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Determination of aldehydes in drinking water using pentafluorobenzylhydroxylamine derivatization and solid-phase microextraction

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Abstract

A headspace solid-phase microextraction (HS-SPME) procedure followed by gas chromatography and electron capture detection (GC–ECD) has been developed for the determination of aldehydes in drinking water samples at μg/l concentrations. A previous derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was performed due to the high polarity and instability of these ozonation by-products. Several SPME coatings were tested and the divinylbenzene–polydimethylsiloxane (DVB–PDMS) coating in being the most suitable for the determination of these analytes. Experimental SPME parameters such as selection of coating, sample volume, addition of salt, extraction time and temperature of desorption were studied. Analytical parameters such as precision, linearity and detection limits were also determined. HS-SPME was compared to liquid–liquid microextraction (proposed in US Environmental Protection Agency Method 556) by analyzing spiked water samples; a good agreement between results obtained with both techniques was observed. Finally, aldehydes formed at the Barcelona water treatment plant (N.E. Spain) were determined at levels of 0.1–0.5 μg/l. As a conclusion, HS-SPME is a powerful tool for determining ozonation by-products in treated water.

Keywords: Water analysis; Derivatization, GC; Solid-phase microextraction; Headspace analysis; Aldehydes

1. Introduction

Chlorine and ozone are the two disinfectants widely used in drinking water disinfection. Despite the benefits of these two disinfectants, disinfection by-products (DBPs) are formed due to the interaction of aqueous free chlorine and/or ozone with natural organic matter present in water. Trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, cyanogen halides, chloral hydrate and chloropicrin have been reported as the main chlorination DBP groups [1–4]. Aldehydes, ketones, carboxylic acids, aldoacids, organic peroxides and epoxides are the main ozone DBP groups, resulted from the reaction between ozone with aromatic compounds, amino acids and polypeptides present in water, which are considered as their precursors [5–9]. Aldehydes are one of the main ozonation DBPs due to their health effects, although no legislation has been established for their control. Formaldehyde is a mutagenic and carcinogen compound [10]; acetaldehyde induces

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tumors [11,12]; propanal, butanal, pentanal, hexanal, nonanal, glyoxal, methyl glyoxal are mutagens in laboratory animals. On the other hand, aldehydes exhibit high biodegradability capable of increasing the microorganism level after the ozonation process [13].

Although the aldehyde formation is associated with the ozonation process, it can be related in minor grade with the chlorination of raw water. Different aldehydes were identified as a result of the chlorination of some aminoacids such as isobutyraldehyde (resulting of valine chlorination), isovaleraldehyde (leucine), 2-methylbutyraldehyde (isoleucine) and phenylacetaldehyde (phenylalanine) [14]. Complaints from consumers related to the presence of these aldehydes were reported in water treatment plants in France [15] and in Canada when their concentrations were 10–50 times higher than their respective odor threshold concentrations (0.9 μg/l for isobutyraldehyde, 0.15–0.2 μg/l for isovaleraldehyde, 12.5 μg/l for 2-methylbutyraldehyde and 4.0 μg/l for phenylacetaldehyde) [16–19].

The high polarity and reactivity of carbonyl compounds in water matrices impose the need for their derivatization prior to their detection by chromatographic techniques. A suitable method involves the direct aqueous derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA), which reacts with low molecular mass carbonyl compounds and aldehydes to form the corresponding oximes. Two geometrical isomers (*E* and *Z*) are formed for simple aldehydes except for formaldehyde or symmetrical carbonyls. Another method commonly applied utilizes 2,4-dinitrophenylhydrazine (DPNH) as a reagent to form hydrazone derivatives (*E* and *Z* isomers). PFBHA derivatization is followed by GC–ECD or GC–MS; aldehyde derivatives present halogen atoms which justifies ECD detection. Meanwhile, DPNH derivatization is followed by GC–MS and HPLC–MS analysis [20–30]. There are also other derivatization agents such as thiazolidine, morpholine, methylhydrazine or *N*-benzylethanolamine which have been less employed [31–34]. Although these methods provide good reproducibility, they involve an extensive work-up, consume materials, and solvents for the derivatization and isolation steps using liquid–liquid (LLE) or solid-phase extraction techniques (SPE).

In recent years, a solid-phase microextraction (SPME) technique developed by Pawliszyn and coworkers has become popular for the analysis of organic compounds from water samples because it combines sampling and preconcentration in one step [35–38]. This technique uses a polymer-coated silica fiber to adsorb the analytes directly from the liquid or from the headspace above the liquid; after extraction, the fiber is inserted into the GC injector to desorb the analytes into the GC column. It requires no solvents, or complicated apparatus and allows to quantify over a wide range of analyte concentrations. Determination of analytes concentrated on SPME fibers is performed using GC followed by ECD, NPD, MS detection and/or HPLC–MS, which have been applied to the determination of organic compounds in water such as VOCs, BTEXs, phenols, surfactants, odor compounds, PAHs, pesticides and disinfection by-products [39–54].

SPME has been also applied for the analysis of carbonyl compounds. Bao and co-workers determined 23 carbonyl compounds formed in a water treatment plant which were derivatized with PFBHA, extracted with a 100-poly(dimethylpolysiloxane) (PDMS) fiber from liquid or headspace and finally analysed by GC–ECD [55] but only the 100-PDMS fiber was tested in this study. A new analytical method was developed to determine formaldehyde in air consisting of on-7 μm-PDMS fiber derivatization, introducing previously the coating in a 2,4-dinitrophenylhydrazine or acetophenone solution, and followed by GC–MS [56]. A similar method considering PFBHA as derivatization reagent and a PDMS–DVB fiber followed by GC–FID analysis was also proposed for this carbonyl compound [57]. A SPME method has been developed using as well on fiber derivatisation applied to the analysis of volatile carbonyl compounds formed during the thermally-induced peroxidation of vegetable oils [58]. Finally, Keszler and coworkers determined the aliphatic aldehydes, which are indicators of rancidity of vegetable oils by headspace-SPME sampling followed by ion-trap GC–MS [59,60].

