10 ng (Sn) mL^{-1} for these three methyltins were in the range of 0.6–1.4% ($n = 5$), and the calculated detection limits ($S/N = 3$) for MMT, DMT and TMT were 0.266, 0.095 and 0.039 ng (Sn) mL^{-1} , respectively. This method was successfully applied to the speciation of methyltins in seawater with spiked recovery in the range of 95.4–106.9%. MMT and DMT were detected in all the seawater samples with concentrations in the range of 1.0–1.5 and 0.30–0.57 ng (Sn) mL^{-1} for MMT and DMT, respectively.

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1. Introduction

Extensive applications of methyltin compounds as biocides, antifouling agents and polyvinyl chloride heater stabilizers have caused serious pollution to the environment because of their high toxicity to organisms [1,2]. Up to date the occurrence of methyltin compounds have been found in many different environmental media such as seawater [3,4], river water [5,6], lake water [6,7], sediments [8] and biological samples [3]. In addition to the anthropogenic sources [1], methyltins can be produced by the biotic and abiotic methylation [9–11].

Although some methods are available for analyzing organotin compounds, there is lack of technique for rapid, direct and sensitive detection for organotins, especially for methyltins. Methyltins are more difficult to be detected than butyltin and phenyltin compounds because of their minor structural difference and higher solubility in water and thus their low extraction efficiencies from aqueous medium. The shortage in rapid, direct and sensitive meth-

ods is often the bottleneck of research on the mechanisms of methyltin biogeochemical cycling in the environment and their toxicity to organisms.

The speciation methods for methyltin compounds mainly focus on hyphenated systems based on gas chromatography (GC) and liquid chromatography (LC). Methods based on coupling GC with different detectors such as atomic absorption spectrometry (AAS) [7], quartz surface-induced luminescence flame photometric detector (QSIL-FPD) [12] and mass spectrometry (MS) [13] are commonly used. However, the major limitation of these methods is that methyltins have to be off-line derivatized with sodium borohydride, sodium tetraethylborate or Grignard reagents [14]. The existence of methyltins as methyltin salts in the environment leads to the utilization of time-consuming steps involving complexation, extraction and derivatization, and is the main sources of errors. When sodium borohydride method is utilized, the hydrides of methyltin compounds have to be trapped using cryogenic purge and trap method [12] or hydride trap method [3] due to the lower boiling points of the hydride generation products of methyltin compounds (CH_3SnH_3 1.4 °C, $(\text{CH}_3)_2\text{SnH}_2$ ca. 35 °C, $(\text{CH}_3)_3\text{SnH}$ ca. 60 °C) [3]. It is more complicated to use Grignard reagent method because this reaction must be conducted under anhydrous condition. Typ-

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ically, organotins in water are complexed with a chelating agent, such as sodium diethyldithiocarbamate (DDTC, 0.2 g) in the presence of sodium chloride [13]. The chelated organotins are then extracted with toluene. After the phase separation, the organic phase collected through a column of anhydrous sodium sulfate was evaporated to ca. 1 mL under reduced pressure. Grignard reagent, such as pentylmagnesium bromide is added to the organic phase and then allowed to stand at 40 °C for 60 min. As can be seen it is a very time-consuming process.

