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Determination of methylmercury in fish and river water samples using in situ sodium tetraethylborate derivatization following by solid-phase microextraction and gas chromatography–mass spectrometry

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Abstract

A solid-phase microextraction (SPME) analytical procedure is described for the quantitative determination of methylmercury and labile Hg^{2+} in fish and river water matrices. The analytical procedure involves aqueous-phase derivatization of ionic mercury species with sodium tetraethylborate in a sample vial and subsequent extraction with a silica fiber coated with poly(dimethylsiloxane). The mercury derivatives are desorbed in the splitless injection port of a gas chromatograph and subsequently analyzed by electron impact mass spectrometry. Both headspace SPME and aqueous-phase SPME are studied, and the linear range of the method spans several orders of magnitude for both procedures. The detection limits of the headspace SPME procedure for a 20-ml sample are 7.5 and 3.5 ng/l as Hg for CH_3Hg^+ and Hg^{2+}, respectively. The detection limits of aqueous-phase SPME for a 1.5-ml sample are 6.7 and 8.7 ng/l as Hg for CH_3Hg^+ and Hg^{2+}, respectively. Analyses of standard reference materials and river water sample demonstrate the suitability of this method for the determination of methylmercury and labile Hg^{2+}.

1. Introduction

Mercury pollution has become a global problem because of its occurrence from natural and anthropogenic sources, and its biogeochemical processes. The determination and monitoring of mercury is a special concern in the field of heavy metal analysis. A number of publications have reported the presence of mercury in a variety of environmental and biological samples [1–3]. It has been demonstrated that mercury can be methylated in the environment and bioconcentrated in biota [4,5]. Ingestion of fish muscle is an important exposure pathway of mercury to humans. The high toxicity of methylmercury has been well recognized. As a result, the US Food and Drug Administration (FDA) has set an Action Level of 1 μg/g (wet mass) for concentration of mercury in fish. Fish containing concentrations of mercury above this level are considered to be hazardous for human consumption and cannot be sold in interstate commerce. Canada and several US States have developed consumption advisories of 0.5 μg/g for mercury in fish [3]. In addition, the European Union (EU) has set environmental quality objectives of 0.3 μg/g (wet mass) for fish, 1 μg/l for continental water, 0.5 μg/l for estuarine water, and 0.3

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μg/l for coastal water as total mercury [6]. As public awareness regarding the toxicity and the environmental impact of mercury contamination increases, the demand for a simple, accurate, reliable speciation analytical method, which can distinguish between organic and inorganic forms of mercury, also increases.

Traditionally, gas chromatography (GC) with electron-capture detection (ECD) was widely used for the determination and speciation of organomercury in many environmental and biological samples [7–9]. The classic method for extracting and separating methylmercury is based on a procedure originally devised by Gage [10] and later modified by Westöö [11], which involves liberation, isolation by multiple liquid–liquid extraction with benzene or toluene, and subsequent analysis by GC–ECD. However, organomercury halides are noted for their poor chromatographic characteristics including severe tailing, decomposition, and low column efficiency. In addition, the halogen-bearing compounds coextracted with methylmercury can interfere with the determination because of the non-specificity of ECD. To overcome these problems, many efforts have been made, involving column passivation using a concentrated organic solution of mercury(II) [8], butylation of methylmercury by a Grignard reagent [9,12] and the coupling of chromatography (gas or liquid) with atomic spectrometry [13]. Most of these methods, however, are time-consuming, require tedious liquid–liquid extraction with organic solvent prior to chromatographic separation and detection, and often lead to the final determination of only the CH_3Hg^+ species. An alternative method has recently been developed for CH_3Hg^+ and Hg^{2+} analysis by using aqueous ethylation with sodium tetraethylborate ($NaBEt_4$), followed by purge and trap and detection by atomic absorption spectrometry (AAS) [14,15] or by atomic fluorescence spectrometry (AFS) [16,17]. The use of $NaBEt_4$ as an ethylation reagent has significant advantages since the derivatization reaction can be performed in the aqueous phase, subsequently reduces the analytical time and eliminates the need for organic solvent extraction.