The aim of this study is to develop an alternative method to EPA Method 556 [61], based on a PFBHA derivatization and solid-phase microextraction (SPME) followed by GC–ECD, for the determination of aldehydes formed as a consequence of

disinfection drinking water. This converts SPME as an alternative to the liquid–liquid extraction (LLE) proposed in the EPA method. Six SPME fibers commercially available were considered. Experimental parameters which affect the adsorption and desorption processes were studied for the most appropriate one. Once optimized the HS-SPME procedure, quality parameters such as precision, linear range and limits of detection were determined. HS-SPME technique was compared with LLE (following the experimental protocol described in EPA Method 556) in spiked water samples analysis; a reasonable agreement between results obtained with both techniques was observed. Finally, aldehyde levels in Barcelona's water treatment plant (N.E. Spain), where the Llobregat river is treated, were measured.

2. Experimental

2.1. Chemical and materials

Standards of 14 carbonyl compounds studied: acetaldehyde (99%), propanal (99%), 2-methylpropanal (99%), butanal (97%), 2-methylbutanal (95%), 3-methylbutanal (97%), pentanal (97%), hexanal (98%), heptanal (95%), octanal (99%), nonanal (95%), decanal (97%), glyoxal and methyl glyoxal (40% aqueous solution) were purchased from Sigma Aldrich (USA). The *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (98%, PFBHA), used as a derivatization reagent of the carbonyl compounds, was purchased from Fluka (Switzerland). The chemical reagents 2,4,5-trifluoroacetophenone (99%) and 1,2-dibromopropane, used as a surrogate and internal standard respectively, and potassium hydrogen phthalate were purchased from Sigma Aldrich. Other reagents were methanol purge and trap grade from Sigma Aldrich; and sodium sulfate ACS–ISO for analysis, sodium chloride ISO for analysis, copper sulfate pentahydrate ACS–ISO for analysis and sulfuric acid form Carlo Erba (Italy). Ultrapure water was from a Milli-Q water purification system (Millipore, USA). For the extraction, water samples were placed in 40 ml EPA vials (Wheaton, USA) equipped with stir bars and sealed with PTFE-faced silicone septa.

2.2. Standard solutions

Stock standard solutions were prepared in methanol by weighing approximately 0.1 g of analyte into 10-ml volumetric flask and diluting to volume; they were kept at −20°C. Secondary standard solutions were prepared by dilution in methanol of primary standard to give concentrations of 50 mg/l. Stock and secondary standard solutions of the substances used as surrogate and internal standard were prepared in the same way. The aqueous solution of PFBHA used as derivatization agent was prepared daily to give concentration of 15 mg/ml. Ultrapure water solutions were prepared by spiking with different amounts of the secondary standard and used in the recovery study and for calibration.

Formaldehyde and acetaldehyde were present in ultrapure water as interferences at levels of 3 μg/l. Munch and coworkers have observed similar carbonyl impurities in purified and bottled reagent water and they reported that purified water rapidly absorbs volatile carbonyl compounds from the air [62]. In order to remove these carbonyl impurities from the air reagent water (1 l), to which potassium permanganate (128 mg) and concentrated sulfuric acid (2 ml) have been previously added, was bidistilled in order to avoid the background levels of aldehydes. The acetaldehyde was completely removed meanwhile residues of formaldehyde were still present and therefore formaldehyde was not considered for quantification.

2.3. SPME coatings

For HS-SPME, 100 μm-polydimethylsiloxane (PDMS), 65 μm-divinylbenzene–polydimethylsiloxane (DVB–PDMS), 85 μm-polyacrylate (PA), 75 μm-carboxen–polydimethylsiloxane (CAR–PDMS), 65 μm-carbowax–divinylbenzene (CWX–DVB) and 50/30 μm divinylbenzene–carboxen–polydimethylsiloxane (DVB–CAR–PDMS) fused-silica fibers were evaluated to determine aldehydes in water samples. The commercially available SPME device and the fibers were purchased from Supelco (Bellefonte, PA, USA). Fibers were initially conditioned according to the manufacturer's instructions in order to remove contaminants and to stabilize the solid-phase. Conditioning was carried out in an extra

split/splitless port (split open) with helium carrier gas prior to each extraction. This procedure prevents the passive extraction of interfering analytes from ambient air.

2.4. Experimental procedure

2.4.1. Sample collection

Water samples from successive stages of the Barcelona's water treatment plant were collected in 100-ml glass bottles with PTFE-faced septa and polypropylene screw caps. A volume of 0.1 ml of 0.1 *M* sodium thiosulfate solution was added to each bottle (100 ml) prior to analysis to eliminate free chlorine and to prevent the production of further disinfection by-products (DBPs). Copper sulfate pentahydrate (50 mg) which acts as a biocide to inhibit bacteriological decay of method analytes was added.

