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Short communication

Determination of chlorinated volatile organic compounds in water and municipal wastewater using headspace–solid phase microextraction–gas chromatography

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Abstract

The aim of this work was to develop a fast and simple analytical method for the determination of 14 chlorinated volatile organic compounds (VOCs) in water and wastewater samples. Headspace–solid-phase microextraction (HS–SPME) and gas chromatography (GC) were used for the determination of the VOCs. The extraction parameters were investigated in order to optimize the HS–SPME–GC method. The quality parameters of the method were also investigated.

Keywords: THMs; Haloacetonitriles; Chlorinated VOCs; SPME; GC; Water; Wastewater analysis

1. Introduction

Chlorination is the most widely used disinfection method for drinking water and wastewater effluents [1,2], but its disadvantage is the formation of disinfection by-products (DBPs). The major DBPs are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketons (HKs), chloral hydrate and chloropicrin (CPN) [3,4]. These DBPs can have adverse health effects.

A wide number of techniques are reported in the literature for the determination of VOCs, such as liquid–liquid extraction (LLE) [5,6] and purge-and-trap (PT) [5,7,8]. Purge-and-trap with GC and mass spectrometric detection can be used for determination of volatile halogenated hydrocarbons in water at ng/L levels [9]. Other methods such as closed-loop stripping analysis (CLSA) [10,11], capillary membrane sampling-flow injection analysis [12], headspace analysis (HS) [5] and SPME [13,14] have been used for analyses of volatile compounds.

In this study, a fast and simple analytical method using HS–SPME–GC was developed for the determination of 14 halogenated VOCs in drinking water samples and chlorinated secondary effluent samples from the Chania Municipal Wastewater Treatment Plant (MWTP) (Crete, Greece).

2. Experimental

A 5000 μg/mL chlorinated disinfectant mixture #B [trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN), bromochloroacetonitrile (BCAN), CPN, 1,1-dichloro-acetone (1,1-DCP), 1,1,1-trichloro-2-propanone (1,1,1-TCP)] in acetone was purchased from Chem Service. The 200 μg/mL THMs mixture [chloroform (TCM), bromodichloro methane (BDCM), dibromochloro methane (DBCM), bromoform (TBM)], 200 μg/mL tetrachloroethylene (PCE), 200 μg/mL trichloroethylene (TCE), 200 μg/mL 1,2 dichloroethane (1,2-DCA) and 200 μg/mL 1-chloro-2-bromopropane (I.S.) in methanol were obtained from Supelco. The NaCl was purchased from Merck (Germany). The working standard solutions were prepared by diluting stock solutions in methanol, except for the standard solutions of the chlorinated disinfectant mixture #B that were prepared in acetone.

The drinking water samples and the chlorinated secondary effluent samples were collected in 60 mL amber glass vials with screw cap and PTFE–silicon septum. Each vial was completely filled with the sample. Four milligrams $Na_2S_2O_3$, as dechlorination agent, had been added in the vials before the addition of the

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water samples. The samples were analyzed immediately after sampling or stored for a maximum of 5 days at 4 °C.

The SPME holder and fiber assemblies used for the SPME extraction were provided by Supelco. Prior to their use, all fibers were conditioned according to the manufacturer's user guide. 25 mL of water sample was placed in a vial (40 mL, Supelco) sealed with screw cap and PTFE–silicon septum. The water sample (drinking water and chlorination effluent sample) was spiked with an appropriate amount of the standard solution and 3.125 g NaCl. The overall methanolic concentration during the experiments was always less than 0.1% (v/v). The sample vials were placed in a water bath, in order to maintain a constant temperature. The fiber was exposed for 30 min to the headspace of the vial at 35 °C, while the water sample was stirred with a PTFE-coated magnetic bar. The fiber was then withdrawn into the needle and immediately transferred into the GC injector. The desorption time was 10 min at 250 °C. The concentration of the compounds during the development of the SPME procedure was: 0.5 μg/L chlorinated disinfectant mixture #B, 0.5 μg/L THMs, 0.05 μg/L PCE, 0.1 μg/L TCE, 10 μg/L 1,2-DCA and 1 μg/L I.S. Distilled water was used for the preparation of the solutions.

Gas chromatographic analysis was carried out on a Carlo Erba gas chromatograph equipped with a Ni^{63} electron capture detector (ECD) at 300 °C. The analytical column was DB-5, 60 m × 0.32 mm I.D., 0.25 μm film thickness (J & W Scientific). The temperature program of the GC was from 35 °C (15 min) to 100 °C (1 min) at 5 °C/min and from 100 °C to 260 °C (2 min) at 15 °C/min and the injector temperature was set at 250 °C. Dissolved organic carbon and NH_4^+ were measured with a Shimadzu 5000A TOC analyzer and Merck ammonium kit (0.013–3.36 ppm NH_4^+), respectively.

