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Determination of methylmercury by solid-phase microextraction inductively coupled plasma mass spectrometry: a new sample introduction method for volatile metal species†

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Direct coupling of solid-phase microextraction (SPME) with inductively coupled plasma mass spectrometry (ICP-MS) is described for methylmercury speciation. A thermal desorption interface, consisting of a heated, glass-lined splitless-type GC injector, was placed directly at the base of the torch to minimize the length of transfer line. This arrangement provides for fast desorption and high sample introduction efficiency. Direct liquid immersion and headspace extraction of methylmercury was studied, including the effect of temperature and time on the extraction efficiency. For clean solutions, immersion sampling SPME provided good sensitivity that was linear over two orders of magnitude whereas headspace sampling showed 15% lower sensitivity, but a linear range of more than three orders of magnitude. The detection limit for headspace methylmercury sampling was 0.2 ng ml^{-1}. Calibration by the method of additions using direct extraction revealed a severe matrix effect with biological tissue samples, diminishing the methylmercury response 70-fold, whereas that obtained by headspace extraction was statistically indistinguishable from signals generated using matrix free standards. Analytical results showed good agreement between certified and measured values for analysis of NRCC DORM-2, (Dogfish muscle) and DOLT-2 (Dogfish liver) reference materials.

Introduction

Methylmercury has attracted considerable attention from the scientific community due to its extreme toxicity. Typically, methylmercury enters the environment either by direct release, through abiotic processes,[1] or *via* methylation of inorganic mercury in biological systems.[2] This latter process provides an alternative route for the bioaccumulation of methylmercury throughout many food chains.[2–7] The resulting biomagnification of methylmercury can have dramatic consequences for top predators such as humans; the best-known example of this being the Minimata catastrophe in which over one hundred people died and many more suffered permanent disability from high-level exposure.[7] Although unfortunate, such events have catalyzed an increased interest in methylmercury toxicology and its biochemical mechanisms.

Methylmercury is one of the few metal species regulated and whose determination is required by law in many countries.[8] There are no current reference materials for human body fluids (urine or blood) for intoxication studies. In some cases,[9] a combination of total mercury determination and pathology evidence can provide indirect evidence of methylmercury poisoning. However, recent reports of the direct determination of methylmercury in body fluids[10] suggest that a more direct approach is possible. This emphasizes the need for the development of certified reference materials to maintain the quality of such analytical measurements. The current status and future needs for methylmercury reference materials have been recently been summarized by Horvat.[11]

Accurate determination of methylmercury in real samples often requires an extraction step coupled with a further separation prior to detection. Uria and Sanz-Medel[12] have recently reviewed some of the most popular extraction/derivatization and separation/detection methods for mercury speciation in environmental samples including: liquid–liquid,[13] acid[14,15] and base[16] leaching, distillation[17] and chemical vaporization, employing hydride-,[18] ethyl-[18] and phenyl-[19] derivatization. Although quite simple, these techniques are often non-selective such that methylmercury is extracted with other alkylated forms. Fortunately, the dominant form of organometallic mercury in the environment is methylmercury. A second, significant problem related to these procedures arises from the possible methylation of inorganic mercury during sample preparation/extraction. Typically, this will generate elevated concentrations of methylmercury and is especially problematic when inorganic mercury is present at high levels. This problem has been discussed at some length in the literature,[20–25] where conversion of inorganic mercury can typically fall between ≈0.01–0.05%, depending on the technique used.

Further separation of methylmercury from other chemical constituents is most commonly performed by gas chromatography,[17,26,27] although liquid chromatographic[28–30] techniques have also been employed. The reactive nature of the methylmercury species can lead to excessive peak tailing (due to its strong interactions with the silica residues in the stationary phase) or even sample decomposition. In addition, the detectors commonly employed tend to lack sensitivity and are not element specific. Greater sensitivity and element selective detection can be achieved through on-line coupling with atomic spectroscopic detectors such as MIP-AES,[31] ICP-MS[32,33] or AFS.[32,33]