2.4.2. Aldehyde derivatization process

Aldehyde derivatization is based on the derivatization procedure described in EPA 556 method [61]. Water samples (30 ml) were placed in 40-ml EPA glass vials. To each sample, 2,4,5-trifluoroacetophenone (4 μl of a methanolic solution of 50 mg/l) was added as an internal standard. Water samples were adjusted to pH 4 with potassium hydrogen phthalate (200 mg) and the carbonyl compounds were derivatized with PFBHA (1 ml of an aqueous solution of 15 mg/l) at 45°C for 1 h and 45 min. Once vials reached room temperature after the derivatization process was finished, sulfuric acid (two drops) was added in order to protonate the residual PFBHA agent. As a result of this process, (*E*) and (*Z*) pentafluorobenzyloxime isomers were obtained for the carbonyl compounds that are not symmetrical. Compounds with two carbonyl groups, such as glyoxal and methyl glyoxal, produced four isomers.

2.4.3. HS-SPME procedure

To each derivatized sample (30 ml), 1,2-dibromopropane (3 μl of a methanolic solution of 50 mg/l) as an internal standard and sodium chloride (6 g) were added before the extraction process. The vial was sealed with a PTFE-faced septum cap and the SPME fiber was exposed to the headspace. The sample was agitated with a magnetic stirring bar at 1100 rev./min at room temperature (22°C) during the extraction process (40 min) to allow the equilibration of analytes between the aqueous phase and the headspace and immediately inserted into the gas chromatographic port for thermal desorption of the extracted analytes.

2.4.4. LLE procedure

Derivatization and extraction processes were performed at the experimental conditions described in EPA Method 556 [61].

2.5. Instruments

Gas chromatography was carried out with a Fisons Top 8000 gas chromatograph equipped with an electron capture detection (ECD) system. A DB-1701 fused-silica column (J&W Scientific) with a 1.0 μm film thickness, 30 m×320 μm I.D., was used. The GC temperature program was 50°C (1 min) to 265°C (5 min) at 5°C/min. Carrier gas was helium (88 kPa) and nitrogen (33 ml/min) as a make-up. Injector and detector temperatures were 200 and 300°C, respectively.

3. Results and discussion

3.1. Development of HS-SPME procedure

In order to develop an HS-SPME–GC–ECD method for the analysis of aldehydes, several experimental parameters such as SPME coating, effect of headspace volume, effect of addition of salt, extraction time and desorption conditions were optimized. HS-SPME sampling was used due to the higher diffusion of the analytes in air than in water [50].

3.1.1. Selection of SPME coating – extraction efficiency

The SPME theory dictates that analytes in water are transferred to the phase coating of the fused-silica fiber; equilibrium process was finally established between the concentration of the analytes in solution and the concentration of analytes in the phase coating. The choice of an appropriate coating

is essential for the establishment of a SPME method and it is dependent of the chemical nature of the target analytes (polarity and volatility). Although aldehydes are polar compounds, derivatization allows to decrease their polarity and therefore the use of apolar coatings/fibers. PDMS presents a non polar phase which extracts efficiently non polar analytes. The PA phase is suitable for more polar compounds. In mixed phases, DVB or CAR porous microspheres are immobilized on the fiber by using CWX or PDMS as glue to hold them together.

Six SPME fiber coatings were evaluated to select the appropriate coating for the method. A fortified aqueous sample (20 ml spiked at a level of 5 μg/l of each carbonyl compound) was analyzed twice with each fiber once the previous derivatization process was finished. The extraction time was 15 min at room temperature and desorption time was 1 min (split mode: 1/125) at 250°C for all fibers. The extraction efficiency of the SPME fibers was evaluated by plotting the ECD areas obtained for each carbonyl compound with the different fibers.

(*E*) and (*Z*) isomers formed as a consequence of the derivatization reaction were obtained for that aldehyde compounds which are not symmetrical. Thus, two chromatographic peaks were observed for many target analytes with all SPME fibers tested. (*E*) and (*Z*) isomers could not be chromatographically resolved in a few cases such as 2-methylbutanal, nonanal and decanal with the chromatographic conditions employed. Compounds having two carbonyls, such as glyoxal and methyl glyoxal, the (*E*) and (*Z*) isomerism occurred from oxime formation with both carbonyl groups, thus increasing the number of isomers to four; a coelution between two signals from glyoxal and methylglyoxal was observed. Undentified peaks labeled as ''d'' peaks were identified as artifacts from PFBHA but they do not interfere with the analysis of the compounds studied. The PFBHA-HS-SPME–GC–ECD profile for the derivatized aldehydes is shown in Fig. 1.

The sum of the isomer peak areas for each compound was considered as the total area for quantitation purposes. Comparison of the oxime derivate amounts adsorbed on the coated fibers can be seen in Fig. 2. Mixed SPME phases are more suitable than the 100 μm-PDMS proposed by Bao and co-workers [55]. Extraction efficiencies for the C_2–C_5 carbonyl compounds decreased following the behavior DVB–CAR–PDMS>DVB–PDMS>100 μm-PDMS>CWX–DVB>CAR–PDMS>PA. However, for butanal, 2-methyl-, 3-methylbutanal and pentanal, the PA extraction efficiency was higher than obtained with CAR–PDMS. For the C_6–C_{10} carbonyl compounds, glyoxal and methyl glyoxal, the PA, 100 μm-PDMS, DVB–CAR–PDMS fibers presented a similar response whereas the CAR–PDMS and CWX–DVB produced a lower response. Due to DVB–PDMS allowing a higher adsorption for the C_6–C_{10} carbonyl compounds, glyoxal and methyl glyoxal than DVB–CAR–PDMS did, DVB–PDMS was chosen as the most appropriate.