HPLC coupled with different detectors, such as AAS [15], MS [16] and inductively coupled plasma mass spectrometry (ICP/MS) [17], are widely used for the speciation of methyltins because they avoid the complex extraction and derivatization step. Some reviews on the speciation of organotins using HPLC coupled with different detectors are available in the literatures [18,19]. One of the major problems for organotin determination is that the shortage of conventional high sensitive detectors limits the application of HPLC-base hyphenated method. ICP/MS is a powerful tool for analyzing organotins due to its high sensitivity and selectivity and has been hyphenated with several modes of LC, such as ion-exchange, reversed phase and ion-pairing. An important issue in the hyphenation of reversed phase LC with ICP/MS is the compatibility of mobile phase and plasma source. The presence of high percent organic solvent in the mobile phase can result in poor plasma stability and may even extinguish the plasma. In addition, carbon deposits may form on the sampler and the skimmer cones within the ICP/MS interface region, and could contribute to higher noise and reduced signals. As a result, it is necessary to add oxygen to the nebulizer argon-gas flow to allow complete combustion of the organic solvent in the plasma. However, many ICP/MS systems are not configured for the oxygen addition, which seriously restricts the applications of reversed phase HPLC–ICP/MS. Furthermore, the traditional nebulizer mode normally has low efficiency, with only 5–10% being delivered to the ICP plasma. For example, the organotins compounds, focused on butyltin and phenyltin compounds, were detected by HPLC–ICP/MS system using traditional mode [20–23]. Sample introduction using hydride generation has proved to be a powerful tool to increase the sensitivity of ICP/MS [24]. For example, a 16-fold sensitivity enhancement is obtained for cadmium determination by using HPLC–HG–ICP/MS rather than the conventional nebulization [24]. So far the HPLC–HG–ICP/MS technique has been applied for the speciation of elements such as cadmium [24] and arsenic [25,26]. Anion exchange chromatographic separation mode was used in these hyphenated systems. However, it is unable to completely separate methyltins with ion-exchange mode. A reversed phase separation mode seems to be a good choice. To our best knowledge, this is the first report on the direct determination of methyltins in water without preconcentration.

In this paper, a reversed phase HPLC–HG–ICP/MS hyphenated system was developed to directly and rapidly determine methyltins without any preconcentration step. This method successfully avoided the extinguishing of plasma resulted from the high percentage of methanol without oxygen addition system or other equipment modification. This technique was applied to the speciation of methyltins in seawaters. Analysis of one seawater sample can be completed within 15 min.

2. Experimental

2.1. Reagents

All reagents were used as purchased without further purification. Three methyltin compounds, including trimethyltin chloride

Fig. 1. Schematic diagram of the HPLC–HG–ICP/MS system. (1) HPLC pump; (2) C₁₈ column; (3) four-way connector; (4) HAc; (5) KBH₄; (6) peristaltic pump; (7) waste; (8) spray chamber; (9) ICP/MS.

(TMT, 98%), dimethyltin dichloride (DMT, 97%) and monomethyltin trichloride (MMT, 97%), were obtained from Aldrich Chemical Co. (USA). Standard stock solutions were prepared by dissolving methyltin compounds in deionized water and stored at 4 °C. The working solutions were prepared daily by appropriately diluting the stock solutions with deionized water. Methanol was HPLC grade solvent (J. T. Baker, Phillipsburg, NJ, USA). Tropolone (98%) was from Acros Organics (NJ, USA). Nitric acid (GR, 65%) was purchased from Merck, Germany. Acetic acid (AR, 99.5%), hydrochloric acid (GR, 36–38%), and potassium hydroxide (GR) were obtained from Beijing Chemical Factory (Beijing, China). Potassium borohydride (95%) was purchased from Institute of Geophysical and Geochemical Exploration (Langfang, China). Deionized water (18.3 MΩ cm) was produced from an ultrapure water system (Barnstead International, Dubuque, IA, USA).

2.2. Apparatus

Fig. 1 shows the schematic diagram of hyphenated HPLC–HG–ICP/MS system, which mainly consists of three parts. Methyltin compounds were first separated by the HPLC system which consists of a DGU-12A degasser, a LC-10A pump (Shimadzu, Japan), an injector valve (Rheodyne 7725i with a 200 µL sample loop), and a C₁₈ separation column (Agilent Zorbax Eclipse XDB-C18, 5 µm particle size, 4.6 mm × 150 mm). In the hydride generation (HG) component, the analytes from the HPLC column reacted with the derivatization reagents, introduced by a peristaltic pump, in a four-way-cross connector to form volatile methyltin hydride. These volatile methyltin hydrides were then introduced into ICP/MS (Agilent 7500ce with Babington nebulizer, USA) for detection. In the third part, the spray chamber of the ICP/MS was used as a gas–liquid separator and the mode of nebulization was changed to make organic mobile phase adapt ICP/MS which would be discussed later in detail. The operating conditions of this hyphenated system are listed in Table 1.

