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Determination of carbonyl compounds in water by derivatization–solid-phase microextraction and gas chromatographic analysis

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Abstract

The solid-phase microextraction (SPME) technique was evaluated for the determination of 23 carbonyl compounds in water. The carbonyl compounds in water were derivatized with *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA), extracted with SPME from liquid or headspace and analyzed by GC with electron capture detection (GC–ECD). The effects of agitation techniques and the addition of salt (NaCl) on extraction, the absorption–time and absorption–concentration profiles were examined. The precision of the SPME technique for the determination of carbonyl compounds was evaluated with spiked bidistilled water, ozonated drinking water, and rain water. The relative standard deviations obtained from different spiked water matrix were similar, and in the range of 5.7–21.1%. The precision can be further improved by using an internal standard. With 4 ml of water sample, the limits of detection for most of the tested carbonyl compounds using liquid or headspace SPME–GC–ECD were similar and in the range of 0.006–0.2 μg/l, except for glyoxal and methylglyoxal, which showed low sensitivity when using headspace SPME. In the analysis of an ozonated drinking water sample, the SPME techniques gave comparable results to those of the conventional liquid–liquid extraction method.

Keywords: Water analysis; Extraction methods; Carbonyl compounds

1. Introduction

Carbonyl compounds play an important role in aquatic and atmospheric oxidation processes. In natural waters, these compounds can be produced by the photodegradation of dissolved natural organic matter [1] and may also be released as metabolites by microbiological processes [2]. In atmospheric systems, these compounds are produced from the photooxidation of hydrocarbons [3] and are also emitted during the combustion of hydrocarbon fuels [4]. In recent years, carbonyl compounds, especially those with low molecular masses, are receiving increasing attention as disinfection and oxidation by-products formed during drinking water treatment processes. Low-molecular-mass carbonyl compounds, such as formaldehyde, acetaldehyde, acetone, glyoxal, and methylglyoxal have been found to

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be major organic by-products in the ozonation of natural waters [5–8]. Presence of these compounds in drinking water is significant because their adverse health effects. Evidence has shown that formaldehyde is mutagenic and carcinogenic [9]. Glyoxal can produce stomach tumors [10]. These compounds may also cause taste and odour problems in drinking water [11].

For the determination of carbonyl compounds in water, derivatization before extraction coupled with gas chromatographic (GC) or liquid chromatographic (LC) analysis is often adopted. For example, derivatization with 2,4-dinitrophenylhydrazine (DNPH) followed by liquid–liquid extraction (LLE) or cartridge extraction and LC analysis has been widely used [1,12–14]. Another commonly used method is based on derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) followed by solvent extraction and GC with electron-capture detection (ECD) or GC with mass spectrometric detection (MS) [5–8].

In recent years, a new extraction technique called solid-phase microextraction (SPME) has been developed by Pawliszyn and co-workers [15,16] which has become more and more popular in the extraction of organic compounds from water samples. This technique uses a polymer-coated silica fiber to adsorb 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. SPME coupled with GC has been applied for the analysis of many classes of environmental organic compounds in water, including alkylbenzenes [17], polynuclear aromatic hydrocarbons and polychlorinated biphenyls [18], chlorinated hydrocarbons [19], phenols [20], organochlorine pesticides [21], nitrogen- and phosphorus-containing pesticides [22], and fatty acids [23]. These applications show that SPME is a simple, solvent-free, inexpensive, reliable, and easily automated technique.

In this paper, we report an approach that uses SPME for the determination of carbonyl compounds in aqueous samples. The method is based on derivatization with PFBHA in the water samples followed by extraction with SPME from liquid or headspace and GC–ECD analysis.

2. Experimental

2.1. Reagents

The standards of 23 carbonyl compounds tested including C_1–C_{10} saturated aliphatic aldehydes, unsaturated aldehydes propenal, 2-butenal, 2-hexenal and heptenal, benzaldehyde, ketones acetone, 2-butanone and 2-pentanone, dialdehydes glyoxal and methylglyoxal, were obtained from Aldrich (Milwaukee, WI, USA). Stock standard solutions of each carbonyl compound at 5 mg/ml were prepared with pure analyte dissolved in methanol and then diluted with bidistilled water to prepare mixed working standard solutions (1–50 μg/ml). Stock standard solutions were kept at −20°C. Aqueous working standard solutions were kept at 4°C and prepared weekly. The derivatizing reagent, *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA), was purchased from Aldrich and prepared as 6 mg/ml solution in bidistilled water.