3.1.2. Effect of headspace volume

SPME theory dictates that the volume of the gaseous phase should be minimized in order to obtain the high sensitivity headspace extraction. To optimize the extraction procedure of the carbonyl compound, the effect of the water sample and the headspace volumes were studied. This experiment was performed using EPA 40-ml vials and increasing the volume of a fortified aqueous sample (spiked at 5 μg/l) from 10 to 30 ml. After the derivatization process, aqueous samples were analyzed twice with the DVB–PDMS fiber. The extraction time was 15 min at room temperature; the desorption time was 1 min (split mode: 1/125) at 200°C.

The obtained results showed that the extraction of the carbonyl compounds is affected by the volume of headspace into which the analytes diffuse. An increase in the peak area was obtained for each analyte when headspace volume decreased from 30 to 10 ml. Further experiments were performed using 30 ml of water sample.

3.1.3. Effect of the addition of salt

With the addition of salt into the aqueous sample previously to the extraction process, an increase of the ionic strength of the solution was obtained. As a consequence, the diffusion of analytes into the headspace is favoured and extraction time for each analyte is reduced. This behavior was observed when fortified aqueous samples (spiked at 5 μg/l) were previously salted with NaCl (6 g) and analyzed following the experimental conditions described above. The addition of salt has a significant effect on

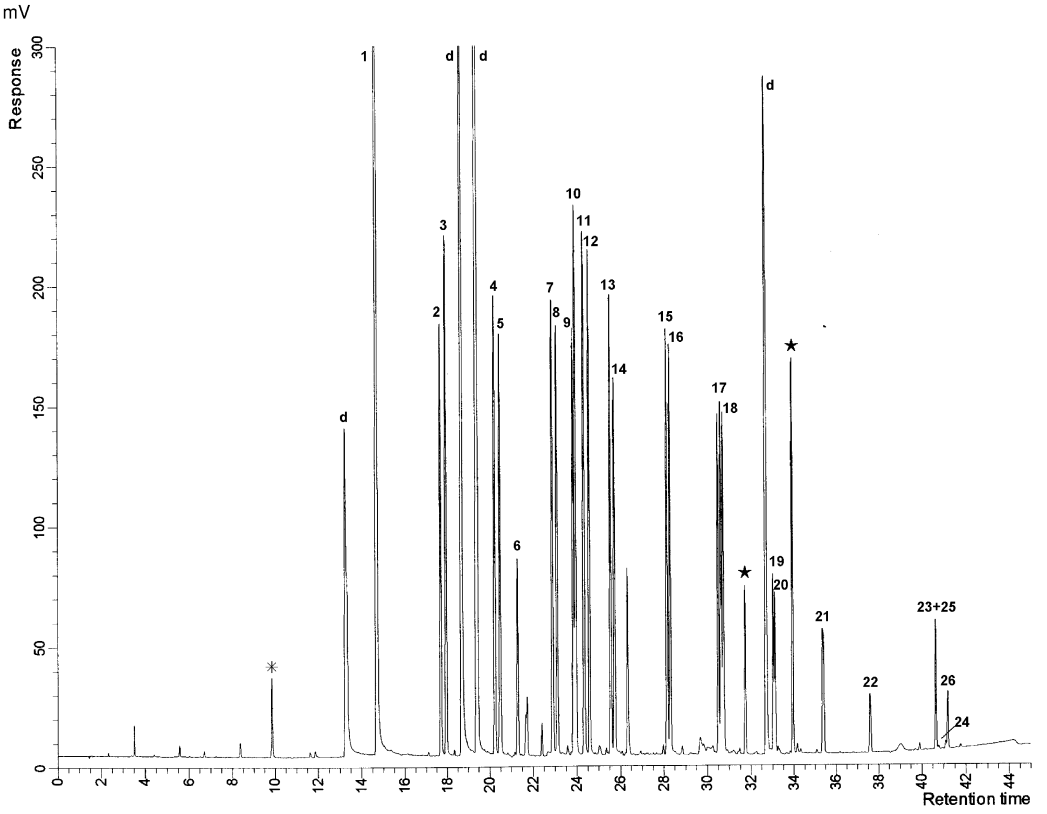

Fig. 1. PFBHA–HS-SPME–GC–ECD chromatogram of a water sample (30 ml) spiked with aldehydes at 5 μg/l. Extraction was performed by HS-SPME with DVB–PDMS fiber under the optimized conditions. Identification of peaks corresponds to same as Table 1 (*, 1,2-dibromopropane; ★, (*E*) and (*Z*) 2,4,5-trifluoroacetophenone; d, artifacts). Chromatographic conditions are described in the Instrumental section.

the extraction of the C_2–C_8 carbonyl compounds meanwhile it was slightly lower on the extraction of nonanal, decanal, glyoxal and methyl glyoxal. As a conclusion, further experiments were performed using 6 g of NaCl.

3.1.4. Sorption time profiles

The DVB–PDMS fiber extracts basically the derivates of carbonyl compounds by total adsorption due to the presence of DVB porous microspheres immobilized on the fiber by using PDMS. The adsorption time profiles of DVB–PDMS fiber were obtained by plotting the ECD response versus the extraction time, as can be seen in Fig. 3; optimum sorption time is defined as the time after which the amount of extracted analyte remains constant. Duplicate water samples were analyzed under the experimental conditions described in the HS-SPME procedure. ECD areas obtained at 20 and 60 min were compared and it was observed that 20 min was not enough to reach the equilibrium, specially for the higher molecular mass compounds. No significant differences were observed in ECD areas registered at 40 and 60 min. As a conclusion, 40 min was considered as the optimized exposure time for all the compounds studied.