As an alternative approach to direct sample extraction, headspace sampling of methylmercury can be achieved using solid-phase microextraction (SPME).[34] Although relatively non-selective, this method may avoid potential analytical errors, such as accidental methylation associated with other extraction techniques. SPME therefore offers the possibility of

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a fast, solvent-free, integrated sampling–extraction–sample introduction system. SPME has already been used for the extraction of organotin,[35] and lead[35] with ethyl generation followed by GC separation. Cai *et al.*[36] utilized direct headspace extraction of methylmercury halides with SPME adsorption on a polydimethylsiloxane coated fiber having a relatively low affinity for very polar methylmercury. The use of a more suitable SPME coating and optimization of the extraction conditions should improve extraction efficiency. In this report, results obtained for the determination of methylmercury in biological samples, associated figures of merit and optimum experimental parameters are presented for both direct immersion and headspace sampling of methylmercury with thermal desorption ICP-MS detection.

Experimental

Reagents

Stock solutions (1000 mg l^{-1}) of Hg(II) and methylmercury ($MeHg^+$) were prepared by dissolution of mercury(II) chloride (Aldrich, Gold Label, Milwaukee, WI, USA) and methylmercury chloride (Alfa Aesar, Johnson Matthey, Ward Hill, MA, USA) salts, respectively. The methylmercury chloride was first dissolved in a small volume of propan-2-ol followed by dilution to volume with dilute hydrochloric acid (prepared in-house by sub-boiling distillation of feedstock). Distilled, de-ionised water (DDW, 18 MΩ cm) obtained from a NanoPure system (Barnstead/Thermolyne, Boston, MA, USA), was used for all solutions. Working standards were prepared by serial dilution of the stocks. As suggested by Lansens *et al.*,[37] all solutions were stored in Pyrex bottles under refrigeration until used. A saturated solution of NaCl was stored in a pre-cleaned polypropylene bottle. National Research Council of Canada CRMs DORM-2 (Dogfish Muscle) and DOLT-2 (Dogfish Liver), certified for methylmercury content, were selected for analysis to assess the accuracy of the technique.

Instrumentation

A Perkin-Elmer SCIEX ELAN 5000 inductively coupled plasma mass spectrometer was used for detection. Fig. 1 schematically illustrates the thermal desorption interface unit, which is fully described in the results section. The SPME fiber, coated with a 65 μm thick, partially cross-linked polydimethylsiloxane/divinylbenzene co-polymer, was conditioned and operated at temperatures specified by the manufacturer (SUPELCO, Bellefonte, PA, USA). The experimental conditions used for ICP-MS detection and the SPME extraction are summarized in Table 1. Evaluation of transient signals was performed using in-house software; peaks were integrated (typically 40 s) following the establishment of a baseline at extreme ends of the signal.

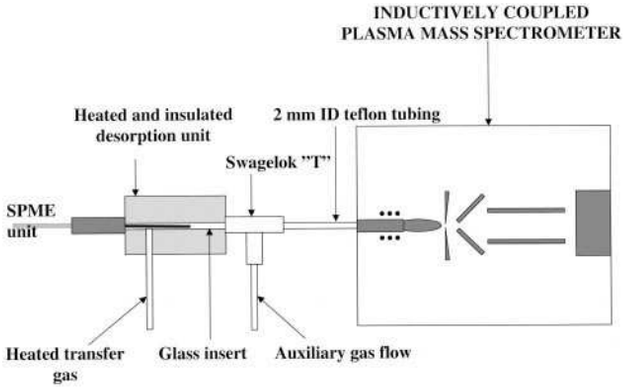

Fig. 1 Schematic illustration of the thermal desorption interface for SPME analyte introduction into ICP-MS.

Sample preparation and extraction

Tissue samples (0.250 g) were leached for one hour in 40 ml glass vials using 5 ml of 3 M hydrochloric acid and subsequently diluted to 30 ml with a saturated solution of sodium chloride. Vials were then sealed with a Teflon-lined septum cap and the headspace subsequently sampled by SPME. Headspace sampling eliminates the need for filtration or centrifugation of the sample.

