

# Simultaneous Speciation of Monomethylmercury and Monoethylmercury by Aqueous Phenylation and Purge-and-Trap Preconcentration Followed by Atomic Spectrometry Detection

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A new method for the detection of trace levels of organomercury species has been developed by combining the high enrichment capacity of purge and trap with aqueous phenylation derivatization. Phenylation products of monomethylmercury (MeHg) and monoethylmercury (EtHg) were first separated by capillary gas chromatography and then detected by atomic fluorescence spectrometry (AFS) or inductively coupled plasma mass spectrometry (ICPMS). This combination made it possible to simultaneously quantify trace or ultratrace level of MeHg and EtHg in environmental samples. Method detection limits were 0.03 ng/L for both MeHg and EtHg when AFS was used as the detector and 0.02 and 0.01 ng/L for MeHg and EtHg with ICPMS, respectively. Certified reference materials, IAEA-405 and DORM-2, were analyzed and the results were in accordance with certified values. Both MeHg and EtHg were detected in sediment samples collected from the Florida Everglades and a Canadian wetland. This new method has been validated for the direct detection of trace organomercury species in freshwater samples and has the additional benefits of being free from interference by  $\text{Cl}^-$  and dissolved organic matter.

Mercury is a global pollutant that is distributed in the environment through natural and anthropogenic processes. Monomethylmercury (MeHg), the most prevalent species of organomercury, has been intensively investigated because it is a neurotoxin that is known to accumulate in food webs. In contrast, information on the levels of other organomercury species in environmental and biological samples is limited. For example, monoethylmercury (EtHg) has been detected in soil, sediment, and biological reference materials; however, the small number of reports are insufficient to support definitive conclusions about the prevalence of this species in the environment.<sup>1–6</sup> The main reason for this

discrepancy in the field is that while methods for MeHg quantification are well developed, reliable and sensitive methods for the analysis of EtHg in various environmental matrixes remain inadequate. Thus the development of new methods that are capable of accurately identifying and quantifying mercury species in environmental and biological matrixes is critical to our understanding of mercury biogeochemistry and toxicity.

One of the most widely used techniques for organomercury speciation is gas chromatography (GC) coupled with various detectors. Prior to GC separation, MeHg and EtHg need to be derivatized to fully alkylated volatile species. Several derivatization techniques, including the Grignard reaction and aqueous ethylation/propylation/phenylation, have been used for this purpose. Aqueous ethylation using sodium tetraethylborate ( $\text{NaBET}_4$ ) is the most commonly used technique and can be easily coupled with a purge-and-trap preconcentration step, followed by detection with an elemental specific detection methods such as atomic fluorescence spectrometry (AFS)<sup>7,8</sup> or inductively coupled plasma mass spectrometry (ICPMS).<sup>9</sup> This combination creates a method that is sensitive enough to detect trace levels of MeHg in environmental samples. Unfortunately, the use of aqueous ethylation with the commonly used reagent,  $\text{NaBET}_4$ , has significant limitations and drawbacks.

The major drawback of aqueous ethylation is that it can only transfer ethyl groups to ionic mercury species. As a consequence, this method cannot distinguish EtHg from inorganic mercury ion ( $\text{Hg}^{2+}$ ) because the ethylation of both ions forms the same product, diethylmercury. In addition, aqueous ethylation using  $\text{NaBET}_4$  suffers from serious matrix effects. High levels of chloride ion and dissolved organic matter (DOM) strongly interfere with the ethylation process and decrease the sensitivity and reproduc-

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ibility of the overall method.<sup>7,10–12</sup> Consequently, seawater and organic-rich freshwater samples have to be “cleaned” by extraction/back-extraction or distillation, prior to aqueous ethylation.<sup>7,13</sup> Although these cleaning processes negate the matrix effects, they make the analysis more tedious and cause potential analytical errors. For instance, artifact formation of MeHg during distillation could be problematic, especially when dealing with sediment and organic-rich freshwater contaminated with divalent mercury ( $\text{Hg}^{2+}$ ).<sup>14</sup> Furthermore,  $\text{NaBEt}_4$  solubilized in water is unstable and needs to be freshly made and handled under protective gas. These additional processes increase the analytical difficulty and cost of using  $\text{NaBEt}_4$  for aqueous derivatization.