Recently, a novel analytical technique, solid-phase microextraction (SPME), has been developed by Pawliszyn and co-workers [18–20]. This technique involves the extraction of volatile or semivolatile organic compounds directly from aqueous or gaseous samples onto a fused-silica fiber that is coated with an appropriate stationary phase. While the fiber is exposed to the sample, the analytes partition from the sample matrix into the stationary phase until equilibrium is reached. The fiber is then directly transferred into a GC injector for thermal desorption and analysis. Such a fast, simple technique has been used for the determination of a number of organic pollutants [18–24]. Recently, a procedure has also been reported for the extraction of bismuth(II) from aqueous nitric acid solution using a fused-silica fiber coated with poly(dimethylsiloxane), which was modified to contain ion-exchanging functions [25]. In the present study, we report an analytical procedure for the determination of CH_3Hg^+ and labile Hg^{2+} using in situ aqueous ethylation with $NaBEt_4$, subsequent SPME sampling and then GC–MS detection. This is, to our knowledge, the first application of SPME to the determination of organometallics. Both aqueous-phase and headspace SPME extraction procedures were studied. This analytical process is much simpler than the methods previously reported, and does not require organic solvent extraction. It is free from chromatographic complications, since the CH_3Hg^+ and Hg^{2+} are derivatized to fully alkylated species before analysis. Compared with the conventional purge and trap method, this procedure eliminates the use of large amounts of liquid nitrogen and the possible blockage of column due to water condensation. Applications to standard reference materials, Dorm-1 and Dorm-2, and river water sample are also presented.

2. Experimental

2.1. Apparatus

SPME device

The SPME fiber holder for manual use and the fiber coated with 100 μm thickness of poly(di-

methylsiloxane) were obtained from Supelco (Bellefonte, PA, USA). This holder was designed to be used with a reusable, replaceable, Supelco SPME fiber assembly. The 25 or 1.5 ml of glass vial were used for headspace and aqueous-phase SPME extraction, respectively. The silicone rubber septa coated with PTFE were used for both vials. The SPME extractions were performed with magnetic stirring to ensure the proper mixing of the sample solution, and a 15×6 mm or a 4×2 mm PTFE-coated magnetic stirring bar was used in headspace or aqueous-phase extraction.

GC–MS

The analysis was performed using a GC 8000 series gas chromatograph coupled with an MD 800 mass spectrometer (Fisons Instruments, Milan, Italy) at 70 eV of ionization energy. Transfer line and ion source temperatures were maintained at 280 and 200°C, respectively. A mass range from m/z 50–450 was recorded in the scan mode, and four ions [m/z 217 and 246 for $CH_3HgC_2H_5$, m/z 231 and 260 for $Hg(C_2H_5)_2$)] were chosen in the selective ion monitoring mode (SIM). A split/splitless injector was used in the splitless mode and maintained at 220°C. A 30-s desorption time was used for all fiber injections. The analytical column used for all experiments was 30 m × 0.32 mm I.D. fused silica coated with 1.8 μm film thickness of DB-624 (J & W Scientific). The column temperature program is given in the chromatograms. Helium at a head pressure of 7.5 p.s.i. (1 p.s.i. = 6894.76 Pa) was used as carrier gas.

2.2. Reagents and materials

Two standard reference materials, Dorm-1 and Dorm-2 (dogfish muscle), were obtained form the National Research Council of Canada (NRCC), Ottawa, Canada. The certified values of CH_3Hg^+ in Dorm-1 and Dorm-2 are 0.731 ± 0.060 and 4.47 ± 0.32 μg/g as Hg, respectively. A subsurface (0.5 m) river water sample was collected from Llobregat river adjacent to Barcelona, Spain.

Methylmercuric chloride (99%), mercury dichloride (99.9995%), and sodium tetraethylborate were purchased from Strem Chemicals (Newburgport, MA, USA). Analytical-grade potassium hydroxide pellets were from Merck (Darmstadt, Germany). Sodium acetate (analytical grade) and acetic acid (analytical grade) were obtained from Aldrich (Steinheim, Germany). All other chemicals were of analytical grade or better.

Stock standards at 1000 mg/l as Hg for methylmercury and inorganic mercury were prepared in acetone and 5% (v/v) nitric acid, respectively. A mixed working solution was prepared weekly by diluting the stock solution with acetone to a range of 0.05–50 mg/l as Hg. A fresh $NaBEt_4$ solution of 1% (w/v) was prepared daily in deionized water and passed through a 0.5-μm FH filter (Millipore, Bedford, MA, USA). Both mercury working solution and $NaBEt_4$ were stored at 4°C. A buffer at pH 4.5 was prepared by mixing appropriate amount of sodium acetate (0.2 *M*) and acetic acid (0.2 *M*).

2.3. Procedure

The liberation of mercury from biological samples was performed using a procedure reported by Fisher et al. [15]. Briefly, 100–200 mg sample of fish tissue was placed in a 50-ml glass bottle. Then 10–20 ml of 25% (w/v) methanolic KOH solution were added, and the sample was shaken in an ultrasonic bath for 3 h. The dissolved sample was stored at 4°C before analysis.

