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Sampling and determination of metal hydrides by solid phase microextraction thermal desorption inductively coupled plasma mass spectrometry

Zoltán Mester,* Ralph E. Sturgeon and Joseph W. Lam

Institute for National Measurement Standards, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9, E-mail: zoltan.mester@nrc.ca

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Direct coupling of solid phase microextraction (SPME) with inductively coupled plasma mass spectrometry (ICP-MS) was used for the non-selective determination of arsenic, selenium, antimony and tin species amenable to hydride generation. 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 the transfer-line. The effects of time and concentrations of sodium borohydride and hydrochloric acid on the extraction efficiency were optimized. Polydimethylsiloxane (PDMS) and polydimethylsiloxane/Carboxen (PDMS/Carboxen) SPME coatings were compared for the headspace extraction of the hydrides. PDMS/Carboxen showed better extraction capacity and enhanced selectivity for tin hydrides. SPME provided good sensitivity and an approximately 3.5 decade linear response range. Detection limits for As, Se, Sn and Sb using a PDMS/Carboxen fiber were 70, 5300, 8 and 310 pg mL^{-1}, respectively. Method validation using NRCC SLRS-4 (Riverine Water) and CASS-4 (Nearshore Seawater) reference materials showed good agreement between certified and measured values for total arsenic.

Introduction

The generation of gaseous metal species and their introduction into atomization/ionization cells offers significant advantages over conventional aqueous phase nebulization of samples.[1] Generally, nebulization efficiency is in the range of a few percent using mL min^{-1} liquid flow rates[2] whereas hydride generation and transport efficiency approaches 100%.[3] Typically, hydride generation is coupled on-line to the detector to provide for either continuous or discrete (flow injection) sample introduction. Continuous sample introduction generates a steady-state response whereas discrete sampling produces a transient signal but accommodates small sample volumes. On-line coupling of hydride generation with ICP–MS also has several limitations, including the large volume of co-generated hydrogen which perturbs plasma stability, and chloride introduction, which leads to the formation of potential isobaric interferences that significantly limit detection power. Reed *et al.*[4] discussed possible interferences by molecular and atomic ions in the *m*/*z* range 24 (Mg) to 76 (Ge) when using a double focusing sector field mass spectrometer. A classical example of this effect is the interference by $^{75}ArCl^{+}$ plasma species on monoisotopic arsenic when using a low-resolution mass analyzer.

Problems experienced with the introduction of chloride and sodium when using on-line coupling can often be minimized using a well-designed gas/liquid separator or application of a membrane separator.[5] Alternatively, gaseous metal species can be separated from hydrogen and the aerosol by selectively collecting the target compounds on a cryogenically cooled sorbent bed.[6] This approach relies on use of chromatographic packing material for the ab- or adsorption of the hydrides at liquid nitrogen temperature. An alcohol-cooled trap is usually placed in front of the cryogenic sorbent to ensure prior removal of moisture. This technique has been used not only for hydride-generated species,[6] but also for the direct sampling of gaseous metal species from ambient air in atmospheres suspected of containing high levels of metals.[7,8]

As an alternative to the above techniques for sample processing, direct headspace extraction of volatile metal species using solid phase microextraction (SPME) can be utilized. Naturally occurring volatile metal species (such as methylmercury chloride) can be extracted from headspaces without prior derivatization.[9] SPME therefore offers the possibility for fast, solvent-free, integrated sampling–extraction–sample introduction methodology. SPME has already been used for the extraction of mercury,[10] organotins[11] and lead[12] (following ethyl generation) in combination with GC separation. Direct liquid phase extraction, applying in-tube SPME, has been described for determination of organolead[13,14] and organoselenium[15] species. To date, no attempt has been made to undertake headspace extraction of inorganic hydride species using commercial SPME coatings. The efficiency of aqueous phase hydride generation is usually higher than that of ethylation or phenylation derivatization; moreover in the absence of a sparging gas to transfer the analyte to the gas phase, the ethylated species exhibit significantly lower vapor pressures above the liquid. Additionally, the number of hydride forming, or potentially hydride forming, elements is significantly larger than their ethyl- or phenyl- counterparts.

In this report, headspace, solid phase microextraction techniques are used for the sampling of As, Se, Sn and Sb hydrides and their subsequent thermal desorption into an inductively coupled plasma mass spectrometer. Experimental parameters are described for their determination and associated figures of merit are presented. The results of this study support the concept of using solid supported ad- or absorption-based extraction techniques for the passive sampling of volatile metal hydrides.

