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Solid-phase microextraction coupled with gas chromatography–ion trap mass spectrometry for the analysis of haloacetic acids in water

M.N. Sarrión, F.J. Santos, M.T. Galceran*

Departament de Química Analítica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

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Abstract

Headspace solid-phase microextraction (SPME) was studied as a possible alternative to liquid–liquid extraction for the analysis of haloacetic acids (HAAs) in water. The method involves derivatization of the acids to their ethyl esters using sulphuric acid and ethanol after evaporation, followed by headspace SPME with a polydimethylsiloxane fibre and gas chromatography–ion trap mass spectrometry (GC–IT-MS). The derivatization procedure was optimized: maximum sensitivity was obtained with esterification for 10 min at 50°C in 30 μl of sulphuric acid and 40 μl of ethanol. The headspace SPME conditions were also optimized and good sensitivity was obtained at a sampling temperature of 25°C, an absorption time of 10 min, the addition of 0.1 g of anhydrous sodium sulfate and a desorption time of 2 min. Good precision (RSD lower than 10%) and detection limits in the ng l^{-1} range (from 10 to 200 ng l^{-1}) were obtained for all the compounds. The optimized procedure was applied to the analysis of HAAs in tap water and the results obtained by standard addition agreed with those of EPA method 552.2, whereas discrepancies due to matrix interferences were observed using external calibration. Consequently, headspace SPME–GC–IT-MS with standard addition is recommended for the analysis of these compounds in drinking water.

Keywords: Water analysis; Derivatisation, GC; Solid-phase microextraction; Haloacetic acid

1. Introduction

Most municipal water supply systems use a form of chlorine for drinking water disinfection. Chlorine can react with naturally occurring organic matter either directly or after hydrolysis to hypochlorous acid; both these reactions lead to the formation of halogenated disinfection by-products (DBPs). In the early days of DBP research, trihalomethanes (THMs) received special attention because chloroform was shown to be an animal carcinogen [1]. In response to public pressure, the United States Environmental Protection Agency (USEPA) initiated a regulatory standard of 100 μg l^{-1} for total THMs, under the 'Safe Drinking Water Act', which has now been reduced to 80 μg l^{-1} under Stage I of the D/DBP Rule (USEPA, 1993) [2]. However, several studies demonstrated the potential formation of non-volatile chlorinated disinfection by-products, whose major components are the haloacetic acids (HAAs) [3–7]. Moreover, these compounds have been found in various environments such as river water [8–10], rain water [8,11,12], wastewater [8,9], seawater [9,10] and even in conifer needles [11].

Because of the very high toxic and carcinogenic

*Corresponding author. Fax: +34-93-4021-233.
E-mail address: galceran@zeus.qui.ub.es (M.T. Galceran)

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risks of some HAAs [13], fast and accurate analytical methods for these substances are needed to monitor their concentration, behaviour and distribution in surface, drinking and groundwater. The EPA has established, in the first stage of the D/DBP Rule, a maximum contaminant level (MCL) of 60 μg l^{-1} for the sum of five haloacetic acids: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA).

Most of the methods used to determine HAAs, including EPA Methods 552 [14] and 552.2 [15], involve liquid–liquid extraction of the acids from the water into an organic phase (typically an ether), followed by derivatization using diazomethane, acidic methanol or BF_3–methanol and analysis of the methyl esters by GC [5,6,14–20]. Nowadays, the new methods tend towards liquid–solid extraction, which requires less solvent and avoids losses due to the concentration step. Some authors have used ion exchange to extract HAAs, followed by elution and esterification of these acids with H_2SO_4–methanol [21,22], H_2SO_4–ethanol [23] or H_2SO_4–propanol [12,24]. In some cases, acid-catalysed derivatization of HAAs was carried out after evaporation of the water sample to dryness and the esters were extracted in organic solvents and analysed by GC [12,24] or directly analysed by headspace GC [25]. Methyl esters of HAAs can also be obtained directly in water and analysed by headspace methods [26]. Methods for direct analysis of HAAs without derivatization have also been reported, such as liquid chromatography [9,10,24,27–29] and capillary zone electrophoresis [30,31], but trace enrichment processes including liquid–liquid extraction and concentration steps or solid-phase extraction were necessary, involving time consuming procedures or detection limits down to low μg l^{-1} levels.

Nowadays, solid-phase microextraction (SPME) developed by Pawliszyn et al. [32–34] is used as a new and practical solvent-free alternative for the extraction of organic compounds from liquid and solid samples [35,36]. SPME uses coated fused-silica fibres to extract analytes from gaseous and liquid phases. After equilibrium is reached or after a well-defined extraction time, the compounds absorbed are thermally desorbed by exposing the fibre in the injection port of a gas chromatograph, or redissolved in an organic solvent if coupled to HPLC [33,34]. So, SPME can integrate sampling, extraction, concentration and sample introduction in a single step and is a fast, inexpensive and easily automated technique. In spite of these advantages, few studies have dealt with the analysis of DBPs in waters using SPME [37–44]. To our knowledge, only Aikawa et al. [39] have reported the analysis of chlorinated acetic acids in drinking water by in situ acidic derivatization to the methyl esters with HCl–methanol followed by headspace SPME and GC–ECD quantitation. Although this is a rapid and sensitive method, decarboxylation of TCAA to chloroform occurred at the extraction temperature (100°C) and a relatively high limit of detection was obtained for MCAA (400 μg l^{-1}).

In this paper, a new method for the analysis for HAAs in water using headspace SPME–GC–IT-MS is proposed. Instead of methylation, ethylation of HAAs was chosen in order to form volatile esters with higher partition constants on the fibre and to obtain low detection limits. In addition, derivatization of HAAs in a non-aqueous medium was performed in order to prevent the hydrolysis of the corresponding esters. Reaction conditions to prevent decarboxylation of TCAA and obtain maximum reaction yields were established, and headspace SPME parameters were optimized to achieve maximum sensitivity in the gas chromatograph. The optimized procedure was applied to the analysis of six HAAs (EPA Method 552) in Barcelona tap water. Finally, the proposed headspace SPME procedure after acidic ethanol esterification (AEE) was evaluated by comparing the results with those obtained with the liquid–liquid extraction and acidic methanol esterification (AME) procedure of the EPA Method 552.2 [15].