For headspace SPME sampling, the magnetic stirring bar, 17 ml of deionized water and 3 ml of acetate buffer solution (pH 4.5) were placed in a 25-ml glass vial. A 100-μl aliquot of the fish extract or 1-μl aliquot of mixed mercury standards (0.5–50 mg/l as Hg), and 200 μl of 1% $NaBEt_4$ solution were added, and the vial was then closed immediately. The fiber was drawn into the needle of the holder, and the needle was used to pierce the septum of the sample vial. The fiber was then lowered into the headspace by depressing the plunger. The fiber within the vial headspace was situated about 0.3 cm above the surface of the aqueous phase, and never came into contact with the liquid. After a predetermined sampling time, the fiber was retracted into the needle and immediately inserted into the GC

injector for thermal desorption. The depth of the fiber in the injection port was 4.4 cm (measured from the holder), which was about 1.5 cm above the column. This position was suggested by the manufacturer for conventional syringe injection, and was found to be suitable in this study. For analysis of the river water sample, 17 ml of real sample was placed in the vial instead of deionized water.

For aqueous-phase SPME sampling, the magnetic stirring bar, 1.0 ml of deionized water, 0.5 ml of acetate buffer solution, 20 μl aliquot of the fish extract or 1 μl of mixed mercury standards (0.05–10 mg/l as Hg), and 20 μl of $NaBEt_4$ were added to the 1.5-ml sample vial. Only about 100 μl of headspace were left in the vial, which prevented the loss of analyte due to the formation of a large headspace. The other steps for aqueous-phase SPME sampling were as described above for SPME sampling of the headspace except that the entire fiber was placed in the solution.

3. Results and discussion

3.1. Development of SPME procedure and GC–MS determination

The SPME procedure, including headspace and aqueous-phase sampling, has been studied extensively for the analysis of organic pollutants [18–24]. SPME, unlike most conventional extraction techniques, is not based on exhaustive extraction of the sample, but on an equilibrium between the analyte concentration in the sample (and/or in the headspace) and that in the solid-phase fiber coating [18]. In the present study, the CH_3Hg^+ and Hg^{2+} were derivatized to ethylmethylmercury and diethylmercury, respectively, and then extracted by the fiber. The derivatization procedure can significantly improve the partitioning of the analytes between fiber coating and sample matrix, since the fully alkylated mercury species have greater affinity for the poly(dimethylsiloxane) coating. As this derivatization reaction can be carried out rapidly in aqueous phase [15,16] and the ethylated products are volatile (b.p. of $Hg(C_2H_5)_2$ = 159°C), it was expected that the extraction equilibration would be reached quickly. Fig. 1 shows the time profile of the in situ ethylation and extraction of CH_3Hg^+ and Hg^{2+} obtained by using the headspace SPME technique. The results indicate that the reaction and extraction equilibration time is approximately 10 min for both compounds at room temperature (25°C). Higher temperature (50°C) of reaction and extraction was investigated, but no significant enhancement in the amount extracted by the fiber was found. The reaction and extraction equilibrium time for the aqueous-phase SPME sampling technique was also estimated. It was found that the equilibration time was extended to approximately 20 min. The reduced sampling time given by the headspace technique can be explained by the fact that the diffusion of analytes is much faster in vapor phase than in aqueous phase. This result agrees with the determination of organic pollutants reported by Zhang and Pawliszyn [20]. To test the effect of salting out as a means of enhancing the amount extracted by the fiber, 1.0 ml of saturated NaCl was added to the vial and a similar procedure to that described for headspace SPME sampling was performed. In contrast to the results obtained for some organic compounds [23], the extraction efficiency for mercury species by the fiber was decreased by the addition of salt. The decreased absorption could be attributed to the high concentration of chloride, which hampers the ethylation reaction of organometallics with $NaBEt_4$ [16,26]. To confirm this explanation, an experiment was performed by injecting 1 ml of saturated NaCl through the septum of the vial after the reaction had been carried out for 5 min, and the result was similar to that obtained without addition of salt. The amount of salt injected to the vial was limited due to the closed system used in this study, and the addition of 1 ml of saturated NaCl did not enhance the amount extracted by the fiber for either $CH_3HgC_2H_5$ or $Hg(C_2H_5)_2$.