Experimental

Reagents

All chemicals used were of reagent grade unless otherwise stated. A 1000 mg L^{-1} stock solution of each of As(III), Se(IV), Sn(IV) and Sb(III) was prepared by dissolving the appropriate salts in 1 M hydrochloric acid. Solutions of $NaBH_4$ (Alfa Chemicals Inc., Newburyport, MA, USA) were prepared daily at a concentration of 8% (m/v) stabilized in 0.1% (m/v) NaOH (BDH Inc., Toronto, ON, Canada). Hydrochloric acid was prepared in-house by sub-boiling distillation of feedstock. High-purity de-ionised water (DDW, 18 MΩ cm), obtained from a NanoPure system (Barnstead/Thermolyne, Boston, MA, USA) and fed with a reverse osmosis supply line, was used for the preparation of all solutions. Working standards were prepared by serial dilution of the stock solutions. National Research Council of Canada CRMs, SLRS-4 Riverine Water and CASS-4 Nearshore Seawater, certified for trace element concentrations were selected for analysis to asses the accuracy of the technique.

Instrumentation

A PerkinElmer SCIEX Elan 5000 inductively coupled plasma mass spectrometer was used for all elemental determinations. A full description of the thermal desorption interface unit is provided in ref. 9 and, for convenience, some details are given in the results section. An evaluation of transient signals was performed using in-house software; peaks were integrated (typically 5–10 s) following the establishment of a baseline at extreme ends of the signal. Two types of commercial SPME coatings were used: a 100 μm thick polydimethylsiloxane polymer and a 75 μm thick polydimethylsiloxane/Carboxen coating. The fibers were conditioned and operated at temperatures specified by the manufacturer (SUPELCO, Bellefonte, PA, USA). The experimental conditions used for the ICP-MS and the SPME extraction are summarized in Table 1.

Sample preparation

Both CRM reference seawater samples were treated as follows for the determination of As: a 10 mL aliquot of sample was acidified by addition of 10 mL of concentrated hydrochloric acid and heated to 50 °C for 1 h. Following cooling, the sample was ready for hydride generation and SPME sampling. This ensured the conversion of all inorganic arsenic to As(III) prior to hydride generation. In all other cases, method development utilized DDW solutions containing the reduced oxidation states of the analytes of interest.

Table 1 Experimental conditions for SPME-TD-ICP-MS

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}	350
Sampler–skimmer	Nickel
Data acquisition	
Measurement mode	Transient
Replicate time/ms	50
Dwell time/ms	50
Scan mode	Peak hop
Number of replicates	1000
SPME	
Fiber coating	100 μm, PDMS or 75 μm PDMS/Carboxen
Extraction time/s	30
Extraction temperature/°C	22
Thermal desorption temperature/°C	200

Solid phase microextractions

Two extraction phenomena can be observed in this study: liquid phase coatings, such as polydimethylsiloxane (PDMS), which show absorption capacity rather than adsorption, and "solid" coatings, such as polydimethylsiloxane/divinylbenzene (PDMS/DVB) or polydimethylsiloxane/Carboxen (PDMS/carboxen), which accumulate analytes *via* adsorption. Absorption-based solid phase extraction, as with liquid–liquid extraction, is characterized by an extraction capacity proportional to the phase volume of extractant (*i.e.*, the coating). Adsorption, however, is dependent on surface phenomena and the extraction capacity is therefore related to the total surface area. In our studies, fibers based on both liquid and solid coatings (PDMS and PDMS/Carboxen, respectively) were used. On an SPME fiber containing a dual coating of Carboxen and polydimethylsiloxane (PDMS), multiple layers of Carboxen are held in place with PDMS which serves as a glue. The PDMS material is cross-linked, not only internally (to itself), but also to the Carboxen particles and the fused silica fiber.

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. As such, the effects of extraction (fiber exposure) time, desorption temperature and matrix concomitants were of interest.

Extraction procedure. Extractions were performed as follows: a 20 mL volume of acidified sample solution was placed in a septum-sealed 40 mL glass vial. The solution was vigorously stirred using a Teflon coated stir bar on a stirring plate. A 250 μL volume of 8 % *m*/*v* sodium borohydride solution was injected through the septum into the stirred, closed vial using a plastic syringe. The septum was also fitted with a 22 gauge syringe needle which served as a 'decompression vent'. The SPME fiber was then inserted into the headspace for a predetermined sampling time, depending on the data of interest. The fiber was then withdrawn and transferred to the desorption unit for introduction of the analyte into the ICP-MS. The glass vials were used only once and disposed of after each analysis. Because the thermal desorption steps completely clean the fiber, no additional clean-up was necessary. The practicality of this step was confirmed by repeated blank extractions, wherein it was ascertained that no sample carry over occurred using the current procedure. After each series of experiments, the stir bars were soaked overnight in a 4 M hydrochloric acid solution to ensure no carryover contamination.