2.2. Apparatus

The SPME device used in this study was a 100-μm film thickness poly(dimethylsiloxane)-coated fiber mounted in a manual syringe holder (Supelco, Bellefonte, PA, USA). The fiber was conditioned for at least 5 h at 250°C before the first experimental use. To agitate the samples two agitation techniques — magnetic stirring or ultrasonication — were investigated in this study. For magnetic stirring, a 12×4.5 mm magnetic stirbar was placed in the sample vial and a magnetic stirrer (VELP Scientifica, Milan, Italy) was used. Previous experiments showed that the optimum stirring rates were 1200 rpm for 4.6-ml vials and 1400 rpm for 8.5-ml vials. For ultrasonic agitation, the sample vial was put in an ultrasonic bath (Model 1200 Brasonic, Branson Europa, Soest, Netherlands).

The PFBHA derivatives of carbonyl compounds were analyzed by using a Hewlett-Packard Model 5890A GC–ECD system. A 30 m×0.25 mm I.D., 0.25-μm film thickness, SPB-5 fused-silica capillary column (Supelco) was used. The GC oven temperature program was as follows: initial 70°C, 5°C/min to 220°C, and then 20°C/min to 280°C. The detector

temperature was 300°C. The temperature of the split/splitless injector, in the splitless mode, was kept at 250°C for SPME fiber injection. According to our preliminary desorption-time (1–10 min) experiments, with 3-min desorption time 0.5–2.5% of carryover for the derivatives of formaldehyde, glyoxal, methylglyoxal, and PFBHA reagent were observed, while with 5-min desorption time, carryovers of the above derivatives and PFBHA reagent were less than 1%. Thus, a 5-min fiber desorption time was chosen. Helium was used as carrier gas at a flow-rate of 2 ml/min. Argon–methane (95:5, v/v) was used as make-up gas at a flow-rate of 60 ml/min.

2.3. Derivatization and SPME procedures

Two SPME sampling techniques, sampling from liquid (liquid SPME) and from headspace above the liquid (headspace SPME), were investigated. For liquid SPME, 4 ml of aqueous sample were placed in a 4.6-ml vial. After addition of 40 μl of 6 mg/ml PFBHA aqueous solution, the vial was closed with a PTFE-lined septum and placed in the dark at room temperature for 2 h. According to our preliminary experiments and to the results reported by other researchers [6,24], the PFBHA derivatization process for most of the carbonyl compounds tested could be completed in 2 h at room temperature. The only exceptions are the three ketones studied, which required a much longer reaction time (>20 h). After derivatization with PFBHA, two drops of 9 *M* H_2SO_4 solution were added via syringe. The SPME needle was pierced into the septum cap and the fiber was exposed to the aqueous phase for a set absorption time with agitation (agitated either with magnetic stirring or with ultrasonication). After sampling, the SPME needle was removed from the sample vial and inserted in the GC injection port for thermal desorption for 5 min.

For headspace SPME, 4 ml of aqueous sample and 40 μl of 6 mg/ml of PFBHA aqueous solution were added into a 8.5-ml glass sample vial. The vial was closed with a septum and placed in the dark at room temperature for 2 h. After derivatization with PFBHA, two drops of 9 *M* H_2SO_4 were added by syringe. The sample was agitated for 5 min to allow the equilibration of analytes between the aqueous phase and the headspace phase. The SPME fiber was then inserted in the headspace of the vial to extract reaction derivatives. The sample was agitated during the sorption process. After sampling, the SPME needle was removed and inserted in the GC injection port for thermal desorption.

The effects of salt (NaCl) addition and agitation techniques (ultrasonication or magnetic stirring) on the SPME extraction efficiency of the derivatives of carbonyl compounds were examined by sampling derivatized water samples spiked at 5 μg/l for 30 min. To obtain an absorption–time profile, bidistilled water samples spiked at 5 μg/l were derivatized with PFBHA and extracted with magnetic stirring for varying lengths of time (5–120 min). For the absorption–concentration curves studies, a range of spiked bidistilled water samples (0.1–100 μg/l) were derivatized and extracted for 30 min with magnetic stirring. All determinations were carried out in duplicate or triplicate.

To determine the precision of SPME techniques, spiked samples of bidistilled water, ozonated drinking water and rain water were analyzed according to the procedure described above. Each type of water sample was analyzed seven times and the relative standard deviation (R.S.D.) was calculated. Additionally, a comparative study using SPME techniques and the conventional LLE method was also performed by analyzing the carbonyl compounds presented in an ozonated drinking water sample. The LLE procedure was similar to that proposed by Glaze et al. [6]. A 10-ml volume of water sample was derivatized with PFBHA in a manner identical to that used for the SPME technique. After derivatization, the water sample was extracted with 1 ml of *n*-hexane containing 100 μg/l of hexachlorobenzene, used as internal standard. The hexane extract was washed with 5 ml of 0.05 *M* H_2SO_4 and then analyzed by GC–ECD.

