

Analysis of haloacetic acids in water and air (aerosols) from indoor swimming pools using HS-SPME/GC/ECD

CHRISTOPHER S. A. SÁ, RUI A. R. BOAVENTURA and ISABEL B. PEREIRA

A solid phase microextraction method was used for the analysis of nine haloacetic acids (HAAs) in water and air (aerosols) from indoor swimming pools (ISPs). The analysis is characterized by derivatization of HAAs to their methyl-esters with dimethyl sulphate, headspace solid phase microextraction (HS-SPME) with a Carboxen–polydimethylsiloxane (CAR-PDMS) fiber and gas chromatography - electron capture detector (GC/ECD). High correlation coefficients were obtained for esters mixture calibration lines and detection limits were found to be at the low ppb level. Repeatability was assessed and coefficients of variation varied from 10 to 20%. Reproducibility was also evaluated and coefficients of variation from 15 to 25% were obtained. Analytical results from four Portuguese ISPs showed that the mean concentration of total HAAs (THAAs) in water ranged from 10 ± 2 to $183 \pm 28 \mu\text{g/L}$ in which $55 \pm 20\%$ corresponded to trichloroacetic and dichloroacetic acids (TCAA and DCAA). THAAs highest concentrations were directly related to higher ISPs' water organic matter content. In the lack of European specific regulation for water from ISPs and taking into consideration that ingestion is a form of exposure, THAAs concentration values were compared with drinking water maximum contamination level (MCL) of $60 \mu\text{g/L}$ proposed by the US EPA for the sum of five HAAs. In 35% of water sampling campaigns the sum of MBAA (monobromoacetic acid), MCAA (monochloroacetic acid), DCAA and TCAA exceeded that MCL value. The concentrations obtained for THAAs in the ISPs' atmosphere ranged from 5 ± 1 to $64 \pm 10 \mu\text{g/m}^3$ ($T = 28^\circ\text{C}$ at 5 cm above the water surface) and were proportional to the aerosols' quantity, which was deeply related to indoor air ventilation system.

Keywords: Haloacetic acids, air aerosols, chlorine, indoor swimming pools, HS-SPME/GC/ECD.

Introduction

Chlorine has commonly been selected as a disinfecting agent because of its proven efficiency and low price. Chlorination is applied to swimming pool water to protect the swimmers, removing effectiveness of malicious microorganisms and preventing their regrowth. When chlorine is added to water, it reacts with organic and inorganic materials, especially those released in the water by swimmers (skin scales, body care products, saliva, sweat and urine) to form several chlorination disinfection by-products (CDBPs).^[1] In consequence, the presence of CDBPs in the atmosphere of indoor swimming pools (ISPs) is highly probable, whenever chlorine is used for water disinfection.

The most frequently measured CDBPs are trihalomethanes (THMs) followed by haloacetic acids

(HAAs).^[2] Between 20% and 60% (w/w) of the total halogenated compounds resulting from chlorination are included in these two groups.^[3]

Excessive exposure to CDBPs may be harmful to humans.^[4-5] Some studies have shown that HAAs are always present in chlorine disinfected waters and are a human health concern.^[6-8] The presence of HAAs in ISPs' water and air (aerosols) is consequently a relevant aspect to be considered when the effects of water and air quality in users and workers' health are evaluated.

At present, there is still no specific regulation in use that establishes maximum concentration of HAAs in water and air from swimming pools either in Europe or in the United States. From the available legal restrictions for water use, it was considered that the more suitable for comparison purposes in the frame of this study were those related to drinking water because water involuntarily ingested is one of the forms of swimmers' exposure. Regulation of the United States Environmental Protection Agency (US EPA) applied to drinking water considers five major HAAs in the group of disinfectants and disinfection by-products: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA),

monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) and establishes the total maximum contamination level (MCL) as 60 $\mu\text{g/L}$.^[9] This agency classified DCAA as a group B2, probable human carcinogen^[7-10] and TCAA as a group C, possible human carcinogen, on the basis of limited evidence of carcinogenicity to the liver in animals.^[7]

Some studies about qualitative or quantitative analyses of HAAs have been reported. In the beginning of the 90's two analytical methods for HAAs determination (US EPA 552 and Standard Method 6233) were being used to evaluate HAAs in drinking water.^[11-12] Nevertheless, diazomethane was used in both methods for derivatization, and that compound was prepared with a potent carcinogen, 1-methyl-3-nitro-1-nitrosoguanidine (MNNG). In 1992 US EPA published Method 552.1 which included a solid-phase extraction and acidic methanol derivatization technique that did not use diazomethane.

