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Speciation analysis of mercury by solid-phase microextraction and multicapillary gas chromatography hyphenated to inductively coupled plasma–time-of-flight-mass spectrometry

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Abstract

This paper reports the development of an analytical approach for speciation analysis of mercury at ultra-trace levels on the basis of solid-phase microextraction and multicapillary gas chromatography hyphenated to inductively coupled plasma–time-of-flight mass spectrometry. Headspace solid-phase microextraction with a carboxen/polydimethylsyloxane fiber is used for extraction/preconcentration of mercury species after derivatization with sodium tetraethylborate and subsequent volatilization. Isothermal separation of methylmercury (MeHg), inorganic mercury (Hg^{2+}) and propylmercury (PrHg) used as internal standard is achieved within a chromatographic run below 45 s without the introduction of spectral skew. Method detection limits (3 × standard deviation criteria) calculated for 10 successive injections of the analytical reagent blank are 0.027 pg g^{-1} (as metal) for MeHg and 0.27 pg g^{-1} for Hg^{2+}. The repeatability (R.S.D., %) is 3.3% for MeHg and 3.8% for Hg^{2+} for 10 successive injections of a standard mixture of 10 pg. The method accuracy for MeHg and total mercury is validated through the analysis of marine and estuarine sediment reference materials. A comparison of the sediment data with those obtained by a purge-and-trap injection (PTI) method is also addressed. The analytical procedure is illustrated with some results for the ultra-trace level analysis of ice from Antarctica for which the accuracy is assessed by spike recovery experiments.

Keywords: Mercury speciation analysis; Solid-phase microextraction; Multicapillary gas chromatography; Inductively coupled plasma–time of flight-mass spectrometry; Antarctica ice; Marine and estuarine sediment

1. Introduction

The interest for speciation analysis of mercury in the environment has been growing rapidly in the last years. It became gradually recognized that organometallic species of mercury are considerable more toxic than their inorganic precursor and the chemical form of mercury controls bioavailability, metabolism, transport, persistence, bio-geochemical cycle and ultimately the impact on the human body and the environment. Speed and simplicity, high accuracy and low detection limits are now considered as important requirements for such determinations. Mercury speciation analysis commonly pays attention to methylated ($MeHg^{+}$) and Hg^{2+} species. In environmental samples, the latter species are usually present in the hydrosphere. Non-polar species such as elemental mercury (Hg^{0}) and dimethylmercury (Me_2Hg) tend to be present in the atmosphere and when present (or brought) in water-based systems are very easily volatilized during sampling, sample transport and storage as well as sample preparation because of their low water solubility [1].

Traditional speciation analysis is based on hyphenated techniques including a gas chromatographic (GC) separation prior to species detection. Conventional capillary gas chromatography (CGC) has been successfully challenged in the last years by multicapillary (MC) systems leading to high-speed separations without sacrificing efficiency [2]. Inductively coupled plasma–mass spectrometry (ICP–MS) is an

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ideal analytical detection technique for direct total mercury determination [3] and speciation studies [4,5], as a result of low limits of detection and high sensitivity and selectivity. Inductively coupled plasma–time-of-flight mass spectrometry (ICP–TOFMS) is suitable for the analysis of very fast chromatographic signals [6], such as those generated by multicapillary gas chromatography (MCGC). The main advantages of ICP–TOFMS are the simultaneous extraction of ions from the plasma and the high speed of data acquisition, which practically eliminate spectral skew. A detailed description of the advantages of ICP–TOFMS for speciation analysis of organometallic compounds is reported elsewhere [7].

In addition to separation and detection, the stabilization of mercury species into solution at ultra-trace levels particularly during storage over long periods of time and the preservation of species integrity during analytical process is important. The species' detection after a chromatographic separation provides basically only a snapshot of their distribution at a particular time [8].

Emphasis is also increasingly placed on the development of 'organic solvent-free' extraction/preconcentration approaches to accomplish state-of-the-art mercury speciation analysis. Both static [9] and dynamic headspace [10–12] (purge-and-trap injection, PTI) techniques, which are the conventional 'organic solvent-free' extraction approaches [13], were successfully applied for mercury speciation analysis. Whereas static headspace suffers from poor sensitivity, PTI is still unsurpassed in sensitivity [14,15] due to its exhaustive extraction/preconcentration capability. Nevertheless, PTI consists of a complex, difficult to operate equipment and is unsuitable for field applications. In addition, it requires the immersion of the purge adaptor into the solution, which may lead to carry-over effects, particularly for Hg^{2+}. Solid-phase microextraction (SPME) has been shown to be a valuable alternative for speciation analysis of mercury from various environmental or biological samples [16–28]. In the headspace (HS) mode of operation, this technique ensures derivatization, extraction and preconcentration in a single step, which significantly increases simplicity and provides a high sample throughput [29]. The analytes' injection with the SPME device is also compatible with most classical split/splitless GC injectors. More details on SPME as a tool for trace element speciation can be found elsewhere [30].

This paper reports the development of a simple, rapid and accurate analytical approach for speciation analysis of mercury at ultratrace levels on the basis of SPME with MCGC separation and ICP–TOFMS detection. The method described is an adaptation and completion of a procedure developed previously for simultaneous speciation analysis of mercury, tin and lead organometallic compounds [31], for which a 65 μm polydimethylsiloxane/divinylbenzene fiber offered the best overall extraction efficiency. Because for the extraction of mercury species the 75 μm carboxen/polydimethylsiloxane fiber was found the best choice [31], evaluation of this fiber for mercury speciation analysis is important. Estuarine and marine sediments with recommended values for total mercury (Hg_T) and MeHg contents were analyzed and the data are compared with those obtained with PTI developed in a previous work [10]. The application to ultra-trace speciation analysis of mercury in ice from Antarctica is also addressed. The results indicate that accurate speciation analysis of mercury is achievable at the pg g^{-1} level both in samples with complex matrix such as sediments and ice from polar regions.