For direct extraction of the acidic digests by fiber immersion, the sample was filtered, the pH was adjusted to 6 and the sample was diluted to 30 ml with a saturated solution of sodium chloride. The vial was then sealed with a Teflon-lined septum cap and the liquid phase subsequently sampled by SPME.

Safety considerations

Inorganic and organo-mercury species are very toxic. Alkylated mercury species are easily absorbed through the skin. As such, these compounds must be handled with maximum precaution and only in an adequately ventilated environment using the appropriate personal protection equipment.

Results and discussion

Two different extraction phenomena can occur with commercially available SPME coatings. Liquid-phase coatings, such as polydimethylsiloxane (PDMS), show absorption characteristics as opposed to "solid" coatings, such as polydimethylsiloxane/divinylbenzene (PDMS/DVB) or carbowax/DVB, which extract analytes *via* adsorption. With absorption-based solid-phase extraction, such as liquid–liquid extraction, the extraction capacity is proportional to the phase volume of extractant (*i.e.*, the coating). Doubling the extractant volume doubles the analyte extraction capacity. Adsorption, however, is dependent on surface phenomena and the extraction capacity is therefore related to the total surface area of the extractant. Generally, absorption-based extraction is more specific and can be used to selectively extract the analyte from complex matrices. Adsorption-based extractions, on the other hand, are non-selective and are therefore limited when more than one extractable compound is present. In practice, this limitation requires a careful method design and a detailed study of potential competitive interferences in real samples. Preliminary results revealed that, whereas the simple PDMS coated fibers do not pick up methylmercury chloride due to their polarity, the efficiency of the PDMS/DVB polymer coating is several orders of magnitude greater.

Because this is a 'solid' coating, severe matrix effects can occur in a competitive environment (such as the liquid phase of a biological extract). SPME is an equilibrium-based extraction technique and, in contrast to exhaustive extraction techniques, only a small fraction of the analyte present in the sampled phase is removed by the polymer.

Fundamental to the SPME-ICP-MS system is the development of an effective desorption-sample introduction method. The interface between the SPME and ICP-MS serves a dual function: to liberate the analyte from the polymer phase of the SPME and to transfer it to the detector. Under optimized conditions, desorption must be rapid and the transfer highly efficient. After extraction, the analyte may be removed from the fiber using either a liquid or thermal desorption process. Liquid desorption simply refers to a back-extraction into a suitable solvent, off-line or on-line, which may then be introduced directly into the ICP-MS. Although this method requires no special modification to the conventional ICP-MS liquid sample introduction system, slow desorption of the analyte from the fiber can cause broadening of the transient peak, in addition to reduced analyte sensitivity as a result of dilution.

Table 1 Experimental conditions for SPME-TD-ICP-MS detection of ^{202}Hg

ICP-MS—	
Rf power/W	800
Outer argon flow rate/l min^{-1}	15.0
Intermediate argon flow rate/l min^{-1}	1.7
Argon flow rate through the desorption unit/ml min^{-1}	35
Auxiliary argon flow rate/ml min^{-1}	280
Sampler–skimmer	Nickel
Data acquisition—	
Transient measurement	
Replicate time/ms	50
Dwell time/ms	50
Scan mode	Peak hop (*m*/*z* 199, 200, 202)
Number of replicates	1000
SPME—	
Fiber coating	65 μm, partially crosslinked polydimethylsiloxane/divinylbenzene
Extraction time/min	10
Extraction temperature/°C	50
Thermal desorption temperature/°C	250

