



Stir bar sorptive extraction with in situ derivatization and thermal desorption–gas chromatography–mass spectrometry for trace analysis of methylmercury and mercury(II) in water sample

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ABSTRACT

A method for the trace analysis of methylmercury (MeHg) and Hg(II) in water sample was developed, which involved stir bar sorptive extraction (SBSE) with in situ alkylation with sodium tetraethylborate and thermal desorption (TD)–gas chromatography–mass spectrometry (GC–MS). The limits of quantification of MeHg and Hg(II) are 20 and 10 ng L⁻¹ (Hg), respectively. The method shows good linearity and the correlation coefficients are higher than 0.999. The average recoveries of MeHg and Hg(II) in tap or river water sample are 102.1–104.3% (R.S.D.: 7.0–8.9%) and 105.3–106.2% (R.S.D.: 7.4–8.5%), respectively. This simple, accurate, sensitive, and selective analytical method may be used in the determination of trace amounts of MeHg and Hg(II) in tap and river water samples.

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1. Introduction

Mercury (Hg) is a well-known environmental pollutant that exists in three major forms: elemental Hg, a common form in air, inorganic Hg(II), and organic Hg, in particular, methylmercury (MeHg) [1]. However some microbes can convert inorganic forms of mercury into organic forms that can be accumulated by aquatic life. And, it has been reported that MeHg is most toxic to human. To evaluate the potential risks of various Hg species, they must be determined with highly sensitive and reliable methods. In the present study, we focused on the determination of MeHg and Hg(II) in water sample.

The maximum contaminant level goal (MCLG) is a non-enforceable level that is based solely on possible health risks and exposure. In the National Primary Drinking Water Regulations formulated by the Environmental Protection Agency (EPA), MCLG for mercury in drinking water is set at 2 ng mL⁻¹ [2]. Based on this MCLG, EPA has set an enforceable standard called maximum

contaminant level (MCL). MCL for mercury has also been set at 2 ng mL⁻¹ by EPA, since it is the lowest level to which water systems can reasonably be required to remove this contaminant should occur in drinking water. The World Health Organization (WHO) has set the guideline value for inorganic mercury in drinking water at 6 µg L⁻¹ [3]. In Japan, the Ministry of Health, Labour and Welfare of Japan has regulated the standard of water-purity for tap water for mercury species at 0.5 µg L⁻¹ [4].

Gas chromatography (GC) is generally used for the speciation of thermally stable and volatile species of Hg. The method generally involves alkylation of analytes prior to preconcentration [5–9]. Recently, solid phase microextraction (SPME) has been proposed as an alternative to liquid–liquid extraction (LLE) due to simplicity of use, high preconcentration ability, and the ability to extract volatile alkylated species [10]. In addition, the use of headspace solid phase microextraction (HS–SPME) for the determination of MeHg or Hg(II) in water sample has been reported [8,11–14]. More recently, stir bar sorptive extraction (SBSE) was introduced by Baltussen et al. [15], as another preconcentration technique in which a stir bar coated with 50–300 µL of polydimethylsiloxane (PDMS) is employed to extract analytes from a variety of matrices [16–18]. In addition, the use of headspace stir bar sorptive extraction (HS–SBSE) for the trace

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Table 1
Figures of merit of SBSE with in situ derivatization and TD–GC–MS

Compound	SIM ^a (<i>m/z</i>)	LOD ^b (ng L ⁻¹)	LOQ ^c (ng L ⁻¹)	Range (μg L ⁻¹)	Correlation coefficient (<i>r</i>)	Amount spiked (0.5 g L ⁻¹)			
						Tap water		River water	
						Recovery (%)	R.S.D. (%) ^d	Recovery (%)	R.S.D. (%) ^d
MeHg	<u>246</u> , 217	5	20	0.02–5	0.999	102.1	7.0	104.3	8.9
Hg(II)	<u>260</u> , 231	2	10	0.01–5	0.999	105.3	7.4	106.2	8.5

^a The underlined number is the *m/z* of the ion used for quantification.

^b LOD: limit of detection (*S/N* = 3).

^c LOQ: limit of quantification (*S/N* > 10).

^d Recoveries and precision were also examined by replicate analysis (*n* = 6) of water samples.

analysis of MeHg and butyltin species in environmental sample has been reported [19]. However, HS-SBSE requires an extraction time of 2 h.

The aim of this study was to determine trace amounts of MeHg and Hg(II) in water samples by SBSE with in situ alkylation with sodium tetraethylborate and TD–GC–MS.

