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# Determination of haloacetic acids in aqueous environments by solid-phase extraction followed by ion-pair liquid chromatography–electrospray ionization mass spectrometric detection

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**Abstract**

Haloacetic acids (HAAs) were determined in different water samples by a new, fast and simple analysis method based on enrichment of 50-ml water samples at pH 1.8 by solid-phase extraction (SPE) followed by liquid chromatography (LC) separation and electrospray ionization mass spectrometric detection in the negative ionization mode. Deprotonated $(M\text{-}H)^-$ haloacetates and decarboxylated $(M\text{-}COOH)^-$ ions were detected. Different polymeric SPE sorbents were tested, and LiChrolut EN was found to be the best material for the extraction. Complete LC separation of all compounds could only be achieved by ion-pair chromatography using triethylamine as volatile ion-pairing reagent. The detection limits were in the low μg/l range. High μg/l concentration levels for the chlorinated and brominated haloacetates were found in drinking water from a drinking water treatment plant in Barcelona, and the corresponding tap water. In swimming pool water samples from Catalonia mg/l levels and in surface river water from Portugal μg/l values were detected. These results confirm other recent reports on the ubiquitous occurrence of HAAs in aqueous environments. 

*Keywords:* Solid-phase extraction; Water analysis; Environmental analysis; Haloacetic acids; Halogenated compounds; Acetic acids

## 1. Introduction

Haloacetic acids (HAAs) are widespread environmental pollutants. Because of their environmental impact, there is a growing interest in their determination in aqueous compartments. HAAs are chemical byproducts of water chlorination and chloramination, the process used for disinfecting drinking water to control infectious microbial contaminants. Chloroacetic acids are directly formed from dissolved humic matter by oxidation of natural waters with chlorine; brominated acetic acids are produced when the water being disinfected contains bromide ions. There are a total of nine HAA species containing chlorine and bromine: (mono)chloro-, dichloro-, and trichloroacetic acid (MCAA, DCAA, TCAA); (mono)bromo-, dibromo-, and tribromoacetic acid (MBAA, DBAA, TBAA); and the mixed species bromochloro-, bromodichloro-, and dibromochloroacetic acid (BCAA, BDCAA, DBCAA). HAAs are highly water-soluble and are toxic to humans, plants and algae. Chloroacetic acids are plant growth inhibitors, e.g. trichloroacetic acid has been used as a herbicide [1,2]. They are of great concern to public health because of their suspected carcinogenicity and mutagenicity as well as developmental, reproductive, and hepatic toxicity [3–7]. The carcinogenicity of DCAA and TCAA has already been proven [8,9],

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and the US Environmental Protection Agency (EPA) has classified them as probable human carcinogens [10].

HAAs are regularly found in drinking water from drinking water treatment plants in the μg/l range [5,11–14], but also in environmental waters such as surface water [1,2,15], rainwater precipitation [1,2,6], seawater [6,16,17] and wastewaters [1]. They also have been recently detected in swimming pools [1,18,19] and tap water [1,2,19] used as drinking water.

The haloacetates represent, after the trihalomethanes (THMs), the second most prevalent class of known disinfection byproducts. Due to their environmental and toxicological impact, the EPA has promulgated a regulation to control disinfection byproducts that establishes a maximum contamination level of 60 μg/l for the sum of five HAAs (MCAA, MBAA, DCAA, DBAA, TCAA and BCAA) [20]. Richardson et al. give a very comprehensive listing of possible disinfection byproducts formed in water by chlorination, chloramination, and ozone treatment, or a combination of these methods [21,22].

HAAs are generally difficult to determine because of their strong acidic and hydrophilic character. Their p$K_a$ values range from 0.63 to 2.9 [23,24], trihalo-substituted acids having lower p$K_a$ values due to the electron-withdrawing effect of the halogens (e.g. MCAA p$K_a$ 2.86, MBAA 2.7, DCAA 1.29, TCAA 0.65). They are usually analyzed after chemical derivatization by gas chromatography with electron-capture (GC–ECD) [3,5,11–13,25], or mass spectrometric (MS) detection [1,7,11,13,22,25–27]. Extraction from water is traditionally performed after acidification by liquid–liquid extraction (LLE) of the acids using organic solvents. However, LLE and derivatization are tedious and labor-intensive. Therefore, new strategies to avoid LLE and derivatization in HAA determinations are desirable to increase simplicity and economize analysis time. It has been suggested that the field has relied too heavily on GC–MS techniques, and that other analytical methods are needed to determine disinfection byproducts [28,29].