The analyte may also be introduced *via* direct thermal desorption (TD) of the volatile components from the fiber into a carrier stream of argon which enters the central channel of the plasma. This method requires a specially designed interface, as illustrated in Fig. 1, which consists of a glass-lined splitless GC injector placed in a heated aluminum block and connected directly to the base of the ICP torch. This minimizes condensation of analyte and reduces the interaction of analyte with the wall of the transfer line so as to minimize sample loss that otherwise can be quite severe with reactive methyl mercury species. An auxiliary gas line was introduced *via* a Swagelok 'T' placed between the injector and the torch to accommodate the gas flow needed for efficient transfer of analyte from the fiber to the plasma and subsequent sampling into the mass spectrometer. Dry sample introduction permits optimal operation of the plasma at a forward rf power of 800 W. Variation in the auxiliary gas flow effectively alters the sampling depth in the plasma; an optimum position reflecting the balance between atomization–ionization processes and subsequent dispersion/neutralization of the analyte. As can be seen in Fig. 2, the effect of auxiliary gas flow rate on the mercury signal shows an optimum. The desorption temperature applied (250 °C) results in rapid release (3–4 s transient peak width) of the methylmercury. At temperatures greater than 250 °C, the polymer coatings are not stable and the TD method is therefore limited to volatile species capable of desorbing at or below this temperature. A significant advantage of this sample introduction method is the very low associated background.

Extraction procedure

Two methods were compared for the solid phase microextraction of methylmercury, (1) direct immersion of the fiber into the sample solution and (2) headspace extraction. The extraction procedure was as follows: a 30 ml volume of sample solution saturated with sodium chloride was placed in a septum-sealed 40 ml glass vial. This solution was vigorously agitated on a stirring plate using a Teflon coated stir bar. The SPME fiber was then immersed into the solution or located in the headspace for a predetermined sampling time, depending on the experiment. The fiber was then withdrawn and transferred to the desorption unit for ICP-MS measurement. The glass vials were used only once and disposed of after each analysis. Because the TD step completely cleans the fiber, no additional clean-up was necessary. The practicality of this procedure was confirmed by repeated blank extractions, wherein it was found that no sample carry-over occurred.

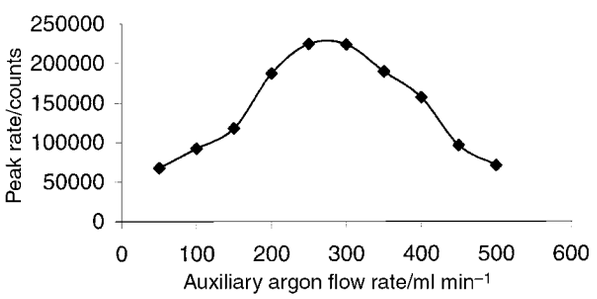

Fig. 2 Effect of carrier gas flow rate on methylmercury signal intensity derived from room temperature headspace sampling of a 100 ng ml^{-1} methylmercury standard solution saturated with NaCl.

Desorption procedure

Analyte desorption was achieved by insertion of the SPME fiber through the septum sealed glass line of the injector, where it was exposed and withdrawn after 40 s. Data collection was arbitrarily started a few seconds prior to the insertion of the fiber to permit establishment of a stable baseline An applied 40 s exposure time resulted in complete clean-up for samples in the ng ml^{-1} concentration range (higher concentrations may require longer desorption times!). The injector temperature was set to the maximum value suggested by the supplier (250 °C) to obtain flash desorption. Higher desorption temperatures resulted in improved transient peak shapes having less tailing, but at the expense of fiber lifetime.

Temporal response for methylmercury extraction by SPME

Fig. 3 shows the effect of extraction time on the signal intensity for methylmercury based on response from the most abundant isotope, $^{202}Hg^{+}$. At room temperature, equilibrium is achieved after $\approx$5–7 min for a 50 ng ml^{-1} analyte solution when immersion liquid-phase extraction is performed. For headspace sampling, equilibration between the gaseous methylmercury fraction and the exposed fiber is significantly slower and is not achieved in the analysis time window ($<$80 min). This temporal characteristic is similar to that reported by Barshick *et al.*[38] For headspace extraction, two parallel equilibration processes arise: one between the sample liquid phase and the (headspace) gas phase and a second between the gas phase and the SPME coating. This double equilibration process may account for the longer equilibration time required with the SPME solid phase.