Desorption procedure. Analyte transfer was achieved by thermal desorption *via* the heated injector unit. The SPME fiber was inserted into the septum-sealed glass line of a standard GC injector port, exposed for 30 s and then withdrawn. The applied 30 s exposure time resulted in the complete removal of the analyte for headspace sampling of solutions in the μg L^{-1} concentration range (higher concentrations may require longer desorption time).

Results and discussion

Optimization of response

Dry sample introduction permits optimal operation of the plasma at a forward rf power of 800 W. Variation of the

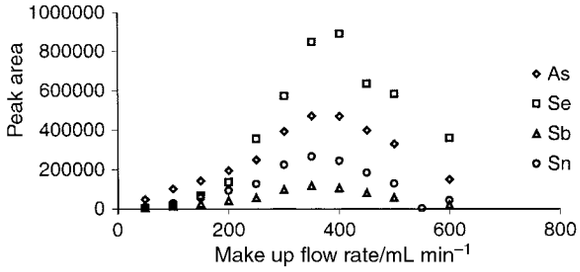

Fig. 1 Effect of carrier gas flow rate on signal intensity. The experiment was conducted at room temperature using a 100 μg L^{-1} multi-element standard solution. Response was normalized to the most intense signal from each element: ◊^{75}As$^+$, □^{82}Se$^+$, ○^{120}Sn$^+$, △^{121}Sb$^+$.

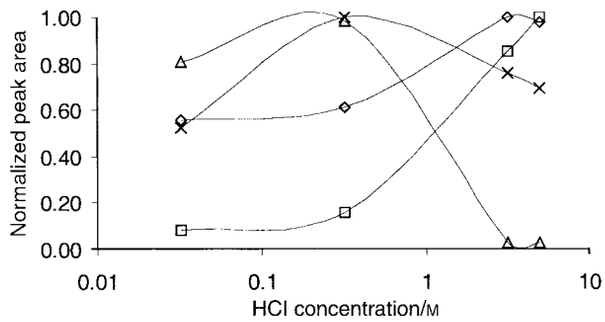

Fig. 2 Effect of HCl concentration on signal intensity. The experiment was conducted at room temperature using a 100 μg L^{-1} multi-element standard solution. Response was normalized to the most intense signal from each element: ◊^{75}As$^+$, □^{82}Se$^+$, △^{120}Sn$^+$, × ^{121}Sb$^+$.

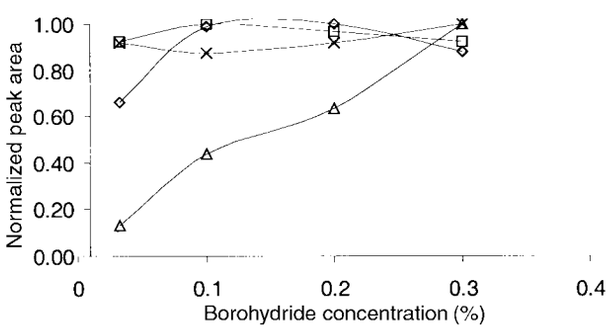

Fig. 3 Effect of sodium borohydride concentration (in the final solution) on analyte signal intensity. The experiment was conducted at room temperature using a 100 μg L^{-1} multi-element standard solution. Response was normalized to the most intense signal from each element: ◊^{75}As$^+$, □^{82}Se$^+$, △^{120}Sn$^+$, × ^{121}Sb$^+$.

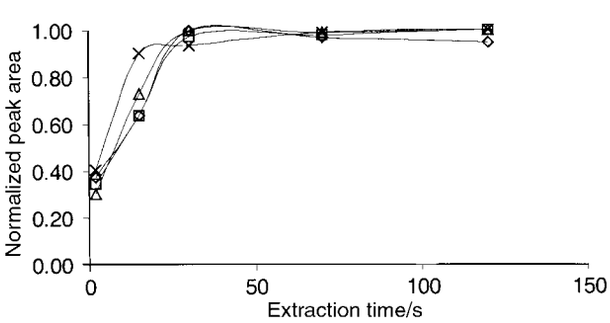

Fig. 4 Effect of extraction time on signal intensity. The experiment was conducted at room temperature using a 100 μg L^{-1} multi-element standard solution. Response was normalized to the most intense signal from each element: ◊^{75}As$^+$, □^{82}Se$^+$, △^{120}Sn$^+$, × ^{121}Sb$^+$.