Due to their polar character, HAAs are principally well suited for analysis by high-performance liquid chromatography (HPLC) or capillary electrophoresis (CE). Indirect UV detection with a mobile phase or an electrolyte containing an ultraviolet-absorbing ion has been performed with these separation techniques [18,23,30,31]. However, indirect UV detection lacks sufficient specificity in complicated matrices such as natural water samples. Moreover, detection of HAAs after HPLC separation was recently proposed with electrochemical methods [4] or ion chromatography followed by conductivity [32] and UV [33] detection.

Considering the difficulties associated with detection, HAAs are well suited for analysis by CE or LC coupled in series to MS with negative electrospray ionization (ESI). One CE–MS method [34] and two LC–ESI-MS procedures [16,17,35] are described in the literature for the analysis of these compounds. Takino et al. [35] recently presented the total separation of all nine chlorinated and brominated HAAs using ion-pair LC–MS, but only analyzed spiked water samples.

Concerning the extraction of HAAs from water, Martínez et al. [31] recently compared four different SPE materials. Ion-exchange extraction with an anion-exchange resin (e.g. EPA method 552.1) [5,6,32] and quaternary amine anion-exchange SPE discs [26] have been used for the extraction of HAAs. Recently, a solid-phase microextraction (SPME) procedure was proposed for the extraction of HAAs [19].

The objectives of this present work were to establish a simpler and faster method for the determination of HAAs in real environmental water samples based on SPE enrichment followed by LC–ESI-MS determination. As far as we are aware, we report for the first time the determination of HAAs in real environmental water samples by LC–ESI-MS analysis.

## 2. Experimental section

### *2.1. Chemicals and reagents*

The ion-pairing reagent triethylamine (TEA) was obtained from Sigma–Aldrich (Deisenhofen, Germany). Individual HAAs were obtained from Merck (MCAA, MBAA, TCAA; Darmstadt, Germany), Fluka (DBAA; Buchs, Switzerland) and Riedel-de

Haën (DCAA, Seelze, Germany). Supelco (Bellefonte, PA, USA) sells a mixture of all nine HAAs (EPA 552.2 acids calibration mix, 1 ml dissolved in methyl *tert*.-butyl ether, No. 47787). This mixture contains the individual compounds in the following concentrations: DBAA, TCAA 200 mg/l; MBAA, BCAA, BDCAA 400 mg/l; MCAA, DCAA 600 mg/l; DBCAA 1000 mg/l; and TBAA 2000 mg/l.

The names of the haloacetic ions, abbreviations and molecular masses of the measured ions ($m/z$) — with respect to the natural halogen distributions — are given in Table 1.

HAA single standard stock solutions of 1000 mg/l were prepared for MCAA, MBAA, DCAA, DBAA, and TCAA by dissolving 50 mg of each compound in 50 ml ultra-pure water (Merck). The other four HAAs were only available within the Supelco mix. The working standard solutions were prepared by further diluting the stock standard solutions with water. For calibration, the Supelco mix was diluted 1/10, 1/20, 1/50, 1/75 and 1/100 with water. The standard mixtures were further diluted for LC analysis, calibrations and preparation of fortified SPE samples. All solutions were stored in a fridge at 4°C.

### 2.2. Samples and sample pretreatment

Different real water samples were analysed. The water used for the SPE recovery experiments and the blanks was Milli-Q water or ground water from the CSIC Institute in Barcelona, which is distinct from the investigated tap water. Drinking water from a drinking water treatment plant for Barcelona (Sant Joan Despí) was investigated and was provided by Aigües de Barcelona (AGBAR). Influent river water of the river Llobregat, after the sandfilter process, and effluent water after postchlorination, were analyzed. The samples were taken in March and May 2000; they were treated for conservation with sodium-sulfite ($Na_2SO_3$), and extracted by SPE after 1–2 days storage in a fridge at 4°C. The influent river water was filtered through glass microfiber filters (Whatman, 0.45-μm pore size). Filtering was not necessary for the other water samples. The swimming pool water samples came from two villages on the Costa Brava north of Barcelona (Sant Feliu de Guixols and Llafranc) and from one town south of Barcelona (Castelldefels). They were collected in September 2000. Moreover, tap water from the apartment of the author close to Plaza España in Barcelona was analyzed. Single samples were taken. In addition, some surface water samples from different places in Portugal were analyzed. All water samples were pH adjusted with sulfuric acid to pH 1.8 and 50 ml was extracted with LiChrolut EN SPE cartridges by the optimized procedure. The extracts were not stored for more than 1 week (in the freezer) before LC–MS determination.