2. Experimental

2.1. Standards and reagents

The HAAs studied were: (1) monochloroacetic acid (MCAA), (2) monobromoacetic acid (MBAA), (3) dichlororoacetic acid (DCAA), (4) bromochloroacetic acid (BCAA), (5) trichloroacetic acid (TCAA) and (6) dibromoacetic acid (DBAA). All

haloacetic acids were obtained at a purity higher than 98% from Fluka (Buchs, Switzerland), except BCAA, which was purchased from Chem Service (West Chester, PA, USA). The compounds, 2,3-dibromopropanoic acid and 1,2-dibromopropane, used as surrogate standard and internal standard, respectively, for the AME procedure were purchased from Fluka and Sigma-Aldrich (Milwaukee, USA) at a purity higher than 98%.

The solvents methanol and ethanol of residue analysis grade and sulphuric acid for analysis were supplied by Merck (Darmstadt, Germany), whereas methyl *tert.*-butyl ether (MtBE) of residue analysis grade was obtained from Fluka. Anhydrous sodium sulfate and copper (II) sulfate pentahydrate were purchased from Panreac (Barcelona, Spain) and Probus (Badalona, Spain), respectively. Water was from Milli-Q water purification system (Millipore, Beldford, MA, USA).

For ethylation and headspace SPME–GC–IT-MS optimization studies, individual stock standard solutions of 1000 mg l^{-1} were prepared by weight in ethanol. Appropriate volumes of a secondary standard mixture prepared in ethanol were always used to derivatize 0.9 μg of each compound (corresponding to an original concentration of 30 μg l^{-1} in water). For water studies, individual stock standard solutions of each HAA of 1000 mg l^{-1} were prepared by weight in Milli-Q water. Standard mixtures were prepared weekly or daily, depending on their concentrations. All solutions were stored at −17°C and warmed to ambient temperature before use.

2.2. Glassware and sampling

One-litre amber glass bottles were used for water sample collection and conical 5- and 40-ml screw-cap vials were used for SPME and AME procedures, respectively. The vials and bottles were cleaned with AP-13 Extran alkaline soap (Merck) for 24 h, rinsed consecutively with water, 1:10 HCl–water, again with water, and finally with Milli-Q water and baked at 110°C overnight. Volumetric glassware was washed as described above, but was air-dried. Anhydrous sodium sulfate was heated to 400°C overnight to remove phthalates and other interfering organic substances and then stored at 110°C until use.

Barcelona tap water was collected in 1-l amber glass bottles with PTFE-faced septa and polypropylene screw caps. To minimize aeration, bottles were filled so that no air remained and they were sealed with no headspace. No dechlorinating agent was added because the analysis was performed immediately after sampling.

2.3. Chromatographic conditions

Analyses using acidic ethanol esterification followed by headspace SPME were performed on a Varian 3400 CX GC capillary gas chromatograph coupled to a Saturn 3 GC–MS ion trap mass spectrometer (Sugar Land, Texas, USA). A DB-5 MS (5% phenyl, 95% methyl polysiloxane) fused-silica capillary column (30 m×0.25 mm I.D.) (J&W Scientific, Folsom, CA, USA) with 0.25 μm film thickness was used, with helium as carrier gas, at a linear velocity of 34 cm s^{-1}. The temperature programme was 40°C (held for 1 min) to 60°C at 20°C min^{-1}, to 120°C (held for 3 min) at 5°C min^{-1}, and finally up to 280°C (held for 10 min) at a rate of 25°C min^{-1}. Injector temperature was maintained at 250°C and splitless injection mode (2 min) was used.

The ion trap mass spectrometer (IT-MS) was operated in the EI positive mode using automatic gain control (AGC). The electron multiplier, emission current and modulation amplitude were set at 2100 V, 79 μA and 2.5 V, respectively, using perfluorotributylamine (FC-43) as reference. The transfer line and the ion trap manifold were set to 270 and 220°C, respectively, and a solvent delay of 2.5 min and an acquisition time of 25 min were applied. The mass range was from m/z 27 to m/z 260 at 0.8 s/scan with ionisation time of 500 ms. For quantification, two characteristic ions of the spectrum obtained for each ethyl haloacetate were selected: m/z 77/94 for ethyl monochloroacetate, m/z 83/85 for ethyl dichloroacetate, m/z 117/82 for ethyl trichloroacetate, m/z 121/138 for ethyl monobromoacetate, m/z 129/109 for ethyl bromochloroacetate and m/z 174/120 for ethyl dibromoacetate. The first ion was used for determination and the second for confirmation. SATURN version 5.2 software was used for data acquisition. Linear dy-

namic ranges of the headspace SPME GC–IT-MS system were determined by derivatization and extraction of standard mixtures in ethanol of the six HAAs between 6 ng and 9 μg (between 0.2 μg l^{-1} and 300 μg l^{-1} expressed as the concentration in the original water samples).

Analyses by acidic methanol esterification were performed on a Carlo Erba 5300 Mega Series gas chromatograph (Milan, Italy), equipped with a ^{63}Ni electron capture detection system (ECD). A DB-1701 (14% cyanopropylphenyl, 86% methylpolysiloxane) 30 m×0.25 mm I.D. fused-silica capillary column (J&W Scientific) of 0.25 μm film thickness was used. The temperature programme was 37°C (held for 21 min) to 140°C (held for 3 min) at 10°C min^{-1}, to 240°C (held for 5 min) at 20°C min^{-1}, and finally up to 300°C (held for 10 min) at a rate of 20°C min^{-1}. Carrier gas was helium (33 cm s^{-1}) and nitrogen was used as make-up (50 ml min^{-1}). Injector and detector temperatures were kept at 200 and 330°C, respectively, and splitless injection mode (1 min) was used. CHROMCARD version 1.3 software (Fisons Instruments, Spain) was used for data acquisition.

