Spectrochimica Acta Part B 111 (2015) 46–51

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Technical note

A miniaturized cryogenic trap design for collection of arsanes

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ARTICLE INFO

Article history:
Received 9 April 2015
Accepted 22 June 2015
Available online 26 June 2015

Keywords:
Hydride generation
Atomic absorption spectrometry
Arsanes
Cryotrapping
Radioactive indicator

ABSTRACT

A new miniaturized design of a cryogenic trap for collection of arsanes generated from inorganic and methyl-substituted arsenic species was developed. The detection was performed by atomic absorption spectrometry. The miniaturization of the cryogenic trap was achieved by replacing the commonly used quartz U-tube (45 cm long, 2.5/4.3 mm i.d./o.d., packed with chromosorb) by a U-shaped quartz capillary (U-capillary, 20 cm long, 0.53/0.65 mm i.d./o.d.). The type and material of the gas phase dryer, an essential part of the cryotrapping system, were necessary to optimize to prevent blockage of the U-capillary by frozen water and to prevent loss of arsanes. A cartridge with solid NaOH was found as the best solution because of a higher absorbing efficiency of water compared to commonly used nafion membrane. The diameter of the NaOH beads was found as a crucial parameter influenced loss of arsane.

Processes during the cryotrapping procedure with the U-tube and U-capillary were investigated by ^{73}As radioactive indicator and arsane trapping and volatilization efficiency were quantified. Trapping and volatilization efficiency of 100% were found in the U-tube as well as in the U-capillary. Relevant experimental parameters for the collection in the U-capillary (carrier gas flow rate, column length and capacity) were studied. Finally, miniaturized, simple and commercially available design of the cryogenic trap based on non-polar fused silica capillary successfully performed the collection procedure of arsanes.

1. Introduction

Arsenic determination plays an important role in the analysis of environmental samples [1–10]. Metabolism studies of arsenic are widely performed [11–16] as well as toxicity studies of arsenic species [17–19]. Since arsenic species, namely inorganic arsenic (iAs), methylarsonate (MAs), dimethylarsinate (DMAs) and trimethylarsine oxide (TMAsO) differ in toxicity, [17,20] appropriate arsenic speciation analysis method is highly desirable.

Although separation by means of high pressure liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICP-MS) detector is the most common approach to arsenic speciation analysis, an alternative technique has also been explored and found its use in analytical applications. It combines selective generation of substituted hydrides (HG) coupled to a cryogenic trap (CT) employed for collection/separation of analytes with subsequent detection most often by atomic absorption spectrometry (AAS). The inherent advantage of this HG-CT approach compared to the common method for arsenic speciation (HPLC-ICP-MS) is a much lower risk of changes of speciation thanks to minimum sample pretreatment and primarily because separation on HPLC column is avoided. The detailed description and several applications to environmental and biological samples of HG-CT can be found elsewhere [21–26].

The general aim of this work was to develop the cryogenic trap with respect to (i) miniaturization, (ii) simplification and (iii) to reach 100% collection (trapping and volatilization) efficiencies. The developed miniaturized cryogenic trap will be used in the future with gas chromatograph and atomic absorption spectrometer for arsenic speciation analysis.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade or higher purity. Deionized water (<0.1 μS cm^{-1}, Ultrapure, Watrex, USA) was used to prepare solutions. Working arsenic standards were prepared from 1000 mg l^{-1} As stock solution of the following compounds: iAs from As_2O_5 in 0.5 mol l^{-1} HNO_3, MERCK, Darmstadt, Germany; MAs from $Na_2CH_3AsO_3 \cdot 6H_2O$, Chem. Service, West Chester, PA, USA; DMAs from $(CH_3)H_2AsO_2$, Strem Chemicals, Inc., Newburyport, MA, USA; TMAsO [15] was obtained by courtesy of Dr. William Cullen, University of British Columbia, Vancouver, Canada and Miroslav Stýblo, University of North Carolina at Chapel Hill, Chapel Hill, USA.