Other aqueous derivatization reagents have been investigated as alternatives to  $\text{NaBEt}_4$ , including sodium (*n*-propyl)borate ( $\text{NaBPr}_4$ )<sup>15–17</sup> and sodium phenylborate ( $\text{NaBPh}_4$ ).<sup>18–21</sup> Coupled with headspace solid-phase microextraction (SPME)-GC-atomic emission detection, propylation using  $\text{NaBPr}_4$  has the potential for organomercury analysis in environmental samples since method detection limits as low as 0.016 ng/L (for MeHg) can be reached after optimization.<sup>17</sup> The advantages of propylation also include the ability of distinguishing  $\text{Hg}^{2+}$  from EtHg. However, aqueous  $\text{NaBPr}_4$  solution is also unstable and the propylation reaction suffers from matrix effects when dealing with seawater.<sup>22,23</sup> Depending on the purity of the derivatization agent used, artifact formation of EtHg during aqueous propylation is sometimes a problem. For example, up to 2.9%  $\text{Hg}^{2+}$  was reported to be converted to EtHg during the propylation reaction in a previous study.<sup>24</sup> In contrast, the aqueous solution of  $\text{NaBPh}_4$  is very stable and the phenylation reaction is not subject to interferences from the presence of chloride ion or decomposed tissues.<sup>18,25</sup> In combination with liquid/liquid extraction (LLE) and SPME, aqueous-phase phenylation has been used for the analysis of organomercury species in biological and soil/sediment samples.<sup>18,19,21,26,27</sup> However, the detection limits when using LLE/SPME-aqueous phenylation are too high for the analysis of trace

level organomercury in some environmental matrixes, especially in water samples.

To overcome this limitation introduced by LLE and SPME, adding a preconcentration step such as purge and trap would be expected to provide a much better enrichment factor. The goal of this study was to develop an aqueous-phase phenylation-purge and trap preconcentration-GC separation and AFS or ICPMS detection method for organomercury speciation analysis. The preconcentration capacity of the purge-and-trap technique combined with the sensitivity of AFS or ICPMS detector created a new method for the simultaneous determination of MeHg and EtHg in environmental samples, with low detection limit, ease in handling, and less interference. This new method was particularly useful for direct analysis of freshwater sample because it was unnecessary to clean the samples by extraction or distillation before the derivatization.