Effect of temperature on extraction efficiency

Fig. 4 shows the effect of the extraction temperature on the uptake of methylmercury using the two different extraction

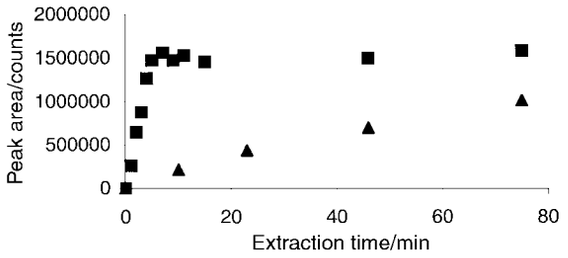

Fig. 3 Effect of extraction time on methylmercury signal intensity derived from room temperature headspace sampling of a 50 ng ml^{-1} methylmercury standard solution saturated with NaCl: ■ direct liquid phase extraction; ▲ headspace extraction.

methods. The temperature was regulated by immersing the extraction vial in a temperature controlled water bath placed on the magnetic stirring plate. The water in the bath was at the same level as the sample solution in the extraction vial as it is beneficial to maintain the fiber temperature as low as possible. As the temperature is increased, the response is enhanced for both methods. The effect is more pronounced with headspace extraction, possibly as a consequence of the increased partial pressure of methylmercury in the headspace which arises with increased temperature. An optimum extraction temperature of 50 °C was selected. Although higher temperatures could be used, the precision of the extraction process degrades from 2.2% RSD at 25 °C to 7.7% RSD at 80 °C. These data could presumably be improved if the process was automated and operated under more controlled environmental conditions.

Analytical figures and merits

Analytical figures of merit, including detection limit (LOD), quantification limit (LOQ), standard deviation, relative standard deviation, sensitivity and linear range for integrated response using both extraction methods, are summarized in Table 2. All of the results were acquired using a synthetic standard solution, an extraction temperature of 50 °C and 10 min extraction time. A headspace LOD of 200 pg ml^{-1} for methylmercury can be achieved for the measurement of this analyte in aqueous solution. This compares favorably with other methodologies[12] (ranging from 0.05 pg ml^{-1} to 10 ng ml^{-1}) when sample preconcentration factors are accounted for. This provides for a method detection limit of 24 ng g^{-1} (dry weight fish tissue). It should be noted that no response above baseline was measurable for blanks processed through this methodology. The LOD was thus derived from a calculation of the standard deviation of the intensity measurements arising from the TD of the blank (every 50 ms) acquired over the duration of the integration window (40 s). As a consequence, the reported LOD is determined primarily by the sensitivity and stability of the instrument. The ELAN 5000 ICP-MS is some 10–100-fold less sensitive than other state-of-the art ICP-MS spectrometers currently available. An absolute LOD was not calculated for sample introduction using the fiber; this could be achieved by introducing known volumes of argon saturated with mercury vapor into the ICP-MS and evaluating the integrated response. Despite availability of alternative species specific techniques possessing enhanced detection power, the methodology described here has the advantage of simplicity, which gives rise to enhanced reproducibility and high throughput. Under these conditions, it appears that direct extraction by immersion of the fiber into the liquid phase gives slightly better performance over headspace sampling, although linear range is sacrificed.

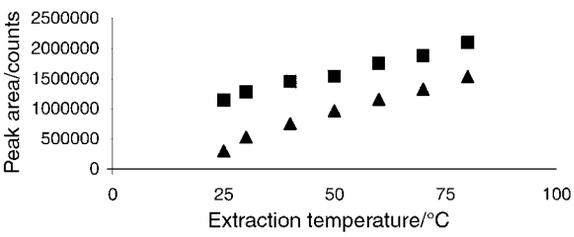

Fig. 4 Effect of extraction temperature on the signal intensity from methylmercury. Ten minute extraction times were applied using a 50 ng ml^{-1} methylmercury standard solution saturated with NaCl: ■ direct liquid phase extraction; ▲ headspace extraction.

As a consequence of the minimal amount of sample manipulation and exposure to reagents, the possibility of species inter-conversion should be minimal. As an example, a selectivity of greater than 10^5 was achieved for methylmercury *versus* inorganic mercury.