2. Experimental

2.1. Instrumentation

A manual SPME device (Supelco, Bornem, Belgium) was used for the extraction/preconcentration of the ethylated mercury species from the solution and their subsequent injection into the MCGC column. Different 1.0 cm length SPME fibers (Supelco) were used as follows: 100 μm (film thickness) polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS–DVB) and 75 μm carboxen/polydimethylsiloxane (CAR–PDMS). Before first use, the fibers were conditioned as recommended by the manufacturer. A magnetic stirrer plate (HB 502, IMLAB, Boutersem, Belgium) and PTFE-coated stir bars were used for stirring the liquid samples during SPME extraction.

The derivatized species were separated using a MCGC column (MC-1 HT, Alltech, Lokeren, Belgium) housed in a gas chromatograph CP 9001 (Chrompack, Bergen-op-Zoom, The Netherlands). High purity helium (99.9999%, Air Liquide, Liège, Belgium) was used as carrier gas.

An axial ICP–TOFMS (LECO Corp., St. Joseph, MI, USA) was used for element-specific detection of the chromatographic signals. Details on the optimization procedures and optimal experimental conditions of the MCGC and ICP–TOFMS can be found in a previous work [10].

For preparation of the sediments, an open focused microwave system Model Microdigest 301 (Prolabo, Paris, France) was used.

2.2. Reagents, standards and certified reference materials

All reagents used were of at least analytical-reagent grade purity. Ultra-pure water obtained by filtration through a reverse osmosis membrane and further purified (18.2 MΩ) using a Milli-Q^{TM} system (Millipore, Milford, MA, USA) was used. A 1.0 g l^{-1} (as Hg) methylmercury chloride aqueous solution (99.87%) from Alfa Aesar, Karlsruhe, Germany, was used throughout for calibration. A 1000 μg g^{-1} mercury(II) chloride solution (99.9999%) was obtained from CPI International (Amsterdam, The Netherlands). Methylmercury chloride solid salt (>98%) and Hg^{2+} (1000 μg g^{-1}) used for internal quality control were purchased from Sigma-Aldrich

(Bornem, Belgium) and Merck Belgolabo NV (Overijse, Belgium), respectively. A stock solution of propylmercury chloride (Pfaltz & Bauer, Waterbury, CT, USA) was prepared by dissolving an appropriate amount of this reagent in methanol (gradient grade, Merck Eurolab, Leuven, Belgium). Stock and intermediate standard solutions of mercury species were prepared in 1% (m/m) HNO_3 (suprapur, Merck, Darmstadt, Germany). Working solutions were prepared daily just prior to analysis in 0.5% (m/m) HNO_3 (Merck).

HNO_3 (10%, v/v) (pro analysi, Merck) was used for washing the extraction vial. The HNO_3 aqueous solution ($\cong$6 mol l^{-1}), used for leaching the mercury species from the sediments, was prepared by diluting 41.3 ml HNO_3 (suprapur, Merck) up to 100 ml with milli-Q water.

Aqueous solution (0.2%, m/v) of $NaBEt_4$ (Galab Products GmbH, Geesthacht, Germany) was daily prepared just prior analysis and kept in the dark refrigerated at 4 °C during analysis to prevent reagent degradation. A 0.1 mol l^{-1} acetate buffer solution (HAc–NaAc) pH 5.0 was prepared by dissolving an appropriate amount of sodium acetate trihydrate (+99.99%, Sigma-Aldrich) in Milli-Q water and adjusting the pH of the solution with concentrated acetic acid (suprapur, Merck).

Teflon bottles were used for gravimetrically preparation of intermediate and working standard solutions of mercury species, $NaBEt_4$ and HAc–NaAc reagents as well as storage of the milli-Q water.

The sediments (IAEA-405 and IAEA-433) were purchased from International Atomic Energy Agency (IAEA, Vienna, Austria).

2.3. Samples and sampling procedure

The ice samples were collected in Antarctica at Dome C within the framework of the European Project for Ice Coring in Antarctica (EPICA). The location, sampling procedure and sample treatment is described elsewhere [32]. Decontamination of the ice core, by removing its external layers contaminated by the drilling fluid and handling in the field was performed in a cold laboratory at the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), CNRS, Grenoble, France in a class 100 clean bench, as described elsewhere [33].

2.4. Analytical procedures

2.4.1. SPME with MCGC separation and ICP–TOFMS detection

The ionic mercury species were derivatized in situ using $NaBEt_4$ and the chemical parameters reported elsewhere were adopted [10]. A standard/sample aliquot (ca. 7.5 g thawed ice and 0.050–0.1 g leached solution of sediments) together with PrHg was buffered at pH 5.0 in a 25 ml sampling vial and then diluted to a volume of 7.9 ml with milli-Q water. For the analysis of ice, 0.5 ml HAc–NaAc buffer was used for the blanks, standard and samples while 4 ml were used for the analysis of sediments. An aliquot of 100 μl $NaBEt_4$ solution was added and the vial was immediately closed and the fiber introduced into HS. The extraction was carried out at room temperature for 8 min while stirring the sample vigorously (1400 rev min^{-1}). The fiber was then withdrawn into the needle and the SPME device transferred into the GC injector in order to transfer the analytes into the separation column. Between two consecutive extractions, the vial was thoroughly washed with 10% (v/v) HNO_3 and rinsed with milli-Q water to avoid carryover.

The operating conditions for the system based on SPME with MCGC separation and ICP–TOFMS detection are given in Table 1. Quantification was carried out on the basis of external calibration and using peak area for evaluation of the signals obtained for the isotope ^{202}Hg. PrHg at 25 pg level was used as an internal standard (IS) and the analytes' intensity was rationed to its intensity throughout quantification (by external calibration).