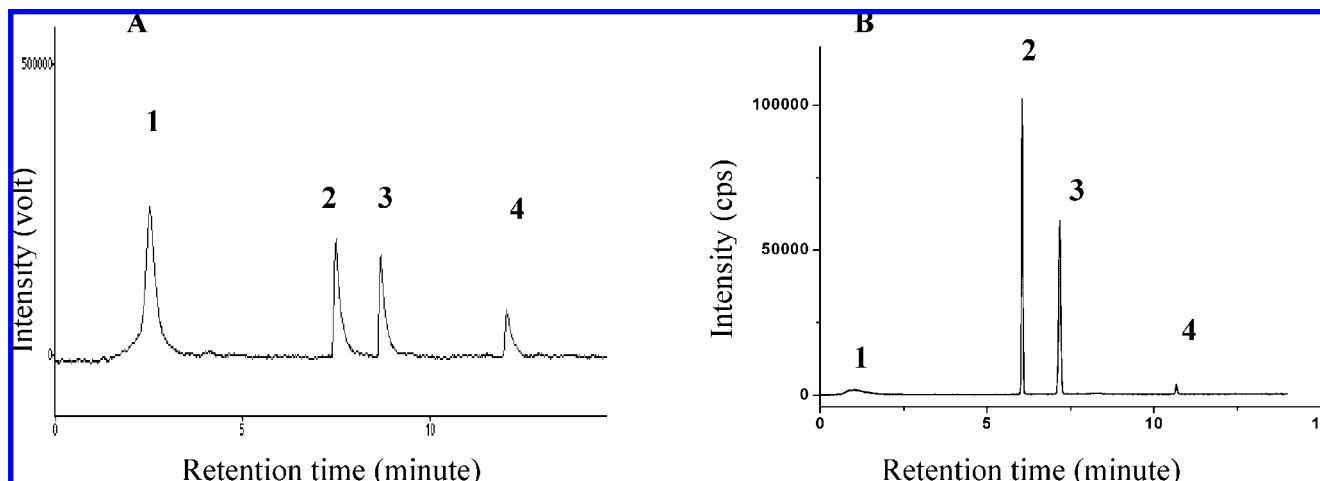
## EXPERIMENTAL SECTION

**Chemicals and Materials.** All mercury standards were purchased from Ultra Scientific (N. Kingstown, RI). Standard solutions of methylmercury chloride ( $\text{MeHgCl}$ ) and ethylmercury chloride ( $\text{EtHgCl}$ ) were prepared by dissolving the standards in methanol and storing the solutions in dark brown glass bottles at room temperature (20 °C).  $\text{NaBPh}_4$  (98%) was purchased from Strem (Newburyport, MA). Solutions of  $\text{NaBPh}_4$  (1%) were prepared monthly in deionized water. Citric buffer (pH 5.0, 1 M) was prepared by dissolving 210 g of citric acid monohydrate (certified ACS) and 423.2 g of sodium citrate dihydrate (certified ACS) in deionized water to give a final volume of 1 L. Humic acid (sodium salt, 50–60% as humic acid) was purchased from Thermo Fisher Scientific Inc. IAEA-405, an estuarine sediment with a certified MeHg value of  $5.49 \pm 0.53$  ng/g (as Hg), was purchased from International Atomic Energy Agency (Vienna, Austria). DORM-2, a dogfish muscle homogenate with a certified MeHg value of  $4.47 \pm 0.32$  mg/kg, was purchased from National Research Council of Canada (Ottawa, Ontario, Canada). Other reagents used were of reagent grade or higher. All the gases used were passed through activated charcoal traps to remove mercury background.

**Instrumentation.** Aqueous phenylation reactions were performed in 200-mL glass bubblers purchased from Brooks Rand LLC (Seattle, WA). The traps used for retaining mercury species were GC inlet liners for ATASOptic 2 (Product No. 2632605, Supelco, Bellefonte, PA). The liners were packed with 0.04 g of Tenax (60/80 mesh, Supelco) and plugged with silanized glass wool on both ends to hold the Tenax grains in place. The end of the liner without the frit faced the bubbler during purge and faced the column when being inserted into the GC injection port. Connections between different components of the system were made by Teflon tubing with various diameters.

A P.S. Analytical mercury speciation system (model PSA 10.723, P S Analytical Ltd., Kent, England) was used to analyze mercury adsorbed on the traps. This system consists of a capillary GC (model GC94, Ai Cambridge, UK) coupled to mercury AFS (PSA Merlin) via a pyrolysis oven maintained at 800 °C. Makeup gas is introduced after the pyrolysis oven via a three-way Teflon Union Tee. This GC possesses a temperature-programmable injection port.<sup>20</sup> A fused-silica capillary column (15 m  $\times$  0.53 mm i.d., coated with DB-1 film of 1.5- $\mu\text{m}$  thickness) was used for mercury separation. The column temperature was programmed

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**Figure 1.** Typical chromatograms of deionized water spiked with MeHg and EtHg standards and analyzed by aqueous phenylation followed by purge and trap-GC-AFS (A) and ICPMS (B): (1)  $\text{Hg}^0$ , (2) MeHgPh, (3) EtHgPh, and (4)  $\text{HgPh}_2$ .

to change temperature as follows: 50 °C for 1 min, ramp from 50 to 150 °C at a rate of 20 °C/min, maintain 150 °C for 1 min, ramp to 250 °C at a rate of 20 °C/min, and maintain 250 °C for 3 min. A split/splitless injector was used in splitless mode and programmed to ramp from 40 to 200 °C at a rate of 16 °C/s. The carrier gas, makeup gas, and sheath gas flows were 4, 30, and 150 mL/min of argon, respectively. A real-time data acquisition system (EZChrom, version 2.10) was used for data processing.

In order to test the feasibility of using a regular GC without a temperature-programmable injection port and using ICPMS as the detector, a PerkinElmer AutoSystem XL GC (PerkinElmer, Waltham, MA) was modified and coupled with an Elan DRC-e ICPMS (PerkinElmer). The GC flame ionization detector was replaced with a quartz tube (12 cm  $\times$  0.635 cm i.d.) wrapped with a nichrome heating coil (2 $\Omega$ ). The temperature of the quartz tube was maintained at 800 °C. An uncoated fused-silica capillary column (20 cm  $\times$  0.53 mm i.d.) passing through the quartz tube was connected to the ICPMS via a Teflon tubing and a three-way Teflon Union Tee, which was used to introduce nebulizer gas to the ICP. The injection port and the detector of the GC were set at 200 and 250 °C, respectively. The GC column temperature program was similar to that of the GC94. The GC injection port was capped quickly after insertion of the trap to avoid any loss of mercury during this time period. The main parameters for ICPMS were set to a nebulizer gas flow 1.05 L/min and an ICP rf power 1300 W.  $^{202}\text{Hg}$  was monitored.