However, this method showed some operating difficulties in the liquid-solid extraction step. In 1995 the US EPA published Method 552.2, proposing a liquid-liquid extraction and acidic methanol derivatization technique with final quantification by electron capture detector (GC/ECD). Later on some modifications to these methods were suggested, as performing the extraction and derivatization simultaneously^[13] or separately by sample evaporation^[14] or by headspace technique.^[15] In 1999, a closed-loop stripping analysis (CLSA) technique was employed for the determination of halogenated DBPs using GC-ECD analysis, but only results for DCAA and DBAA were reported.^[16]

The determination of HAAs without derivatization was possible with ion chromatography^[17-18] or capillary zone electrophoresis.^[19] These methods are able to achieve low detection limits, but still with a significant consumption of time and labor. Also in 1999 a method for the analysis of six HAAs using headspace solid-phase microextraction gas chromatography with ion-trap mass spectrometry (HS-SPME/GC/ITMS) was developed.^[20]

Acid-catalysed ethylation was used to obtain low detection limits and good sensitivity (detection limits from 10 to 200 ng/L), but still with a significant cost of time and labor. In 2000 the same authors^[21] proposed a new method also based on HS-SPME/GC/ITMS with direct derivatization of HAAs in water by dimethyl sulphate (DMS) or diethyl sulphate (DES) in order to avoid long pre-concentration steps and reduce the analysis time. DMS was already known as a derivatizing agent that can convert polar substances into hydrophobic compounds and thus increase volatility for a determination by headspace gas chromatography.^[15-22]

In 2003, the US EPA published Method 552.3, by which the sample is extracted with methyl tert-butyl ether (MTBE) or tert-amyl methyl ether (TAME) containing an internal standard. The derivatization and detection techniques are similar to those of Method 552.2, but do not use

the advantages of SPME.^[23] Another method was reported in 2007 which uses solid-phase extraction followed by capillary electrophoresis analysis.^[24] According to the authors of that study, the main advantages of the method are the saving in solvent and the fact that it avoids the hazards and complexity of the derivatization step. In 2008 a method that combines simultaneous liquid-liquid microextraction with methylation for the determination of haloacetic acids in drinking waters by headspace gas chromatography was reported.^[25] Recently in 2010 the same authors optimized and compared several microextraction/methylation methods for determining HAAs in water using GC/MS^[26] and propose a method that includes solvent bar microextraction (HS-SBME/GC/MS) as a candidate for routine determination of HAAs in tap water.

Some studies^[21-26-27] present HAAs' quantification in water of swimming pools. These works report concentrations of individual HAAs determined in water samples from Spanish and German ISPs and the obtained results will be presented later in this article together with those of the present study. Analysing the values of HAAs concentrations from those three studies it is possible to conclude that DCAA and TCAA are the two major constituents of HAAs. No reported values for HAAs in the air (aerosols) of ISPs were found in the literature.

Based on the latest knowledge and the best practices of recent techniques this study uses an analytical method capable of analyzing 9 HAAs in water and air (aerosols) from ISPs with good sensitivity, repeatability and reproducibility. This method is environmentally friendly and less time and labor consuming than many of those referenced earlier. The analytical procedure includes the derivatization of HAAs to their methyl-esters with dimethyl sulphate (DMS), headspace solid phase microextraction (HS-SPME) with a Carboxen-polydimethylsiloxane (CAR-PDMS) fiber and gas chromatography analysis with an electron capture detector (GC/ECD). The developed method was validated and applied to analyse the water and the air of four ISPs in Northern Portugal.

Materials and methods

The experimental conditions were established to obtain high efficiency in the derivatization and extraction steps and HS-SPME parameters were optimised to achieve good sensitivity in the GC/ECD analysis. The optimised procedure was applied to the determination of HAAs – monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA) and bromochloroacetic acid (BCAA) – in water and air from indoor swimming pools.

The individual standards necessary to enable peak identification by retention time were purchased from Supelco (Bellefonte, PA) with the following purity: Monochloroacetic acid (MCAA), 98.8%, Monobromoacetic acid (MBAA), 99.9%, Dichloroacetic acid (DCAA), 98.3%, Dibromoacetic acid (DBAA), 97.3%, Trichloroacetic acid (TCAA), 97.5%, Tribromoacetic acid (TBAA), 99.9%, Bromodichloroacetic acid (BDCAA), 99.9%, Chlorodibromoacetic acid (CDBAA), 98.9% and Bromochloroacetic acid (BCAA), 98.0%.

Commercially available esters calibration mixture in MTBE (Methyl tert-butyl ether) was also used (EPA 552.2). This mixture, also supplied by Supelco, contains the 9 corresponding methyl-esters (Methyl chloroacetate, 600 $\mu\text{g}/\text{mL}$, Methyl bromoacetate, 400 $\mu\text{g}/\text{mL}$, Methyl dichloroacetate, 600 $\mu\text{g}/\text{mL}$, Methyl dibromoacetate, 200 $\mu\text{g}/\text{mL}$, Methyl trichloroacetate, 200 $\mu\text{g}/\text{mL}$, Methyl tribromoacetate, 2000 $\mu\text{g}/\text{mL}$, Methyl bromodichloroacetate, 400 $\mu\text{g}/\text{mL}$, Methyl chlorodibromoacetate, 1000 $\mu\text{g}/\text{mL}$, Methyl bromochloroacetate, 400 $\mu\text{g}/\text{mL}$).