The GC injector temperature and the appropriate desorption time were also evaluated to ensure that oxime derivates were completely desorbed from the fiber in order to reach the highest sensitivity and to avoid carryover. For the DVB–PDMS fiber, different GC injector temperatures between 200 and 270°C

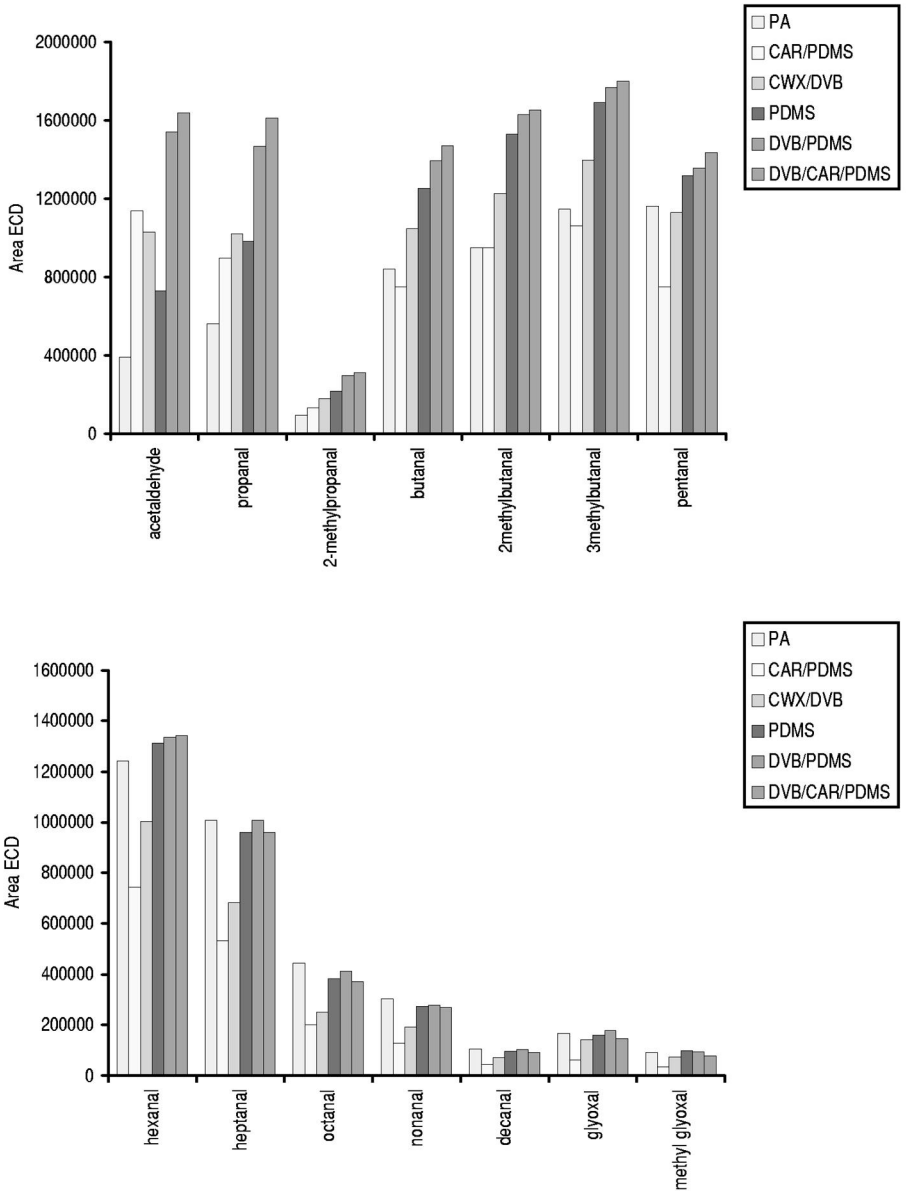

Fig. 2. Extraction efficiencies of fiber coatings for sampling C_2–C_5 aldehydes (top) and C_6–C_{10}, glyoxal and methyl glyoxal aldehydes (bottom) by PFBHA–HS-SPME–GC–ECD.

were tested, it was found that 200°C was the most appropriate to avoid thermal degradation of the derivates. Desorption profiles (Fig. 4) showed that 5 min was enough to ensure total desorption and no peaks appeared in the chromatogram corresponding to the analysis of the fiber prior to re-exposure.

3.2. Linear range, limits of detection and precision

Quality parameters such as linearity, limits of detection and precision were calculated when the optimum conditions for the HS-SPME–GC–ECD procedure were established.