**Experimental Design.** MeHg and EtHg standards were used for method development and optimization. Several factors that could affect the performance of the method, such as purge time and temperature, were tested and optimized separately. Method performance was validated by analyzing Certified Reference Materials (CRMs) and real samples. Details of each trial are described in the Supporting Information.

Freshwater samples were collected from several locations in the Florida Everglades. Nylon screen (100  $\mu\text{m}$ ) was used to remove large particles from water. The samples were acidified using concentrated HCl (4 mL/L sample) and then analyzed directly without any pretreatment.

Surface sediment/soil samples from the Florida Everglades and a Canadian wetland were collected in polyethylene specimen

cups, which were doubly bagged with polyethylene Zip-lock bags. The samples were kept on ice in a cooler during transport and were transferred into a refrigerator (4 °C) upon arrival in the laboratory. Organomercury species in sediments and IAEA-405 were isolated following the  $\text{KBr}/\text{CuSO}_4$  extraction method.<sup>19</sup> DORM-2 was digested using a modification of Bloom's method.<sup>7</sup> Details of the isolation of organomercury from soil/sediment samples and CRMs can be found in the Supporting Information.

## RESULTS AND DISCUSSION

**Identification of Phenylation Products.** MeHgPh and EtHgPh generated by aqueous phenylation were identified previously and confirmed again in this study by GC/MS.<sup>19</sup> When GC-AFS or GC-ICPMS were used, identification of the derivatives was made according to their retention times. Figure 1A shows the typical chromatogram of a DI water aliquot spiked with MeHg (24.62  $\mu\text{g}$  as Hg) and EtHg (23.85  $\mu\text{g}$  as Hg) standards using aqueous phenylation, purge and trap, and GC-AFS. Elemental  $\text{Hg}^0$  and  $\text{HgPh}_2$  also appeared on the chromatogram.

Phenylation derivatives of the three mercury species, MeHgPh, EtHgPh, and  $\text{HgPh}_2$ , were also clearly separated and detected using the modified PerkinElmer GC coupled to ICPMS (Figure 1B, MeHg 78.78  $\mu\text{g}$  as Hg, EtHg 76.32  $\mu\text{g}$  as Hg). This indicates that, after a simple modification, regular GC without a programmable injection port can be utilized to analyze the mercury species adsorbed on the Tenax trap. Applying isothermal temperature to the injection port did not deteriorate desorption of the mercury species from the trap or their separation on a GC column. The combination of aqueous phenylation and conventional GC coupled to ICPMS is simple and provides a powerful tool for mercury stable isotope tracer experiments.

**Optimization of Phenylation Reaction and Purge-and-Trap Parameters.** Successful development of this speciation technique required demonstration of rapid and quantitative aqueous phenylation of mercury species in the bubbler, efficient purge of the derivatives from the bubbler, retention of derivatives on the Tenax trap, and accurate analysis by GC-AFS or GC-ICPMS. The phenylation reaction is rapid and can be carried out at variable pH.<sup>19</sup> The reaction time was set to 15 min, and a citric buffer solution (pH 5) was used according to previously optimized



conditions.<sup>19</sup> A complete factorial experiment and analysis of variance (ANOVA) indicated that 1 mL of 1% NaBPh<sub>4</sub> was sufficient for all samples analyzed.<sup>28</sup> This study was focused on the purge-and-trap method because it is the key step for this approach.