Table 1
Optimal operating conditions for SPME with MCGC separation and ICP–TOFMS detection

SPME conditions	
SPME fiber	CAR–PDMS (75 μm film thickness)
Extraction temperature	25 °C (±2)
Extraction mode	Headspace
Sample volume (vial capacity)	8 ml (25 ml)
Extraction time	8 min
Stirring rate	1400 rev min^{-1}
Injection time	30 s
Injection conditions	
Injection port (desorption) temperature	250 °C
SPME fiber position in injector port	3 cm
Injection mode	Splitless
Injection port liner	0.75 mm i.d.
Connection of MCGC column to injector	25 cm × 0.53 mm i.d. fused silica capillary
Separation and analytes transport conditions	
Column	MC-1 HT: 900 capillaries × 1 m × 40 μm i.d. × 0.2 μm film thickness (100% PDMS)
Carrier gas/column flow (linear velocity)	He/105 ml min^{-1} (155 cm s^{-1})
Separation temperature (isothermal)	100 °C
Transfer line set-up	Fused silica capillary: 170 cm × 0.25 mm i.d.
Transfer line temperature	150 °C
Make-up gas flow (Ar)	1.4 ± 0.2 l min^{-1}
ICP–TOFMS conditions	
RF-power	1.3 kW
RF-frequency	40.68 MHz
Auxiliary gas flow	1.4 ± 0.2 l min^{-1}
Plasma gas flow	14.5 l min^{-1}
Integration time	204 ms
Scanning mode	Transient
Isotopes monitored	^{202}Hg, ^{201}Hg, ^{200}Hg, ^{199}Hg, ^{198}Hg
Spectral generation frequency	20 kHz

2.4.2. Preparation of sediments

A procedure reported elsewhere [34] was used for leaching the mercury species from sediments. In brief, approximately 1.0 g sediment was accurately weighed directly into an extraction vessel and then 10 ml HNO_3, 6 mol l^{-1}, were added. After manually shaking for 5 min to ensure homogenization of phases, the mixture was exposed to 60 W microwave power for 3 min. After cooling at room temperature the phases were separated by centrifugation (10 min at 2000 min^{-1}). The supernatant solution was quantitatively transferred into a 50 ml propylene tube and stored at −20 °C until analysis.

3. Results and discussion

Method optimization was carried out by analysis of a standard solution containing 100 pg of MeHg, Hg^{2+} and PrHg using univariate optimization. The normalized intensities (%) reported in this study are calculated by rationing the actual value to the maximum. HS-SPME was carried out at ambient temperature (25 ± 2 °C) throughout the study. A CAR–PDMS fiber was used for extraction/preconcentration and subsequent injection of the ethylated mercury species into the separation column. This fiber proved to be the most efficient for HS extraction of MeHg and Hg^{2+} after their derivatization with $NaBEt_4$ [31], hence justifying its use in this study.

3.1. Derivatization/volatilization conditions

Commonly used as derivatization agents for the ionic mercury species are $NaBEt_4$, sodium tetrapropylborate ($NaBPr_4$) and sodium tetraphenylborate ($NaBPh_4$). Since the first application of SPME for speciation analysis of mercury [25], $NaBEt_4$ is most often used. Its main advantages are the relatively short equilibration times and the high extraction efficiency [31]. In addition, using ethylation, PrHg can be used as an IS because its presence in the environment is highly unlikely. Conversely, when using propylation, the use of PrHg is hampered because of loss in species-specific information (both Hg^{2+} and PrHg lead to the same propylated product). An alternative IS is ethylmercury (EtHg) but this species is sometimes present in environmental or biological samples [35]. Phenylation suffers from both long equilibration times (in excess of 30 min for mercury species) and low extraction efficiency [18]. Consequently, this derivatization method is seldom used in combination with HS-SPME. Due to all this, ethylation of the mercury ionic species was adopted for this study.

The necessary amount of $NaBEt_4$ for the ethylation of MeHg and Hg^{2+} was optimized at pH 5.0. In previous work [31], it was found that by increasing the amount of $NaBEt_4$ up to 0.05% in the extracting solution (milli-Q water used as matrix) the extraction yield for MeHg decreased by over 50%. This behavior might be caused by triethylborate (BEt_3), the product of both derivatization and hydrolytic degradation reactions of $NaBEt_4$ taking place in acidic medium [36]. However, to measure BEt_3 (by monitoring ^{10}B or ^{11}B isotopes) was not possible in this study, because mass per charge ratios (m/z) of 10 and 11 were deflected as a consequence of deflection of m/z 12 (^{12}C isotope), whose deflection is mandatory to avoid overloading the detector. It is worth noting that the narrowest setting of a deflection window affects minimum 2–3 amu, hence ^{10}B and ^{11}B are inherently deflected together with the ^{12}C isotope. At high $NaBEt_4$ concentrations of ca. 0.05% in the extracting solution the BEt_3 level was five orders of magnitude higher than that of MeHg and Hg^{2+}. BEt_3 then could compete with the ethylated mercury species in the transfer into HS and their sorption by the SPME fiber. Hence, the amount of $NaBEt_4$ should be carefully optimized to ensure optimum extraction efficiency. In this respect attention should be paid to the method employed for optimization of the derivatization step when using HS-SPME. The use of liquid–liquid extraction for this purpose as reported by other authors [37] or direct SPME might lead to erroneous results. Also, at concentrations of $NaBEt_4$ over 2% in the extracting solution self-ignition of the SPME fiber could occur [18]. The amount of buffer solution added for derivatization should also be kept to a minimum to ensure a low reagent blank, especially for the analysis at ultra-trace levels, as both $NaBEt_4$ and HAc–NaAc buffer [38] are known to contain trace levels of Hg^2. In this respect, the purity of the IS must also be checked; MeHg and Hg^{2+} were not detected in the reagent blank solution when 100 pg amounts of PrHg was added.

In order to assess the contribution of HAc–NaAc and $NaBEt_4$ reagents to the contamination of the blank solution, MeHg and Hg^{2+} signals were monitored while increasing separately the volumes of HAc–NaAc and $NaBEt_4$ added to the blank solution, from 100 to 1000 μl. To ensure that increasing MeHg and Hg^{2+} levels reflect only the contamination, their signals were rationed to the intensity of the IS, which then compensates small variations of chemical and instrumental parameters. Apart from the rationed signals (MeHg/IS and Hg^{2+}/IS) the absolute signal of IS was also monitored. The addition of 100 μl of HAc–NaAc was sufficient to ensure a pH 5.0 of the standard solution used for optimization. Hence, theoretically the increase in MeHg and Hg^{2+} signal should be correlated only to the contamination caused by the increase in buffer amount rather than variation of chemical parameters such as pH.