3. Results and discussion

3.1. Optimization of SPME procedures

Fig. 1 shows the GC–ECD chromatograms obtained after PFBHA derivatization and extraction

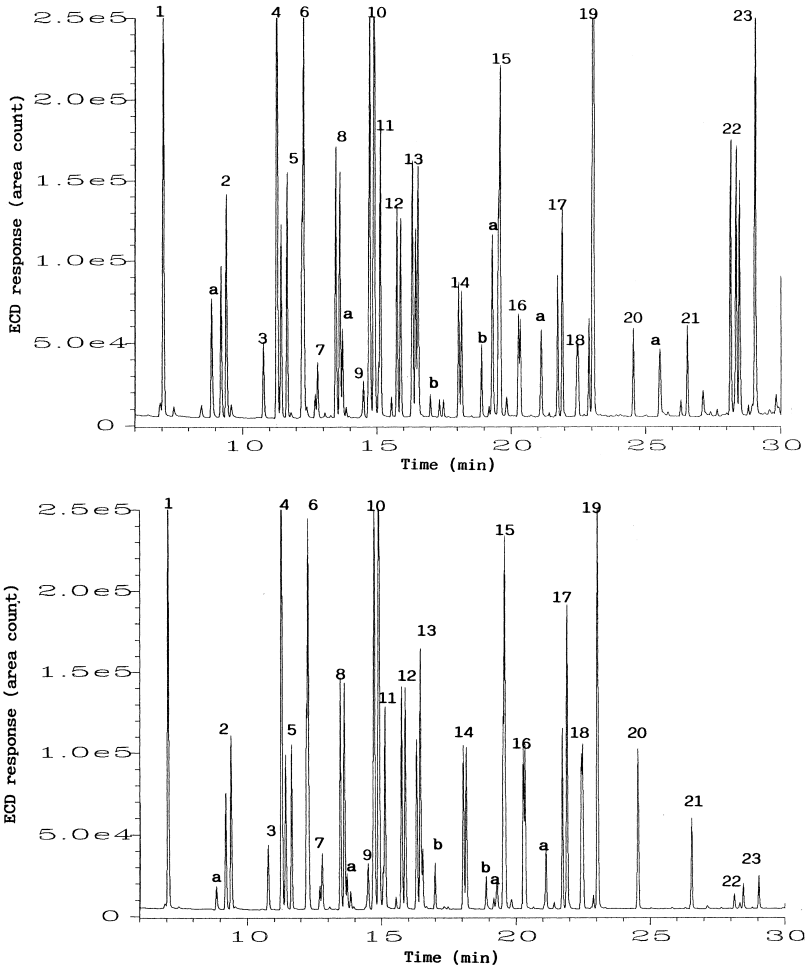

Fig. 1. GC–ECD chromatograms obtained after PFBHA derivatization of a bidistilled water sample spiked with 5 μg/l of each tested carbonyl compound followed by SPME from liquid (top) or from headspace (bottom). Sample volume was 4 ml. SPME sampling time was 30 min with magnetic stirring. Peaks are numbered in the order in which they appear in the Tables 1–3. Peaks noted as (a) were PFBHA reagent by-products. Peaks noted as (b) were SPME fiber bleed.

by SPME from liquid (top) and headspace (bottom) of a bidistilled water spiked with 5 μg/l of each of the carbonyl compounds studied. The SPME sampling time was 30 min. The GC resolution, peak shapes and sensitivity are perfectly acceptable for this type of application. The identity of all peaks in Fig. 1 was confirmed by the analysis of the same derivatized standard samples with GC–MS. The extraneous peaks present in the chromatograms, especially in the chromatogram obtained by liquid SPME, were identified as PFBHA reagent by-products or SPME fiber bleed. The presence of these extraneous peaks does not interfere with the determination of the analytes of interest. For most derivatives of carbonyl compounds tested in this study, the sensitivity obtained by headspace SPME was similar to that obtained by liquid SPME, with the exception of the derivatives of glyoxal and methylglyoxal, for which headspace SPME gave a much very lower extraction efficiency. This is to be expected since the PFBHA derivatives of these two dialdehydes have the highest molecular masses (448 and 462 for the derivatives of glyoxal and methylglyoxal, respectively) and lowest volatility.