### 2.3. Solid-phase extraction

The SPE procedure for the concentration of water

Table 1
Names, abbreviations and measured ions ($m/z$) of haloacetic acids

| HAAs | $m/z$ | | |
|---|---|---|---|
| | Acetate $[M\text{-}H]^-$ | $[M\text{-}COOH]^-$ | $[2M\text{-}H]^-$ |
| (Mono)chloroacetic acid (MCAA) | 93 ($^{35}Cl$) | | 187 |
| (Mono)bromoacetic acid (MBAA) | 137 ($^{79}Br$) | | |
| | 139 ($^{81}Br$) | | |
| Dichloroacetic acid (DCAA) | 127 ($^{35}Cl_2$) | | 257 |
| | 129 ($^{35}Cl^{37}Cl$) | | |
| Bromochloroacetic acid (BCAA) | 173 ($^{35}Cl^{81}Br$ or $^{37}Cl^{79}Br$) | | |
| Dibromoacetic acid (DBAA) | 217 ($^{79}Br^{81}Br$) | | |
| Trichloroacetic acid (TCAA) | 163 ($^{35}Cl_2^{37}Cl$) | 117 ($^{35}Cl_2^{37}Cl$) | |
| Bromodichloroacetic acid (BDCAA) | 207 ($^{35}Cl_2^{81}Br_2$ or $^{35}Cl^{37}Cl\ ^{79}Br$) | 163 ($^{35}Cl_2^{81}Br_2$ or $^{35}Cl^{37}Cl\ ^{79}Br$) | |
| Dibromochloroacetic acid (DBCAA) | 251 ($^{37}Cl^{79}Br_2$ or $^{35}Cl^{79}Br\ ^{81}Br$) | 207 ($^{37}Cl^{79}Br_2$ or $^{35}Cl^{79}Br\ ^{81}Br$) | |
| Tribromoacetic acid (TBAA) | 295 ($^{79}Br_2^{81}Br$) | 251 ($^{79}Br_2^{81}Br$) | |
| | | 253 ($^{79}Br^{81}Br_2$) | |

samples was performed off-line but automatically with an ASPEC XL apparatus (Gilson, Villiers-le-Bel, France). The solid-phase adsorption material LiChrolut EN was obtained from Merck, Isolute ENV+ from International Sorbent Technology (IST, Cambridge, UK), HR-P from Macherey–Nagel (Düren, Germany), and Oasis HLB (a macroporous poly(divinylbenzene–co-*N*-vinylpyrrolidone) copolymer), from Waters (Milford, MA, USA). Disposable 3- or 6-ml SPE cartridges with 200 mg sorbent were used in the case of LiChrolut EN, HR-P, and Isolute ENV+; the Oasis HLB cartridges only contained 60 mg sorbent.

The sorbents were activated and conditioned first with 5 ml methanol, then with 3 ml water (acidified to pH 2.5 with sulfuric acid) at a flow-rate of 1 ml/min. The sorbents were not allowed to dry, and subsequently the water samples (usually 50 ml) were passed through the cartridges at a flow-rate of 5 ml/min. For recovery studies, ground or Milli-Q water was spiked with known quantities of an HAA mixture and were pH-adjusted with sulfuric acid (96%) to pH 1.8. The SPE recoveries were determined at two different spike levels. The concentrations for the individual compounds are reported in Table 2; 100 or 10 μl of the Supelco mix were diluted in 200 ml water for four extractions of a 50-ml volume.

After the extraction, the cartridges were not allowed to dry, were washed with 1 ml water (pH 2.5) and immediately eluted with 4 ml of a solvent mix of 0.5 ml water + 3.5 ml methanol–acetone (1:1, v/v). The compounds were eluted into 10 ml ASPEC glass vials. The solvent mixture was evaporated under a gentle stream of nitrogen until only the water was left. If necessary (if some water had been evaporated), the vials were filled up with water. The overall SPE enrichment factor was 166.6 as the samples were evaporated (or filled up) until 300 μl water was left. Absolute recoveries were determined using external calibrations.

### *2.4. Liquid chromatography–mass spectrometry*

LC separations were carried out with a Hewlett-Packard (HP) 1090A LC system coupled in series

Table 2
Recoveries of HAAs from 50 ml spiked ground water at pH 1.8 ($n=4$): comparison of different SPE sorbents