2.4. Acidic ethanol esterification (AEE) and headspace SPME procedure

SPME was performed with a 100-μm film thickness polydimethylsiloxane (PDMS) fibre housed in a manual holder (Supelco, Bellefonte, PA, USA). Before use, PDMS fibre was conditioned for 2 h in the GC injector port at 250°C. First, esterification conditions were optimized. Reaction time and reaction temperature, were consecutively established using a mixture of 30 μl of sulphuric acid and 70 μl of an ethanol solution containing the HAAs placed in a screw-capped septum conical vial (5 ml). The solution was vortex mixed and incubated for different times (from 10 to 40 min) at 60°C or different temperatures (from 50 to 70°C) at 10 min in order to derivatize the HAAs. After cooling, the vial was placed in a thermostatic bath and the 100-μm PDMS fibre was exposed to the headspace to extract the haloacetic ethyl esters. During the esterification optimization, an exposure time of 25 min, an extraction temperature of 25°C and a desorption time of 1 min were used. Volumes of sulphuric acid and ethanol between 10 and 100 μl were consecutively tested at the optimized time and temperature of reaction, in the headspace SPME conditions as above.

For headspace SPME optimization, the exposure time (from 1 to 30 min), the extraction temperature (from 20°C to 45°C), the ionic strength (from 0.1 to 0.6 g of sodium sulfate) and the desorption time (up to 3 min) were studied to obtain maximum sensitivity on the gas chromatograph responses after esterifying the HAAs at the optimum conditions.

For water analysis, 30 ml of sample solution was placed in a 50-ml flask. The sample was concentrated at 50°C to ~400 μl (15 min) using a rotary evaporator, and the residue was transferred to a conical 5-ml screw-capped septum vial. Temperatures higher than 50°C were not used in order to avoid decarboxylation of TCAA. Three additional aliquots of 400 μl were used to clean the 50-ml flask and added to the 5-ml vial. Three samples were evaporated in parallel using a laboratory-made glass adapter to the rotary system that allowed multiple sample evaporation in 50 min. After evaporation to dryness, 0.1 g of sodium sulfate, 30 μl of concentrated sulphuric acid and 40 μl of ethanol were added to the dried vial, which was sealed with the septum. The solution was vortex mixed and the HAAs were derivatized at 50°C for 10 min. The ethyl haloacetates were extracted with the 100-μm PDMS fibre and desorbed in the injection port of the gas chromatograph as described above. An exposure time of 10 min, an extraction temperature of 25°C and a desorption time of 2 min were used. Possible carryover of unknown compounds was prevented by keeping the fibre in the injector for an additional time with the injector in the split mode (purge on). Moreover, blanks were run periodically during the analysis to confirm the absence of contaminants. Since this method used a highly acidic ethanol phase, the fibres were often cleaned (2 or 3 times a day) by immersing them in Milli-Q water for 10 min, and desorbing in the GC injector at 250°C. The durability of the PDMS fibre under these extreme conditions is shorter than usually because sulphuric acid can oxidize the coating. However, each fibre can be used approximately more than 35–40 times without a loss of efficiency or precision in the results. To avoid the possible degradation of the fibre, Aikawa and Burk

[39] used HCl instead of H_2SO_4 to methylate HAAs in water. However, Shorney et al. [45] reported that HAAs were more susceptible to speciation shifts in the presence of HCl rather than H_2SO_4 when methanol was used. For this reason, H_2SO_4 was chosen as acid in the ethylation procedure. HAAs from tap water sample were analysed in triplicate using an external calibration curve generated by derivatizating and extracting 30 ml of Milli-Q water samples spiked with HAAs at seven different levels between 0.5 and 20 μg l^{-1}. In a preliminary study, HAAs losses in the evaporation process between 29 and 6% were observed when 30 ml Milli-Q water samples spiked at 5 μg l^{-1} for each HAA ($n=3$) were analysed using external calibration with direct derivatization and extraction of HAAs in ethanol solutions. So, aqueous calibration standards were used to compensate losses in the evaporation step. To take account of matrix effects, three water samples were also analysed by standard addition spiking the sample at different levels between 50 and 200% of the concentration in the water sample.

2.5. Acidic methanol esterification (AME) procedure

AME procedure for the determination of HAAs in drinking water was performed in triplicate as described by EPA Method 552.2 with some modifications [15]. Briefly, 11 μl of a MtBE solution of 2,3-dibromopropionic acid 22 μg ml^{-1}, as surrogate standard, 3 ml of concentrated sulphuric acid (to obtain pH<0.5), 12 g of anhydrous sodium sulfate, 3 g of copper(II) sulfate pentahydrate and 2 ml of MtBE were added to 30 ml of water placed in a vial of 40 ml. The vials were sealed with PTFE-faced septa, shaken for 15 min in a mechanical shaker, placed upright and allowed to stand for 5 min. In order to derivatize the HAAs, 1 ml of the MtBE extract and 2 ml methanol–sulphuric acid (9:1, v/v) were transferred to a 10-ml vial, which was placed in a thermostatic water bath at 50°C for 1 h. After cooling to 4°C, 5 ml of a $CuSO_4$–Na_2SO_4 solution was added and the mixture was shaken by hand for 2 min. An aliquot of 300 μl of MtBE extract was transferred to a 2-ml vial and 3 μl of a MtBE solution of 1,2-dibromopropane of 10 mg l^{-1} (as internal standard) were added. Finally, 1 μl of the MtBE extract was injected into the gas chromatograph. Water samples were analysed using a calibration curve obtained by spiking 30 ml of Milli-Q water with HAAs at seven concentration levels between 0.25 and 20 μg l^{-1}.

3. Results and discussion

3.1. Acidic ethanol esterification (AEE) and SPME optimization

3.1.1. Derivatization conditions

First, optimal conditions for the ethanol esterification procedure were established in order to obtain maximal reaction yields for all HAAs. This optimization was developed by consecutively changing derivatization times, temperatures and volumes of sulphuric acid and ethanol, whereas the headspace SPME temperature and time were maintained at 25°C and 25 min, respectively. This extraction time was considered long enough to achieve the equilibrium for all the esters taking into account previous studies that used a PDMS fibre to extract methyl chloroacetates by headspace SPME [39].

The first parameter to be evaluated was the esterification time. For this purpose, the derivatizing temperature, sulphuric acid volume and ethanol volume were fixed at 60°C, 30 μl and 70 μl, respectively. These values were chosen according to the results reported by Mori et al. [25] for the analysis of fluoroacetate ion in aqueous solution by headspace GC, before derivatization to its ethyl ester. The results obtained at derivatization times from 10 to 40 min showed that this parameter had no significant effect on ethylation of HAAs. Since 10 min was enough for efficient production of haloacetates, all subsequent reactions were carried out using this time.