A suitable desorption temperature is critical, since the thermal decomposition of mercury derivatives in the process of desorbing from a

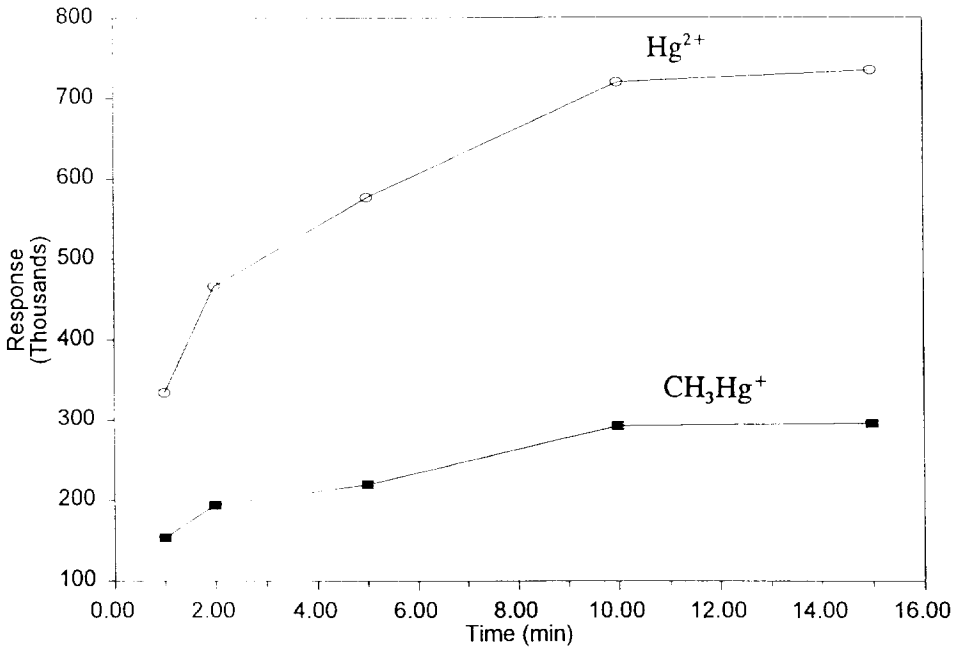

Fig. 1. Time profile of the in situ ethylation and absorption of CH_3Hg^+ and labile Hg^{2+} obtained by using headspace SPME technique with an initial concentration of 0.5 μg/l as Hg.

Carbotrap column has been observed [17]. We found that at 220°C fast desorption of the analytes can be ensured and the decomposition can be eliminated. A significant advantage of this analytical procedure is that the fiber is directly exposed to the high-temperature injection port for desorption. This is in contrast to the conventional purge-and-trap technique, in which the analyte on the trap column is desorbed by heating the column with a resistance wire. Rapid desorption has been shown to eliminate the thermal decomposition [17].

Carryover or memory effect is a common problem encountered in the analysis of mercury using conventional techniques [13,15]. It was also observed in the determination of organic compound by the SPME method [21,23]. To determine whether the analytes remained on the fiber after desorption, two types of carryover experiment were performed for both the headspace and aqueous-phase SPME sampling procedures. The first consisted of running a second desorption of the same fiber after the initial desorption, following exposure to a standard solution. The second involved running a blank using a same procedure, except that no standard was added, after the initial desorption of the same fiber. In the first case, no memory effect was observed for either headspace or aqueous-phase sampling procedures. This result suggests that the ethylated mercury absorbed on the fiber can be efficiently desorbed under the experimental conditions used. In the latter experiment, neither compound showed any sign of carryover when the headspace SPME method was used. For the aqueous-phase SPME sampling procedure, however, an evident peak of diethylmercury was found. This can be attributed to Hg^{2+}, which was absorbed in the first sampling, but remained in the coating after desorption. It was ethylated during the next sampling, then desorbed with the subsequent injection. The extent of carryover relies mainly on the type and thickness of the fiber, and the concentration of analyte. When 100-μm thickness fiber coated with poly(dimethylsiloxane) was used, and a 0.67 μg/l solution was sampled, the carryover was less than 1% for a subsequent blank. The mem-