The ultrapure type I deionised water used in the preparation of standard solutions and for material washing was obtained from a Barnstead water purification system. The derivatization reagent dimethyl sulphate (DMS), purity $\geq 99\%$, was obtained from Riedel-de-Haën. Tetrabutylammonium hydrogen sulphate (TBA- HSO_4) and anhydrous sodium sulphate (both salts with 99% purity) were purchased from Fluka. Anhydrous sodium sulphate was heated up to 400°C to remove phthalates and other interfering organic substances and stored at 45°C until use.

Samples and standard solutions were poured into screw capped vials (4 and 40 mL), sealed with a Teflon lined silicon septum. These vials were washed prior to use, first with deionised water, then with acetone (Prolab), again with deionised water and finally with Barnstead water. At the end they were heated and kept at 400°C for 30 min to loose any organic matter adsorbed. Septa were also washed with deionised water and further baked at 100°C for 1 h before use. Other glassware used in the HAAs analysis was washed in the same way of the vials and dried at 45°C. Some preliminary tests have showed that this procedure for septa, vials and glassware avoided all probable contamination.

A commercially available Carboxen-Polydimethylsiloxane (CAR-PDMS), 75 μm , fiber supplied by Supelco was used in the SPME technique. This option took into consideration previous results of HAAs analysis by HS-SPME/GC/ITMS.^[21]

HAAs analysis

Preparation of HAAs standards. Each stock individual calibration standard (1000 $\mu\text{g}/\text{L}$) was prepared using the pure HAA standard either by weight or volume depending on reagent phase. Other work standard solutions were pre-

pared daily and stored together with stock solutions at -18°C. A similar procedure was adopted to prepare mixture calibration standards, from the commercial calibration mixture.

Individual standards and the standard calibration mixture were used for the determination of residence times of every haloacetate. A chromatogram of the standard calibration mixture with the 9 methyl-esters (concentrations from 0.066 to 0.325 $\mu\text{g}/\text{L}$) is presented in Figure 1, together with a blank chromatogram. Every compound was well separated with the exception of DBAA and BDCAA methyl-esters that were co-eluted. Although several tests were performed to overpass this problem, none of the other conditions tested was more satisfactory, as the separation of the other methyl-esters was negatively affected.

Procedure for HS-SPME. Previous tests were executed in the interest of studying possible interferences from materials in air lab, glassware, reagents, septa, fiber glue and purge gas in the analytical procedure to keep them under control.

First, a volume of 1.6 mL of water (deionised water, ISP water sample or water in which ISP air was bubbled) was poured into a 4 mL amber vial containing a Teflon coated magnetic stirring bar. If deionised water had been poured, then the required volume (some μL) of the 1 ppm haloacetic acid standard solution was added to achieve the desired concentration in the vial.

The effect of an ion pairing agent on the derivatization of HAAs was studied adding different volumes of TBA- HSO_4 (0.45 M) to the water (from 10 μL (2.8 mM in the vial) to 40 μL (11.2 mM in the vial)). The highest recoveries for most compounds were obtained using 20 μL of 0.45 M TBA- HSO_4 (5.6 mM in the vial) for the sample volume used.

The dimethyl sulphate (DMS, 10.6M) was used as derivatization agent (injecting it through the vial septum with a syringe) and different volumes ranging from 10 μL (0.066 M in the vial) to 40 μL (0.264 M in the vial) were tested. The addition of 20 μL (0.132 M in the vial) of DMS ensured the maximum responses.

After the addition of the two agents, the CAR-PDMS fiber was exposed to the headspace for 20 min at $55 \pm 1^\circ\text{C}$ with the liquid stirred at 300 rpm. Different values of time (1 to 45 min) and temperature of extraction (30 to 65°C) were previously tested, and the best results were in agreement with corresponding values used by Sarrión et al.^[21]

The importance of ionic strength in the extraction process is known^[23] and normally the amount of analytes adsorbed onto the fiber increases when a salt (namely sodium sulphate) is added. This was also observed in the present study. Nevertheless, at concentrations of sodium sulfate higher than 62.5 $\mu\text{g}/\text{L}$, the peak area increase was only obtained for some compounds (MCAA, TBAA and CDBAA), whereas a decrease was observed for others (DCAA, TCAA, MBAA, DBAA+BDCAA and BCAA). Another negative aspect was that after using the SPME fiber for