The reductant was 1% (m/v) solution of $NaBH_4$ (Sigma-Aldrich, Germany) in 0.1% (m/v) KOH (p.a., Merck, Darmstadt, Germany) filtered after preparation and stored frozen. The buffer was 0.75 mol l^{-1} Tris (hydroxymethyl) aminomethane (TRIS·HCl buffer was prepared

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http://dx.doi.org/10.1016/j.sab.2015.06.014
0584-8547/

from a reagent grade Trizma® hydrochloride (Sigma)) and adjusted by 10% NaOH (Lachema, Czech Republic) to pH 6.

L-Cysteine hydrochloride monohydrate ($(C_3H_8ClNO_2S \cdot H_2O)$ Merck, Darmstadt, Germany) was used for pre-reduction of pentavalent arsenic species.

1 mol l^{-1} HCl (p.a., Merck, Darmstadt, Germany) was used for cleaning the hydride generator. 38% (m/v) HF (p.a., Spolchemie, Ústí nad Labem, Czech Republic) and 65% HNO_3 (p.a., Lach-Ner, Czech Republic) mixed in the ratio of 3:7 (v/v) were used to clean the multiatomizer.

The sodium hydroxide beads (NaOH, purum, pearls, bead diameter of 2–3 mm usually with 3% (w) of particles under 2 mm, Lach-Ner, Czech Republic) and (NaOH, purum, micro pearls, bead diameter of 1–1.9 mm, Lach-Ner, Czech Republic) were used as a filling of a dryer cartridge for water vapor and aerosol removal.

A filling of the U-tube was realized by CHROMOSORB, OV-3 WAW-DMCS 45/60, Supelco, Bellefonte, USA. The silanization agent was REJUV-8 (hexamethyldisilazan, N,O-bis (trimethylsilyl) acetamid, (n-trimethylsilylimidazole) Supelco, Bellefonte, USA).

2.2. AAS instrumentation

A Perkin Elmer AAnalyst 800 (Norwalk, Mass, USA) atomic absorption spectrometer equipped with FIAS 400 flow injection accessory (FIAS) was used as a detector. An arsenic electrode discharge lamp (EDL) powered by Perkin Elmer EDL System II was operated at 376 mA using 193.7 nm arsenic line. Deuterium background correction was used. The slit width was set to 0.7 nm. A multiple microflame quartz tube atomizer (multiatomizer, model MM5 in Ref. [27]) heated resistively to 900 °C and supplied with 35 ml min^{-1} of air as outer gas was employed.

The transversally heated graphite furnace atomizer (THGA, on AAnalyst800, Perkin Elmer with Zeeman correction, with end cap and platform modified with 40 μl 1000 mg/l iridium) was employed to check the concentration of standard solution of each arsenic species after its preparation.

2.3. Hydride generator and cryogenic traps

The setup consists of a flow injection hydride generator (3 channels with the same flow rates of: 1% $NaBH_4$ in 0.1% KOH; 0.75 mol l^{-1} TRIS buffer; deionized water with sample coil) described earlier [24] coupled to a cryogenic trap (CT) via a dryer. Two dryer set-ups are employed: (i) a nafion membrane (MD-110-12FP, Perma Pure, Toms River, N.J., USA, with 2 l min^{-1} N_2); (ii) a polypropylene cartridge filled with solid NaOH. The usability of these two types of dryers is described below (Section 3.1.1 Elimination of the non-specific absorption and selection of a dryer).

Two designs of CT are used. The first CT design (see Ref. [24] for details), further termed here as the U-tube, is based on a U-shaped tube (borosilicate tube i.d./o.d. 2.5/4.3 mm, 45 cm long) partially filled with chromosorb and treated with REJUV (100 μl and flow of helium for 5 h). The U-shaped tube, wrapped with a resistance Ni–Cr wire (15 Ω), is fixed in a special glass flask which serves for automatic filling of liquid nitrogen and immersed in a Dewar flask (5 l).