2.3. Preparation of seawater sample

Seawater samples from Yantai (Bohai Sea, China) were stored at –20 °C in the refrigerator. The samples were analyzed without any pretreatment except being filtered with a 0.4 µm filter membrane before injected into the HPLC system.

Table 1
Optimum operating conditions for the HPLC–HG–ICP/MS system

Parameter	Optimized value
HPLC	
Column	Agilent Zorbax Eclipse XDB-C ₁₈ , 5 μ m, 4.6 mm $\times$ 150 mm
Mobile phase	70% (v/v) methanol, 3% (v/v) HAc, 27% (v/v) water, 0.1% (m/v) tropolone; pH 3.5
Flow rate of mobile phase	0.3 mL min ⁻¹
Sample injection	200 μ L
Derivatization reagent	
HAc	1% (v/v), flow rate: 0.36 mL min ⁻¹
KBH ₄	0.5% (m/v), (containing 0.2% KOH), flow rate: 0.36 mL min ⁻¹
ICP/MS	
S/C Temperature	2 °C
Makeup gas (Ar)	0.72 L min ⁻¹
Carrier gas (Ar)	0.22 L min ⁻¹
RF power	1550 W
Isotope monitored	¹¹⁸ Sn, ¹²⁰ Sn

3. Results and discussion

3.1. Optimization of HPLC–HG–ICP/MS

HPLC separation of methyltin compounds was conducted as described in our previous paper [23] and the adopted parameters are listed in Table 1. In these liquid chromatographic conditions, three methyltins were baseline separated in less than 15 min and the eluent sequence of these three methyltins is TMT, MMT and DMT because of the function of tropolone as complexant in the mobile phase. As for the operational parameters of ICP/MS, the isotope ¹²⁰Sn signal intensity was selected to optimize the instrumental performance. HAc (2% v/v, containing 3.0 ng (Sn) mL⁻¹ MMT) and KBH₄ (0.5% (m/v) containing 0.2% (m/v) KOH), introduced via the peristaltic pump of ICP/MS, were mixed in a four-way-cross connector, and the produced volatile MMT hydride was introduced into the spray chamber (2 °C) of ICP/MS. The instrumental parameters were adjusted until the ¹²⁰Sn signal intensity reaches maximum value. The signal intensity was strongly dependent on flow rate of the carrier gas and makeup gas of the HPLC–HG–ICP/MS system. Generally, the flow rate of carrier gas was higher than that of makeup gas in order to improve the nebulization efficiency and sensitivity. However, the carrier gas flow rate used in this HPLC–HG–ICP/MS system was lower than that of makeup gas for the following two purposes: (1) the Babington nebulizer with bigger spray pore than concentric nebulizer used in this system can easily decrease the nebulization efficiency by changing the flow rate of carrier gas to reduce the influence of methanol in mobile phase to the plasma and (2) increasing the flow rate of makeup gas can efficiently carry the volatile hydride to the plasma and thus greatly increases the sensitivity. As a result, the optimum flow rates of the carrier gas and the makeup gas in this hyphenated system were 0.22 and 0.72 L min⁻¹, respectively. Furthermore, there is no interference of other elements to the methyltin determination because only the isotope of ¹¹⁸Sn and ¹²⁰Sn were selected to be detected. Overall, it is very easy to set up this HPLC–HG–ICP/MS system as no special auxiliary equipment was needed, and the only difference of using ICP/MS procedure with the conventional mode is to adjust the flow rate ratio of the carrier and makeup gases.