Secondly, the effect of the derivatizing temperature on the reaction yield of the HAAs was studied. No differences in the responses were observed for any of the compounds when the temperature increased from 50°C to 70°C, and 50°C was thus chosen as the optimum temperature. In contrast, the volume of sulphuric acid significantly affected the responses obtained for the HAAs (Fig. 1A). Generally, the area of the esters increased, reached a

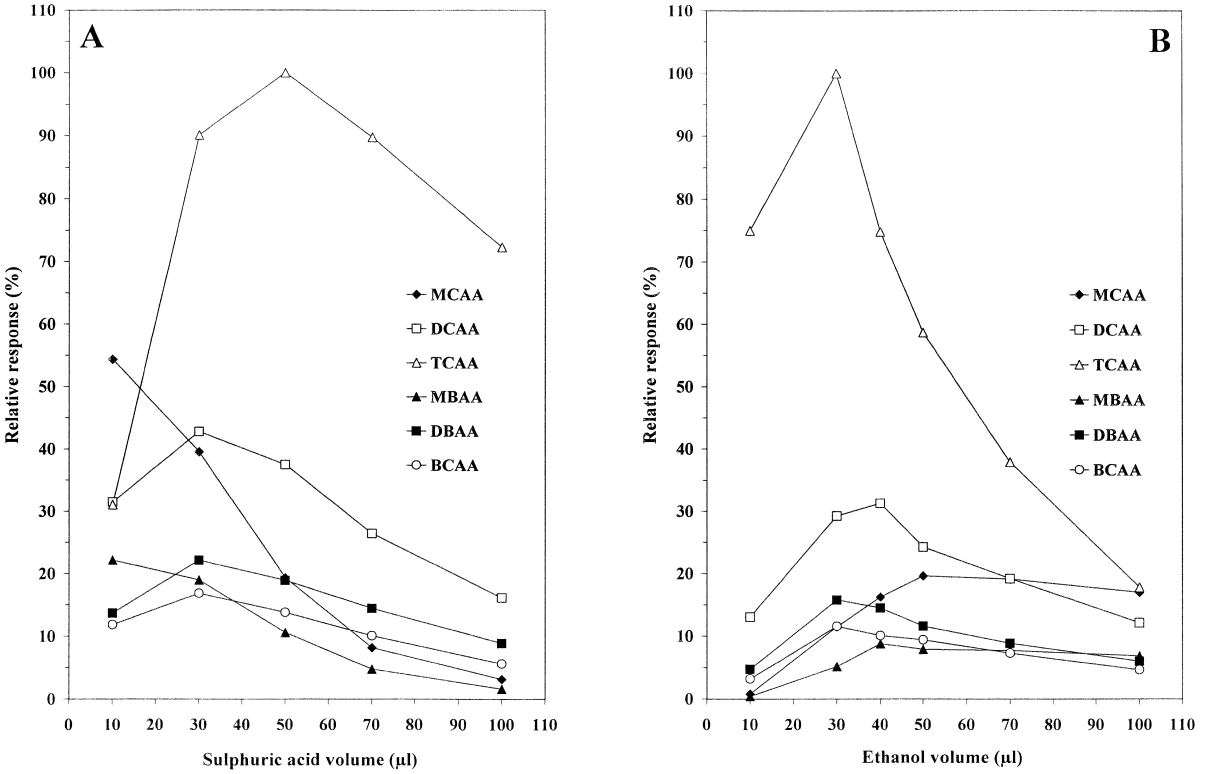

Fig. 1. Effect of volume of (A) sulphuric acid and (B) ethanol on the reaction yield of HAAs, expressed as the areas of the corresponding ethyl esters normalised to the maximum response. In (A) 0.9 μg of each HAA were derivatized with 70 μl of ethanol at 50°C for 10 min. Headspace SPME–GC–IT-MS with a 100-μm PDMS fibre, extraction temperature 25°C, extraction time 25 min and splitless injection mode. The same conditions were used for (B) with the sulphuric acid fixed at 30 μl.

maximum and then decreased, except for MCAA and MBAA ethyl esters, whose sensitivity decreased continuously with the acid volume. For three di-halogenated acetates (DCAA, DBAA and BCAA), the highest responses were obtained for 30 μl of sulphuric acid, although in these conditions, a loss in the sensitivity for MCAA and MBAA ethyl esters was observed. The response for the trichlorinated ester was higher at 50 μl of sulphuric acid than at 30 μl, although only by 11%. At volumes of sulphuric acid higher than 50 μl, a decrease for all compounds was observed that could be due to lower esterification efficiency or decomposition of the esters. In addition, the presence of high amounts of sulphuric acid in the headspace can oxidize the fibre coating giving diethyl sulfate, which appeared as an important component in the chromatogram (Fig. 4B). So, in order to obtain good responses for all the compounds, 30 μl of sulphuric acid was chosen for the reminder of this study.

Finally, the effect of ethanol volume when the sulphuric acid volume was fixed at 30 μl is shown in Fig. 1B. Maximum sensitivity for some di- and tri-halogenated ethyl esters (TCAA, DBAA and BCAA) was achieved when the sulphuric acid/ethanol ratio was 1, i.e. at 30 μl of ethanol. A decrease in the responses was observed for high ethanol volumes, for instance, the responses of TCAA and BCAA ethyl esters at 100 μl of ethanol were 18 and 30% of the maximum, respectively. This decrease could be due to lower derivatization efficiency or to a decrease in the fibre absorption capacity at high percentages of organic solvents, as has been previously reported [32]. For MBAA and DCAA ethyl esters, the maximum peak areas were obtained for 40 μl of ethanol, although for MCAA ethyl ester

increased till 50 μl. The different behaviour of these compounds can be related with their higher volatility, which does not appear to be influenced by the phase matrix. In order to obtain adequate responses for all the esters, 40 μl of ethanol was chosen as a compromise for subsequent studies.

3.1.2. Headspace SPME conditions

After optimal conditions for an efficient derivatization of HAAs had been established, parameters that affect the sensitivity of the headspace SPME, such as the extraction temperature, the exposure time of the fibre in the headspace, the effect of adding an inorganic salt and the desorption time in the gas chromatograph injector were optimized, using a derivatization temperature of 50°C, a derivatization time of 10 min and sulphuric acid and ethanol volumes of 30 and 40 μl, respectively.