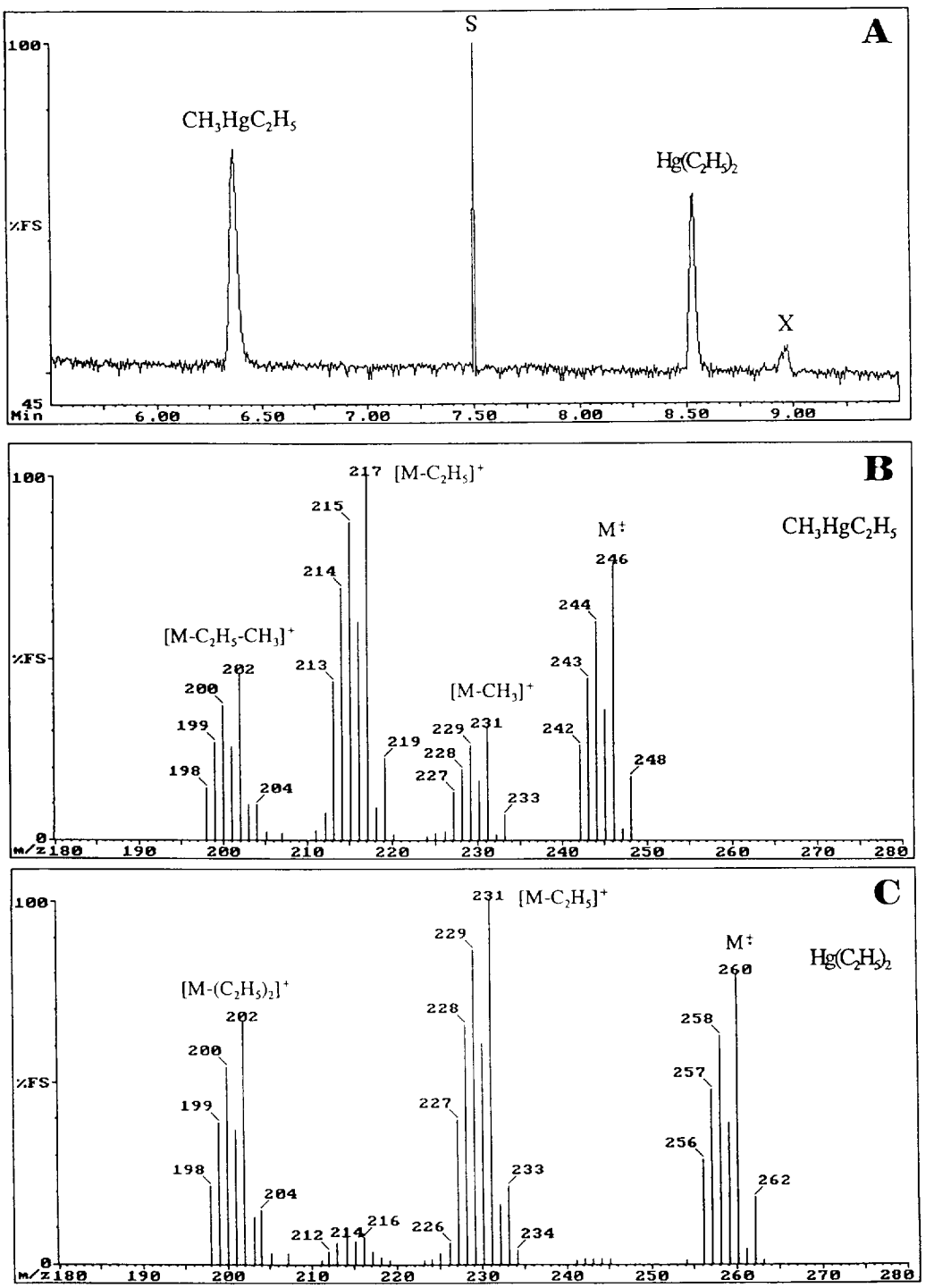

Fig. 2. (A) Selected ion mode GC–MS chromatogram for CH_3Hg^+ and labile Hg^{2+} spiked at 0.25 μg/l as Hg in water using headspace SPME. The unidentified peak X was from blank. Peak S was an electric noise resulting from changing the retention window of the acquisition pragram. The column temperature was initially held at 30°C, programmed at 10°C/min to 80°C, then increased to a final temperature of 260°C at a rate of 15°C/min, and held there for 2 min. (B, C) Electron impact mass spectra of $CH_3HgC_2H_5$ and $Hg(C_2H_5)_2$, respectively, obtained at 70 eV.

Table 1
Detection limits and linear range for the determination of CH_3Hg^+ and Hg^{2+} by SPME

	Absolute detection limits (ng as Hg)		Concentration detection limits Water sample (ng/l as Hg)		Fish tissue (μg/g as Hg)[b]		Linear range[a] (ng/l as Hg)	
	CH_3Hg^+	Hg^{2+}	CH_3Hg^+	Hg^{2+}	CH_3Hg^+	Hg^{2+}	CH_3Hg^+	Hg^{2+}
Headspace	0.15	0.07	7.5	3.5	0.15	0.07	25–2500	25–2500
Aqueous phase	0.01	0.013	6.7	8.7	0.1	0.13	30–6700	30–6700

[a] Correlation coefficients ranged from 0.9959 to 0.9999.
[b] Dry mass.

ory effect can be significantly reduced by using a longer desorption time, or by running blanks. In contrast to the aqueous-phase SPME sampling, the fiber did not contact the liquid solution in headspace SPME sampling and only the ethylated mercury species escaping to the headspace were extracted. This greatly reduces the possibility of Hg^{2+} carryover, and consequently eliminates interference in the analysis of subsequent samples.