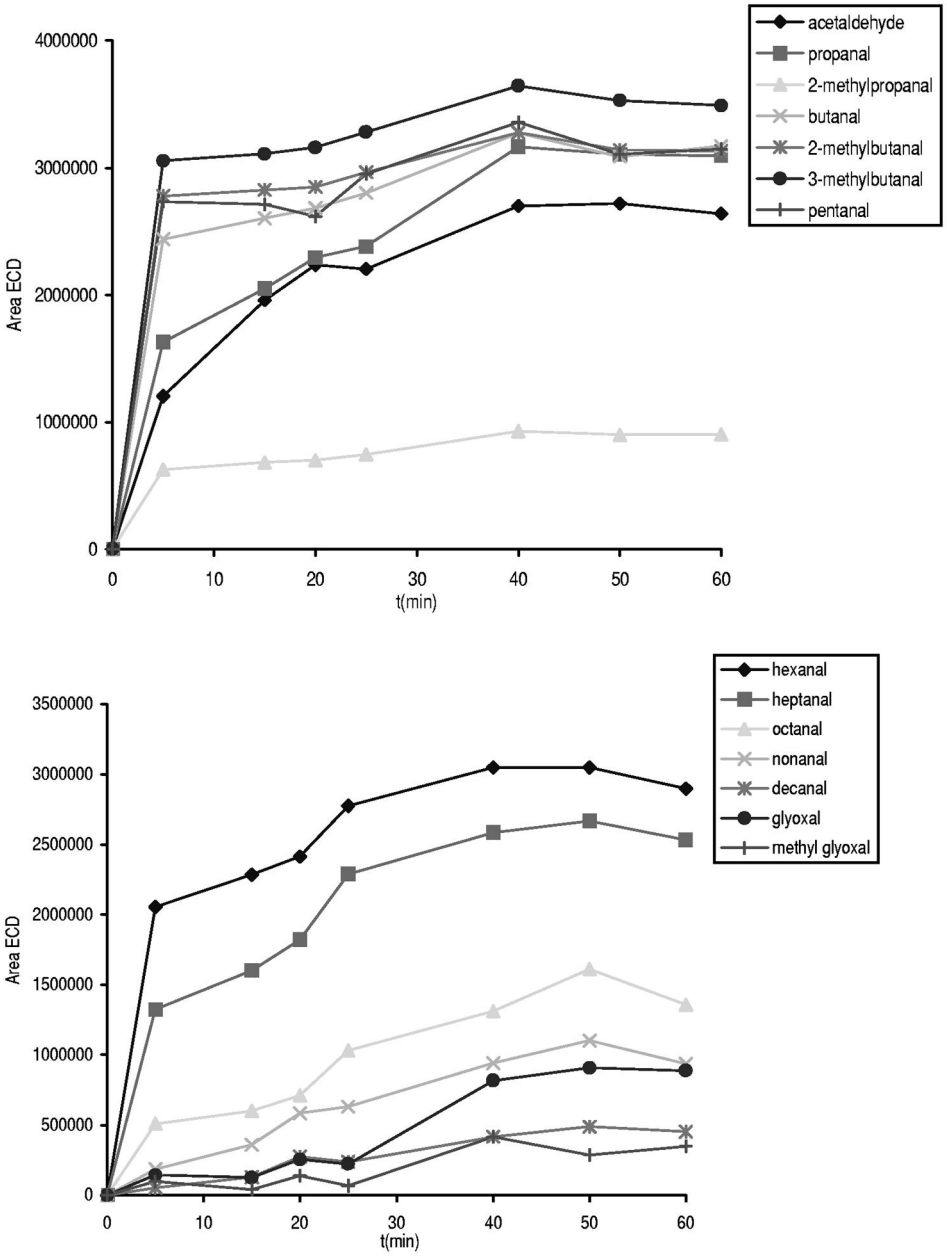

Fig. 3. Adsorption profiles (DVB–PDMS fiber) for C_2–C_5 aldehydes (top) and C_6–C_{10}, glyoxal and methyl glyoxal aldehydes (bottom) by PFBHA–HS-SPME–GC–ECD.

The linearity of the HS-SPME method was obtained by plotting the calibration curves of the total area (sum of (*E*) and (*Z*) isomers) relative to the internal standard 1,2-dibromopropane (A_{E+Z}/A_{is}) versus the concentration of each carbonyl compound (C_i). Standard calibration curves were plotted for concentrations from 0.1 to 30 μg/l. The linear ranges and the correlation coefficients (r^2) obtained for each compound are given in Table 1. The seven-point calibration curve was found to have good