Table 2 Figures of merit

	As/ng ml^{-1}	Se/ng ml^{-1}	Sn/ng ml^{-1}	Sb/ng ml^{-1}
PDMS				
DL^a	0.32	12	3.2	1.8
QL^b	0.98	36	9.7	5.3
Carboxen				
DL^a	0.06	5.3	0.008	0.31
QL^b	0.20	16	0.024	0.92

^{a}Limit of detection (3σ). ^{b}Limit of quantification (10σ).

auxiliary gas flow effectively alters the sampling depth in the plasma, an optimum position reflecting the balance between atomization–ionization processes and subsequent dispersion/ion–electron recombination of the analyte. As can be seen from the data in Fig. 1, the effect of auxiliary gas flow rate on response, based on intensities from ^{75}As$^+$, ^{82}Se$^+$, ^{120}Sn$^+$ and ^{121}Sb$^+$, shows an optimum at 350 mL min^{-1}. No significant difference in this trend is observed for the various metal hydrides, irrespective of their ionization energy.

Effect of reagent concentration. Fig. 2 shows the effect of HCl concentration on response. As expected, and in agreement with other studies, higher acid concentration is favorable for arsenic and selenium whereas lower concentrations enhance efficiency for tin and antimony. With the exception of tin, hydride generation efficiency is not strongly influenced by the concentration of sodium borohydride, as evident from the data presented in Fig. 3. For tin, the higher concentration results in a dramatic increase in the signal intensity.

Fiber exposure time. Fig. 4 shows the effect of fiber exposure time on analyte signal intensity. In the case of headspace sampling, two equilibration processes are of significance. One establishes the distribution of the analyte between the liquid and gas phase (headspace) and a second governs the relative concentrations of analyte in the gas phase and the SPME coating. Evidently, in the present case, the target compounds not only escape easily from the liquid phase due to their low solubility and the large surface area presented by the stirred gas–liquid interface, but equilibration between the metal hydrides present in the headspace and the exposed fiber is also very fast. At room temperature, overall equilibrium is achieved in ≈20–30 s for all analytes using a 100 μg L^{-1} analyte solution. No significant difference was observed between the two SPME coatings regarding their equilibration times.

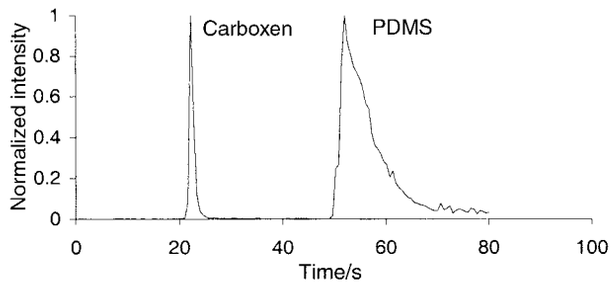

Fig. 5 Transient signals arising from desorption of arsenic hydride from a Carboxen and PDMS coated fiber. (Based on response from ^{75}As$^+$.)

Table 3 Analytical results

Sample	Measured/ng ml^{-1}	Certified/ng ml^{-1}
SLRS-4	0.63 ± 0.12^a	0.68 ± 0.06^b
CASS-4	0.99 ± 0.21^a	1.11 ± 0.16^b

^{a}Standard deviation, n = 5. ^{b}95% confidence interval.

Table 4 Comparison of detection limits for various hydride generation systems

System	As/ng mL^{-1}	Se/ng mL^{-1}	Sb/ng mL^{-1}	Sn/ng mL^{-1}
HG-ICP-AES (ref. 16)	0.6	—	0.8	1.7
HG-ICP-MS (quadrupole) (ref. 17)	0.02	0.03	—	—
Molecular absorption spectrometry (ref. 18)	50	120	20	1100
HG-SPME-ICP-MS(quadrupole) (this study)	0.067	5.3	0.008	0.31