| HAA | Conc. (μg/l) | Recovery (%) (RSD, %) | | | |
|---|---|---|---|---|---|
| | | LiChrolut EN | HR-P | Isolute ENV+ | Oasis HLB |
| MCAA | 300 | 26 (3) | 27 (2) | 21 (2) | 18 (3) |
| MBAA | 200 | 42 (6) | 57 (3) | 28 (15) | 29 (9) |
| DCAA | 300 | 55 (5) | 54 (3) | 50 (4) | 42 (7) |
| BCAA | 200 | 60 (8) | 53 (4) | 44 (3) | 38 (5) |
| DBAA | 100 | 56 (7) | 45 (3) | 37 (1) | 30 (4) |
| TCAA | 100 | 75 (5) | 74 (3) | 65 (3) | 51 (4) |
| BDCAA | 200 | 45 (2) | 39 (3) | 33 (6) | 28 (3) |
| DBCAA | 500 | 37 (2) | 22 (2) | 37 (1) | 33 (6) |
| TBAA | 1000 | 33 (2) | 25 (1) | 31 (3) | 27 (6) |
| MCAA | 30 | 35 (8) | | | |
| MBAA | 20 | 51 (9) | | | |
| DCAA | 30 | 45 (12) | | | |
| BCAA | 20 | 53 (6) | | | |
| DBAA | 10 | 48 (9) | | | |
| TCAA | 10 | 69 (8) | | | |
| BDCAA | 20 | 56 (7) | | | |
| DBCAA | 50 | 45 (5) | | | |
| TBAA | 100 | 39 (8) | | | |

The relative standard deviations (RSD) are given in brackets.

with the HP 1100 mass-selective single quadrupole detector equipped with an orthogonal interface and a standard atmospheric pressure ionization (API) source using ESI in the negative mode.

Ion-pair reversed-phase LC was used for the separation of the polar HAAs with a 250×4-mm LiChrospher RP-$C_{18}$ column (LiChroCART 250-4, LiChrospher 100, 5-μm particle diameter, Merck) using TEA, a volatile tertiary alkylamine, as ion-pairing reagent. Eluates were acetonitrile and water containing 5 m*M* TEA and 5 m*M* acetic acid. The water was pH adjusted to 7.0 with acetic acid. A linear gradient from 85 to 50% water in 12 min at a flow-rate of 0.5 ml/min was used for the separations. The injection volume was usually between 20 and 50 μl, and was performed automatically by the HP (Agilent) autosampler.

After the LC separation, detection was performed by negative electrospray ionization. The operating conditions of the MS system were optimized in order to achieve the highest sensitivity (Table 3). The optimum parameters were: drying gas flow 11 l/min; drying gas temperature 350°C; nebulizer pressure 55 p.s.i. (1 p.s.i.=6894.76 Pa); vaporizer temperature 400°C; capillary potential 5000 V. The fragmentation voltage was set to quite a low value of only 40 V for inhibiting fragmentation of the HAAs. External quantification was applied to the measurements of the real samples. The concentrations were corrected with the recoveries of the recovery experiments.

Table 3
Optimized LC–MS conditions used for HAA determinations

| Parameter | Value |
|---|---|
| LC column | 250×4 mm LiChrospher RP-$C_{18}$ |
| Ion-pairing reagent | Triethylamine (TEA) |
| Eluates | Acetonitrile and water containing 5 m*M* TEA and 5 m*M* acetic acid |
| Gradient | 85 to 50% water in 12 min |
| Flow rate | 0.5 ml/min |
| Drying gas flow | 11 l/min |
| Drying gas temperature | 350°C |
| Nebulizer pressure | 55 p.s.i. |
| Vaporizer temperature | 400°C |
| Capillary potential | 5000 V |
| Fragmentation potential | 40 V |

## 3. Results and discussion

### 3.1. Solid-phase extraction

The extraction of the HAA compounds from water by SPE is difficult because of their low molecular masses and highly water-soluble character. Therefore we studied the SPE for HAAs precisely using various polymeric adsorbent materials. Of the SPE materials investigated (polystyrene–divinylbenzene sorbents LiChrolut EN, HR-P, Isolute ENV+, and Oasis HLB), the highest recoveries were obtained with LiChrolut EN (Table 2). HR-P gave very similar extraction results, while the recoveries with Isolute ENV+ and Oasis HLB were slightly lower. However, it should be considered that the Oasis HLB cartridges only contained 60 mg sorbent material and the other sorbents 200 mg. For LiChrolut EN the recoveries were determined at two different concentration levels, expanding the range between 5 and 500 μg/l (Table 2).

Also Martínez et al. [31], who recently compared four different SPE extraction materials for the extraction of HAAs (quarternary ammonium anion-exchanger, LiChrolut EN, graphitized carbon black, and Oasis HLB), reported that LiChrolut EN was, with recoveries >64%, the best sorbent for the extraction of HAAs. They acidified the water before the extraction to pH 0.5 for protonation of the acetates. Sarzanini et al. [33] even reported higher recovery results for five different HAAs using LiChrolut EN SPE at pH 1.0. These high recovery values are a little bit astonishing, considering that normally the retention of aromatic compounds — in comparison to aliphatic substances — on polymeric sorbents is due to the π–π interactions between the polymeric sorbent and the aromatic analyte preferred [36–40].