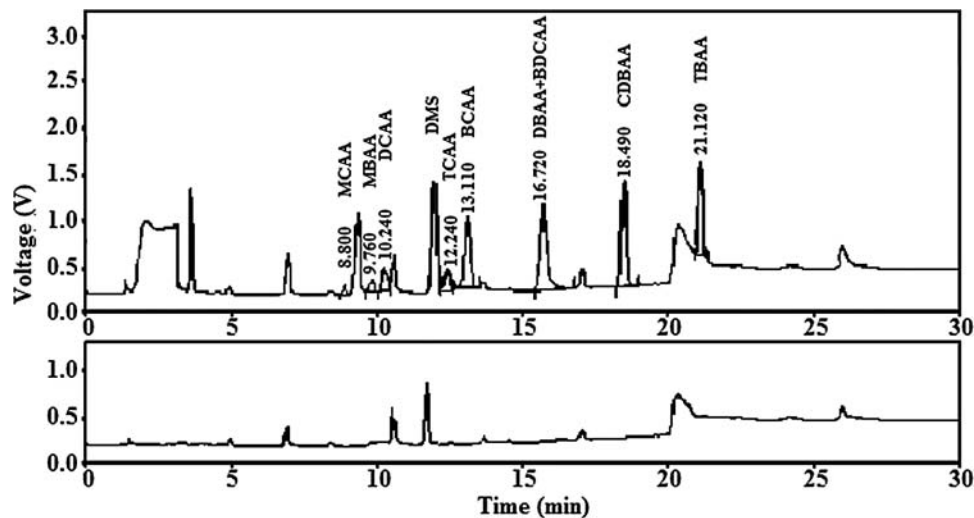


Fig. 1. Chromatograms of a blank (deionized water + DMS + TBA-HSO₄) and of a methyl-haloacetates standard mixture with concentrations from 0.066 to 0.325 $\mu\text{g/L}$.

some time, salt residues were detected on its surface, and they were responsible for pulling out the Carboxen coating. For these reasons, it was decided not to use any inorganic salt to improve volatilization of haloacetic esters.

Finally, the compounds retained in the fiber were desorbed at the injection port of the GC for 10 min in splitless mode and 200°C. Another desorption temperature, 250°C, was tested but as there were no differences between both chromatographic responses, the temperature of 200°C was selected in order to increase fiber lifetime. As the total chromatographic analysis of a sample took about 30 min, the needle (containing the fiber) was kept in the injection port during 10 min. After that the fiber was immediately positioned in another vial, for another 20 min sample extraction. This procedure prevented the adsorption of other compounds from surrounding air by the hot fiber which would interfere with subsequent chromatographic analysis.

The proposed method allows the analysis of HAAs in about 40 minutes, which is less than for example the analysis' time required by EPA 552.2 method (more than 2 hours) and by Sarrión and coworkers' procedure^[21] (about 68 min).

Water sampling

The swimming pool water samples were collected in 40 mL amber glass bottles with PTFE faced septa and polypropylene screw caps, avoiding the presence of headspace at the top of the bottles. Water samples were collected in four different points of the pool (at the corners, 1 m away from the sides and at 20 cm depth). Samples were transported in isothermal containers directly to the laboratory and their

analysis started immediately, otherwise they were stored at low temperature ($T < 5^\circ\text{C}$). In any case all analyses were performed during the 2 subsequent days after sampling.

Air sampling

The air (aerosols) samples were collected at one corner of the swimming pool, 10 cm away from the two walls and 5 cm above water surface. Samples were vacuum pumped during 1 hour at a flow rate of 1 L/min ($\pm 5\%$) into 2 midjet fritted glass bubblers placed in series, each one with 100 mL of ultrapure deionised water. The two glass bubblers were then sealed, transported in isothermal containers directly to the laboratory and their analysis started immediately. The two volumes of water from the bubblers (200 mL) were mixed for further analysis of HAAs. Air temperature was measured during sampling and registered.

Gas chromatographic system and conditions

The GC capillary gas chromatograph used was a DANI 1000 with an electron capture detector (ECD). Separations were conducted in a ValcoBond VB-624 ((6% Cyanopropyl-phenyl)-methylpolysiloxane) fused silica capillary column, 30 m length, 0.53 mm i.d., 3 μm film thickness with nitrogen as carrier gas (5.8 mL/min) at a linear velocity of 40 cm/s and as auxiliary gas (1.1 mL/min). The column was held at 40°C for 1 min, then was ramped at 10°C/min to 65°C, 6°C/min to 106°C, 3°C/min to 115°C, 6°C/min to 160°C, 10°C/min to 175°C and then held at this temperature for 8 min (total time 30.33 min). Injection port (splitless mode) and detector temperatures were set at 200°C and 300°C, respectively.

Results were confirmed using a different capillary column (J&W Scientific DB-210 (50%-Trifluoropropyl)-methylpolysiloxane)) with 30 m length, 0.32 mm i.d. and 0.5 μm film thickness.

Results and discussion

Linearity, limits of detection, reproducibility, repeatability

Quantification with external calibration, as it is frequently done in SPME, was chosen. Calibration linearity was checked performing 3 extractions/injections for each calibration mixture standard. A correlation coefficient of 0.990 was obtained for concentrations of methyl-tribromoacetate between 0.325 and 52.0 $\mu\text{g/L}$. With other methyl-haloacetates the results were similar (correlation coefficients of 0.972 to 0.995).

Limits of detection (LOD) for the seven well-separated methyl-esters and the corresponding haloacetic acids, considering the peaks with a signal-to-noise (S/N) ratio of 2:1 are presented in Table 1. The concentration values thus obtained for the sum of DBAA and BDCAA methyl-esters (0.099 $\mu\text{g/L}$), that were co-eluted, and for the sum of the corresponding haloacetic acids (0.086 $\mu\text{g/L}$) do not strictly represent limits of detection but were used as reference values for results evaluation.