Initial experiments indicated that the phenylation products of mercury were not purged because of their poor volatilities in deionized water. The "salt out" technique, which is the addition of NaCl to the deionized water, was therefore used to enhance the purge efficiency. Considering that the limit of the solubility of NaCl in water is 35.9 g/100 mL at 25 °C, three NaCl concentrations (10, 20, and 30% (w/v)) were tested. The efficiency of the purging of the two mercury species increased significantly as NaCl was added to the bubbler. The responses of MeHgPh and EtHgPh increased by ~130 (when 20% NaCl was used as the purge matrix) and ~300% (when 30% NaCl was used), with comparison to the purge matrix of 10% NaCl. When a 30% NaCl solution was used as the matrix, the solution became cloudy after adding NaBPh<sub>4</sub>. The precipitate was likely to be NaBPh<sub>4</sub> because of its decreased solubility in NaCl solutions.<sup>29</sup> The precipitate suspended in the solution was partially purged from the solution and attached to the wall of the upper part of the bubblers. When analyzing real samples, the aqueous sample solution should be adjusted to contain an appropriate NaCl concentration. It is difficult to dissolve enough NaCl in the sample to reach a concentration of 30% without disturbing the integrity of the sample. Instead, we found that mixing the aqueous sample with 30% NaCl to get a homogeneous solution with a final NaCl concentration lower than 30% is easier and more consistently maintains the integrity of the sample. For these experiments, 22% NaCl was optimal (35 mL of aqueous sample solution combined with 100 mL of 30% NaCl). The purge-and-trap efficiency was slightly sacrificed because the matrix had a NaCl concentration lower than 30%.

Purge flow significantly affected the purge-and-trap efficiency of the mercury derivatives. Slow purge flow dramatically prolonged the analytical time, while high flow increased the deposition of solid NaCl on the frit of the purge tube, consequently causing clogging of the pores of the frit. High purge flow also intensified the foaming during purge for real sample analysis, which could deteriorate the purge-and-trap efficiency. Under the experimental conditions of this study, a flow rate of 200 mL/min was found to be optimal.

Increasing the purge temperature significantly improved the purge efficiency. The response of MeHgPh increased by 130%, and the response of EtHgPh increased by 60% when the purge temperature was increased from 20 to 50 °C (data not shown). Higher temperatures are not recommended because they caused more water vapor to be purged and to condense on the trap packing material. Consequently, the adsorption efficiency of the mercury species was reduced by the blockage of the gas passage through the Tenax grains.

The purge time is another important parameter that affects the purge efficiency. Purge times of 15, 30, and 45 min were tested. The signals for both mercury species increased rapidly in the first 15 min of purge time and then slowed. When the purge time increased from 15 to 45 min, increments of ~80 and ~35% on the

signals of MeHgPh and EtHgPh were obtained, respectively. Different solubility and volatility of the two mercury species could account for the higher efficiency enhancement of MeHgPh than EtHgPh. A purge time of longer than 45 min is not recommended because it generates a large amount of water vapor, which interferes with the adsorption of the derivatization products.

The aqueous phenylation and purge-and-trap parameters were optimized as follows: reaction and purge-and-trap matrix, 22% NaCl solution; purge temperature, 50 °C; purge flow rate, 200 mL/min; purge time, 45 min. The figure of merits was investigated under these optimized conditions. The reproducibility was tested using six replicates of MeHgCl (24.62 pg) and EtHgCl (23.85 pg) standards. The relative standard deviations (RSDs) were found to be 9 (MeHg) and 12% (EtHg). When the AFS detector was used, the concentration ranges that could be run directly (dilution required for higher concentration) were 0.03–1.12 ng/L (linear response,  $y = 121011x - 88238$ ,  $R^2 = 0.9976$ ) for MeHg and 0.03–1.09 ng/L ( $y = 88523x$ ,  $R^2 = 0.9820$ ) for EtHg. Much broader ranges were obtained when ICPMS was used (0.02–17.99 ng/L for MeHg, 0.01–17.41 ng/L for EtHg and linear response for both species). The detection limits, calculated as three times the standard deviation of blank signals in seven replicates, were found to be 0.03 ng/L for both MeHg and EtHg with AFS as detector when 35 mL of aqueous sample was analyzed and 0.02 and 0.01 ng/L for MeHg and EtHg, respectively, with ICPMS. These detection limits are much lower than those reported for other preconcentration techniques, such as LLE (0.3 µg/L)<sup>19</sup> and SPME (0.12 µg/L),<sup>27</sup> and comparable with the method of aqueous ethylation followed by purge-and-trap AFS detection for MeHg analysis.<sup>30</sup> Such low detection limits make it possible to simultaneously determine MeHg and EtHg levels in natural water samples without preconcentration using this new technique. As for soil and sediment samples, the detection limits were 0.003 ng/g wet weight (using AFS as the detector) for both MeHg and EtHg, or 0.002 and 0.001 ng/g wet weight (using ICPMS as the detector) for MeHg and EtHg, respectively.