The new miniaturized CT design, further termed as U-capillary in the text, is realized by a U-shaped nonpolar fused silica capillary (20 cm, 0.53/0.65 mm i.d./o.d. covered by polyimide, nonpolar fused silica capillary, Supelco, USA) with 90% of the length inserted into a teflon tube of 0.75/1.56 mm i.d./o.d. to protect the capillary against mechanical and overpressure damage. A piece of polyethylene foam insulation serves as a holder for stable shape of the capillary. The input end of the capillary was sealed in a teflon tube (0.50/1.52 mm i.d./o.d., 10 cm length). The output end of the capillary is interfaced to the multiatomizer in the same way (see Fig. 1). The heating of the U-capillary in the volatilization step of the collection procedure is performed by ambient temperature only. The U-capillary was immersed in a Dewar flask (2 l) with liquid nitrogen during the trapping step. A special lid on the top of the Dewar flask made from polyethylene foam was designed (see Fig. 1) to reduce the risk of U-capillary blockage by frozen water (see Section 3.2.1 for detailed explanation).

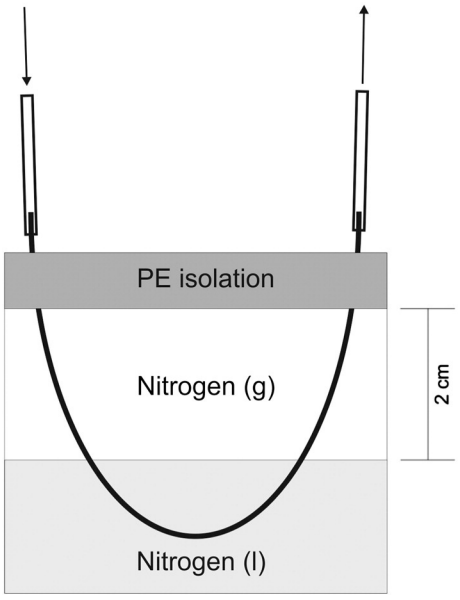

Fig. 1. The U-capillary immersion in the Dewar flask with a polyethylene foam lid on the top; the input and output ends of the U-capillary are heat-sealed in the teflon tubes; the arrows show the input and output of the carrier gas.

In both CT designs the gaseous phase containing arsanes has to pass through a drying tube (dryer) to reduce the water vapor content to the tolerable extent before reaching the cryogenic trap. Otherwise blockage of the cryogenic trap by frozen water occurs which presents a serious problem.

2.4. Procedure

Two solutions containing arsenic species are prepared: i) a mixture of iAs, MAs, DMAs and TMAsO and ii) only TMAsO. The first solution is mixed with solid L-cysteine hydrochloride monohydrate to the final concentration of 2% m/v at least 1 h prior to analysis. The second is not [24,28]. All arsenic species are converted to trivalent forms in order to reach 100% efficiency of hydride generation. TMAsO is converted by L-cysteine to $(CH_3)_3As$ which is gradually released from the solution before hydride generation procedure can start [15,29]. That is the reason to prepare the second solution containing only TMAsO.

The cryotrapping procedure was similar for both CT designs. It consisted of two steps, trapping and volatilization. In the first step, arsines released from the hydride generator are trapped in a CT. Subsequently, after finishing hydride generation, trapped arsines are released from a CT and transported to the multiatomizer in the volatilization step. The detailed description of the HG-CT-AAS procedure can be found in Ref. [24], only a brief description is thus presented here.

During hydride generation in the trapping step, all the investigated arsenic species are converted to corresponding arsanes. Three reagent flows are pumped at the same flow rate into three respective channels of the hydride generator [24]: water as the carrier, the buffer and the reductant. 0.5 ml sample volumes were injected into the carrier water flow. Arsanes released from the gas–liquid separator of the hydride generator are dried and trapped in the CT cooled by liquid nitrogen.

In the volatilization step the CT is heated to volatilize trapped arsanes, stepwise according to their boiling points (the first AsH_3, the second CH_3AsH_2, the third $(CH_3)_2AsH$, the last $(CH_3)_3As$). and transport