To validate the calibration lines, a condition referred by Sousa^[28] was adopted: $S_b/b \leq 5\%$, where S_b is the standard deviation of the calibration line slope and b is the calibration line slope. S_b/b (%) values obtained for the eight calibration lines were equal to 1.0, 1.0, 1.2, 0.7, 1.2, 1.0, 0.4 and 0.5%. As all the values were below 5%, calibration lines were validated.

Repeatability was assessed by analyzing 12 times the same methyl-esters standard with concentrations from 1.32 to 13.0 $\mu\text{g/L}$. Coefficient of variation (CV), defined as the ratio of standard deviation by mean, for each HAA varied from 10 to 20%.

Table 1. Limits of detection for 7 methyl-esters and for the corresponding haloacetic acids when analyzed by HS-SPME/GC/ECD.

Compound	Limit of detection ($\mu\text{g/L}$)	
	Methyl-ester	Haloacetic acid
MCAA	0.098	0.085
MBAA	0.098	0.085
DCAA	0.066	0.057
TCAA	0.033	0.029
BCAA	0.066	0.057
CDBAA	0.163	0.142
TBAA	0.325	0.283

Reproducibility was evaluated by injecting the same standard mixture once a day and during 12 consecutive days. Results showed coefficients of variation from 15 to 25%. These values are high when compared with EPA Method 552.2 for water spiked at similar concentrations of HAAs and allow us to conclude that ECD has significant variations. Therefore, it was decided to check the calibration lines daily or every time the analysis was done and adjust them if needed. Comparing the achieved CV values for repeatability (10% to 20%) and the LODs (29 to 283 ng/L) with the ones presented by Sarrión and coworkers^[21] (9.8 to 13.9% for CV and 10 to 450 ng/L for LODs, using HS-SPME/GC/ITMS, and 6 to 13% for CV and 200 to 1500 ng/L for LODs, using EPA Method 552.2) it is possible to conclude that performance of the herein proposed method is similar.

Giving the matrix complexity of ISPs' samples, some tests were performed to check the interferences in retention times and HAAs' peak areas. As slight changes were observed in real samples' HAAs separation times, the sample was spiked with standard calibration mixture in order to validate the peaks' identification. Moreover the quantification of HAAs was confirmed by the addition of standard mixtures of adequate concentration to real samples. For every case tested, the comparison of the peak areas (standard mixture alone, sample alone and sample with the standard mixture) led to the conclusion that sample matrix did not interfere in the HAAs' quantification.

HAAs in ISP's water

Eighty water samples from four public swimming pools (F, MC, MSMF, MPL) located at the North of Portugal were collected in 5 different days and analyzed in duplicate using the optimized HS-SPME/GC/ECD method. Each concentration value presented in Figures 2 and 3 as well as in Table 2 (*present study* column) corresponds to the mean concentration of the four water samples from each swimming pool collected in each day.

Figure 2 presents the results obtained for the sum of the 9 HAAs concentrations. The total HAAs' mean concentration in swimming pool water ranged between 10 ± 2 and $183 \pm 28 \mu\text{g/L}$. Other authors report THAAs' values of $330 \mu\text{g/L}$ ^[21] and 201 to $363 \mu\text{g/L}$ ^[26] in ISPs' water.

Another result displayed in Figure 2 is that MSMF swimming pool water presented the highest THAAs values ($183 \pm 28 \mu\text{g/L}$, 179 ± 27 and $164 \pm 25 \mu\text{g/L}$), much probably due to its highest organic matter values. In fact, TOC (total organic carbon) average values in the four swimming pools water were $6.72 \pm 0.05 \text{ mg/L}$ for MSMF, $4.34 \pm 0.24 \text{ mg/L}$ for MC, $3.66 \pm 0.08 \text{ mg/L}$ for F, $1.13 \pm 0.06 \text{ mg/L}$ for MPL and permanganate oxidability values in the feed water were $3.0 \text{ mgO}_2/\text{L}$ for MSMF (drawn from an artesian well), $0.4 \text{ mg O}_2/\text{L}$ for MPL and $1.1 \text{ mg O}_2/\text{L}$ for both F and MC.

Table 2 presents the ranges of mean concentration values obtained in the present study for every HAA in ISPs' water

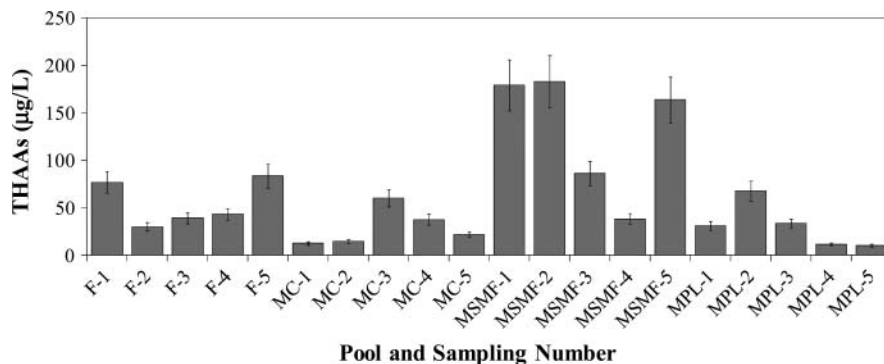


Fig. 2. THAAs mean concentration values in water samples from four Portuguese indoor swimming pools.