Both approaches were evaluated for external and internal calibration strategies by analysis of DORM-2 dogfish muscle CRM. Slightly different results were obtained, as summarized in Table 3. Calibration curve data for methylmercury, generated using headspace extraction from synthetic solutions (external calibration) and from spikes to the DORM-2 matrix (internal calibration–standard addition), show reasonable agreement. Headspace sampling using external calibration therefore offers sufficient accuracy for screening purposes. Where higher accuracy is required, the method of standard additions is recommended, employing more than one standard to ensure linearity. Typical $^{202}Hg^+$ signal transients based on a headspace SPME extraction of 10 and 100 ng ml^{-1} methylmercury solutions with TD-ICP-MS are given in Fig. 5. A significant integration time (40 s) is required to ensure that the full signal is measured. A relatively high background count of 300 Hz is evident and probably arises as a consequence of desorption of mercury within the instrument, as it is used for routine sample analysis. No attempt was made to identify the specific source to minimize it. A cleaner instrument may generate improved LODs. It is evident that there is a shift in the level of the baseline signal on the extreme tail of the transients which coincides with the withdrawal of the fiber from the desorption unit. Mercury, initially desorbed from the fiber, may be condensed onto cooler regions of the needle and then only slowly, and incompletely, released within the measurement window. A comparison of the data acquired using external calibration and standard additions for the direct immersion liquid-phase extraction method reveals much poorer agreement. It appears that competition in the liquid phase significantly reduces the extraction efficiency of methylmercury. For complex samples containing volatile components, headspace extraction is therefore recommended.

Results for the determination of methylmercury by headspace SPME-TD-ICP-MS in DORM-2 and DOLT-2 certified reference materials are summarized in Table 4. The data generated using the current method indicate good agreement with the certified values. In particular, the relative standard deviation is small, which may reflect the very simple and reproducible sample handling/extraction procedures involved.

Several fibers were consumed during the method development, but all analytical data presented here were obtained using only 2 fibers. All measurements detailing the analytical characteristics of the technique (Tables 2, 3 and 4) are based on a single fiber. All precision and accuracy data reflect results obtained with a single fiber. Close examination of the data presented in Figs. 3 and 4 for comparison of the two extraction methods reveals some inconsistencies in the absolute intensity results. Between the two measurement studies, the SPME fiber was changed and the two fibers show about 20% difference in their uptake rate. This aspect of fiber performance was investigated in more detail. Table 5 shows results for a intra- and inter-fiber performance for 5 repetitive headspace samplings of a 10 ng ml^{-1} sample of methylmercury. The 3 fibers had not been used prior to this process, they were in their original condition as provided by the supplier. For any given

Table 2 Figures of merit

	LOD[a]/ng ml^{-1}	LOQ[b]/ng ml^{-1}	RSD[c] (%)	Sensitivity/counts per ng ml^{-1}	Upper range of linearity[d]/ng ml^{-1}
Headspace	0.19	0.64	2.4	2250	1500
Direct	0.16	0.53	2.7	2600	300

[a]Limit of detection (3σ). [b]Limit of quantification (10σ). [c]Relative standard deviation, $n=5$, using 5 ng ml^{-1} solution. [d]Defined as concentration at which response deviates by 10% from a linear relationship.

Table 3 Calibration parameters

	External calibration		Internal calibration[a]	
$y=ax+b$	Headspace	Direct	Headspace	Direct
a	2244	2601	2169	34.9
b	163.5	151.5	—	—

[a]Obtained by standard additions to DORM-2 reference material.

fiber, the (intra-) reproducibility of measurement is quite good, averaging about 2.3% RSD. However, the RSD of the means for the three fibers is greater than 20%. More alarming is the difference between the two extrema which is more than 30%. These data are probably a reflection of the quality of manufacture of the fibers. Surprisingly, over the past several years of commercial history of SPME and the hundreds of research papers (organic analysis) utilizing this technology, no discussion has arisen concerning the quality of the results with respect to fiber-to-fiber performance. The unique aspect of manufacture of SPME fibers is the extremely low volume of the extraction medium (*i.e.*, the polymer coating on the surface of the silica fiber support). Any irregularity or inhomogeneity of the polymer phase/surface, may result in a significant difference in its extraction characteristics. This effect could be more pronounced in the case of non- equilibrium extraction with solid coatings where the extraction is based on adsorption phenomena rather than absorption.