First, in order to study the effect of the temperature on the extraction efficiency, different extraction temperatures between 20 and 45°C were tested, using a sampling time of 25 min. The relative responses are given in Fig. 2A, showing that 25°C gave the best results. Moreover, a rise in the temperature increased the vapour pressure of the sulphuric acid in the headspace, which can damage the fibre and reduce its lifetime.

As a second step, the time required to reach the equilibrium between the stationary phase and the acidic ethanol solution at 25°C was determined. Fig. 2B shows the absorption time profiles for ethyl haloacetates absorbed on the 100-μm PDMS fibre. Different responses were found for the compounds, depending on their volatility and distribution constants. Although some compounds (MCAA, MBAA ethyl esters) achieved the equilibrium in a very short time, the other compounds needed 5 or 10 min. Consequently, an exposure time of 10 min was chosen as optimal for all the haloacetates.

The effect of ionic strength on the SPME sensitivi-

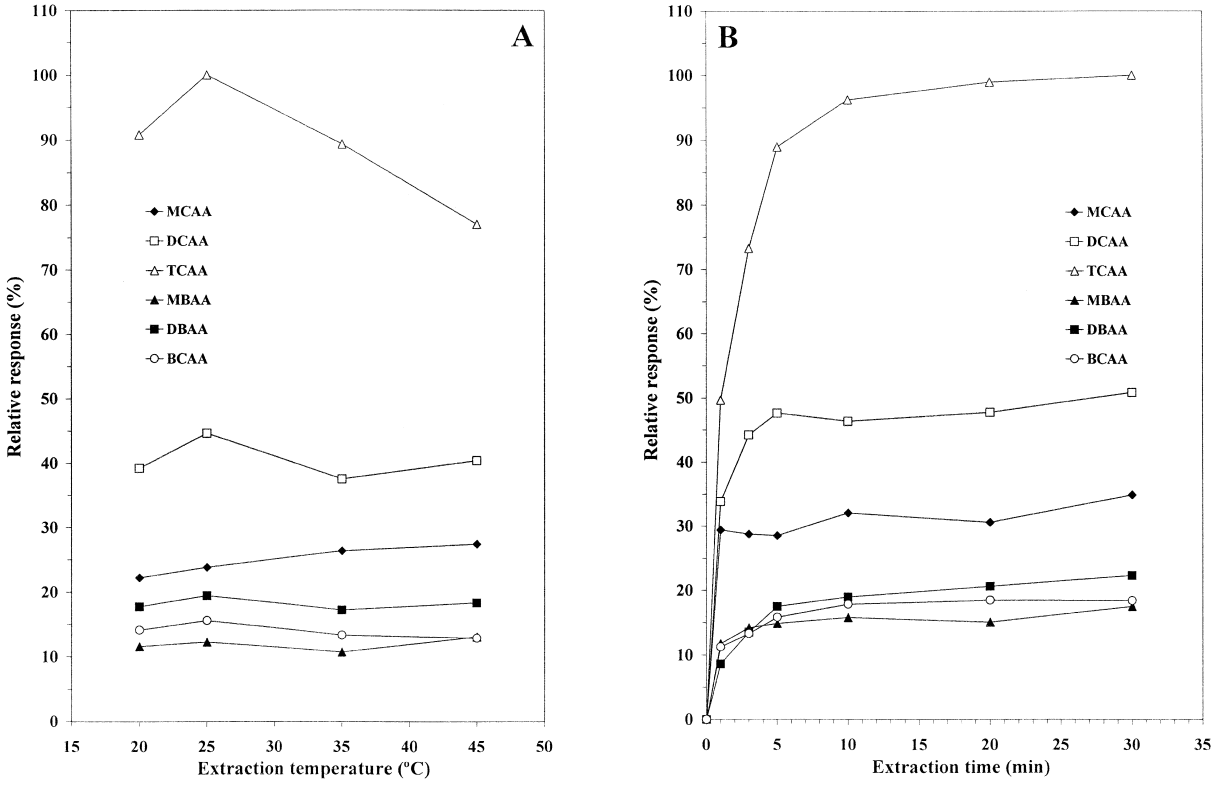

Fig. 2. Effect of (A) extraction temperature and (B) extraction time on absorption of ethyl haloacetates by headspace SPME–GC–IT-MS. Fibre and conditions as in Fig. 1B, with 40 μl of ethanol. In (B) extraction was carried out at 25°C.

ty was also studied. For this purpose, anhydrous sodium sulfate up to 0.6 g was introduced into the 5-ml conical vial before the addition of 40 μl ethanol solution containing the HAAs and 30 μl of sulphuric acid. The mixture was derivatized and extracted in the conditions previously established. The results are shown in Fig. 3A. Generally, the addition of salt up to 0.6 g progressively improved the absorption capacity of the fibre coating for all the compounds, although a decrease in the response of trichloroacetate was observed for amounts of sodium sulfate higher than 0.1 g. Taking these results into account and the fact that the small volume of liquid phase did not allow complete wetting of the walls of the vial in the presence of amounts of salt higher than 0.1 g, this value was chosen. Moreover, an additional peak that interfered with TCAA ethyl ester, which has been identified as the diethyl ester of the oxalic acid, increased progressively for quantities of sodium sulfate higher than 0.1 g.

Finally, desorption time was studied, and the profiles obtained for the six haloacetates in the optimum derivatization and extraction conditions for the 100-μm PDMS fibre are shown in Fig. 3B. As can be seen, 2 min was enough to desorb the compounds.