As illustrated in Fig. 1(a), the MeHg/IS and Hg^{2+}/IS signals increased steadily with addition of buffer solution from 100 to 750 μl. The IS intensity also increased over the whole range of buffer amounts studied. In this case, the increase in extraction efficiency for MeHg, Hg^{2+} and PrHg could be explained by the enhancement of the ionic strength of the solution with the addition of buffer rather than contamination as the buffer solution was found to be free of PrHg. The ionic strength of the solution is an important parameter that favors volatilization and hence, global extraction efficiency [39]. In this particular case, the differentiation between contamination and salting out effects would imply additional ex-

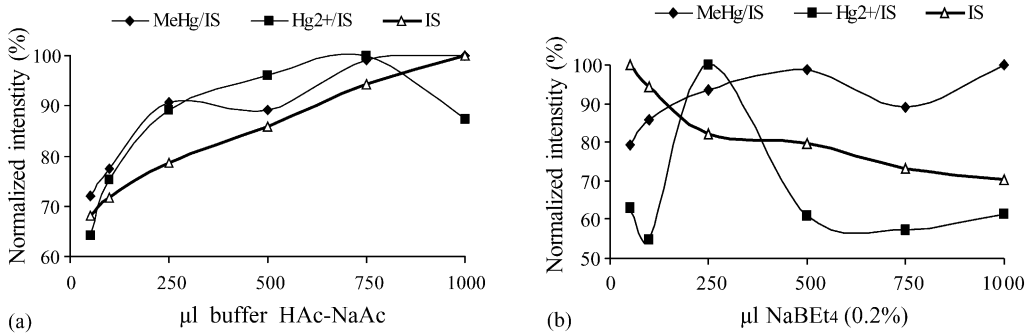

Fig. 1. Influence of volumes of HAc–NaAc (a) and $NaBEt_4$ (b) added to the blank solution on extraction efficiency and contamination.

periments where variation in buffer amount is carried out in solutions of the same overall ionic strength, but this was not attempted. For further experiments, 500 μl HAc–NaAc buffer solution was used as a compromise between the reagent blank level and the optimum ionic strength for enhanced volatilization.

Similar considerations can be formulated for explaining the effects when increasing the $NaBEt_4$ concentration, but the interpretation is more complex as apart from contamination and salting out effects, signal suppression as a result of the elevated amount of BEt_3 might occur. A compromise in terms of contamination and extraction efficiency was found by using 250 μl $NaBEt_4$ as illustrated in Fig. 1(b). In order to compensate the basicity introduced by $NaBEt_4$ (pH 10.0 for 0.2% concentration), 2 ml HAc–NaAc buffer solution was maintained while increasing the amount of $NaBEt_4$ from 100 to 1000 μl.

The stability of $NaBEt_4$ solution (0.2%) during storage at 4 °C in the dark was also evaluated. After 1 day of storage, only 15% of the reagent is degraded whereas 60% degradation occurs after 4 days.

3.2. SPME optimization

3.2.1. Extraction time

Extraction time profiles for mercury species are shown in Fig. 2. The extraction time was optimized using magnetically stirring at 1400 rev min^{-1} and a pre-equilibration time of 1 min, as described in previous work [31]. An extraction of >90% (the ratio, % between the actual value and the maximum) was obtained for MeHg and PrHg within 3 min whereas >7 min were required to reach this level for Hg^{2+}. Extraction efficiencies were identical for 8 min extraction from headspace and 7 min extraction after 1 min equilibration time without fiber into headspace, which confirms that derivatization/volatilization and sorption of analytes by the fiber takes place simultaneously. In order to avoid loss of analytes through the septum piercing during a pre-equilibration step, extraction was carried out by introducing the fiber into HS immediately after the vial was closed and 8 min sampling was adopted (1 min pre-equilibration + 7 min, optimum). This procedure prevents also loss of analytes because of the adsorption onto the vial walls or the silicone rubber septum [40].

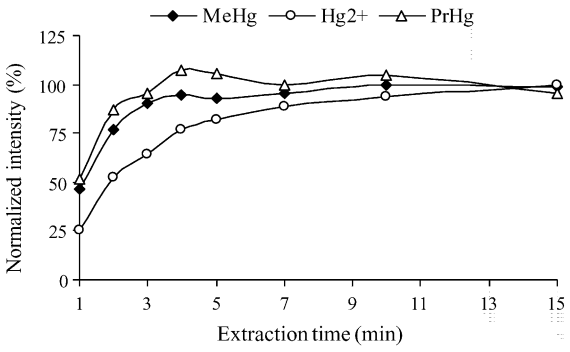

Fig. 2. Influence of extraction time on extraction efficiency for MeHg, Hg^{2+} and PrHg.

3.2.2. Desorption/injection conditions

Injection speed is critical in MCGC to ensure satisfactory peak profiles. Hence, thermal analytes' desorption from the fiber should be fast and quantitative to obtain narrow chromatographic peaks and maximum sensitivity. This commonly implies the use of a high temperature (above 200 °C) of the GC injector port. On the other hand, the ethylated mercury species become somewhat thermally unstable at high temperature and the formation of Hg^0 could take place during thermal desorption, particularly when carbon-based adsorbents are employed [41] as is the case of CAR–PDMS fiber.