3. Results and discussion

3.1. SPME parameters

In this study four types of fibers [70 μm carbowax/divinylbenzene (70 μm CW/DVB), 65 μm polydimethyl siloxane/divinylbenzene (65 μm PDMS/DVB), 85 μm carboxen/polydimethyl siloxane (85 μm CAR/PDMS), 50/30 μm divinylbenzene/carboxen/polydimethyl siloxane (50/30 μm DVB/CAR/PDMS)] were tested. The best extraction efficiency for most compounds was achieved using the fiber 85 μm CAR/PDMS.

The volume of the gaseous phase, in the HS–SPME, should be minimized for higher recoveries according to the SPME theory [14]. In order to optimize the ratio of sample to headspace volume, a 40 mL vial was used, while the water volume in the vial ranged from 15 to 25 mL (headspace volume from 25 to 15 mL, accordingly). The best results were obtained at 15 mL headspace volume (minimum headspace volume studied).

The addition of salt can improve the extraction of the more polar compounds [14]. So, the addition of 12.5 and 25% (w/v) NaCl was studied. The results of these experiments showed that the optimum recoveries of the compounds were obtained with the addition of 12.5% (w/v) NaCl.

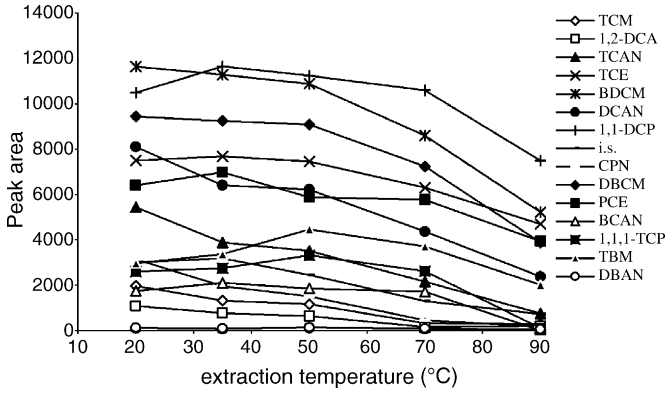

Fig. 1. Effect of extraction temperature on extraction efficiency.

The pH of the water sample was set at 6, because the HANs hydrolyze at high pH [15]. Stirring the water sample can increase extraction efficiency, because stirring can speed up the transfer of the compounds from water to headspace. The water samples were stirred at 750 and 1000 rpm and the best recoveries for all compounds were observed at 1000 rpm.

The influence of temperature on the extraction yield was studied varying the temperature between 20 and 90 °C, using 85 μm CAR/PDMS and 30 min extraction time. It can be seen from Fig. 1 that better recoveries for most of the compounds were obtained at or below 35 °C.

The HS–SPME is an equilibrium process of the analytes between the vapour phase and the fiber coating, so it is important to determine the time that analytes reach equilibrium. Analytes with high molecular weight or low Henry's constant values need longer equilibrium times [14]. In order to evaluate the extraction efficiency, the extraction time ranged from 5 to 120 min at 35 °C, using 85 μm CAR/PDMS. Acceptable equilibrium states were achieved for most of the compounds at 30 min as shown in Fig. 2. It was therefore decided to keep the extraction time at 30 min. For those substances that extraction time had not quite reached equilibrium, the measurements were also valid as long as the extraction time remained constant for both standards and samples [14].

The desorption time was studied using 85 μm CAR/PDMS, extraction time 30 min at 35 °C and increasing time from 0.5 to 15 min at 250 °C. All compounds were completely desorbed at 10 min.

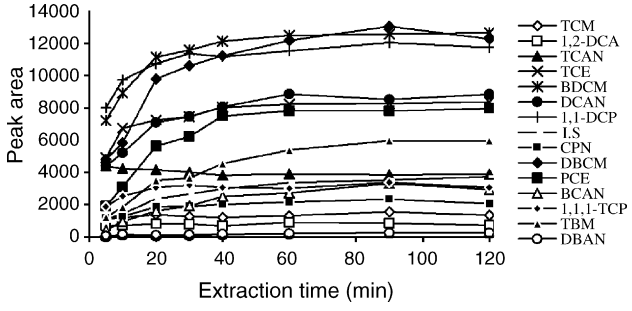

Fig. 2. Effect of extraction time on extraction efficiency.