Generally, the commonly used temperature of spray chamber, precisely controlled by Peltier cooling device, is 2 °C. Peltier cooling spray chamber can remove some of the water from the sample, delivering only the smallest droplets to the plasma. Consequently, this Peltier cooling device can provide the plasma with a very stable ion signal and produce low levels of polyatomic

Fig. 2. Effects of KBH₄ concentrations on signal intensities of methyltins. Analyte concentrations (as Sn): 10 ng mL⁻¹ of MMT, DMT, and TMT. Derivatization reagents: 2% (v/v) HCl and different concentration of KBH₄ (containing 0.2% (m/v) KOH).

oxide species, which in turn reduces the interferences on certain analytes. Considering the boiling points of (CH₃)₂SnH₂ (35 °C) and (CH₃)₃SnH (60 °C), we initially speculated that the low spray chamber temperature at 2 °C would liquefy the methyltin hydrides and lead to low transfer efficiency to the plasma. Therefore, the effect of spray chamber temperature on the signal intensities of the three methyltins was investigated at 10 ng (Sn) mL⁻¹ of methyltins. The signal intensities of methyltins varied slightly with the spray chamber temperature increased from 2 to 15 °C, which is because the total flow rates of carrier gas and makeup gas is about 1 L min⁻¹, which can carry the methyltin hydrides to pass through the spray chamber rapidly and give almost no chance to liquefy these hydrides. As the reflected power of ICP/MS, normally at 1 W, increases from 1 to 25 W and becomes very unstable by increasing the temperature of spray chamber from 2 to 15 °C, the selected temperature of spray chamber was 2 °C in the following experiments.

3.2. Optimization of derivatization reagents

The concentrations of derivatization reagents have a great influence on the hydride generation of methyltins and thus on the detection limit of ICP/MS. Low KBH₄ concentration results in low hydride reaction efficiency, whereas too high KBH₄ produces too much hydrogen that could affect the stability of plasma, even extinguish the plasma. Fig. 2 displays the effect of KBH₄ concentrations on the peak height of methyltins when the flow rate of KBH₄ was set at 0.36 mL min⁻¹. As can be seen, the best signal intensities for these three methyltins were obtained at 0.5% (m/v) KBH₄, which was adopted in the following studies.

With a constant flow rate of 0.36 mL min⁻¹ for both the acid and 0.5% (m/v) KBH₄, the influence of acid type and concentration were studied (Fig. 3). Similar signal responses were observed for hydrochloric acid, nitric acid and acetic acid at their optimum concentrations. Relatively lower acid concentrations in this experiment seem to have higher signals. For example, the signals of methyltins obtained at 1% (v/v) HCl were higher than those at 2% and 3% HCl. However, too lower acidic concentrations may lead to incomplete hydride reaction, which produces lower signal intensity. Overall, relatively higher signal were obtained using 0.6% (v/v) nitric acid or 1.0% (v/v) acetic acid. Considering acetic acid is a weak acid and is used in the mobile phase, 1.0% (v/v) acetic acid was adopted in the following experiments. The final operating conditions were shown in Table 1.

Fig. 3. Effects of the types and concentrations of acids used for derivatization on the signal intensities of methyltins. Analyte concentrations (as Sn): 10 ng mL⁻¹ of MMT, DMT and TMT. Derivatization reagents: 0.5% (m/v) KBH₄ (containing 0.2% (m/v) KOH) and various acids.

3.3. Analytical performance

The three methyltins were baseline separated in less than 15 min. Table 2 shows the analytical performance data of this developed HPLC–HG–ICP/MS system. Linear calibration curves, based on peak heights to concentrations, were obtained in the range of 0.5–50 ng (Sn) mL⁻¹ of methyltins with correlation coefficients of 0.9990, 0.9990 and 0.9996 for MMT, DMT and TMT, respectively. The relative standard deviations measured at 10 ng (Sn) mL⁻¹ level were in the range of 0.6–1.4% ($n = 5$). Based on the relative standard deviations measured at 2.0 ng (Sn) mL⁻¹, the calculated detection limits ($S/N = 3$) for MMT, DMT and TMT were 0.266, 0.095 and 0.039 ng (Sn) mL⁻¹, respectively.