(excepting DBAA and BDCAA that were co-eluted and are presented as a sum concentration) and also the individual HAAs' concentrations reported in other works.^[21–26–27] Some variability of values is observed among the three studies. A common feature is that TCAA and DCAA constituted the greatest fraction of total HAAs ($55 \pm 20\%$, in the present study).

As referred to previously US EPA establishes a MCL of $60 \mu\text{g/L}$ for the sum of MCAA, DCAA, TCAA, MBAA and DBAA in drinking water. In the absence of specific regulation for ISPs and bearing in mind that water involuntarily ingested is one form of swimmers' exposure to HAAs, the US EPA MCL was used for comparison purposes. In Figure 3, the values obtained during all the campaign for the sum of those HAAs' concentration (excluding DBAA as it was co-eluted with BDCAA) are presented, together with the US EPA MCL value for HAAs in drinking water. The results indicate that in 35% of all water sampling campaigns that MCL value is exceeded.

Taking into consideration estimations^[29] of the volume of water involuntarily swallowed by a child, 0.090 L, or an adult, 0.022 L, or even an athlete, 0.056 L (considered as a mean value between child and adult ingestion), and total

water consumed during 1 normal life day (1 L for children, 2 L for adults) one might be led to conclude that users are not in health danger. However other forms of exposure exist

Table 2. Mean concentration values for individual HAAs in the water of ISPs (^[21–26–27] and present study).

Haloacetic acid	Mean concentration values in ISPs' water ($\mu\text{g/L}$)			
	[21]	[26]*	[27]	Present study
MCAA	4.22	34–42	2.6–81	0.6–13.2
MBAA	–	–	< 0.5–3.3	0.5–20.1
DCAA	45.2	94–130	1.5–192	0.4–54.1
TCAA	155	55–195	3.5–199	0.5–72.9
BCAA	10.5	–	–	0.4–24.7
CDBAA	32.8	–	–	0.2–0.9
TBAA	18.9	–	–	0.4–0.9
DBAA	2.76	1.4–1.6	< 0.2–7.7	0.1–11.9**
BDCAA	60.6	3.0–8.2	–	–

*HS-SBME/GC/MS method; **The range values refer to the sum (DBAA+BDCAA).

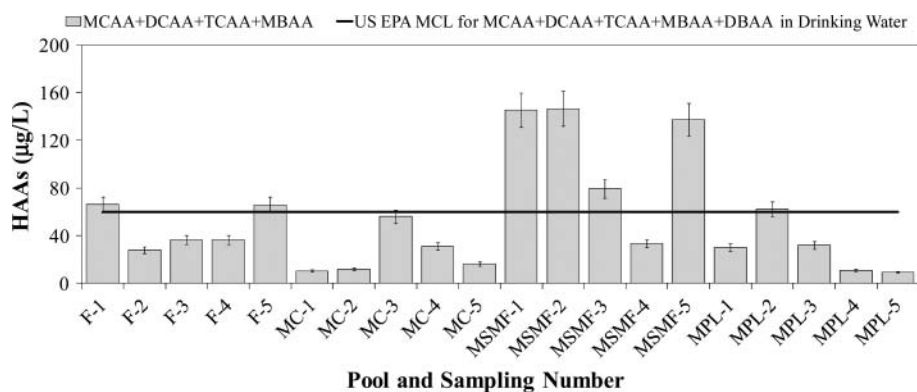


Fig. 3. Mean concentration values for the sum of four HAAs in water samples from four Portuguese indoor swimming pools compared with US EPA maximum contamination level for drinking water.

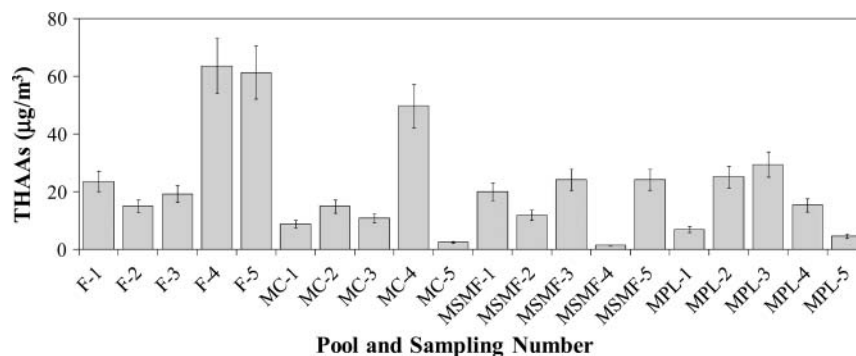


Fig. 4. THAAs mean concentration values in air (aerosols) at 5 cm above water surface from four Portuguese indoor swimming pools.

and HAAs may affect ISPs' users and workers differently, namely by inhalation.