Although solid-phase extraction (SPE) or capillary GC column technology is similar, the resultant effects of inhomogeneities in these coatings are not as serious because in both cases the extraction or separation is based on bulk characteristics of the polymer phase. If the particle size distribution in the case of SPE falls within specified limits, the variation between individual particles has no impact. If the capillary GC column coating exhibits fluctuation in thickness or eventually surface cracks appear along the length of the column, these effects are buffered by the 1–100 m length of the column. If these or any other type of manufacturing irregularities occur on the surface of a 1 cm long SPME fiber, the extraction characteristic could be seriously altered.

Table 4 Analytical results

Reference material	Measured/g g^{-1}	Certified/g g^{-1}
DORM-2	4.72 ± 0.16[a]	4.47 ± 0.32[b]
DOLT-2	0.727 ± 0.014[a]	0.693 ± 0.053[b]

[a]Standard deviation, $n=5$. [b]95% confidence interval.

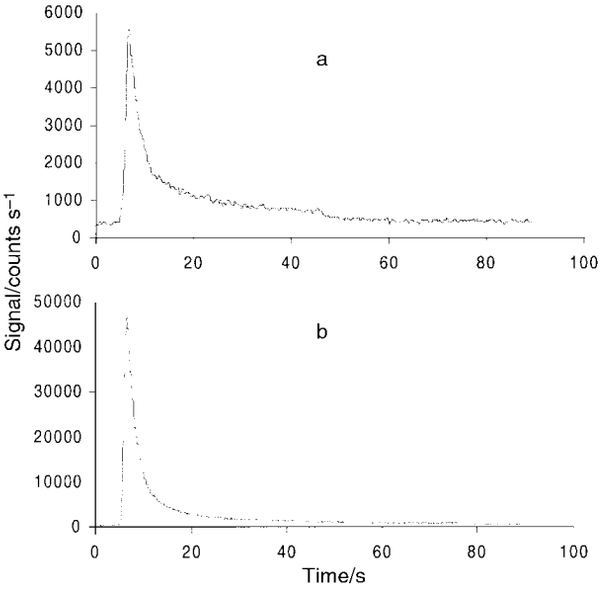

Fig. 5 Transient signals from SPME extraction of methylmercury solutions using TD-ICP-MS: (a) 10 ng ml^{-1}; (b) 100 ng ml^{-1}.

Conclusion

Direct coupling of SPME with ICP-MS *via* a simple thermal desorption-gas introduction interface provides a new approach for both the sampling and sample introduction of volatile metal species into an atomic spectroscopic detector. The compact design of the interface lends itself to direct placement at the base of the torch, significantly minimizing the length of the transfer zone, particularly important for the analysis of very reactive methylmercury chloride. This interface design also offers the possibility for direct introduction of small amounts of organic solvents containing metals into the plasma, thereby expanding the scope of application to include liquid–liquid extraction techniques. Particularly attractive is the significant preconcentration factor arising from application of the thermal desorption interface with SPME. Headspace extraction of methylmercury chloride from a biological reference material shows acceptable analytical characteristics. Selective extraction is particularly attractive as this can significantly reduce the

Table 5 Intra- and inter-fiber(s) precision (10 ng ml^{-1} solution concentration; $n=5$)

	Intensity/counts					Intra-fiber precision		
	1	2	3	4	5	Average	s	RSD (%)
Fiber 1	23528	24362	22845	23456	23345	23507	547	2.33
Fiber 2	18635	18523	18856	17854	18886	18551	418	2.25
Fiber 3	15525	16124	15256	15856	16032	15759	362	2.30
	Inter-fiber precision				Average	19272		
					s	3924		
					RSD (%)	20		

analysis time and the number of sample manipulation steps. The commonly used ethylation method requires a separation step (generally GC) because the reductant also reacts with inorganic mercury. This combination of sensitive ICP-MS detection with the high efficiency of the sampling/sample introduction system may also offer a new approach to the passive sampling of volatile metals in different environments. (*i.e.*, exposure studies).

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