In addition to the different cartridges, the pH effect of the water was studied. HAAs are strong acidic compounds with p$K_a$ values ranging between 0.63 and 2.9. Therefore, the water samples should be acidified before SPE for protonation of the acetate groups. However, our experience [39] has shown that LiChrolut EN should not be used at pH values below 1 to avoid degradation of the sorbent material, low recoveries and reduced precision and accuracy. The

optimal pH value found in this present study for the SPE of the HAAs with LiChrolut EN was between 1.5 and 2.0. Moreover, acidification of water samples to pH 0.5 is tedious.

### 3.2. Liquid chromatography–mass spectrometry

A comprehensive investigation of the LC separation of the nine HAAs was carried out testing different conditions such as LC eluates and gradients (using acetonitrile and water), flow-rates, acetic acid content, and the addition of ion-pairing reagents. Moreover, the instrumental MS parameters were optimized. Noteworthy is the low fragmentation potential of only 40 V used which gave the highest response. Deprotonated $(M\text{-}H)^-$, decarboxylated $(M\text{-}COOH)^-$, and dimer ions (Table 1) were detected. The abundance of the deprotonated ions for the trihalogenated HAA species was very low; the decarboxylated ions were the base peaks for these compounds [35].

Takino et al. [35] recently reported the separation of all nine chlorinated and brominated HAAs by ion-pair LC–MS. However, they only analyzed spiked water samples. They tested different ion-pairing reagents: TEA, di-, and tributylamine. The amines with longer alkylchains gave stronger retention of the HAAs in the column.

Due to their polar character the compounds in our study showed quite low retention in the RP-$C_{18}$ column. Due to limitations in the choice of solvents for LC–ESI-MS, the resolution of all nine HAAs was difficult in a reasonable run time. Acetic acid [16,17] did not improve the separation, and moreover caused severe noise problems; we could not reproduce the separation results of Takino et al. [35]. Our investigations showed that tributylamine as ion-pairing reagent was not totally volatile. Using this amine, the sensitivity of the MS decreased from injection to injection, indicating MS contamination or ionization suppression.

Fig. 1 shows the selected ion monitoring (SIM) LC–MS chromatograms under the optimized conditions. Completely satisfactory resolution of the compounds only could be achieved by ion-pair chromatograhy (IPC) using TEA as ion-pairing reagent. Without TEA no complete separation of the HAAs was possible. TEA increases the retention

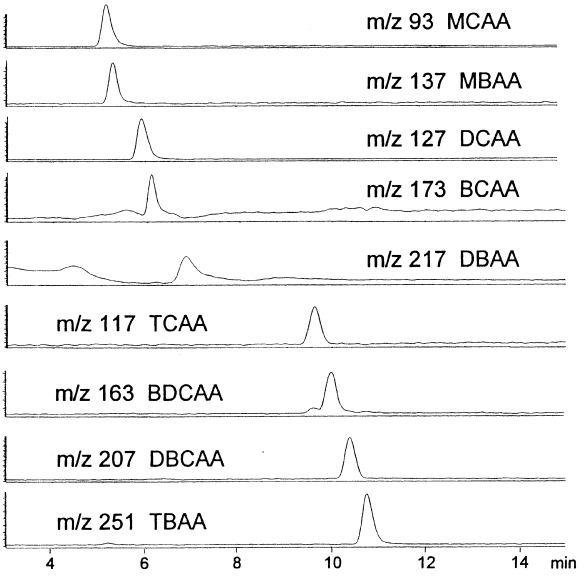


Fig. 1. Ion-pair LC–MS chromatogram of HAAs. Mobile phase: acetonitrile and water (pH 7.0) containing 5 m*M* TEA and 5 m*M* acetic acid. Linear gradient from 85 to 50% water in 12 min. Concentrations: DBAA, TCAA 4 mg/l; MBAA, BCAA, BDCAA 8 mg/l; MCAA, DCAA 12 mg/l; DBCAA 20 mg/l; TBAA 40 mg/l.

times of the trihalogenated species TCAA, BDCAA, DBCAA, and TBAA considerably and only slightly reduces MS detection sensibility.

### 3.3. LC–MS calibration and LODs

Calibration for the ion-pair LC–MS method was carried out in a concentration range between 0.03 and 200 mg/l, depending on the individual compounds. Table 4 shows the quality parameters for the HAAs. Calibration graphs were linear with good correlation coefficients (number of points $n=6$–7). LC–MS concentration sensitivity for the injection of standards was in the range between 0.01 and 0.5 mg/l ($S/N=3$).