**Interferences.** A strong interfering effect of Cl<sup>-</sup> on aqueous ethylation has been observed.<sup>7,10,11</sup> This interference has greatly limited the application of the aqueous ethylation method to direct analysis of high-salt-containing waters, such as seawater. The usage of high NaCl concentration in this study indicates that aqueous phenylation does not suffer from Cl<sup>-</sup> interference. However, the interference of K<sup>+</sup> with the phenylation reaction has to be considered when dealing with seawater. K<sup>+</sup> can precipitate BPh<sub>4</sub><sup>-</sup> and reduce the amount of BPh<sub>4</sub><sup>-</sup> available for Hg phenylation. In this study, a depression in the system response of ~50% was observed when artificial seawater (salinity 35‰, K<sup>+</sup> 0.38‰)<sup>31</sup> was analyzed. While increasing the amount of NaBPh<sub>4</sub> failed to overcome the depression, dilution could partially overcome the depression. The system response recovered to ~70% of the normal values when the artificial seawater was diluted with deionized water at a ratio of 1:1. Nevertheless, good linearity ( $R^2 > 0.95$ ) was obtained when calibration curves were prepared with both artificial and diluted artificial seawaters. We therefore suggest that standard addition method be used for real seawater analysis. Another choice is a "matrix match" technique, whereby a calibra-

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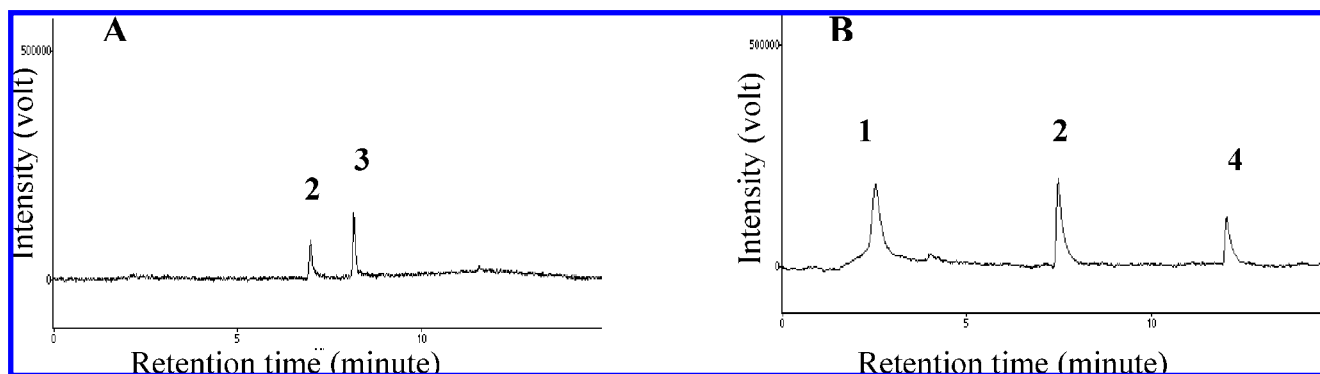
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**Table 1. Detection of MeHg and EtHg in the CRMs and Sediment Samples Collected from the Florida Everglades and a Canadian Wetland<sup>a</sup>**

sample ID	MeHg		EtHg	
	concentration (ng/g)	recovery (%)	concentration (ng/g)	recovery (%)
IAEA-405	4.99 ± 0.39	91 ± 7	4.80 ± 0.66	85 ± 12
DORM-2	(4.62 ± 0.22) × 10 <sup>3</sup>	103 ± 5	(3.00 ± 0.49) × 10 <sup>3</sup>	91 ± 15
1	1.13 ± 0.30	60 ± 16	4.55 ± 0.05	68 ± 12
2	1.07 ± 0.06	97 ± 14	1.09 ± 0.10	77 ± 7
3	1.75 ± 0.19	82 ± 13	1.05 ± 0.35	89 ± 25
4	10.90 ± 1.64	107 ± 38	0.15 ± 0.03	65 ± 6

<sup>a</sup> Sample 4 was collected from a Canadian wetland. All other samples were collected from the Florida Everglades. Concentrations are on dry weight basis. For CRMs,  $n = 7$ . For all the sediment samples,  $n = 3$ .

**Figure 2.** Typical chromatograms of sediment (A) and water (B) samples collected from the Florida Everglades: (1) Hg<sup>0</sup>, (2) MeHgPh, (3) EtHgPh, and (4) HgPh<sub>2</sub>.

tion curve is prepared with artificial seawater having K<sup>+</sup> concentrations similar to the real samples. Dilution could be also used to reduce this precipitation effect if the detection limit is not a consideration.

