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Dielectric barrier discharge induced atomization of gaseous methylethylmercury after $NaBEt_4$ derivatization with purge and trap preconcentration for methylmercury determination in seawater by GC-AFS

Qian He[a], Xueke Yu[b], Yanbin Li[a], Huijun He[a], Jing Zhang[a,c,*]

[a] Key Lab of Marine Chemistry Theory & Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China
[b] College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China
[c] Earth and Environmental System, Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, Japan

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ABSTRACT

A novel method suitable for methylmercury (CH_3Hg) analysis in seawater by gas chromatography (GC)-atomic fluorescence spectrometry (AFS) based on dielectric barrier discharge (DBD) induced atomization of gaseous methylethylmercury ($CH_3HgC_2H_5$) after sodium tetraethylborate ($NaBEt_4$) derivatization with purge and trap preconcentration was developed in this work. In the proposed method, with $NaBEt_4$ used as derivatization reagent, the nonvolatile CH_3Hg could be converted to the gaseous $CH_3HgC_2H_5$ and trapped in a quartz tube with Tenax sorbent for preconcentration. A DBD atomizer was employed for the atomization of $CH_3HgC_2H_5$ to Hg^0 between the GC separation and AFS detection instead of the conventional thermal decomposition atomizer, which had not been reported before. The DBD atomizer not only produces a comparable atomization efficiency for $CH_3HgC_2H_5$ to the thermal decomposition atomizer, but also can be operated at room temperature with low power consumption (5 W). The effects of DBD input discharge voltage, DBD discharge distance, N_2 gas purge time, and thermal desorption time on CH_3Hg determination were evaluated. The method provided good reproducibility (RSD, 2.0%) and low detection limits of CH_3Hg (LOD, 0.0008 ng L^{-1}). The proposed method was validated by the analysis of a certified reference material (GBW08675) and successfully applied to the determination of CH_3Hg in sub ng L^{-1} level in different seawater samples.

1. Introduction

Among the most concerned heavy metals, mercury has been considered as one of the most toxic elements for human health, while methylmercury (CH_3Hg) has been proved to be the most toxic mercury species [1]. As CH_3Hg is liable to enter and finally accumulated in human body through the seafood chain, detection of CH_3Hg at trace levels in seawater is of great significance to evaluate the risk of mercury exposure to human beings.

The detection limits of CH_3Hg by the common method were usually in sub μg L^{-1} level [2,3]. However, CH_3Hg in seawater is normally at trace and even ultra-trace levels (< 1 ng L^{-1}) [4]. In these cases, a preliminary preconcentration step is preferred [5]. Prevailing preconcentration techniques, such as solid-phase extraction [6–12], cation or anion exchange column preconcentration [1,13], sodium tetraethylborate ($NaBEt_4$) or sodium tetraphenylborate ($NaBPr_4$) derivatization with purge and trap preconcentration [14,15] or headspace extraction preconcentration [16] had been utilized for the determination of CH_3Hg in seawater or other samples. Among them, $NaBEt_4$ or $NaBPr_4$ derivatization with purge and trap preconcentration was most attractive and commonly utilized, attributed to its virtues of low detection limits of CH_3Hg (< 5 pg L^{-1}) [14,15] (see Table 1) and easy operation. Taking $NaBEt_4$ derivatization for example, in the process of $NaBEt_4$ derivatization with purge and trap preconcentration for CH_3Hg determination, the sample is first reacted with $NaBEt_4$, to convert the nonvolatile CH_3Hg to gaseous methylethylmercury ($CH_3HgC_2H_5$). This volatile adduct is then purged from solution, and trapped on a graphitic carbon column at room temperature. The $CH_3HgC_2H_5$ is then thermally desorbed from the column and separated by gas chromatography (GC) and finally analyzed by cold vapor atomic fluorescence spectrometry (AFS) or inductively coupled plasma mass spectrometry (ICP-MS). To detect the level of CH_3Hg in seawater, AFS is more simple than ICP-MS. However, the 900 °C thermal atomizer between the GC separation and cold vapor AFS detection to decompose $CH_3HgC_2H_5$ to Hg^0 limits the analysis to some extent, due to its high temperature and high electric power. Thus, there is a need to develop an atomizer with low

* Corresponding author at: Key Lab of Marine Chemistry Theory & Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China.
E-mail address: jzhang@sci.u-toyama.ac.jp (J. Zhang).

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Table 1
The LODs in different preconcentration methods for CH_3Hg determination in seawater.

Preconcentration method	Detection method	CH_3Hg LOD (ng L^{-1})	References
Derivatization and dynamic headspace in-tube extraction	GC-ICPMS	0.08	[16]
Sulfhydryl cotton fiber as adsorbent for solid-phase extraction	GC-AFS	0.01	[7]
Fe_3O_4/polyaniline nanoparticle as adsorbent for solid-phase extraction	GC–MS	100	[9]
Thiol-functionalized silica microspheres as adsorbent for solid-phase extraction	HPLC-ICPMS	0.013	[8]
Sulfur-based sorption material as adsorbent for solid-phase extraction	HPLC-CV-AFS	0.04	[6]
Cation exchange column preconcentration	HPLC-ICPMS	0.016	[1]
Anion exchange guard column preconcentration	HPLC-ICPMS	0.01	[13]
$NaBEt_4$ derivatization purge and trap preconcentration	GC-Pyr-AFS	0.003	[14]
$NaBPr_4$ derivatization purge and trap preconcentration	GC-Pyr-AFS	0.001–0.002	[15]
$NaBEt_4$ derivatization purge and trap preconcentration	GC-DBD-AFS	0.0008	This work