Analytical figures of merit

Analytical figures of merit, based on peak integration, are summarized in Table 2 and include, for both fibers, the detection limit and quantification limit. All results were generated using a multi-element synthetic standard solution and a 30 s extraction time, 1 M hydrochloric acid and a 0.3% sodium tetrahydroborate solution (effective concentration in the final sample solution). Naturally, the responses vary by changing the acid concentration of the analyte solution. Use of a 1 M acid concentration reflects a compromise between the optimum sensitivity for individual elements and the requirements of a multi-element approach. Comparison of the results for the two fibers shows that the volatile metal hydrides were extracted with higher efficiency using the carbon fiber. The desorption process from the PDMS coating was significantly slower than from the Carboxen coating. This phenomenon was most pronounced for arsine. Fig. 5 shows typical transient signals obtained with Carboxen and PDMS fibers. The slow desorption from PDMS may be a consequence of some degree of decomposition of the hydride species with subsequent enhanced interaction with the polymer coating. This effect could be related to the fundamental absorption phenomenon occurring during extraction with the PDMS coating; adsorption based surface phenomena dominate with the Carboxen coating.

SPME thermal desorption sample introduction of metal hydrides also serves to eliminate some interferences normally accompanying continuous hydride generation. Because gaseous hydrogen is not efficiently trapped by the fiber at room temperature, no hydrogen introduction into the plasma occurs with SPME sampling. SPME sample introduction also accomplishes a complete gas–liquid separation. The transport of small droplets (aerosol) from the bulk solution to the plasma, which may arise from the relatively violent reaction between sodium borohydride and the acidified solution, can be eliminated. Isobaric interference from argon chloride molecular ions may present a severe limitation to determination of ultra trace concentrations of arsenic using low resolution mass detection. Sorbent sampling can potentially decrease introduction of HCl into the plasma, thereby minimizing interference by chloride molecular species when sorbent materials with high selectivity for the metal hydrides are used. In this study, a significant difference was be observed between the Carboxen and PDMS fiber coatings regarding uptake of gaseous HCl. Virtually no HCl uptake was found using the non-polar PDMS polymer as the extracting phase. The HCl that is collected on the PDMS fiber probably arises as a result of some surface related adsorption phenomena rather than by absorption, which is the principal mechanism of uptake with liquid polymers. Using a Carboxen fiber, where extraction is based primarily on adsorption (which is less selective than the absorption process), the amount of HCl extracted is higher. These results were deduced from ICP-MS data, where the signal intensity for $ArCl^+$ species was measured at both *m*/*z* 75 and 77. An attempt was made to determine molecular HCl on the fiber using direct electron impact ionization mass spectrometry, but insufficient sensitivity was available for the low HCl concentration encountered.

The performance of the method was evaluated by analysis of SLRS-4 Riverine Water and CASS-4 Nearshore Seawater reference materials. Table 3 summarizes the certified and measured values obtained for total arsenic in the reference materials using a PDMS/Carboxen fiber. Results are in good agreement with the certified values but precision is relatively poor. Poor precision probably occurred as a result of the uncontrolled loss of analyte during the decompression (venting) process. This can be eliminated by using closed, pressurized reaction vessels or by using continuous hydride generation. Using the reagent concentrations described in the Experimental section, the calculated volume of hydrogen released gives rise to a pressure in the reaction vial (40 mL vial with 20 mL headspace volume) of about 3 atmospheres. As a consequence, about 70% of the analyte is expelled during the venting process. Determination of Se, Sb and Sn in SLRS-4 and CASS-4 was not possible as their concentrations were below the detection power of the current methodology.

Table 4 presents a comparison of detection limits for several hydride generation based methods. Detection limits obtained in this study are comparable to other reported values. It should also be noted that the Elan 5000 ICP-MS used here is some 10–100-fold less sensitive than other state-of-the art ICP-MS spectrometers currently available

Conclusion

Passive collection and sampling on a single SPME fiber presents a new approach for quantitation of metal hydrides. Collection can be preformed following continuous or batch generation. In the latter case, SPME offers the advantage of high efficiency in the sampling process. Naturally, the amount of analyte collected on the fiber is relatively small, which limits application to the high ng L^{-1}–low μg L^{-1} range. On the other hand, this methodology eliminates some molecular ion isobaric interferences as well as the quenching effect of hydrogen on the argon plasma, which may accompany many direct sample introduction methodologies. The direct coupling of SPME with ICP-MS *via* a thermal desorption–gas introduction interface provides a simple 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. This interface design also offers the possibility for direct introduction into the plasma of small amounts of organic solvents containing sequestered metals, thereby expanding the scope of application to include liquid–liquid extraction techniques. Particularly attractive is the significant preconcentration factor, which arises from application of the thermal desorption interface with SPME. The 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).

Acknowledgements

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