3.4. Determination of methyltins in seawater samples

The proposed method was successfully applied to directly measure methyltins in seawater samples collected from Bohai Sea at

Fig. 4. Typical chromatograms for methyltin analysis in water. (A) Seawater sample; (B) seawater sample spiked with standards (2.0 ng (Sn) mL⁻¹); (C) methyltin standards.

Yantai city (Shandong Province, China). The chromatograms of seawater sample analyses with and without addition of standards, as well as standard of methyltins are shown in Fig. 4. Three methyltins can be well separated. The results of seawater samples were shown in Table 3. Good spiked recoveries (%) of 5 samples, 95.8–108 for MMT, 95.4–106.9 for DMT, and 97.0–103.7 for TMT, were obtained at 2.0 ng (Sn) mL⁻¹ spiking level. MMT and DMT were detected in all seawater samples and the concentration of MMT (1.0–1.5 ng (Sn) mL⁻¹) is higher than that of DMT (0.30–0.57 ng (Sn) mL⁻¹). TMT was not detected in any of these seawater samples, even though the proposed method has the highest sensitivity for TMT. This could be due to the fact that TMT is less stable than MMT and DMT in the environment. TMT can be degraded to DMT and MMT by biotic and abiotic demethylation [28]. In addition, biotic and abiotic methylation of inorganic tin in seawater could also lead to the formation of MMT.

The concentrations of methyltins in our results are consistent with the previous work conducted in Ontario Lake water [7], which contains 0.53–1.22 ng (Sn) mL⁻¹ MMT, 0.10–0.40 ng (Sn) mL⁻¹ DMT, and below detection limit of TMT. Furthermore, the omnipresent

Table 2
Some analytical performance data of the proposed method

Compound	Calibration curve ^a	Correlation coefficient	Detection limit (ng mL ⁻¹)	RSD (% , $n = 5$) ^b
MMT	$Y = 1.56 \times 10^5 X + 7.87 \times 10^4$	0.9990	0.266	1.4
DMT	$Y = 5.08 \times 10^5 X - 3.63 \times 10^5$	0.9990	0.095	0.6
TMT	$Y = 1.00 \times 10^6 X - 2.54 \times 10^5$	0.9996	0.039	0.6

^a The methyltins concentration range was 0.5–50 ng (Sn) mL⁻¹.

^b Obtained at concentration of 10 ng (Sn) mL⁻¹ for each tin species.

Table 3
Recoveries and concentrations of methyltin compounds in seawater samples collected in Bohai Sea (Yantai) ($n = 3$) by HPLC–HG–ICP/MS

Sampling site	Recovery (%) ^a			Concentration found (ng mL ⁻¹) ^b		
	MMT	DMT	TMT	MMT	DMT	TMT
Huangzhuang	104.0 ± 4.0	95.4 ± 2.0	97.0 ± 2.5	1.44 ± 0.06	0.57 ± 0.02	ND
Jiulaojumatou	95.8 ± 0.6	104.9 ± 1.0	98.0 ± 2.0	1.06 ± 0.05	0.31 ± 0.02	ND
Yueliangwan	108.0 ± 4.3	106.9 ± 1.5	103.7 ± 3.2	1.16 ± 0.08	0.33 ± 0.03	ND
Haishuiyuchang	106.0 ± 1.1	104.0 ± 0.7	101.7 ± 1.8	1.25 ± 0.05	0.35 ± 0.04	ND
Yugangmatou	96.0 ± 1.8	101.0 ± 1.6	96.7 ± 2.6	1.14 ± 0.06	0.33 ± 0.02	ND

^a Standards were spiked at 2 ng (Sn) mL⁻¹ for each tin species.

^b Values are means of three measurements ± standard deviation. ND = not detectable.