3.1.3. Quality parameters

Linear dynamic ranges of the headspace SPME–GC–IT-MS system were established from the curves obtained by plotting areas of the ethyl haloacetates versus concentration of each haloacetic acid (expressed as the concentration in the aqueous sample), after derivatization and extraction of the HAAs at the optimal conditions previously established. Detection limits, defined as the concentration of the HAAs in water that produced a signal-to-noise ratio (S/N) of 3 for the respective ethyl haloacetates, were calculated using Milli-Q water without detectable quantities of the HAAs, spiked at low levels of these acids. The results obtained for linear dynamic ranges and detection limits are given in Table 1. Good correla-

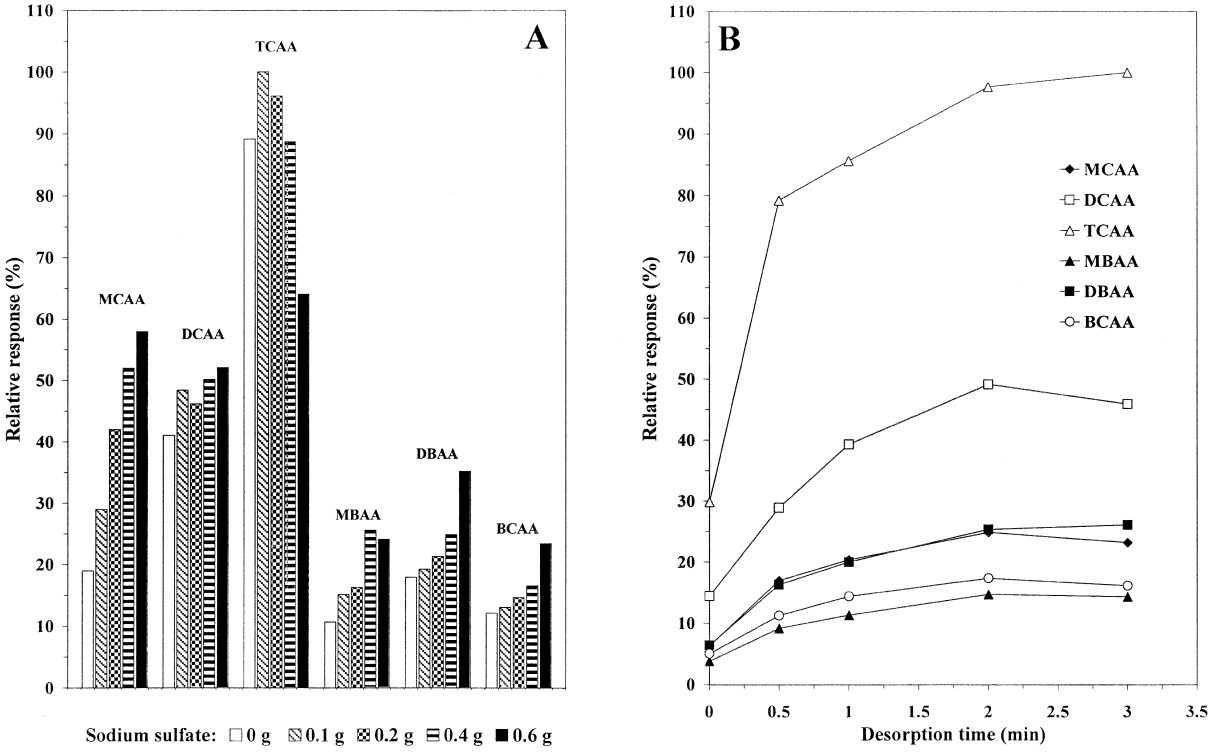

Fig. 3. Effect of (A) sodium sulfate and (B) desorption time on absorption of ethyl haloacetates by headspace SPME–GC–IT-MS. Fibre and conditions as in Fig. 2B, extraction time 10 min. In (B) 0.1 g of sodium sulfate was added.

Table 1
Quality parameters

Compound	Linear dynamic range ($\mu g\ l^{-1}$)	Correlation coefficient (r^2)	LOD[a] ($\mu g\ l^{-1}$)	Precision						
				Target value ($\mu g\ l^{-1}$)	Run-to-run[b]			Day-to-day[c]		
					Mean ($\mu g\ l^{-1}$)	SD ($\mu g\ l^{-1}$)	R.SD (%)	Mean ($\mu g\ l^{-1}$)	SD ($\mu g\ l^{-1}$)	RSD (%)
MCAA	1.00–125	0.998	0.20	10.1	10.0	0.72	7.2	10.3	1.03	10.0
DCAA	0.50–125	0.999	0.04	5.11	5.33	0.41	7.7	5.15	0.41	7.9
TCAA	0.50–125	0.998	0.01	5.08	5.37	0.34	6.3	5.33	0.54	10.1
MBAA	0.85–120	0.998	0.10	10.0	10.1	0.80	7.9	10.1	1.01	10.0
DBAA	0.50–125	0.998	0.02	5.10	5.00	0.33	6.7	5.20	0.54	10.3
BCAA	1.00–135	0.999	0.03	10.2	10.9	0.78	7.2	10.3	0.99	9.6

[a] LOD = Limit of detection.
[b] $n = 5$.
[c] $n = 5$ replicate × 3 days.

tion ($r^2 \geq 0.998$) and detection limits as low as 0.01–0.20 $\mu g\ l^{-1}$ were obtained for all the compounds.

To determine the run-to-run and day-to-day precision of the proposed AEE and headspace SPME–GC–IT-MS procedure, five replicates of spiked Milli-Q water were consecutively analysed at the optimized conditions using external calibration on one day and in three days, respectively. Relative standard deviations for run-to-run precision ranged between 6.3 and 7.9% and for day-to-day precision between 7.9 and 10.3% (Table 1).

3.2. Analysis of water samples

In order to show the applicability of the method, the acidic ethanol esterification coupled to headspace SPME procedure was used to determine HAAs in tap water from Barcelona, Spain. GC–IT-MS total-ion chromatograms obtained by headspace SPME with splitless injection (100-μm PDMS fibre), as well as the single-ion chromatograms selected for HAAs esters in a water sample are given in Fig. 4A. The total-ion chromatogram of a Milli-Q water sample spiked at 20 $\mu g\ l^{-1}$ for each haloacetic acid is also given in Fig. 4B. As can be seen, headspace SPME–GC–IT-MS is a highly selective procedure for the analysis of HAAs in drinking water, showing no interferences from other compounds potentially present in the sample matrix, except for TCAA, whose peak at m/z 117 was interfered with the contribution of another compound present in the matrix sample. For this reason, a second ion was used for quantitation, m/z 82, and a third ion (m/z 84) was used for confirmation. For comparison, the same sample was also analysed using the AME procedure (EPA Method 552.2) and HRGC–ECD. The chromatogram obtained using a DB-1701 column as well as the chromatogram of methyl haloacetates obtained from a Milli-Q water sample spiked at 10 $\mu g\ l^{-1}$ of each haloacetic acid are given in Fig. 5A and B, respectively. A high number of peaks appeared in the chromatogram which can interfere with the identification and quantitation. For instance, the internal standard recommended by the EPA Method 552.2, 1,2,3-trichloropropane, could not be used because it coeluted with another compound present in the sample. For this reason, 1,2-dibromopropane, which is recommended in the Standard Method 6251B, was used.