The limits of detection (LODs) or quantification (LOQs) of environmental analytical methods have to be determined by applying a blank sample to the whole analytical extraction and detection procedure. Milli-Q or ground water from our Institute was used as blank water. Table 4 reports these blank value dependent LODs and LOQs of the combined SPE–LC–MS procedure for the extraction of 50 ml water

Table 4
Quality parameters for the SPE–LC–MS analysis method of the HAAs

| HAA | $m/z$ | Linear range (mg/l) | Corr. coeff. ($r^2$) | Sensitivity (mg/l) | LOD (μg/l) | LOQ (μg/l) |
|---|---|---|---|---|---|---|
| MCAA | 93 | 0.3–60 | 0.996 | ~ 0.1 | 1.6 | 2.4 |
| MBAA | 137 | 0.2–40 | 0.994 | ~ 0.1 | 0.8 | 1.5 |
| DCAA | 127 | 0.03–60 | 0.994 | ~ 0.03 | 0.8 | 1.1 |
| BCAA | 173 | 0.02–20 | 0.974 | ~ 0.01 | 0.1 | 0.1 |
| DBAA | 217 | 0.1–20 | 0.985 | ~ 0.05 | 1.3 | 1.7 |
| TCAA | 117 | 0.1–20 | 0.996 | ~ 0.05 | 0.9 | 1.3 |
| BDCAA | 163 | 0.2–40 | 0.993 | ~ 0.1 | 0.8 | 1.2 |
| DBCAA | 207 | 0.5–100 | 0.999 | ~ 0.2 | 0.4 | 0.5 |
| TBAA | 251 | 1–200 | 0.997 | ~ 0.5 | 0.2 | 0.4 |

$m/z$: most abundant ions used for quantification. The number of points $n$ of the calibration curve was between 6 and 7. The sensitivity is the concentration of an injected standard at a signal-to-noise ($S/N$) ratio of ~3. LOD, limit of detection = blank value + 3·RSD of the blank value; LOQ = blank value + 6·RSD of the blank value (at the retention time of the analyte peak).

with 200 mg LiChrolut EN. Some positive blanks were observed which are the reason for the quite high LODs.

### *3.4. Analysis of real water samples*

HAAs are widespread environmental pollutants. Recently, their occurrence has been reported in Europe and the USA in surface waters [1,2], rainwater [1,2], seawater [16,17], swimming pools [1,18,19], and drinking water [1,2,5,14,19].

In this study, surface water (from Portugal), swimming pool water (from Catalonia, NE Spain), drinking water from a drinking water treatment plant and tap (drinking) water from Barcelona were analyzed for the target HAA compounds. The Llobregat river — heavily polluted, bearing a lot of industries including textile, galvanic, tannery, mines etc. — supplies drinking water to Barcelona and its surrounding area. The drinking water treatment plant of this river (Sant Joan Despí) carries out a complicated and cost-effective treatment consisting of prechlorination, flocculation (settling), sand filtration, ozonization, granular activated carbon filtration and postchlorination. The raw river water entering the water treatment plant contains quite high levels of total organic carbon (TOC) and bromide ions; the average levels are in the range of 6 and 0.7 mg/l, respectively [14].

Entrance river water, samples after the sand filtration process, and effluent drinking water after the postchlorination of this drinking water treatment plant, were examined by the developed SPE–LC–MS analysis method. Table 5 reports the calculated concentrations for all HAAs found in the drinking water treatment plant by SPE–LC–MS. BCAA and DBAA were the compounds found most frequently and in the highest concentrations in the water samples (up to 78 μg/l for DBAA). The HAAs were also detected in the influent river water, but their concentrations in the effluents of the plant were higher, clearly indicating that they are disinfection byproducts formed during the water chlorination treatment process. Mostly, higher concentrations were found in the effluents than after the sandfilter. The dihalogenated and trihalogenated species constituted the greatest molar fraction of the total HAA concentration; the monohalogenated species MCAA and MBAA were only detected in low concentration ranges close to the detection limits. Total HAA concentrations (Σ HAAs) were between 100 and 200 μg/l in the effluent water of the drinking water treatment plant as average level, clearly exceeding the maximum contamination level of 60 μg/l for the sum of five HAAs established by the EPA.

The swimming pool and tap water samples were determined in duplicate. The mean concentration values of both measurements are given in Table 6. The precision for repeated analysis of the real samples was >90%, as the calculated concentrations of the two analyses were very similar. In the tap water from Plaza España (Barcelona), MCAA, DCAA, TCAA, BDCAA and DBCAA were identified. The total HAA (Σ HAAs) concentration found