The speed of the desorption/injection process in SPME is related to the nature of the extracting phase of the fiber and consequently the sorption mechanism. In principle, the fastest injection should be obtained using fibers with solid extracting phases, such as PDMS–DVB and CAR–PDMS. In this case, the extraction is carried out predominantly by adsorption and hence thermal desorption is a surface process. Conversely, when using fibers with liquid extracting phases such as PDMS, the analytes need to diffuse through the liquid (polymeric) layer, which leads to slower desorption/injection. To check this, three fibers namely PDMS (100 μm), CAR–PDMS (75 μm) and PDMS–DVB (65 μm) were compared in terms of injection speed. The full width at half height (FWHM) for MeHg (the most volatile species)

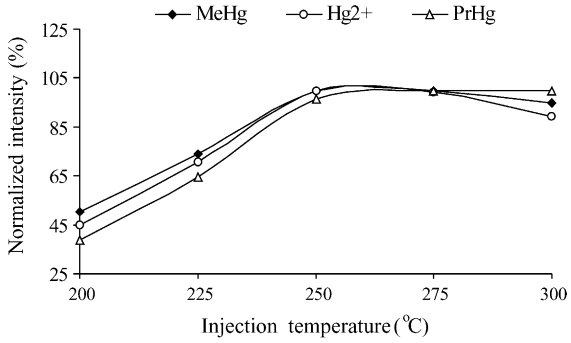

Fig. 3. Influence of injector port temperature on desorption/injection efficiency.

was used as a criterion for desorption/injection speed. The experiment was carried out during the same day to avoid instrumental bias. Among the fibers compared, the PDMS–DVB fiber ensured the fastest injection and FWHM values down to 0.4 s were obtained, while both CAR–PDMS and PDMS provided slower injection (but similar to each other) with FWHM ≅0.8 s. Theoretically, the FWHM for CAR–PDMS should be lower than that for PDMS and comparable with PDMS–DVB, as the extraction by both CAR–PDMS and PDMS–DVB fibers takes place predominantly by adsorption. The slower desorption from CAR–PDMS is probably the result of the nature of the coating. In comparison to other solid extracting phases used in SPME, the carbon particles (Carboxen) have pores with extremely small diameters, which can lead to capillary condensation of the analytes inside the pores [42]. This directly influences the thermal desorption of the analytes. In addition, significant carryover can also occur [42] if the temperature of the GC injection port is not carefully optimized.

The desorption/injection temperature for the CAR–PDMS fiber was optimized in the range 200–300 °C. As shown in Fig. 3, the most efficient desorption/injection was obtained at 250 °C, which was chosen for further experiments. Desorption at temperatures below 225 °C led to low efficiency and unsatisfactory peaks profile as illustrated in Fig. 4(a). On the other hand, a more elevated formation of Hg^0 was observed at 300 °C (Fig. 4(b)).

In a previous work [31], the maximum desorption efficiency was obtained when the SPME needle was withdrawn 3 cm from the fiber holder; most likely, this position corresponds to the hottest region of the injector and leading, therefore, to the enhanced desorption characteristics.

The speed of injection is also influenced by the internal diameter (i.d.) of the injector inlet liner [43] as well as the fused silica tubing used for connection of the MCGC column to the injector port. In this context, three fused silica capillaries with 0.25, 0.32 and 0.53 mm i.d. were compared as connectors of the MCGC column to the injector port. In each case, the FWHMs were determined at three different head column pressures (30, 60 and 90 psi, 1 psi ≅ 0.069 bar) but no significant difference in terms of peak width was obtained. Similarly, differences below 10% in peak width were obtained between injector inlet liners with 0.75 and 4 mm i.d. This indicates that reducing the diameter of the injector inlet liner or connecting tubing does not necessarily improve the injection performance when high carrier gas flows are employed. Nevertheless, for further experiments, a 0.75 mm i.d. injector inlet liner and a 0.53 mm i.d. × 25 cm length connector (of the MCGC column to the GC injector port) was used to ensure maximum achievable velocity of the carrier gas at the column entrance.

3.2.3. Assessment of distribution constants

Besides the practical aspects of method development, a more fundamental approach dealing with the determination of distribution constants of both ethylated mercury species under the optimized experimental conditions was also considered in this study. Such information is lacking in the literature and to the authors' knowledge, this is the first determination of distribution constants of ethylated mercury species such as methylethylmercury (MeHgEt) and diethylmercury (Et_2Hg) by HS-SPME with MCGC separation and ICP–TOFMS detection. The following distribution constants were assessed:

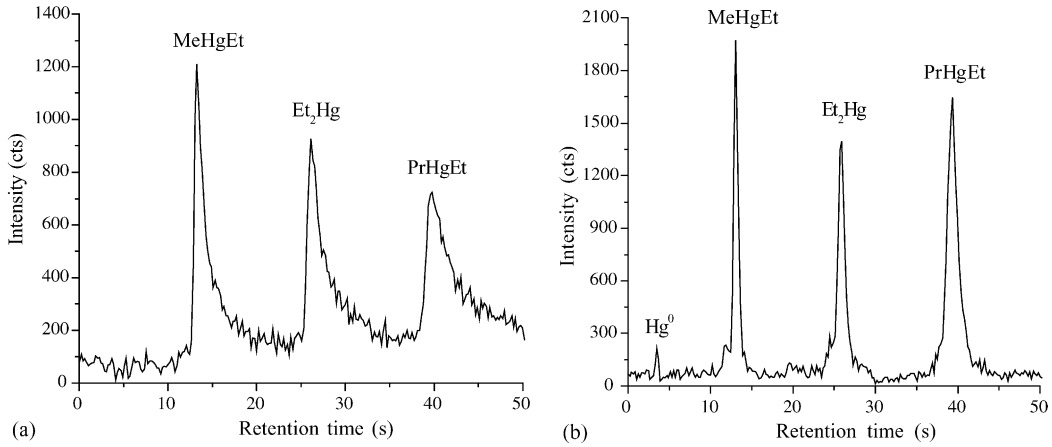

Fig. 4. Influence of injection temperatures: (a) 200 °C and (b) 300 °C on chromatographic peak profile.

headspace-solution (K_{hs}), coating-solution (K_{cs}) and coating-headspace (K_{ch}). A method based on multiple HS-SPME experiment proposed by Ezquerro et al. [44] was used. For this, five successive SPME runs were carried out from the same solution with milli-Q water as a matrix. The solution initially contained a standard mixture of 25 pg of MeHg, Hg^{2+} and PrHg. Calculation of K_{cs} is based on Eq. (1), which describes the equilibrium in a three-phase (headspace) SPME system [45].

$$K_{cs} = \frac{m_c}{m_0 - m_c}\left(\frac{V_s}{V_c} + K_{hs}\frac{V_h}{V_c}\right) = \frac{m_c}{m_s}\left(\frac{V_s}{V_c} + K_{hs}\frac{V_h}{V_c}\right) \quad (1)$$

where m_c is the amount of analyte extracted by the coating at equilibrium; m_0, initial amount of analyte in solution; m_s, amount of analyte remained in solution at equilibrium; K_{cs}, coating-solution distribution constant; K_{hs}, headspace-solution distribution constant; V_s, volume of liquid sample; V_c, volume of fiber coating; V_h, volume of headspace.