For SPME it is often used external calibration for quantification, assuming that the matrix does not significantly interfere with the extraction. In this study, two methods, external calibration and standard addition have been used to study the effect of sample matrix.The results obtained for HAAs with the AEE and headspace SPME–GC–IT-MS procedure in the analysis of a water sample with both calibration methods are given in Table 2, where the values obtained using the AME procedure (EPA Method 552.2) are also given. The analytical significance of the mean values of the two quantification headspace SPME methods as well as the AME procedure was

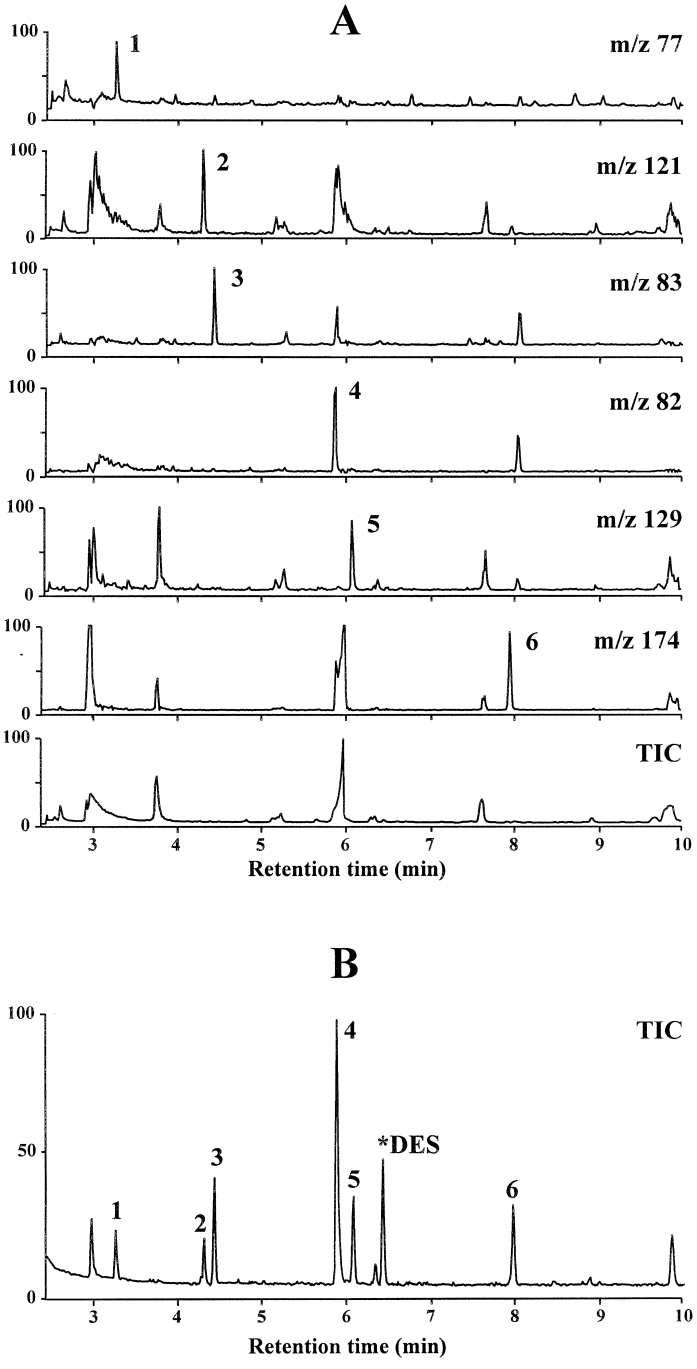

Fig. 4. (A) Headspace SPME–GC–IT-MS total-ion chromatogram and single-ion chromatograms of ethyl haloacetates from Barcelona tap water and (B) total-ion chromatogram of a Milli-Q water sample spiked at 20 μg l^{-1} for each haloacetic acid. Conditions as in Fig. 3B. Peaks: 1=MCAA; 2=MBAA; 3=DCAA; 4=TCAA; 5=BCAA; 6=DBAA ethyl esters; *DES=diethyl sulfate.