A thicker stationary phase column (DB-624, 1.8 μm film thickness) was employed, and in this study the desorption temperature was high enough (220°C) for the desorption to be fast. This eliminated the need for a cryofocusing step, which is often included to refocus the analytes onto the capillary column, and to avoid band broadening when volatile compounds are analyzed by SPME [20]. Fig. 2A shows a GC–MS chromatogram in SIM mode for determination of CH_3Hg^+ and Hg^{2+} spiked at 0.25 μg/l as Hg in deionized water, using headspace SPME sampling. Mass spectra of $CH_3HgC_2H_5$ and $Hg(C_2H_5)_2$ in scan mode are shown in Fig. 2B and C for confirmation of the ethylation products.

The headspace SPME and the aqueous-phase SPME techniques were calibrated with a series of CH_3Hg^+ and Hg^{2+} standard. The linearity ranges for both CH_3Hg^+ and Hg^{2+} are at least from 0.025 to 2.5 μg/l and from 0.03 to 6.7 μg/l for headspace and aqueous-phase SPME procedures, respectively. Detection limits were determined for both sampling methods. The linear ranges and absolute detection limits, calculated as three times the baseline noise are shown in Table 1. The concentration detection limit is a function of the sample size that can be used in

Table 2
Results of mercury speciation in fish tissue and river water samples

	Measured values (μg/g as Hg)		Certified CH_3Hg^+ (μg/g as Hg)
	CH_3Hg^+	Hg^{2+}	
Dorm-1[a]	0.77 ± 0.03 (n = 2)	0.38 ± 0.078 (n = 2)	0.731 ± 0.060
Dorm-2[b]	4.41 ± 0.55 (n = 5)	0.13 ± 0.01 (n = 5)	4.47 ± 0.32
River sample[b,c]	ND	9.30 ± 0.03 (n = 2)	NC

ND = Not detectable; NC = not certified.
[a] Using aqeuous-phase SPME.
[b] Using headspace SPME.
[c] Values given in ng/l as Hg.

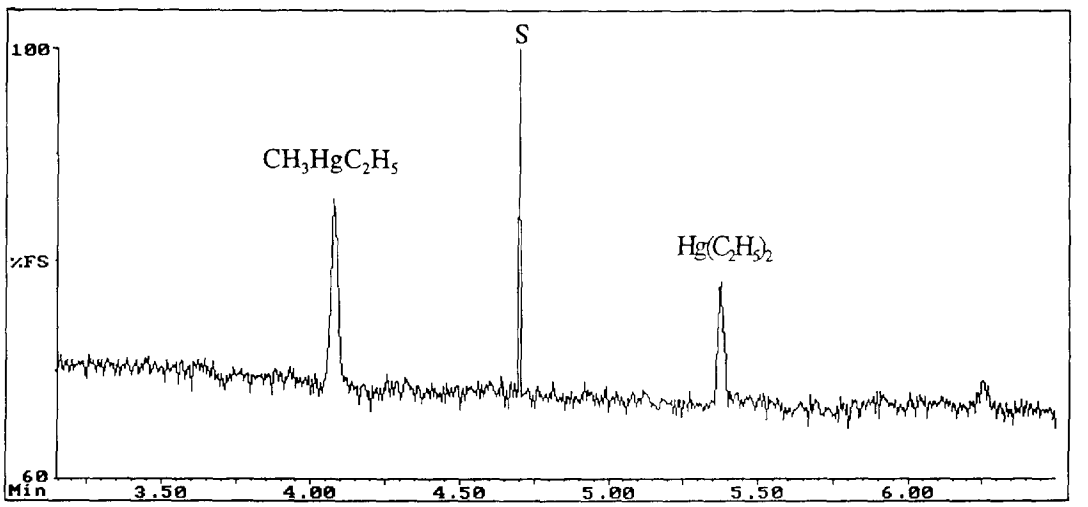

Fig. 3. GC–MS chromatogram in SIM mode for Dorm-1 analysis with aqueous-phase SPME technique. The column temperature was initially held at 30°C, programmed at 25°C/min to 90°C, then increased to a final temperature of 260°C at a rate of 20°C/min, and held there for 2 min. Peak S was an electric noise resulting from changing the retention window of the acquisition program.