The practical relationship derived from Eq. (1) used for calculation of distribution constants based on the multi-headspace SPME experiment is as follows [44]:

$$\ln A_i = (i-1)\ln\beta + \ln A_1 \quad (2)$$

where A_i is peak area during extraction i; A_1, peak area during the first extraction step and β is defined by Eq. (3).

$$\beta = \frac{K_{hs}V_h + V_s}{K_{cs}V_c + K_{hs}V_h + V_s} \quad (3)$$

As illustrated by Eq. (2), β can be calculated from the slope of the linear plot of $\ln A_i$ versus $(i-1)$ obtained from successive HS-SPME determinations of the same standard solution. Once β is experimentally determined, K_{cs} can be calculated using Eq. (4).

$$K_{cs} = \frac{1-\beta}{\beta}\left(\frac{V_s}{V_c} + K_{hs}\frac{V_h}{V_c}\right) \quad (4)$$

As shown in Eq. (4), in order to calculate K_{cs}, the knowledge of K_{hs} is necessary. Whereas for the corresponding salts, MeHgCl and $HgCl_2$, K_{hs} can be calculated using Henry's law constants (H) ($K_{hs} = H/RT$) found in the literature [46], these constants are not available for the ethylated derivatives. Hence, an additional experiment for the determination of K_{hs} for MeHgEt and Et_2Hg was carried out for which the method proposed by Bierwagen and Keller [47] was adopted. The experiment consists in spiking the same bulk amount of analyte into different volumes of solution and measuring the extracted amount of analyte from headspace; K_{hs} (dimensionless) is calculated using Eq. (5).

$$\frac{1}{AV_s} = \frac{1}{kn_0K_{hs}} + \frac{1}{kn_0}\left(\frac{V_h}{V_s}\right) \quad (5)$$

where n_0 is the initial amount of analyte in solution (mol); k, calibration factor; A, peak area corresponding to the measurement of the sample with volume V_s. In this study, a 500 pg mixture of MeHg, Hg^{2+} and PrHg were spiked into five different volumes of solution, ranging from 4.2 ml up to 16.5 ml. Using Eq. (5), K_{hs} can then be calculated as the ratio of the slope and the intercept of the plot $(1/AV_s)$ versus (V_h/V_s). It is worth noting that in this case, determination of K_{hs} is independent of the amount of analyte present in solution and the nature of fiber coating used for extraction.

Based on Eq. (2), β values obtained for MeHgEt and Et_2Hg were 0.49 and 0.58; using Eq. (5), K_{hs} = 0.76 for MeHgEt and 0.63 for Et_2Hg. Because the experiments were conducted with mixed standards instead of solutions of single species, K_{hs} values as reported here are indicative. On the other hand, the determination of K_{hs} is inherently affected by the presence of volatile BEt_3 in the system as the product of derivatization and degradation (of $NaBEt_4$) reactions. Moreover, as Eq. (4) illustrates, K_{hs} has a relatively low contribution to the global distribution constant, K_{cs} when large volumes of headspace and extraction phases with low thickness of the coating are used. In Eq. (4), the ratio V_h/V_c is approximately 10^4, therefore, small variations in K_{hs} do not significantly affect the calculation of K_{cs}. The coating volume of the CAR–PDMS fiber was calculated as described elsewhere [48] using $V_c = \pi L(f^2 + af)$ and taking into account the coating thickness (f = 75 μm), the diameter of the supporting rod (a = 0.011 cm) and the fiber coating length (L = 1 cm). Using experimentally determined β and K_{hs} values and taking into account that in our experiments, V_s = 8 ml, V_h = 17 ml and V_c = 0.436 μl, K_{cs} values calculated for MeHgEt and Et_2Hg are 4.9×10^4 and 3.0×10^4. Finally, K_{ch} was calculated given that $K_{cs} = K_{ch}K_{hs}$. Hence, $K_{ch} = 6.5 \times 10^4$ for MeHgEt and 4.8×10^4 for Et_2Hg.

3.3. ICP–TOFMS detection: forward power optimization

Apart from the parameters that are daily optimized for optimum plasma conditions, the forward power (RF) is the main factor influencing the signal intensity. Heisterkamp [36] showed that optimum RF is related to the make-up gas flow. When higher RF is applied, the location of the plasma analytes' ionization zone is shifted towards the induction coil. Thus, to reposition the ionization zone, a higher make-up gas flow should be applied [36]. On the other hand, in a previous work [10], it was found that re-optimization of the make-up gas flow in transient mode in comparison with the optimized value for ^{124}Xe in the bulk mode (steady state signal) is not necessary when MCGC is used in combination with ICP–TOFMS. This is the consequence of considerable higher carrier gas flows used for separation by MCGC (carrier gas flow >100 times higher than in CGC). In this particular situation, there is no need of additional make-up gas (compared to values optimized for ^{124}Xe in bulk mode) to improve the analytes transport efficiency as the case of CGC [10].

In this study, the RF influence on the signal intensity was evaluated while the make-up gas flow was kept constant. Sig-

nal intensity of mercury species at RF ranging from cold plasma (0.8 kW) up to hot plasma conditions (1.5 kW) was determined. An identical behavior for MeHg, Hg^{2+} and PrHg was found over the whole range of RF studied as was expected since the RF power is element but not species dependent. The most efficient ionization was obtained at 1.3 kW, and this value was adopted for further experiments. In a similar study by Leenaers et al. [49] where ICP–TOFMS was used for mercury species detection after separation by CGC, an optimum RF between 1.0 and 1.1 kW was obtained. The higher RF obtained in the present work is consistent with the ionization conditions for mercury; this element has a high first ionization potential (10.4 eV), which, in principle, requires hotter plasma conditions, particularly when higher flows of carrier gas are introduced into the plasma.

