



The application of gas chromatography-time-of-flight mass spectrometry to the analysis of monomethyl mercury at sub-picogram levels

Yong-Hyun Kim ^a, Ki-Hyun Kim ^{a,*}, Hye-On Yoon ^b, Richard J.C. Brown ^c

^a Department of Environment & Energy, Sejong University, Seoul, Korea

^b Korea Basic Science Institute, 126-16, 5th St., Anam-dong, Seongbuk-gu, Seoul, Korea

^c Analytical Science Division, National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK

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ABSTRACT

The analysis of sub-picogram-range methyl mercury generally requires complicated hyphenated instrumentation combining chromatographic systems for the separation and identification of organic Hg components (by GC–MS or LC–MS) and inorganic mass spectrometric techniques for their quantification. To eliminate the complexities and possible biases associated with such complicated hyphenated systems, it is highly desirable to develop a simplified but reliable single-stage instrumental method for the analysis of methyl mercury in environmental samples. To this end, this paper presents an analytical technique based on thermal desorption (TD) – GC – time of flight (TOF) mass spectrometry (MS) for the quantitative analysis of monomethyl mercury (MMHg) prepared in a liquid phase standard. This optimized system was calibrated using standards in the range of 18 pg to 45 ng and yielded a coefficient of correlation of $R^2 = 0.9996$. This GC-TOF-MS system allowed very low detection limits for MMHg (MDL = 1.86 pg and LOD = 0.031 pg) with good reproducibility (RSE = 1.82%). The potential applicability of the GC-TOF-MS system is highlighted for the trace-level analysis of sub-pg-range of methyl mercury.

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1. Introduction

Mercury is a well-known toxic environmental pollutant that exists mainly in its elemental form [1–3]. Elemental mercury can be converted into highly toxic organo-mercury compounds by biological processes such as biomethylation [1,4,5]. Although organic mercury is generally much less abundant than its inorganic counterparts, it may easily bioaccumulate in terrestrial and aquatic biosystems, resulting in highly Hg-contaminated environmental reservoirs (e.g., landfill gas). As a result, mono-methyl mercury (MMHg), which is more toxic than any inorganic Hg species, is the principal form of Hg found in fish [6]. In this way, MMHg may be concentrated in the human body as a result of the dietary intake of fish [7,8]. Indeed, consumption of fish accounts for over 99% of the total human intake of methyl mercury [9]. Consequently, the World Health Organization (WHO) and the U.S. Environmental Protection Agency (US EPA) have established regulatory guidelines to limit the allowable concentration of methyl mercury in water and fish [10].

Evidence collected over the past decades suggests that increases in the atmospheric deposition of Hg have been observed both regionally and hemispherically [11]. Although methylated species represent at any one time only a minor fraction of compounds in the Hg cycle, global atmospheric changes are expected to exert an influence on

their presence in the atmosphere [12]. Hence, similar to the case of fish and the aquatic reservoir, it is thus important to monitor and regulate methyl mercury in air, as its presence poses significant threats to human health [13,14].

In order to analyze methyl mercury at the sub-picogram range, a combination of two separate analytical systems (steps) has commonly been employed. The first stage most usually employs GC or GC–MS to separate (and identify) methyl mercury from other organic species. The next stage determines the quantity of methyl mercury separated during the first step by spectrometric approaches such as atomic fluorescence spectrometry (AFS) [15,16], atomic absorption spectrometry (AAS) [17,18], and inductively coupled plasma mass spectrometry (ICP-MS) [15,19–21]. Alternatively, GC–MS with a derivatization approach has been examined as a possible means to analyze methylated Hg in environmental samples [22,23]. In fact, the application of hyphenated analytical systems has been favored in the literature because it can provide the optimum balance between separation and detection. However, as a hyphenated system is generally built by two or more independent instrumentations, many laboratories cannot afford such an investment. Moreover, for the application of such system, a number of practical issues should be resolved [24]. As the system is difficult to operate (e.g., complicated conditions for the synchronization of the operation parameters), it generally requires highly trained staff to reduce or suppress systematic biases due to the interface structure.

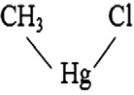
It is well known that a single GC-time of flight-mass spectrometry (GC-TOF-MS)-based platform is a superior tool for the analysis of

* Corresponding author. Tel.: +82 2 499 9151; fax: +82 2 3408 4320.

E-mail address: khkim@sejong.ac.kr (K.-H. Kim).

Table 1

Basic information concerning the target compound, methyl mercury chloride and preparation of its standard solutions.

A. Basic information of methyl mercury chloride (MMC)			
MW (g mol ⁻¹):	251.08		
Density (g mL ⁻³):	4.063		
Melting point (°C):	170		
Formula:	CH ₃ HgCl		
CAS number:	115-09-3		
B. Preparation of liquid phase MMC primary standard (PS)			
	Compounds	6 N HCl	MMC
Primary grade	Concentration (%)	100	95.0
Chemical	Density (g mL ⁻¹)	1.10	4.06
Primary standard (PS)	Bulk mass (mg)	220,400	316
	Real mass (mg)	220,400	300
	Volume (mL)	201	0.08
	Concentration		1492
	(ng μL ⁻¹)		
C. Eight-point calibration of MMC using both the first and second working standards (WSs)			
Order	Mixing volume (μL)	Concentration ^a	
		Standard	Methanol
			MMC
[1] The second working standard (2-WS) at four concentration levels			
	1st WS ^b		
1	40	19,960	0.018
2	100	19,900	0.045
3	200	19,800	0.090
4	2000	18,000	0.895
[2] The first working standard (1-WS) at four concentration levels			
	PS		
5	60	19,940	4.48
6	120	19,880	8.95 ^b
7	240	19,760	17.9
8	600	19,400	44.8

^a Equivalent to the absolute mass (ng) of MMC loaded on the sorbent tube (ST) for the actual 1 μL injection.