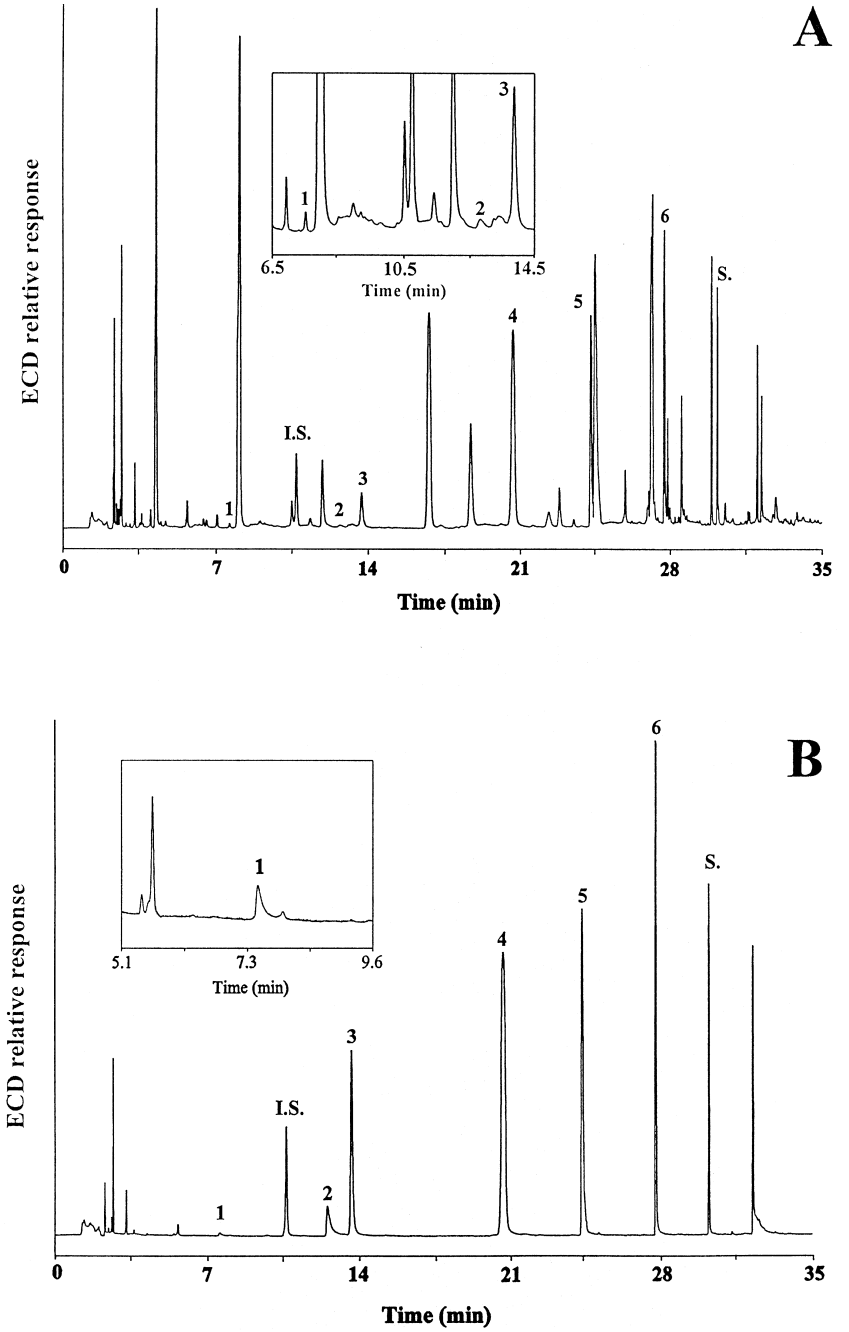

Fig. 5. (A) HRGC–ECD chromatogram of methyl haloacetates from Barcelona tap water. (B) HRGC–ECD chromatogram of Milli-Q water sample spiked at 10 μg l^{-1} for each haloacetic acid. Column: 30 m DB-1701 column, I.S. = 1,2-dibromopropane, S. = 2,3-dibromopropionic acid. Peaks: 1 = MCAA; 2 = MBAA; 3 = DCAA; 4 = TCAA; 5 = BCAA; 6 = DBAA methyl esters.

Table 2
Analysis of HAAs in Barcelona tap water

Compound	Concentration ($\mu g\ l^{-1}$)									Significance level (P-value)[c]		
	Headspace SPME External calibration[a] (A)			Headspace SPME Standard addition[a] (B)			Acidic methanol esterification[a,b] (C)			A vs. B	B vs. C	A vs. C
	Mean	SD	RSD (%)	Mean	SD	RSD (%)	Mean	SD	RSD (%)			
MCAA	12.4	0.88	7.1	8.06	0.51	6.3	8.07	0.61	7.6	0.005	0.989	0.002
DCAA	8.27	0.92	11.1	3.15	0.28	8.9	3.35	0.18	5.3	0.011	0.356	0.012
TCAA	9.01	0.93	10.3	9.92	0.41	4.1	8.47	0.76	9.0	0.196	0.062	0.482
MBAA	1.93	0.10	5.0	1.06	0.08	7.7	0.92	0.04	4.1	0.0003	0.064	0.0005
DBAA	9.37	0.66	7.0	9.58	0.68	7.1	9.02	0.27	3.0	0.727	0.261	0.443
BCAA	5.69	0.62	11.0	6.04	0.31	5.1	5.62	0.52	9.2	0.429	0.292	0.894
Total HAAs	46.7			38.1			35.4					

[a] $n=3$.
[b] EPA Method 552.2.
[c] Significant differences between procedures for $P<0.05$ (at the 95% confidence level).

statistically studied using the t-test. In case of obtaining unequal variances (F-test), the Cochran's test was applied. The significance values (P) obtained by comparing the three procedures are given in Table 2. Generally, the results with headspace SPME using standard addition agreed with those obtained with AME, whereas significant differences were observed between these methods and headspace SPME using external calibration for three compounds, MCAA, DCAA and MBAA ($P<0.05$). In general, the mean values obtained for these compounds with external calibration were 2 or 3 times higher than the values obtained with the other two procedures. Taking these discrepancies into account, the matrix may have had a significant effect on evaporation and extraction due to the presence of numerous organic and inorganic substances (as can be seen by the dried residue obtained in the vial after evaporation), that can enhance extraction, so standard addition is the method to be recommended to overcome the matrix effects. The total HAAs concentration found in the tap water using headspace SPME and standard addition was 38.1 $\mu g\ l^{-1}$, below the MCL of 60 $\mu g\ l^{-1}$.

AEE and headspace SPME–GC–IT-MS showed some advantages over AME and GC–ECD procedure, such as a shorter analysis time, the avoidance of hazardous organic solvents and the higher selectivity of the mass spectrometric detection. In addition, lower detection limits (between 2 and 20 times) were obtained with the proposed method.

4. Conclusions

HAAs in water were derivatized to their volatile ethyl esters under strongly acidic and alcoholic conditions and analysed by headspace SPME–GC–IT-MS using a 100-μm polydimethylsiloxane fibre. Good precision was obtained for the optimized procedure (run-to-run precision lower than 7.9% and day-to-day precision lower than 10.3%). The method was applied to the analysis of tap water and the results obtained using standard addition agreed with those obtained using the liquid–liquid extraction and acidic methanol esterification (AME) (EPA Method 552.2), whereas significant differences were observed between these methods and headspace SPME using external calibration for some analytes ($P<0.05$) because of matrix effects. To overcome these problems and obtain good reproducibilities (RSD between 4.1 and 8.9%), the use of standard addition is recommended. Consequently, AEE and headspace SPME procedure using standard addition can be proposed as an alternative accurate method for the analysis of HAAs in water at low $\mu g\ l^{-1}$ levels which avoids the need for large amounts of toxic organic solvents and tedious concentration steps that

may cause loss of the analytes and are time consuming.

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