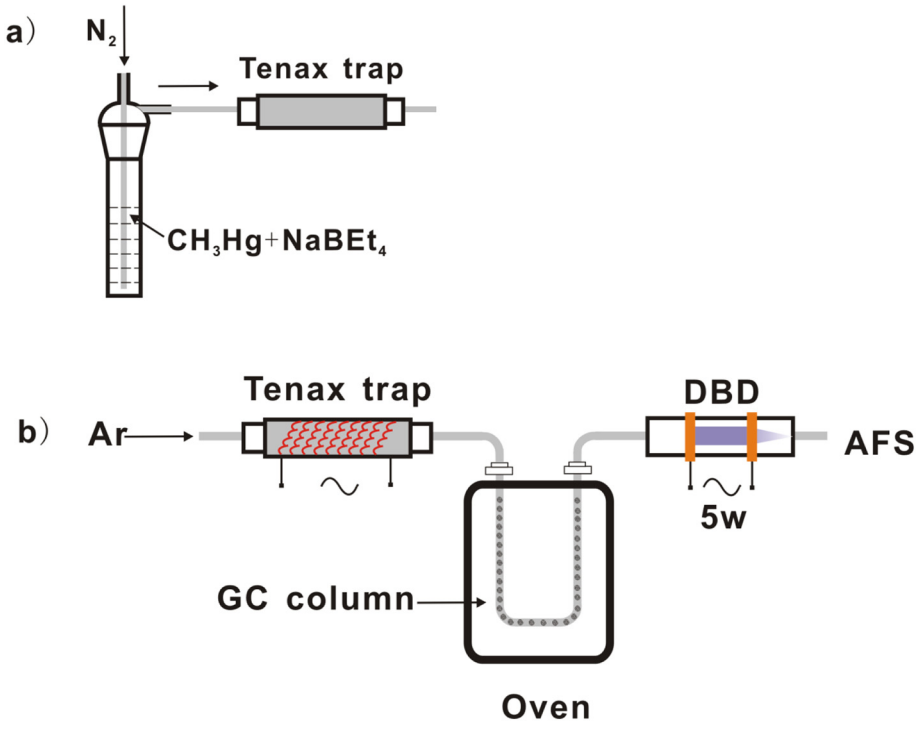

Fig. 1. Schematic diagram of DBD induced atomization after $NaBEt_4$ derivatization with purge and trap preconcentration for CH_3Hg determination by GC-AFS. a) The schematic diagram of $NaBEt_4$ derivatization following with purge and trap; b) the schematic diagram of thermal desorption following with determination by GC-AFS with DBD as atomizer.

temperature and low power for $CH_3HgC_2H_5$ atomization.

In the previous studies, dielectric barrier discharge (DBD) was widely used in the field of atomic spectrometry [17], *i.e.*, excitation source [18], ionization source [19], induced vapor generation [20], and atomizer [21–33]. It is highly efficient for the atomization of hydrides and can be operated at room temperature with low power consumption (5 W). Zhu et al. [25] and Yu et al. [26] all validated the feasibility of methylmercury hydride (CH_3HgH) atomization by a DBD atomizer. Thus, it makes sense to study the atomization behavior of $CH_3HgC_2H_5$ by DBD atomizer.

In this work, a new method suitable for CH_3Hg analysis in seawater by GC-AFS through DBD induced atomization of $CH_3HgC_2H_5$ after $NaBEt_4$ derivatization with purge and trap preconcentration was described. The DBD could be effectively used to atomize $CH_3HgC_2H_5$ into Hg^0 at room temperature with low power consumption (< 5 W). The effects of instrument configuration, including DBD input discharge voltage, DBD discharge distance, N_2 gas purge time, and thermal desorption time, on CH_3Hg determination were evaluated in this work. Finally, the applicability of the proposed method on determination of CH_3Hg at sub ng L^{-1} level in seawater was tested.

2. Experiment

2.1. Instrument

A Model III AFS (Brooks Rand, USA) with a low pressure mercury lamp (253.7 nm) was used to detect the Hg^0 species. The PMT voltage of AFS was set as −620 V. A GC column (Dalian Zhonghuida Scientific Instrument Co., Ltd., China) was used to separate the derivative $CH_3HgC_2H_5$ from other species. The GC column consisted of a 4 mm (inner diameter) × 6 mm (outer diameter) U-shaped silanized glass column packed with 15% OV-3 (phenyl methyl dimethyl silicone 10% phenyl) on Chromasorb White (acid-washed, dimethyldichlorosilane treated). The column temperature of GC was set as 70 °C. The Ar gas flow rate of GC was set as 30 mL min^{-1}. A DBD atomizer was used to atomize the derivative mercury species to Hg^0. In DBD atomizer, two pieces of copper foil (6 mm wide, 20 mm length) pasted around a quartz tube (4 mm i.d., 6 mm o.d.) parallelly with a distance about 10 mm were operated as the electrodes, and the quartz tube was operated as the dielectric. A commercial ozone generator power supply (5 W, Guangzhou Jinshi Electronic Equipment Co., Ltd., Guangzhou, China) was connected to the two copper foil electrodes to sustain the DBD plasma.