Table 4

Comparisons of the pretreatment procedures for methyltin analysis in water using AAS, GC and HPLC-based methods

Method	Sample	Pretreatment method	Reference
AAS	100 mL seawater or lake water	Volatile hydrides were generated using NaBH ₄ and then trapped in liquid nitrogen followed by sequential elution with increasing temperature and detection using AAS	[3]
GC-AAS	4–5 L water, Ontario Lakes and Rivers	Saturation with NaCl, extraction of 4–5 L water with 100 mL of benzene/0.5% tropolone. Extracts were evaporated to a small volume, butylated with butylmagnesium bromide. Then samples were cleaned up and concentrated	[6]
GC-AAS	Lake water (5–10 L)	Extraction with benzene containing tropolone from water saturated with sodium chloride, butylation to form tetramethylbutyltins. Then samples were cleaned up and concentrated	[7]
GC-FPD	SnCl ₂ reaction solution (1–2 mL)	Samples were placed in a centrifugation tube together with citric acid–NaH ₂ PO ₄ buffer solution (pH 5.0). The internal standard (MeSnPr ₃) and 0.1% tropolone–cyclohexane were added. The mixture was extracted in an ultrasonic bath and centrifuged twice at 3000 r min ^{−1} . Then, the organic phases were dried using anhydrous Na ₂ SO ₄ and reacted with <i>n</i> -PeMgBr (Grignard reagent) in an ultrasonic bath. Excess Grignard reagent was eliminated by the addition of 5% (v/v) H ₂ SO ₄ solution, and the organic phase was purified by anhydrous Na ₂ SO ₄ and Florisil. Finally, the eluted organic phase was concentrated to 2 mL under a stream of nitrogen	[11]
HPLC–HG–ICP/MS	200 µL water	Without any other pretreatment except being filtered with 0.4 µm filter membrane	This work

Table 5

Comparisons of the detection limits for methyltin analysis using HPLC coupled with different detectors

Method of detection	Detection limits (ng(Sn) mL ^{−1})	Reference
HPLC–HG–QSIL–FPD	MMT: 1.69; DMT: 0.51; TMT: 0.36	[27]
HPLC–Flame AAS	MMT: 380; DMT: 340; TMT: 320	[30]
HPLC–ICP/MS (with DIN)	MMT: 20; DMT: 16; TMT: 18	[31]
HPLC–ICP/MS	MMT: 0.46; DMT: 0.26; TMT: 1.26	[32]
MLC–ICP/MS	DMT: 1.02; TMT: 0.70	[33]
HPLC–HG–ICP/MS	MMT: 0.266; DMT: 0.095; TMT: 0.039	This work

existence of the methyltin compounds in different seas has been reviewed in previous literature [29].

Comparison of the pretreatment methods listed in Table 4 suggests that direct AAS method and GC-based methods need the more volume of natural waters and the solvent- and time-consuming pretreatment procedures. Compared with these methods, HPLC-based method reported in this paper has a great advantage due to no pretreatment step involved. The detection limits of methyltins for methods reported in literature using HPLC coupled with various detectors are listed in Table 5. The detection limits obtained with the present technique are markedly lower than HPLC–Flame AAS and HPLC–ICP/MS with direct injection nebulizer (DIN), and are about 5–20 times better than HPLC–HG–QSIL–FPD, micellar liquid chromatography (MLC)–ICP/MS and conventional HPLC–ICP/MS. This is the reason why this HPLC–HG–ICP/MS technique, rather than other techniques, can direct detect the methyltins in seawater.

4. Conclusions

HPLC was on-line coupled with hydride generation and ICP/MS for the speciation of methyltins in water samples. Speciation of methyltins in seawater samples can be rapidly and directly performed with high sensitivity and without interferences. Sample pretreatment steps can be avoided and the use of time and toxic

organic solvents can be greatly reduced. This hyphenated system also broadens the application of reversed phase HPLC and ICP/MS without the oxygen addition system for ICP/MS. This technique could also speciate methyltins in beverage, wine and other natural waters, such as tap water, lake water and river water. It is expected that this system could also be used for direct speciation of butyltins and phenyltins with appropriate modification of the interface (e.g. maintaining the temperature of the transfer line).

Acknowledgments

This work was supported by the National Natural Science Foundation of PR China (20577057 and 40503014) and by the State High Tech Development Plan (2006AA06Z424).

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