^b The second out of the four level 1-WS (8.95 ng μL⁻¹) used for the 2-WS.

low-level VOC samples [25]. Hence, if GC-TOF-MS is coupled with thermal desorption (TD) technique, this combined method can be applied further to cover virtually all concentration levels of complex target components in diverse environmental matrices. In light of a

wide feasibility of TD-GC-TOF-MS, its applicability has been investigated for the analysis of mono-methyl mercury (MMHg) as an alternative to more complicated hyphenated systems.

2. Materials and methods

2.1. Preparation of working standards

In this study, primary-grade methyl mercury chloride (MMC) with a purity of 95.0% was used (Alfa Aesar, UK) (Table 1) to prepare calibration standards. 37% hydrochloric acid (HCl) was used as a solvent (Merck, Germany) to dissolve the MMC. The working standards (WSs) were then made by multi-step gravimetric dilution of this stock solution with methanol (Burdick & Jackson, USA) (Table 1).

A 37% HCl solution was diluted with distilled water to make a 6 N HCl solution. For the preparation of the primary standard (PS), 316 mg of MMC was mixed with 220,400 g of the 6 N HCl solution to yield a concentration of 1492 ng μL⁻¹. The 1st WS was then prepared by dilution of the PS (8.95 ng μL⁻¹). Eight final working standards (F-WS) (0.018, 0.045, 0.090, 0.895, 4.48, 8.95, 17.9, and 44.8 ng μL⁻¹) were prepared as dilutions of the PS and 1st WS.

2.2. Instrumental system

In this study, a GC system (Agilent GC 7890A, USA) equipped with TOF-MS (Almsco Bench TOF-dx, UK) was used for the quantitation of MMC. For the preconcentration of MMC, a TD trap and desorption system (Unity, Markes International, Ltd, UK) was used. In order to perform adsorption and desorption of MMC inside the TD system, the cold trap was packed with a thoroughly mixed equi-volume ratio of Tenax TA and Carboxen B. The temperatures (and times) of adsorption and desorption for the TD system were set at -10 °C (5 min) and 320 °C (20 min), respectively. The MMC was separated on a CP-Wax column (diameter: 0.25 mm, length: 30 m, and thickness: 0.25 μm, Agilent). The column temperature was ramped up at 20 °C min⁻¹ from an initial temperature of 100 °C to the final temperature of 210 °C. The MMC was separated in a splitless injection mode with helium carrier gas at a flow rate of 1.2 mL min⁻¹ for the detection by TOF-MS. Total ion chromatogram (TIC) mode was used over a mass range of 35 to 260 m/z with the interface and ion source temperatures set at 230 °C. The results from the TIC mode were then converted to extracted ion chromatogram (EIC) mode for optimum detection of the MMC. Four mass ranges, including the main spectrum

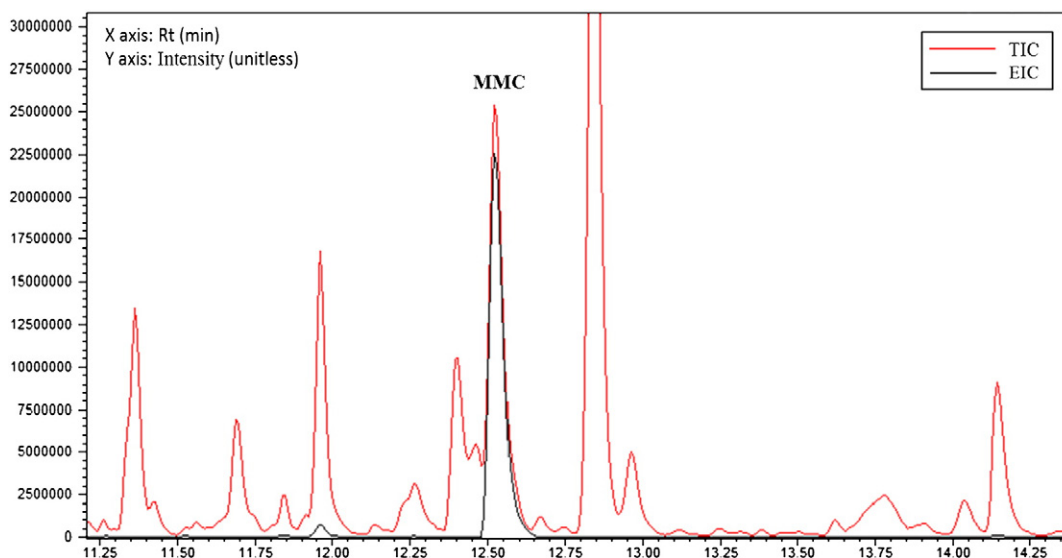


Fig. 1. Chromatogram of 4.48 ng μL⁻¹ of F-WS determined by the two scan modes (TIC vs. EIC).

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