HAAs in ISP's air (aerosols)

Twenty air (aerosols) samples from the same public swimming pools (F, MC, MSMF, MPL) were collected in five different days and analyzed in duplicate using optimized HS-SPME/GC/ECD method. After determining each HAA total mass in the water volume of 200 mL collected from the two glass bubblers used in air sampling, the HAA air concentration was finally obtained dividing that quantity by the total volume of sampled air (60 L).

The THAAs concentration values ranged from 5 ± 1 to $64 \pm 10 \mu\text{g}/\text{m}^3$ ($T = 28^\circ\text{C}$) at 5 cm above the water surface and are presented in Figure 4. Curiously, the THAAs highest values found in the swimming pools atmosphere (64 ± 10 and $61 \pm 9 \mu\text{g}/\text{m}^3$ in ISP F) didn't occur in the same swimming pool where the highest THAAs values in the water were detected (ISP MSMF). The number of air changes per hour and the relative humidity mean values were measured, giving results of 2.3 and 70.4% for swimming pool F and 5.1 and 44.5% for swimming pool MSMF, respectively. These values may explain a greater amount of aerosols in swimming pool F and therefore higher concentrations of HAAs in the air when compared with swimming pool MSMF.

The results of air (aerosols) analysis obtained confirm that users of the ISPs studied are also exposed to HAAs via inhalation. A third way of human exposure to these compounds is the absorption through the skin.^[19] So, taking into consideration the results of water and air analysis, only an accurate evaluation of the summative effects of the three types of exposure for the tested conditions would allow a correct conclusion regarding health concern for swimmers and workers of those swimming pools.

Conclusions

The HS-SPME/GC/ECD procedure proposed in this study was a suitable analytical methodology for the analysis

of HAAs in water and air (aerosols) from indoor swimming pools after derivatization with dimethyl sulphate and using TBA- HSO_4 as an ion pairing agent. High correlation coefficients were obtained for calibration lines of standard esters mixtures and detection limits were at the low ppb level. The total HAAs mean concentration in the water of the studied ISPs ranged between 10 ± 2 and $183 \pm 28 \mu\text{g}/\text{L}$.

The highest THAAs concentration values found in water, where TCAA and DCAA constituted the greatest fraction ($55 \pm 20\%$), were related to its organic matter content. In the lack of more specific regulation for water from ISPs and taking into consideration that water involuntarily ingested is a form of exposure for users, THAAs concentration values were compared with drinking water maximum contamination level ($60 \mu\text{g}/\text{L}$) proposed by US EPA for the sum of five major HAAs (MBAA, MCAA, DCAA, DBAA and TCAA). In 35% of the results, the concentration sum of MBAA, MCAA, DCAA and TCAA exceeded that MCL value.

The fifth major HAA considered by US EPA (DBAA) was not individually quantified in this study. The THAAs mean concentration values in the atmosphere of the ISPs, 5 cm above the water surface, ranged from 5 ± 1 to $64 \pm 10 \mu\text{g}/\text{m}^3$ ($T = 28^\circ\text{C}$) and the highest values were directly related to the amount of aerosols in the atmosphere, which depends on the indoor air ventilation system. Although no definite conclusion may be taken directly from the results regarding health concern, this study gives a contribution for the easiest evaluation of HAAs in water and air from ISPs and provides data that may be useful for toxicologists and rulers in the establishment of specific regulation.

References

- [1] WHO, *World Health Organisation, Environmental Health Criteria 216*, International Programme for Chemical Safety (IPCS), Geneva, 2000; 499 pp.
- [2] Weinberg, H.S.; Krasner, S.W.; Richardson S.D.; Thurston A.D. *The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study*, EPA/600/R-02/068, US EPA, 2002; 455 pp.