Table 5
Concentrations of HAAs (μg/l) found in the drinking water treatment plant of Barcelona using SPE–ion-pair LC–MS

| HAA | *m/z* | LOQ | Influent | Sandfilter | | Effluent | |
|---|---|---|---|---|---|---|---|
| | | | May 2000 | March 2000 | May 2000 | March 2000 | May 2000 |
| MCAA | 93 | 2.4 | (1.1[a]) | ND | (1.2[a]) | ND | (2.4[a]) |
| MBAA | 137 | 1.5 | ND | ND | (2[a]) | 8 | 4 |
| DCAA | 127 | 1.1 | (3[a]) | 11 | (3[a]) | 11 | 10 |
| BCAA | 173 | 0.1 | 7 | 15 | 5 | 39 | 21 |
| DBAA | 217 | 1.7 | 25 | 44 | 23 | 78 | 33 |
| TCAA | 117 | 1.3 | 16 | 9 | 7 | 12 | 11 |
| BDCAA | 163 | 1.2 | (3[a]) | 27 | (1[a]) | 27 | 9 |
| DBCAA | 207 | 0.5 | 5 | 17 | (1[a]) | 18 | 11 |
| TBAA | 251 | 0.4 | 5 | 9 | ND | 10 | 5 |
| Σ HAAs | | | 58 | 132 | 35 | 203 | 104 |

LOQ, limit of quantification.
[a] Close to the LOQ.

in this tap water was 70 μg/l which is higher than the threshold value proposed by the EPA. Our results are in good correlation to Sarrión et al. [19], who also analyzed Barcelona's tap water; they found a Σ HAA concentration of 30 μg/l. In the swimming pool water samples, MCAA, TCAA, BDCAA, DBCAA and TBAA were detected; the highest concentrations were quantified for TCAA, >1 mg/l for all three investigated swimming pools. The Σ HAA values for the swimming pools were between 1.3 and 3.2 mg/l. These concentrations are higher than reports from the literature [1,18,19].

Fig. 2 shows the corresponding LC–MS chromatograms of the investigated tap (drinking) water for MCAA and DCAA, and Fig. 3 the chromatograms of the different swimming pool waters for the compounds MCAA and TCAA (in SIM detection mode and after SPE enrichment). Castelldefels, Llafranc and Sant Feliu (de Guixols) are the names of Catalonian villages. For peak comparison, a standard and an SPE blank sample are also given. The retention times of the peaks in the real samples were in good agreement with the standards. Some weak blank interferences were detected which are the reason for the (blank value-dependent) elevated LODs.

Table 6
Concentrations of HAAs (μg/l) found in different real water samples using SPE–ion-pair LC–MS

| HAA | *m/z* | Swimming pool water | | | Tap water | River water |
|---|---|---|---|---|---|---|
| | | Castelldefels | Llafranc | Sant Feliu | Plaza España | Portugal |
| MCAA | 93 | 1000 | 15 | 120 | 4 | 36[a] |
| MBAA | 137 | ND | ND | ND | ND | ND |
| DCAA | 127 | ND | ND | ND | 35 | 1–3 |
| BCAA | 173 | ND | ND | ND | ND | 29[a] |
| DBAA | 217 | ND | ND | ND | ND | ND |
| TCAA | 117 | 1700 | 1500 | 1000 | 14 | 4.2–308 |
| BDCAA | 163 | 480 | 912 | 208 | 9 | 7–48 |
| DBCAA | 207 | ND | 62 | ND | 8 | ND |
| TBAA | 251 | ND | ND | 15 | ND | 26–42 |
| Σ HAAs | | 3200 | 2500 | 1300 | 70 | – |

The swimming pool water and tap water samples were measured in duplicate.
[a] Found in one sample.

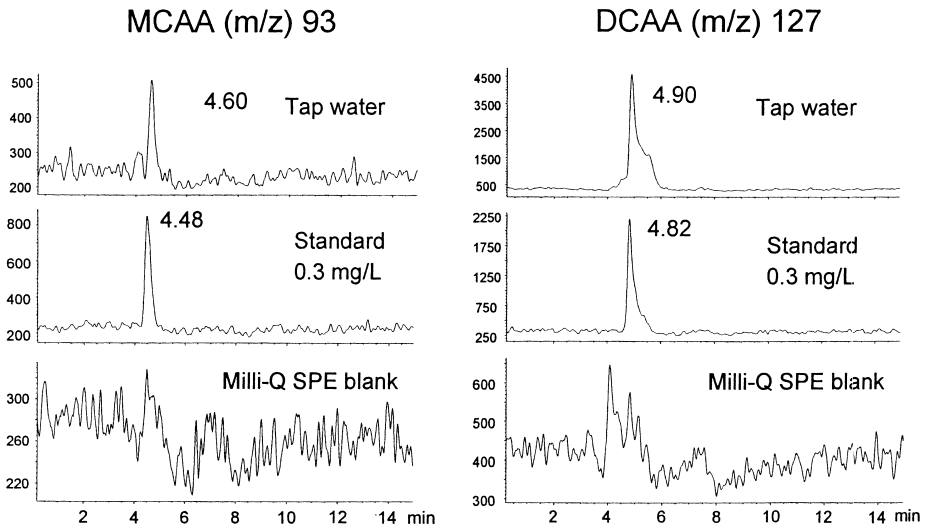


Fig. 2. LC–MS chromatograms of tap water from Barcelona after SPE enrichment with LiChrolut EN: comparison with standards and blanks, SIM-MS detection of MCAA ($m/z$ 93) and DCAA ($m/z$ 127); conditions as in Fig. 1.