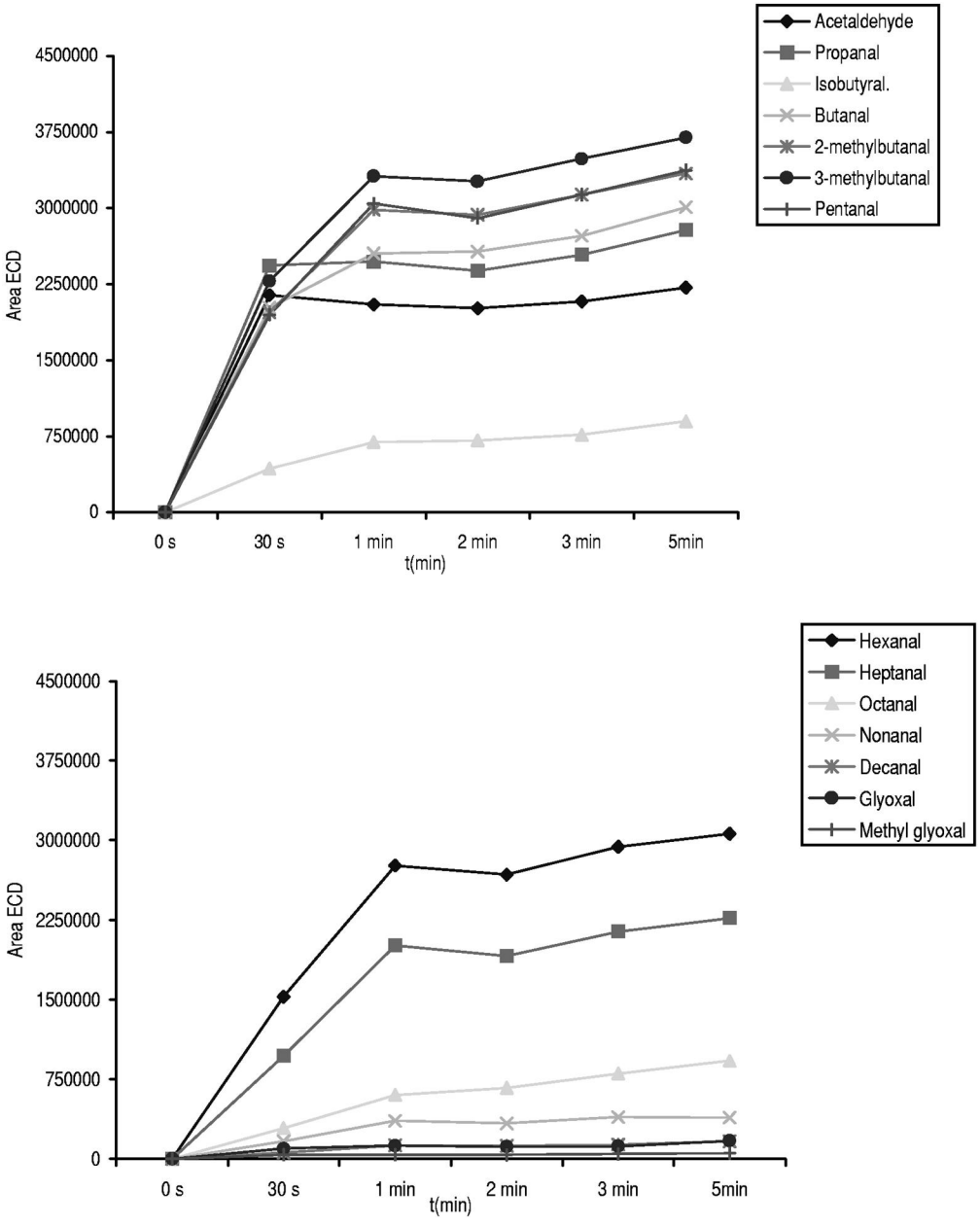

Fig. 4. Desorption profiles (DVB–PDMS fiber) for C_2–C_5 aldehydes (top) and C_6–C_{10}, glyoxal and methyl glyoxal aldehydes (bottom) by PFBHA–HS-SPME–GC–ECD.

linearity with linear ranges between 0.5 and 15 μg/l for greater part of aldehydes and correlation coefficients better than 0.994. These calibration ranges differ from the 0.1–100 μg/l for C_2–C_{10} carbonyl compounds and 0.1–50 μg/l for glyoxal and methyl glyoxal obtained by Bao et al. [55]. Linear behaviour indicated that there was not adsorption of PFBHA-derivatives on the magnetic stir bar.

The sensitivity of the HS-SPME method was evaluated in terms of limit of detection (LOD). This

Table 1
Peak identification, linear dynamic ranges, coefficients (r^2), limits of detection (LODs), repeatability and reproducibility of the optimized PFBHA–HS-SPME method using the DVB–PDMS fiber

Aldehydes	Peaks	t_r (min)		Linearity[b]		LOD[c] (μg/l)	Repeatability[d] RSD (%)	Reproducibility[e] RSD (%)
		(*E*)	(*Z*)	range (μg/l)	r^2			
Acetaldehyde	2,3	17.71	17.97	0.5–19.4	0.996	0.04	10.3	12.7
Propanal	4,5	20.27	20.52	0.1–8.9	0.997	0.15	8.7	14.9
2-Methylpropanal[a]	6	21.33		0.5–14.5	0.994	0.07	6.9	9.1
Butanal	7,8	22.93	23.15	2.0–15.3	0.994	0.05	4.7	9.9
2-Methylbutanal	9,10	23.89	24.00	0.5–27.7	0.995	0.06	2.9	5.2
3-Methylbutanal	11,12	24.38	24.63	0.5–19.7	0.996	0.05	2.6	6.1
Pentanal	13,14	25.59	25.78	0.5–13.3	0.999	0.07	3.8	4.9
Hexanal	15,16	28.20	28.35	0.5–18.0	0.996	0.18	9.3	8.6
Heptanal	17,18	30.69	30.79	0.4–16.9	0.997	0.16	12.1	10.1
Octanal	19,20	33.10	33.18	0.4–16.9	0.997	0.13	10.2	9.8
Nonanal[a]	21	35.41		0.4–12.4	0.997	0.14	15.8	22.6
Decanal[a]	22	37.50		0.4–12.2	0.997	0.20	13.0	22.6
Glyoxal	23,24	40.67	40.73	1.2–23.5	0.996	0.40	11.7	12.8
Methyl glyoxal	25,26	40.67	41.22	1.5–24.0	0.998	0.30	10.5	12.1

[a] Single peak for (*E*) and (*Z*) isomers under the chromatographic conditions used.
[b] $n=7–10$ aqueous calibration solutions.
[c] Mean of five determinations.
[d] Mean of seven determinations.
[e] Mean of nine determinations (3 days).

parameter was calculated experimentally by spiking ultrapure water with aldehydes at concentration levels close to the theoretical LODs and produced a signal three times greater than the baseline noise. Under the experimental conditions, LODs were between 0.04 and 0.16 μg/l, as can be seen in Table 1. Glyoxal (0.40 μg/l) and methyl glyoxal (0.30 μg/l) exhibit high LODs versus the $C_2–C_{10}$ carbonyl compounds due to the PFBHA derivates of these two dialdehydes presented the highest molecular masses and the lowest volatility.

