Desalination 250 (2010) 414–417

Contents lists available at ScienceDirect

Desalination

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

Development of solid-phase microextraction for the determination of trihalomethanes in drinking water from Bizerte, Tunisia☆

M. Bahri, M.R. Driss *

Laboratoire de Chimie Analytique et Environnement, 05/UR/12-03, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisia

ARTICLE INFO

Available online 12 October 2009

Keywords:
Trihalomethanes (THMs)
Disinfection by-products (DBPs)
Headspace-solid-phase microextraction (HS-SPME)
Drinking water analysis

ABSTRACT

Headspace-solid-phase microextraction (HS-SPME) combined with gas chromatography-electron capture detector (GC-ECD) has been developed and studied for the determination of trihalomethanes (THMs) in treated water samples. Experimental parameters such as the selection of thickness of the polymer coating, addition of salt, magnetic stirring, extraction temperature, and extraction time were studied. Extraction of the analytes was performed using HS-SPME with a 100 μm poly(dimethylsiloxane) coating followed by thermal desorption at 250 °C and GC analysis. The optimized conditions were 20 min extraction time at 35 °C with 25 w/v% NaCl. Analytical parameters such as linearity and limit of detection were also evaluated. The linear range of 1–100 μg/l was established with relative standard deviations (%RSD) within the range, 1.3–11.7%. The limits of detection (LODs) were ranged from 1.4 ng/l to 6.1 ng/l. The average THM concentration was 88.16 μg/l which was well within the proposed European Union directive of 100 μg/l.

1. Introduction

Chlorination is the most widely used disinfection method for drinking water [1,2], but its disadvantage is the formation of disinfection by-products (DBPs). The major DBPs are trihalomethanes (THMs). They are formed when free available chlorine reacts with natural organic matter in raw water during water disinfection [3,4].The frequently formed THMs are chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$) and bromoform ($CHBr_3$). They can have adverse health effects. The US Environmental Protection Agency [5], the European Union (EU) [6] has set maximum contaminant levels 80 or 100 μg/l, respectively, for total THM concentrations in drinking water. The World Health Organization (WHO) provides guidelines for individual THM compounds [7].

A wide number of techniques are reported in the literature for the determination of THMs and other volatile organic compounds in water samples, such as liquid–liquid extraction (LLE) [8], purge-and-trap [9] and solid-phase microextraction (SPME).SPME developed by pawliszyn [10] is a practical solvent-free alternative for the extraction of organic compounds. SPME integrates sampling, extraction, concentration and sample introduction into a single solvent-free step. Analytes in the sample are directly extracted and concentrated to the extraction fiber. This technique has been successfully applied to the analysis of THMs [11–13], BTEX [14], organochlorine pesticides [15], PAHs [16], PCB [17] and volatile organic compounds [18] in water samples.

The main objective of this work was to develop, evaluate and improve a simple, rapid and sensitive method for extraction and determination of THMs in drinking water by headspace-solid-phase microextraction (HS-SPME) combined with a capillary gas chromatography-electron capture detector (GC-ECD). Analytical methods are needed for monitoring THMs directly in the drinking water distribution system and applied for an investigation program concerning the THM concentration in Tunisia drinking water supplies.

2. Experimental

2.1. Standard solutions

A stock solution of a THM mixture ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) containing each compound at 2 mg/ml MeOH were purchased from Supelco. Working aqueous standard solutions were prepared daily by diluting the methanolic standards with high quality water (ultrapure) obtained using a Milli-Q water purification system (Millipore, Bedford, MA, USA) and also stored at 4 °C in the refrigerator. Final concentrations were in the range of 1–100 μg/l for each analyte together.

2.2. HS-SPME procedure

The SPME holder and fiber assemblies for manual sampling were provided by Supelco. The fiber coatings assayed was poly(dimethylsiloxane) (PDMS, 100, 30 and 7 μm).Before measurements the fiber was conditioned according to Supelco's recommendations. The HS-

☆ Presented at the 1st Maghrebian Conference on Water Treatment and Desalination, Hammamet, Tunisia, 7–10 December 2007.

* Corresponding author. Tel.: +216 72 591906; fax: +216 72 590 566.
E-mail address: MR.DRISS@fsb.rnu.tn (M.R. Driss).

0011-9164/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2009.09.067

SPME extractions were performed by placing 2 mL of aqueous sample into 4 mL vials capped with PTFE-coated septa. The aqueous standard solutions were freshly prepared by spiking appropriate amounts of the working standard solution. The samples were immersed in a temperature-controlled water bath during the sampling process. The HS-SPME equilibrium was conducted with stirring the sample for an appropriate time period, during which analytes sorb on the stationary phase of the fiber. After extraction, the fiber was thermally desorbed for 4 min into the glass liner of the gas chromatograph injector at 250 °C. Every day before use, the SPME fiber was conditioned for 5–15 min at 250 °C. Identification of the four analytes was deduced from their retention times and quantification was performed using the peak area measurement as well as comparison with responses of a mixed THMs standard based on multi-level calibration from 1 to 100 μg/l ($n=6$).

2.3. SPME-GC-ECD analysis

A Hewlett-Packard 6890 gas chromatograph equipped with a split/splitless injection port, an ^{63}Ni electron capture detector (GC-ECD) and operated by HP Chemstation software was used for the experiments to optimize HS-SPME conditions. The injector was used in splitless mode (4 min) and held isothermally at 250 °C. The column used for analysis was VOCOL (60 m × 0.32 mm ID, 1.8 μm film thickness, Supelco). The initial oven temperature was set at 60 °C for 4 min, ramped at 15 °C/min to 210 °C and held for 15 min. The ECD system was maintained at 300 °C. The Carrier gas was helium at a flow rate of 1.5 ml/min and the flow rate of the make-up gas was 60 ml/min with nitrogen.