the experiment. In the present study, 1.5 ml for aqueous-phase sampling and 20 ml for headspace sampling were used. For analysis of biological samples, 100 mg of sample was dissolved in 20 ml of methanolic KOH solution and from this solution 200 μl (headspace SPME) and 20 μl (aqueous-phase SPME) were analyzed. The concentration detection limits calculated for water sample and biological sample are also listed in Table 1. These detection limits are adequate to meet the requirements of FDA and EU for monitoring mercury in fish or water samples. The relative standard deviation (R.S.D.) of the signal (peak area) was also examined. For headspace SPME, the R.S.D.s for a 0.25 μg/l as Hg of CH_3Hg^+ and Hg^{2+} standards were 4.8 and

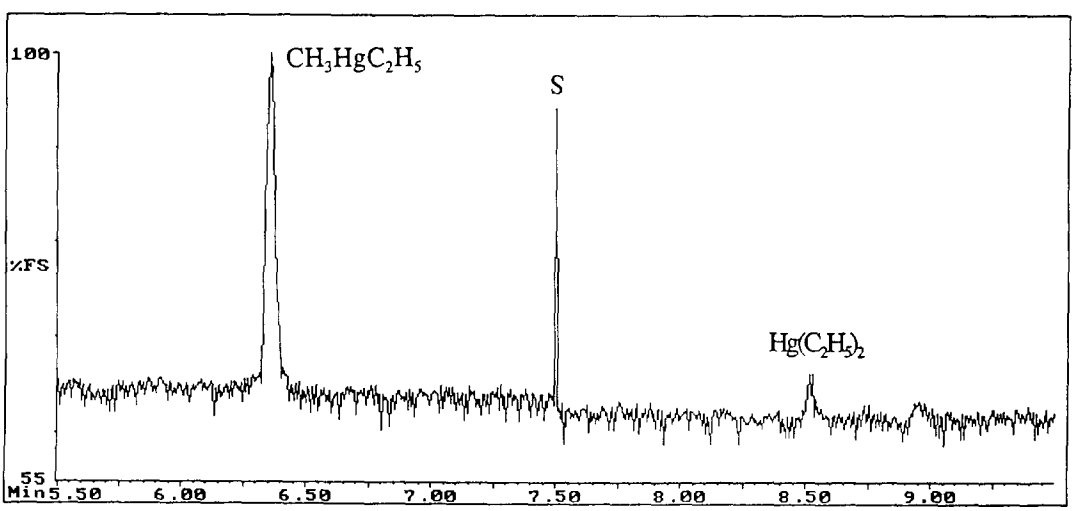

Fig. 4. GC–MS chromatogram in SIM mode for Dorm-2 analysis with headspace SPME technique. Column temperature program as in Fig. 2. Peak S was an electric noise resulting from changing the retention window of the acquisition program.

2.4% ($n = 3$). For aqueous-phase SPME the R.S.D.s for a 0.67 μg/l as Hg of CH_3Hg^+ and Hg^{2+} standards were 3 and 11% ($n = 3$), respectively.

3.2. Application to real samples

To evaluate the reliability of the analytical technique developed for the analysis of real-world samples, two standard reference materials and a river water sample were analysed. The method of standard addition was used to account for the matrix effects. The analytical results are listed in Table 2. Typical GC–MS chromatograms in SIM mode for Dorm-1 analysis with aqueous-phase SPME procedure and for Dorm-2 analysis with headspace SPME procedure are presented in Figs. 3 and 4, respectively. The analytical result for Dorm-2 indicates that the mercury present in this material is almost entire-