- [3] US EPA. *Research Plan for Microbial Pathogens and Disinfection By-Products in Drinking Water*. EPA/600/R-97/122, Washington, DC, **1997**; 173 pp.
- [4] Chu, H. A report to estimate the amount of DBP exposure and the possible health effects to pregnant women who attend indoor swimming pools in London, MSc Report, Imperial College of Science, Technology and Medicine, University of London, London, England; **2000**.
- [5] Nieuwenhuijsen, M.J.; Toledano, M.; Eaton, N.; Fawell, J.; Elliott, P. Chlorination disinfection by-products in water and their association with adverse reproductive outcomes: a review. *J. Occup. Environ. Med.* **2000**, *57*, 73–85.
- [6] Norwood, D.L.; Thompson, G.P.; Johnson, J.D.; Christman, R.F. In *Water Chlorination: Chemistry, Environmental Impact and Health Effects* (Jolly, R.L.; Bull, R.J.; Davis, W.P.; Katz, S.; Roberts, Jr. M.H.; Jacobs, V.A. Eds.), Lewis Publishers Inc., Chelsea, MI, **1985**, vol. 5, pp. 1115–1122.
- [7] Bull, R.J.; Sanchez, I.M.; Nelson, M.A.; Larson, J.K.; Lansing, A.J. Liver tumor induction in B6C3F1 mice by dichloroacetate and trichloroacetate. *Toxicology* **1990**, *63* (3), 341–359.
- [8] Reckhow, D.A.; Singer, P.C. Chlorination by-products in drinking waters: From formation potentials to finished water concentrations. *J. Am. Water Works Asso.* **1990**, *82* (4), 173–180.
- [9] US EPA, United States Environmental Protection Agency, EPA Proposed Rule, Fed. Reg. 59(145): 38668–38829, Washington, DC, 1994; 38668–38829.
- [10] DeAngelo, A.B.; Daniel, F.B.; Most, B.M.; Olson, G.R.; The carcinogenicity of dichloroacetic acid in the male Fischer 344 rat. *Toxicology* **1996**, *114* (3), 207–221.
- [11] Fair, P.S.; Barth, R.C.; Flesch, J. Measurement of Disinfection By-Products in Chlorinated Drinking Water. In: *Proceedings of AWWA Water Quality Technol. Conference* **1988**, *15*, 339–353.
- [12] Xie, Y.; Rajan, R.V.; Reckhow, D.A. Mass spectra of synthesized mixed bromochloroacetic acids. *Org. Mass Spectrom.* **1992**, *27* (7), 807–810.
- [13] Benanou, D.; Acobas, F.; Sztajn bok, P. Analysis of haloacetic acids in water by a novel technique: simultaneous extraction-derivatization. *Water Res.* **1998**, *32* (9), 2798–2806.
- [14] Scott, B.F.; Alaee, M. Determination of haloacetic acids from aqueous samples collected from the Canadian environment using an in situ derivatization technique. *Water Qual. Res. J. Can.* **1998**, *33* (2), 279–293.
- [15] Neitzel, P.L.; Walther, W.; Nestler, W. In-situ methylation of strongly polar organic acids in natural waters supported by ion-pairing agents for headspace GC-MSD analysis. *J. Anal. Chem.* **1998**, *361* (3), 318–323.
- [16] Kampioti, A.A.; Stephanou, F.G. Simultaneous determination of halogenated neutral and acidic disinfection by-products in drinking water by closed-loop stripping analysis extraction and capillary gas chromatography. *J. Chromatogr.* **1999**, *857* (1–2), 217–229.
- [17] Sarzanini, C.; Bruzzoniti, M.C.; Mentasti, E. Preconcentration and separation of haloacetic acids by ion chromatography. *J. Chromatogr.* **1999**, *850* (1–2), 197–211.
- [18] Lopez-Avila, V.; Liu, Y.; Charan, C. Determination of haloacetic acids in water by ion chromatography—Method development. *J. AOAC Int.* **1999**, *82* (3), 689–704.
- [19] Martinez, D.; Borrull, F.; Calull, M. Evaluation of different electrolyte systems and on-line preconcentrations for the analysis of haloacetic acids by capillary zone electrophoresis. *J. Chromatogr.* **1999**, *835* (1–2), 187–196.
- [20] Sarrión, M.N.; Santos, F.I.; Galceran, M.T. Solid-phase microextraction coupled with gas chromatography-ion trap mass spectrometry for the analysis of haloacetic acids in water. *J. Chromatogr. A.* **1999**, *859* (2), 159–171.
- [21] Sarrión, M.N.; Santos, F.I.; Galceran, M.T. In-situ derivatization/solid phase microextraction for the determination of haloacetic acids in water. *J. Anal. Chem.* **2000**, *72* (20), 4865–4873.
- [22] Neu, H.-J.; Ziemer, W.; Merz, W. Ein neuartiges Derivatisierungsverfahren zur Bestimmung von Spuren polarer organischer Substanzen in Wasser mittels statischer Dampfraum-Gaschromatographie. *Fresen. J. Anal. Chem.* **1991**, *340* (2), 65–70.
- [23] Pawliszyn, J. *Solid Phase Microextraction: Theory and Practice*, Wiley-VCH, New York, **1997**; 264 pp.
- [24] Zhang, L.; Capel, P.D.; Hozalski, R.M. Development of a solid phase extraction-capillary electrophoresis method for the analysis of haloacetic acids in drinking water. *J. Am. Water Works Asso.* **2007**, *99* (3), 83–94.
- [25] Cardador, M.J.; Serrano, A.; Gallego, M. J. Simultaneous liquid-liquid microextraction/methylation for the determination of haloacetic acids in drinking waters by headspace gas chromatography. *J. Chromatogr. A* **2008**, *1209* (1–2), 61–69.
- [26] Cardador, M.J.; Gallego, M. Optimisation and comparison of several microextraction/methylation methods for determining haloacetic acids in water using gas chromatography. *Anal. Bioanal. Chem.* **2010**, *396* (3), 1331–1343.
- [27] Stottmeister E.; Naglitsch F. *Human exposure to other disinfection by-products than trihalomethanes in swimming pools*. Annual report of the Federal Environmental Agency, Berlin, Germany, **1996**.
- [28] Sousa S. Implementação de uma instalação piloto para tratamento de águas contaminadas com pesticidas. MSc thesis, Faculdade de Engenharia da Universidade do Porto, Porto, Portugal, **2000**.
- [29] WHO, Guidelines for Safe Recreational-Water Environments, Swimming Pools, Spas and Similar Recreational-Water Environments; World Health Organization Press; **2006**; 2, 146 pp.