To test the effect of DOM on aqueous phenylation, two solutions with different concentrations of humic acid (100 and 250 mg/L) were spiked with MeHg (0.70 ng/L) and EtHg (0.68 ng/L). In both cases, the recoveries of MeHg were very high (101 ± 2 and 102 ± 8% for 100 and 250 mg/L humic acid solutions, respectively,  $n = 3$ ). The recoveries of EtHg were lower than for MeHg (75 ± 2 and 71 ± 2% for 100 and 250 mg/L humic acid solutions, respectively,  $n = 3$ ). It has been reported that DOM interferes with the aqueous ethylation reaction. This interference could be the result of the consumption of the ethylation reagent by DOM.<sup>7,12</sup> Extraction or distillation was generally necessary before the aqueous ethylation step. However, the result described above indicated that this cleaning step is likely to be unnecessary when NaBPh<sub>4</sub> is used as the derivatization reagent. Potassium, ammonium, cesium, rubidium, thallium, silver, and alkaloids are the only ions known to react with NaBPh<sub>4</sub>.<sup>32–34</sup> Those ions are not expected to be present in normal freshwater systems at high enough concentrations to interfere with aqueous derivatization with NaBPh<sub>4</sub>.

**CRMs and Sediment Sample Analysis.** MeHg recoveries from IAEA-405 and DORM-2 CRMs were calculated and compared to the certified values. Recoveries of EtHg were evaluated by spiking the CRMs with known amounts of EtHgCl. Both materials

did not contain measurable EtHg without spiking, and the measured MeHg concentrations were in accordance with the certified values (Table 1). The reproducibility and the recovery of EtHg from the spiked CRMs were also high, indicating that MeHg and EtHg in samples could be simultaneously analyzed using this aqueous phenylation and purge-trap technique with precision and accuracy. In support of this, both MeHg and EtHg were both detected in all the sediment samples from the Florida Everglades and the Canadian wetland (Table 1). Figure 2A gives a representative chromatogram of those sediment samples. Concentrations of MeHg and EtHg were similar in the Everglades sediment samples, while the MeHg concentration was much higher than that of EtHg in the Canadian wetland sample. These results agreed with the findings of Cai et al.<sup>3</sup> and Holmes and Lean.<sup>4</sup>

**Water Sample Analysis.** A representative chromatogram of the Florida Everglades water samples is shown in Figure 2B. These water samples contained MeHg, but not EtHg. Using this direct aqueous phenylation-purge-and-trap-GC-AFS method, both MeHg (original, 0.03–0.16 ng/L) and EtHg (spiked, 0.10–1.44 ng/L) were determined with good precision (RSD < 33%) and accuracy (recovery 72–105%) (See Table S-1 in the Supporting Information). Furthermore, the results agreed with those obtained using a distillation-aqueous ethylation-GC-AFS method, which is recommended by USEPA as the standard method for analysis of MeHg in water samples,<sup>30</sup> indicating that the matrix effects, mainly from DOM (ranging from 6.50 to 23.75 mg/L), can be minimized with the application of aqueous phenylation. This is a very important result which shows that MeHg artifacts that often resulted from the distillation of high DOM-containing waters can

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be avoided by using aqueous phenylation. Elimination of the tedious distillation step substantially decreases cost of analysis and possible artifact of MeHg in water samples.

## CONCLUSIONS

We have developed a method for the simultaneous measurement of MeHg and EtHg levels in environmental and biological samples, which is based on aqueous phenylation derivatization, purge-and-trap preconcentration, GC separation, and AFS or ICPMS detection. After a simple modification, regular GC can be applied to analyze the phenylation products retained on the traps and both AFS and ICPMS can be used as the detectors. The method has been successfully applied to the analysis of two CRMs for different matrixes, IAEA-405 and DORM-2, and real freshwater and soil samples. This method allows direct analysis of freshwater samples without tedious and troublesome pretreatment steps. The low detection limits obtained under optimized conditions make it suitable for the analysis of trace amounts of MeHg and EtHg in environmental samples, including water samples. In addition, this

aqueous phenylation-purge and trap-GC-ICPMS method provides a powerful tool for studying mercury biogeochemistry using stable isotope tracer techniques.

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## SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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