2. Experimental

2.1. Materials and reagents

Methylmercury(II) chloride standard and mercury(II) chloride standard were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Other reagents and solvents were purchased from Wako Pure Chemical Inc. (Osaka, Japan). Sodium tetraethylborate (NaBEt₄) was purchased from Hayashi Pure Chemicals Inc. (Osaka, Japan). NaBEt₄ was used as the derivatization reagent, and was dissolved in purified water prior to use. The water purification system was a Milli-Q gradient A 10 equipped with an EDS polisher (Millipore, Bedford, MA, USA).

Calibrators for eight-point calibration (0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 μg L⁻¹) of MeHg and nine-point calibration (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 μg L⁻¹) of Hg(II) were prepared by the addition of purified water and calibrators were analyzed by using SBSE with in situ derivatization.

2.2. Instrumentation

TD was performed with a Gerstel TDS 2 thermodesorption system equipped with a Gerstel TDS A autosampler and a Gerstel Cooled Injection System (CIS) 4 programmable temperature vaporization (PTV) inlet. GC–MS was performed with an Agilent 6890N gas chromatograph equipped with a 5973N mass-selective detector with an ultra ion source (Agilent Technologies).

Stir bars coated with a 0.5-mm-thick PDMS layer (24 μL; TwisterTM) were obtained from Gerstel (Mülheim an der Ruhr, Germany). The stir bars were conditioned for 1 h at 300 °C in a flow of helium. Then, the stir bars were kept in new 2 mL vials until immediately prior to use. The stir bars could be used more than 50 times with appropriate re-conditioning. For the extraction, a 20-mL headspace vial from Agilent Technologies (Palo Alto, CA, USA) was used.

2.3. TD–GC–MS conditions

The TDS 2 temperature was programmed from 20 (held for 1 min) to 200 °C (held for 5 min) at 60 °C min⁻¹. The desorbed compounds were cryofocused in the CIS 4 at –150 °C. After the desorption, the CIS 4 temperature was programmed from –150 to 300 °C (held for 10 min) at 12 °C s⁻¹. Injection was performed in the splitless mode. Separations were conducted on a DB-1 fused silica

column (60 m × 0.25 mm i.d., 1 μm film thickness, J&W Scientific, Agilent Technologies). Oven temperature was programmed from 40 to 220 °C (held for 2 min) at 10 °C min⁻¹. Helium was used as the carrier gas at a flow rate of 1.0 mL min⁻¹. The mass spectrometer was operated in the selected ion-monitoring (SIM) mode with electron ionization (ionization voltage: 70 eV). SIM monitoring ions are shown in Table 1.

2.4. Sample preparation

Ten millilitres of tap water or river water was pipetted into a 20-mL headspace vial. A PDMS stir bar, 2 M sodium acetate buffer (pH 5, 200 μL) for pH adjustment, and NaBEt₄ as the derivatization reagent were added and the vial was crimped with a Teflon-coated silicone septum cap. SBSE with in situ derivatization was performed at room temperature for 15 min while stirring at 1000 rpm. After the extraction, the stir bar was easily removed with forceps (due to magnetic attraction), rinsed with purified water, dried with lint-free issue, and placed inside a glass TD tube. The TD tube was then placed in the TD system where the stir bar was subjected to TD–GC–MS.

3. Results and discussion

3.1. Optimization of GC–MS conditions

Stir bar sorptive extraction with in situ derivatization followed by GC–MS analysis of the standard solutions of MeHg and Hg(II) in the scan mode was performed by EI–MS. The mass spectra of the derivatives of MeHg and Hg(II) are shown in Fig. 1. As shown in Fig. 1, isotopic ions of mercury were observed. As for mercury, the maximum isotopic abundance (approx. 29.86%) is ²⁰²Hg, following to ²⁰⁰Hg (approx. 23.1%).

For SIM, the following ions were monitored: *m/z* 246, 217 for the derivative of MeHg, and *m/z* 260, 231 for the derivative of Hg(II). The underlined number is the *m/z* of the ion used for quantification.

3.2. Optimization of derivatization conditions

One important parameter affecting SBSE with in situ derivatization was the volume of the derivatization reagent. In this regard, optimization of the volume of 0.5% NaBEt₄ solution was performed using 0.5 μg L⁻¹ standard solutions of MeHg and Hg(II). The derivatives of MeHg and Hg(II) in 10 mL of respective standard solutions, which were obtained by SBSE with in situ derivatization, were subjected to TD–GC–MS, and the results are shown in Fig. 2. When the volume of 0.5% NaBEt₄ solution was 10 μL, the derivatives of MeHg and Hg(II) in 10 mL of the respective standard solutions after SBSE with in situ derivatization gave a maximum response. Therefore, 10 μL was considered to be the optimal volume of 0.5% NaBEt₄ solution added.

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