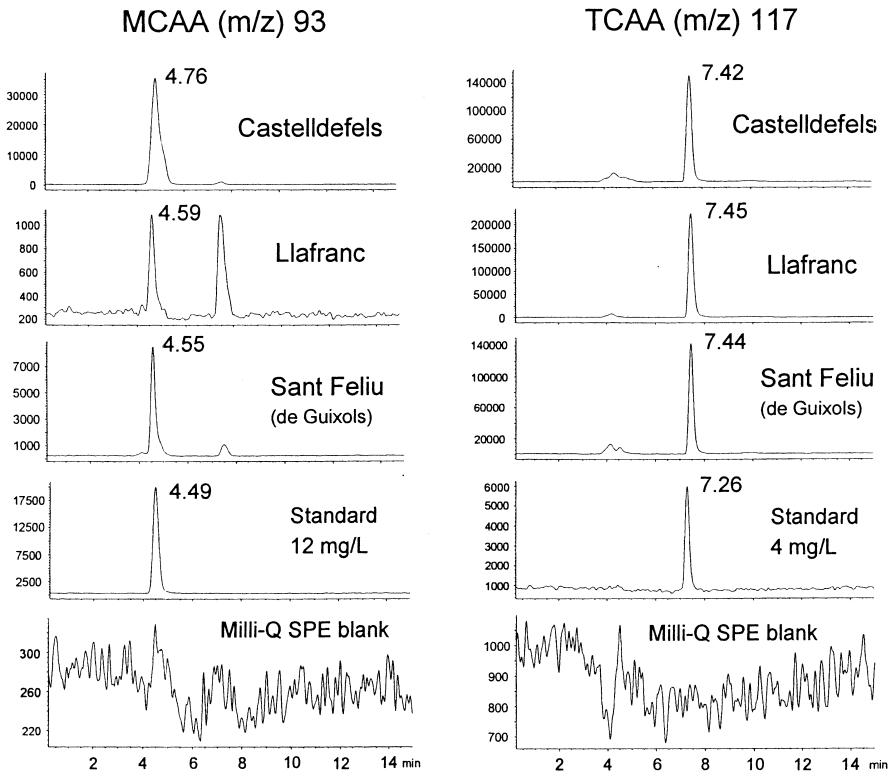


Fig. 3. LC–MS chromatograms of swimming pool water from Catalonia (NE Spain) after SPE enrichment with LiChrolut EN: comparison with standards and blanks, SIM-MS detection of MCAA ($m/z$ 93) and TCAA ($m/z$ 117); conditions as in Fig. 1.

The concentrations found for the HAAs with the SPE–ion-pair LC–MS method are comparable with the standard derivatization–GC–MS results of Cancho et al. [14] and Sarrión et al. [19], who also analyzed drinking water from Barcelona.

## 4. Conclusions

New reliable techniques are needed for disinfection byproducts analysis, as the field has relied too much on GC–MS. Therefore, a simple, rapid and selective SPE–LC–MS analysis method for the determination of all nine chlorinated and brominated HAAs in water has been developed. Adsorption of the polar low molecular mass haloacetates by SPE is difficult. Nevertheless, satisfactory recovery rates were achieved for the extraction of 50-ml water samples with LiChrolut EN at pH 1.5–2. Polystyrene–divinylbenzene sorbent materials should not be used at pH values $<1$. However, in the future maybe ion-pair, ion-exchange or graphitized carbon black SPE could help in achieving better extraction efficiencies. Ion-pair chromatography is a well suited method for the separation of polar compounds, such as the HAAs. ESI–MS in the negative ion mode is the method of choice for detection. High concentration values exceeding the EPA threshold value of 60 μg/l were found in water from a drinking water treatment plant and the corresponding tap water, which is used as drinking water. These results show the environmental significance of this supposed carcinogenic disinfection byproducts. Moreover, the compounds were detected in river and swimming pool water showing their ubiquitous occurrence in the aquatic environment. More drinking water controls should be performed in the future. The developed SPE–ion-pair LC–MS method proved to be useful for the detection of HAAs in different water samples, and is a fast and simple alternative to conventional derivatization GC techniques. Moreover, the stability and persistence of the individual HAAs in different matrices should be studied in detail in the future.

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