3.4. Analytical characteristics: repeatability, detection limits and linearity

The repeatability in terms of relative standard deviation (R.S.D., %) calculated for 10 successive injections of a standard mixture (10 pg) using integrated peaks and analog detection mode is reported in Table 2. R.S.D.s below 5% were obtained using the IS. As the detection in analog mode is not limited by the need to record single-ion events as the case of ion-counting, multiple ions can be detected simultaneously, hence, worse precision can be obtained in the ion-counting mode [7]. Using the ion-counting mode a repeatability of 7.9% for MeHg and 10.6% for Hg^{2+} was obtained. The repeatability obtained for 10 successive injections of the reagent blank with R.S.D. up to 8% is also reported in Table 2. These values reflect determinations at concentration levels close to the detection limit. Values calculated without corrections on the basis of IS for both blank and standard are given in parenthesis (Table 2). As can be seen, PrHg used as IS proved to correct adequately for errors related to experimental procedures, such as derivatization, extraction, injection, separation and instrumental drift especially at levels close to the MDL; R.S.D. values between 15 and 20% were obtained at blank level without using the IS.

Ensuring identical extraction times and solution volumes for blanks, standards and samples is important for accurate and precise quantification, particularly when using HS-SPME before reaching full equilibrium [50]. In such circumstances, the use of IS is recommended. In this study, successful compensation (deviation below ± 10%) for variations in extraction time up to 2–3 min was obtained for both species by using PrHg as an IS. The compensation for large variations in solution volume was shown to be more critical. Nevertheless, excellent compensation (deviations < 15%) was obtained for a variation in solution volume up to 2 ml, a situation, however, unlikely to be encountered in practice.

Method detection limits (MDL) are reported as three times the standard deviation for 10 successive injections of the analytical reagent blank in the analog mode. MDLs considerably below the pg g^{-1} level, namely 0.027 pg g^{-1} (as metal) for MeHg and 0.27 pg g^{-1} for Hg^{2+} were obtained. These values are slightly higher than those obtained by PTI in a previous work [10]. This can be explained by incomplete (equilibration) extraction by SPME, which intrinsically leads to lower sensitivity. In opposition, PTI enables an exhaustive continuous extraction. It should be noted that using both SPME and PTI, the MDL for Hg^{2+} is about one order of magnitude higher than that of MeHg. This is the consequence of the higher reagents blank of Hg^{2+} as can be seen in Fig. 5(a), which shows a typical chromatogram obtained for the reagent blank spiked with IS.

The linearity of the method was assessed by analyzing in duplicate MeHg and Hg^{2+} at seven levels of concentration between 0 and 1500 pg (as cation) using the analog detection mode. The calibration graphs show good linearity over this concentration range, correlation coefficients higher than 0.99 were obtained. A comparison of the SPME and PTI methods in terms of analytical performance characteristics is given in Table 2.

3.5. Analysis of sediments: comparison with PTI method

The developed method was applied to the analysis of marine and estuarine sediments with recommended values for MeHg and Hg_T. Quantification was carried out using external calibration and IS. Derivatization by using propylation (qualitatively only) was initially carried out to assess the eventual presence of EtHg, which could hamper the determination of Hg^{2+} when using ethylation; no traces of EtHg were found in the sediments analyzed. Table 3 shows the agreement between the recommended levels of MeHg and Hg_T for both IAEA-405 and IAEA-433 and concentrations

Table 2
Analytical performance characteristics of SPME asnd PTI based methods in combination with MCGC separation and ICP–TOFMS detection (in analog mode)

Analyte	MDL (pg g^{-1}, as metal)		Precision[a] (R.S.D., %, n = 10)				Correlation coefficient (R^2)[b]	
	PTI	SPME	Reagent blank		Standard[c]		PTI	SPME
			PTI	SPME	PTI	SPME		
MeHg	0.016	0.027	6.2 (6.1)	5.5 (16)	1.2 (3.4)	3.3 (5.7)	0.9999	0.9995
Hg^{2+}	0.26	0.27	6.4 (8.7)	7.1 (19)	4.1 (3.5)	3.8 (5.5)	0.9981	0.9978

[a] Values reported in parenthesis: repeatability calculated without IS.
[b] 0–1000 pg for PTI and 0–1500 pg for SPME.
[c] Successive injections of a standard mixture containing 10 pg MeHg (as Hg) and Hg^{2+}.