2.4. Sample collection

Duplicate samples for THM analysis were collected from the districts' water treatment plants (WTPs) and its distributive system in Bizerte area (north of Tunisia). All the samples were collected in 22-ml amber glass vials and were capped with PTFE-faced silica septa. Before sampling, a sodium sulfite (50 μl of a 1.5 g/l Na_2SO_3 solution) was added to bottles to eliminate any remaining residual chlorine and to stop further chlorination by-products (CBP) formation. The vials were completely filled to avoid evaporation of volatile compounds. The samples were transported to the laboratory, transferred to a refrigerator (set at 4 °C) and analyzed within 2 days of collection.

3. Results and discussion

3.1. Development of HS-SPME procedure

The transport of analytes from the matrix into the extraction medium begins as soon as the coated fiber has been placed in contact with the sample. In most cases, SPME extraction is considered to terminate when the analyte concentration has reached distribution equilibrium between the sample matrix and the fiber coating. The amount of analytes adsorbed by the fiber depends on the thickness of the polymer coating, salt addition, extraction temperature and extraction time. Experimental parameters were optimized and used for the analysis of THM in drinking water.

3.1.1. Effect of film thickness

In this study three fibers with different film thickness, 7-μm poly (dimethylsiloxane) (7-PDMS), 30-μm poly(dimethylsiloxane) (30-PDMS) and 100-μm poly(dimethylsiloxane) (100-PDMS) were chosen to select the appropriate fiber for the analysis. New fibers were conditioned, following the manufacturer's recommendations. Water samples (2 ml spiked at a level of 80 μg/l of THMs) were analyzed with each fiber. The extraction time was 20 min at 35 ± 1 °C and desorption time was 4 min at 250 °C for all fibers. In order to evaluate the extraction efficiency,

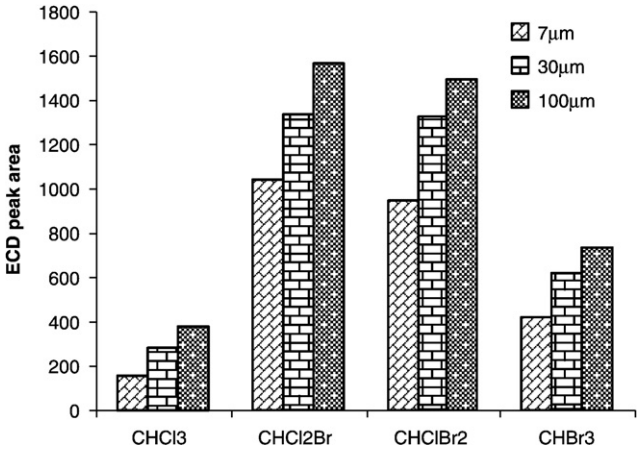

Fig. 1. Extraction efficiencies with different film thicknesses of the PDMS fiber: extraction time of 20 min at 35 °C, desorption time of 4 min at 250 °C. THM concentration: 80 μg/l, $n=5$.

the peak areas obtained for each THMs with the different fibers are shown in Fig. 1. Extraction efficiencies for the THMs were increased according to the following order: 7-PDMS < 30-PDMS < 100-PDMS. The 100-PDMS fiber was found to be able to extract these compounds from aqueous solution by HS-SPME method.

3.1.2. Effect of the addition of salt and magnetic stirring

The addition of salt can improve the extraction efficiency for compounds. So, sodium chloride at various concentrations (from 0 to 25%, w/v) was studied. The results of these experiments showed that the optimum responses of the compounds were obtained with the addition of 25 w/v% NaCl (Fig. 2).

Stirring the water sample can increase extraction efficiency, because stirring can speed up the transfer of the compounds from water to headspace. Fig. 3 shows that stirring (at 750 rpm) affects significantly the response of THM.

3.1.3. Effect of extraction temperature

The influence of temperature on the extraction yield was studied varying the temperature between 20 and 60 °C, using 100 μm PDMS and 20 min extraction time. I t can be seen from Fig. 4 that better response for most of the compound s were obtained at 35 °C.

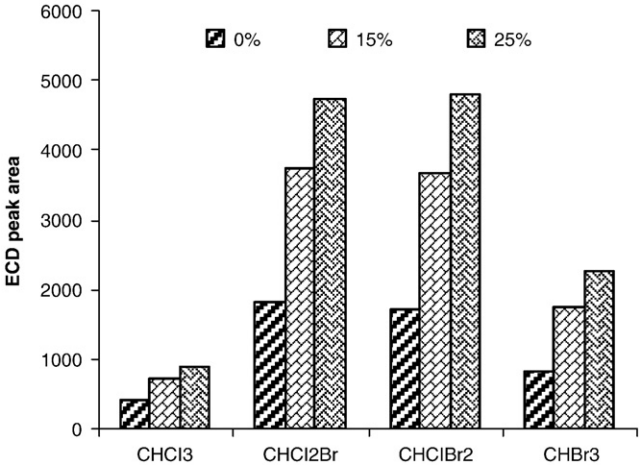

Fig. 2. Effect of the addition of salt and magnetic stirring on extraction: extraction time of 20 min at 35 °C, desorption time of 4 min at 250 °C. THM concentration: 80 μg/L, $n=5$.