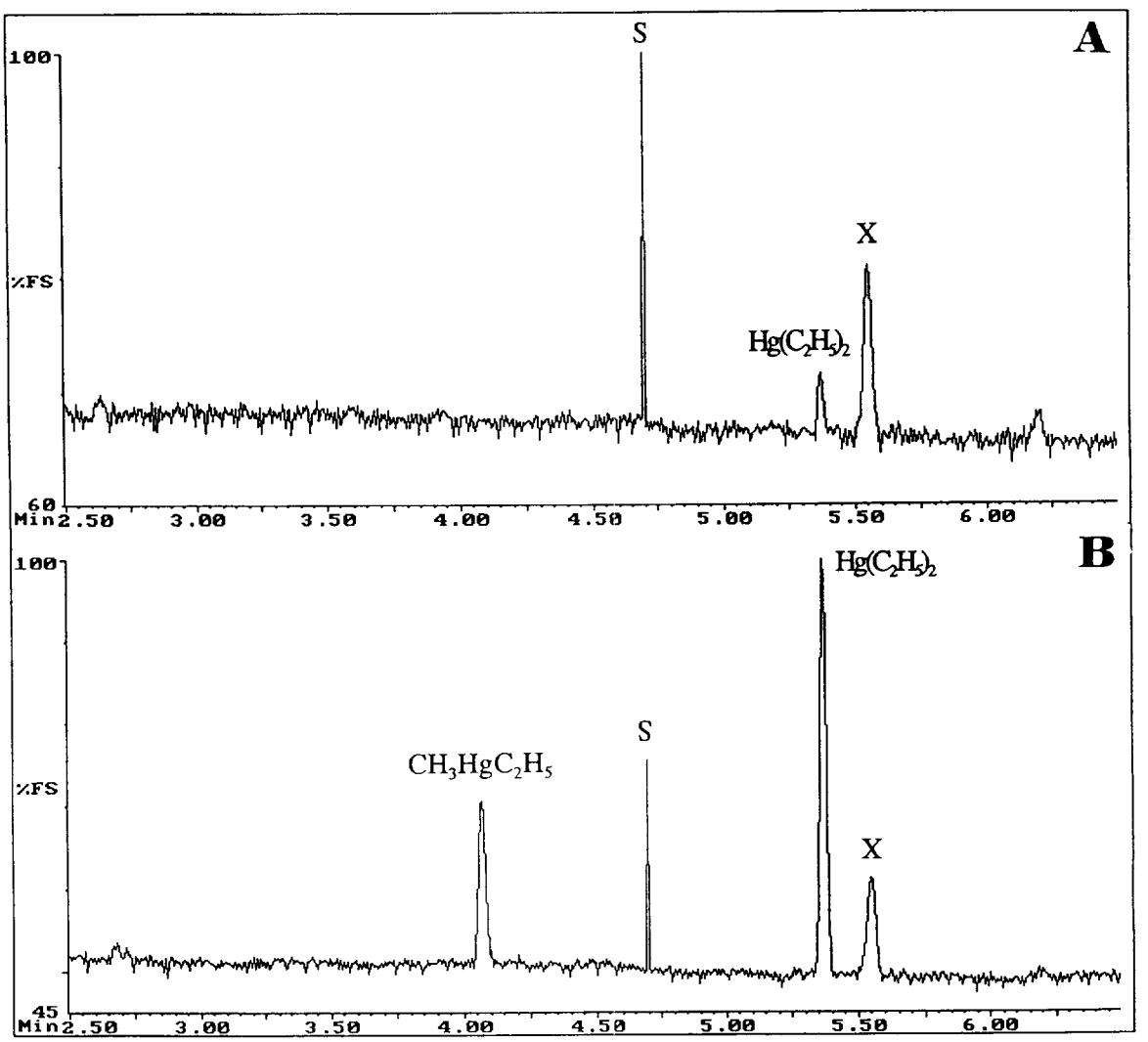

Fig. 5. GC–MS chromatogram in SIM mode for river Llobregat sample analyses with headspace SPME technique. (A) Unspiked, (B) spiked at 100 ng/l as Hg for both CH_3Hg^+ and Hg^{2+}. The unidentified peak X was from blank. Peak S was an electric noise resulting from changing the retention window of the acquisition program. Column temperature program as in Fig. 3.

ly methylmercury. This is in good agreement with the NRCC's report for this certified reference material. No methylmercury was found in the Llobregat river sample. The inorganic mercury, however, was measured at a concentration of 9.3 ng/l as Hg. Fig. 5 shows the GC–MS chromatograms of the river sample in SIM mode for the samples unspiked and spiked at 100 ng/l as Hg for CH_3Hg^+ and Hg^{2+} using headspace SPME techniques.

In summary, the results of this study demonstrate that the quantitative, simultaneous determination of CH_3Hg^+ and labile Hg^{2+} from fish and water samples can be achieved using an in situ aqueous derivatization followed by SPME and GC–MS detection. Compared with the direct SPME sampling from aqueous phase, the headspace SPME sampling procedure is more suitable since it eliminates the memory effects of Hg^{2+}. This analytical method is simple, rapid, solvent-free, and cost-effective. It uses an existing GC injector, and hence could be extended for use with other hyphenated techniques. Taking these advantages into account, this technique could be used to monitor and screen mercury species in the environment.

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