The repeatability and reproducibility of the HS-SPME method were evaluated by analyzing five ultrapure water samples (spiked at 5 μg/l of each aldehyde) on the same day and a total of a nine samples on 3 different days, respectively. Results reported in Table 1 showed that the relative standard deviation (RSD%) for repeatability ranged from 2.6 to 15.8%, being higher for the heaviest carbonyl compounds; whereas the RSD for the reproducibility ranged from 4.9 to 14.9%, following the same tendency as repeatability, except for nonanal and decanal which presented a RSD value of 22.6%. These values are in the same order that those reported by Bao et al. [55].

3.3. Comparison of HS-SPME with EPA Method 556: determination of aldehydes in a water treatment plant

The optimized HS-SPME–GC–ECD method was compared with EPA Method 556 for the determination of carbonyl compounds by spiking samples of ultrapure water at 1.0 and 3.0 μg/l ($n=3$). Quantitation was performed using the calibration curve for each compound relative to the internal standard (1,2-dibromopropane). Results are shown in Table 2.

Standard deviation and mean values were compared using the *F*-Fischer test (95% probability) and the Student's *t*-test (95% probability and two sides), respectively [63]. No significant differences were found between the results given by these two extraction techniques except for heptanal, octanal and nonanal. HS-SPME method can be considered a good alternative to LLE extraction with hexane proposed in EPA method with the advantage that solvent is not needed and it is faster due to the fact that intensive manual labor is avoided.

Aldehydes formed as a consequence of the disinfection process was monitored at the Barcelona treatment plant (Table 2). Salt mines located in the

Table 2
Estimated concentrations and standard deviations of aldehydes in ultrapure spiked water determined by HS-SPME (DVB–PDMS) and EPA Method 556

	PFBHA–HS-SPME–GC–ECD[a]				PFBHA–LLE–GC–ECD[a]				Treated water (μg/l)[a]
	1.0 μg/l		3.0 μg/l		1.0 μg/l		3.0 μg/l		
	Mean	±SD	Mean	±SD	Mean	±SD	Mean	±SD	
Acetaldehyde	0.9	0.1	2.8	0.2	0.9	0.1	3.3	<0.1	0.08
Propanal	1.1	0.1	2.9	<0.1	1.1	<0.1	2.9	0.1	0.5
2-Methylpropanal	0.9	0.2	2.6	<0.1	0.9	<0.1	2.6	0.1	–
Butanal	1.0	0.1	2.7	<0.1	1.1	0.1	2.8	0.1	–
2-Methylbutanal	1.1	0.1	3.0	0.7	1.4	0.5	3.0	0.1	–
3-Methylbutanal	1.0	0.1	2.6	0.1	1.1	<0.1	3.1	0.2	–
Pentanal	0.5	<0.1	1.7	<0.1	0.6	<0.1	1.9	<0.1	–
Hexanal	1.3	0.1	3.5	0.1	1.5	0.1	3.7	<0.1	–
Heptanal	0.9	<0.1	2.9	0.1	1.5	0.1	2.9	0.3	–
Octanal	0.7	<0.1	1.5	<0.1	1.0	0.1	2.9	<0.1	–
Nonanal	0.9	<0.1	2.5	<0.1	1.2	0.2	3.1	<0.1	–
Decanal	1.0	0.2	3.3	<0.1	1.2	<0.1	3.1	<0.1	–
Glyoxal	–	–	–	–	0.9	<0.1	2.5	0.1	0.25
Methyl glyoxal	1.4	<0.1	2.6	<0.1	1.1	0.1	3.1	<0.1	0.15

Average aldehyde levels (μg/l) in Barcelona's treated water (October, 1999). –: below LOD. Average raw water quality characteristics (October 1999): volume, 12.7 m^3/s; pH, 7.32; temperature, 18°C; conductivity, 1665 μS/cm; total organic carbon, 2.4 mg C/l; bromide, 0.27 mg/l; break-point, 1.8 mg Cl_2/l.

[a] (n=3) mean of three determinations for each sample and method.

upper course of the river are responsible for the high bromide concentration in raw water. The plant carries out conventional treatment, consisting of prechlorination (to break-point), flocculation (settling), sand filtration, ozonization, GAC filtration and postchlorination with a lower dosage of chlorine, to guarantee a 0.5–1 mg/l concentration in the distribution system. Aldehydes were determined at the postchlorinated water. Results obtained showed that acetaldehyde (0.8 μg/l), propanal (0.5 μg/l), glyoxal (0.25 μg/l) and methyl glyoxal (0.15 μg/l) are the main ozonation DBPs formed. Total concentration of these by-products was lower than 2.0 μg/l and no health effects can be associated to this level. On the other hand, no aldehydes resulting from the chlorination of raw water were identified which decrease the presence of odour episodes.

4. Conclusions

The optimized HS-SPME–GC–ECD method allows to determine aldehydes in water at sub-μg/l levels. A previous derivatization process with PFBHA is necessary in order to obtain the corresponding oxime derivates which are less polars and unstables. The DVB–PDMS fiber is the most suitable for extracting quantitatively the oxime derivates of these ozonation by-products. Equilibrium tooks place at room temperature and the sensitivity was improved by the addition of salt. The optimized method has an acceptable linearity in the range of concentrations formed in water treatment plants with an associated precision between 3 and 10% for practically all the compounds studied.

The HS-SPME–GC–ECD method can be considered as a good alternative to LLE proposed in the EPA Method 556 for monitoring aldehydes in drinking water samples. The optimized method presents the following advantages: it is faster, inexpensive, no solvents are consumed and no intensive manipulation is performed.

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