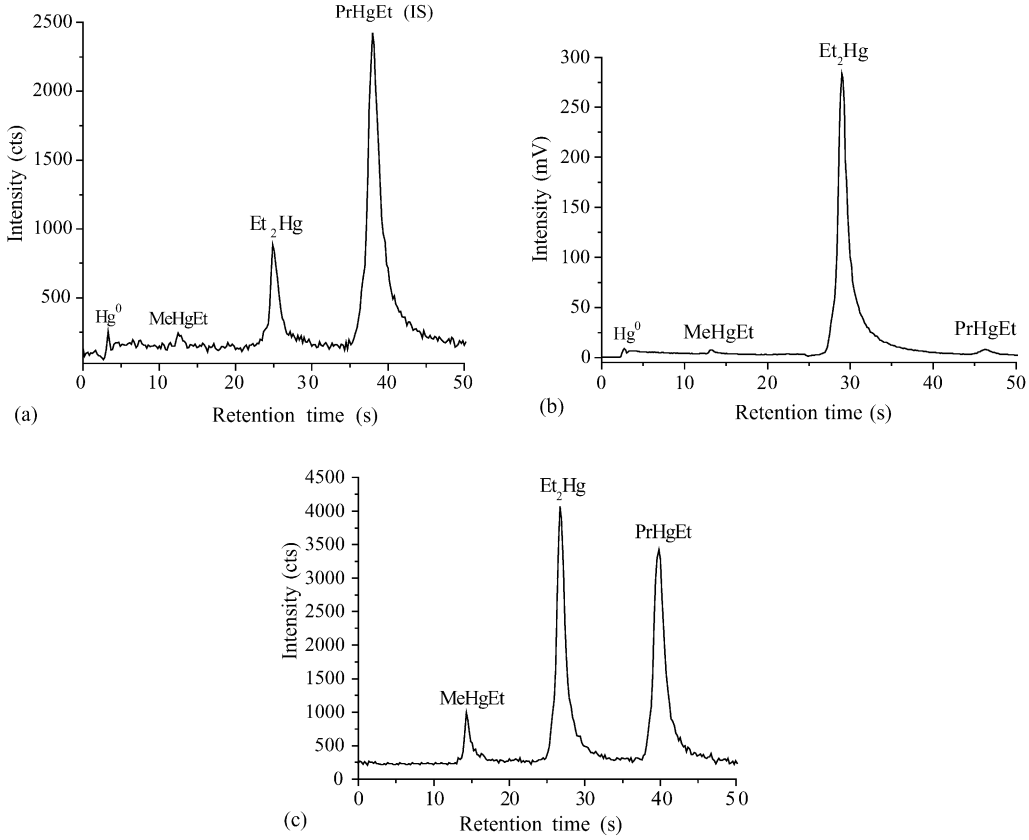

Fig. 5. Typical chromatogram obtained for the reagent blank (a), IAEA-405 sediment (b) and ice (c) spiked with internal standard.

measured by SPME method developed in this study. Also, a comparison with the PTI method is addressed. Only for IAEA-433, a higher level was obtained for MeHg when using the PTI method developed earlier [10], which was employed for an intercomparison exercise of the marine sediment IAEA-433 [51]. The values obtained for Hg_T and MeHg by the PTI method were considered for the calculation of the recommended value. A typical chromatogram of a sediment (IAEA-405) spiked with IS is shown in Fig. 5(b).

The simultaneous determination of MeHg and Hg^{2+} in complex matrices such as sediments is an analytical challenge, especially when the level of MeHg is orders of magnitude below that of Hg^{2+} as in the case of IAEA-433. In this case, when 10–15 pg MeHg (as metal) is present in the aliquot of leached solution subjected to SPME, the concentration of Hg^{2+} is 1000–1500 pg. Such high levels of Hg^{2+} can saturate both the SPME fiber and the detector. Considerable memory effects occur for Hg^{2+}, hence monitoring the blank level between replicates is mandatory. Monitoring the intensity of the IS is an efficient way to asses the effects of saturation and the sample matrix on the derivatization and/or extraction efficiency. In general an IS can successfully compensate for errors if the deviation of its signal in samples compared to blank/standards is less than ±30% [52]. For the sediments analyzed in this work, the fluctuation of the IS intensity compared to the standards was generally well below 20%.

3.6. Application to speciation analysis of mercury in Antarctica ice

The method was applied to speciation analysis of mercury in ice from Antarctica. Similarly to the case of sediments, no traces of EtHg were found in the ice, which allowed the use of

Table 3
Results (mean ± standard deviation, $n = 3$) of the analysis of sediments

Analyte	IAEA-405			IAEA-433		
	Recommended	Found		Recommended	Found	
		PTI	SPME		PTI	SPME
MeHg[a]	5.49 ± 0.53	5.93 ± 1.28	5.31 ± 0.30	0.17 ± 0.07	0.51 ± 0.088	0.25 ± 0.022
Hg_T[b]	0.81 ± 0.04	0.84 ± 0.10	0.75 ± 0.10	0.168 ± 0.017	0.195 ± 0.016	0.150 ± 0.012

[a] $\mu g\,kg^{-1}$, as metal.
[b] $mg\,kg^{-1}$ total mercury: sum of MeHg and Hg^{2+}.

Table 4
Results obtained by SPME and MCGC coupled to ICP–TOFMS for mercury speciation analysis in ice from Antarctica

No.	Concentration (pg g^{-1}, as Hg)[a]			
	Depth (m)	Age (years BP)	MeHg	Hg_T[b]
1	229.35	7100	0.14 ± 0.02	0.97 ± 0.01
2	515.9	22000	0.17 ± 0.01	9.13 ± 1.26
3	1313.4	93300	0.36 ± 0.09	3.85 ± 0.54
4	1643.4	124700	0.12 ± 0.05	0.12 ± 0.05

[a] Mean ± standard deviation (n = 3).
[b] Total mercury, sum of MeHg (as Hg) and Hg^{2+}.

derivatization by ethylation. The preliminary results reported in this work correspond to four ice core sections taken at depths of 229, 516, 1313 and 1643 m, which cover a period of about 125,000 years before present (BP) from the Holocene back to at least the penultimate glacial–interglacial transition. As listed in Table 4, concentrations of Hg_T are spread over a rather wide range, from 0.1 pg g^{-1} up to 9 pg g^{-1} whereas MeHg values are generally below 0.4 pg pg^{-1}. A typical chromatogram of an ice sample spiked with IS is shown in Fig. 5(c).

The accuracy of the measurements was assessed on the basis of recovery studies on ice samples spiked with MeHg (5 pg) and Hg^{2+} (10 pg), just prior to the analysis. The recovery factor was calculated as the ratio (%) of analyte's amount determined in the blend sample + spike (by subtracting the analyte's amount measured in the real sample just prior the measurement of the mixture sample + spike) and the known amount of analyte added. Recovery factors of 100% for MeHg and 104% for Hg^{2+} were obtained. In addition, internal quality control of the experimental procedure was carried out by using standard solutions of MeHg and Hg^{2+} purchased from a different source than that used for calibration. More than 90% recovery was obtained.

4. Conclusions

This study demonstrates that the combination of HS-SPME with MCGC separation and ICP–TOFMS detection allows rapid, simple, accurate and precise speciation analysis of mercury at ultra-trace levels in sediments and ice from polar regions. SPME with CAR–PDMS fiber is comparable in terms of analytical performance characteristics with PTI, but in terms of cost, simplicity and sample throughput SPME is preferable. Very fast chromatographic signals (with FWHM below 1 s) as obtained by MCGC systems can be recorded with ultra-trace sensitivity without loss in precision due to the simultaneous character and very high data acquisition rate of ICP–TOFMS.

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