Fig. 2 shows the effects of salt (NaCl) addition and the agitation of the solution on the extraction efficiency of PFBHA derivatives of carbonyl compounds by SPME. The addition of 10% NaCl (w/v) was found to have no significant effect on the extractability of the PFBHA derivatives of the tested carbonyl compounds, either for liquid SPME or for headspace SPME. The only exceptions are the derivatives of benzaldehyde and the unsaturated aldehydes 2-hexenal and 2-heptenal, which demonstrated significant increases in headspace SPME extractability by addition of NaCl. As previous SPME studies reported [16], the agitation of the solution can strongly improve the SPME extraction process. For liquid SPME, we have found that magnetic stirring is more effective than ultrasonication for improving the extraction efficiency of the derivatives of carbonyl compounds, especially for the derivatives of benzaldehyde, glyoxal and methylglyoxal. For headspace SPME, ultrasonication was as effective as magnetic stirring for improving the extraction efficiency of the derivatives of the tested carbonyl compounds, except for the derivatives of benzaldehyde, decanal, glyoxal, and

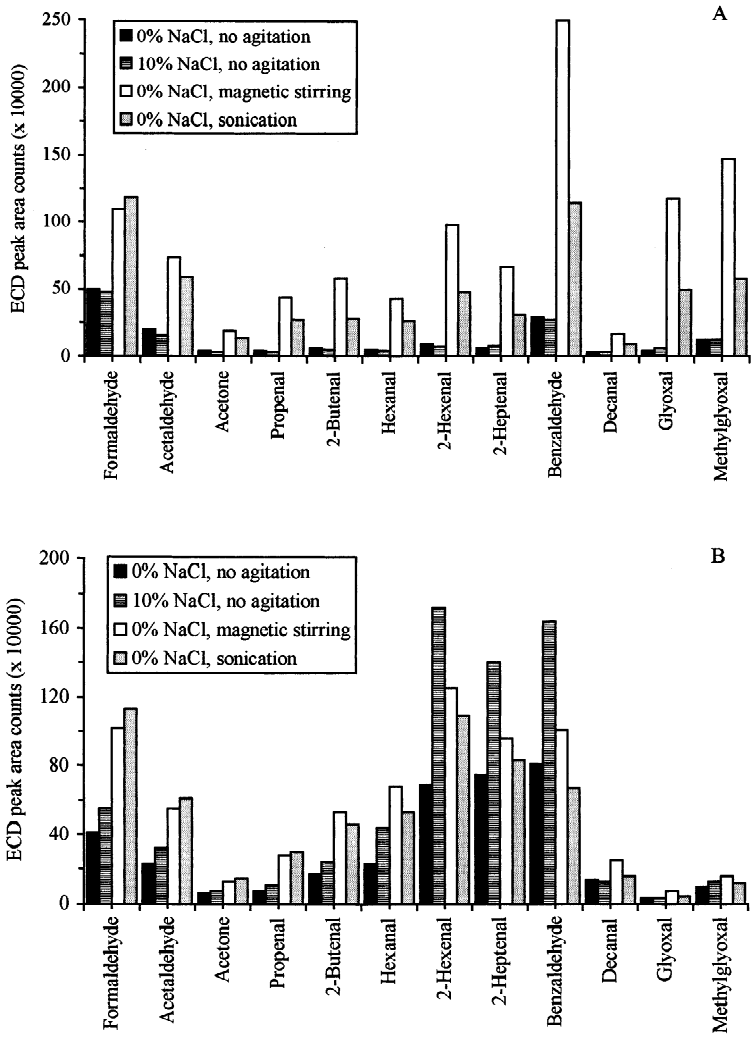

Fig. 2. Effects of salt (NaCl) addition and agitation techniques on the extraction of PFBHA derivatives of carbonyl compounds by SPME from liquid (A) or from headspace (B). Sample volume was 4 ml. Spiking level was 5 μg/l. SPME sampling time was 30 min.

methylglyoxal, for which magnetic stirring was more effective for improving the extraction process. As a result of these data, all subsequent SPME performances, either in liquid or headspace, were carried out with magnetic stirring. The effects of magnetic stirring/salt addition on the SPME extraction efficiency of PFBHA derivatives have also been investigated. The results (not shown in the paper) indicate that, in comparison with those obtained by magnetic stirring/without salt addition, magnetic stirring/salt addition showed higher extraction efficiency only for the derivatives of unsaturated aldehydes and benzaldehyde using headspace SPME. Since the extraction efficiency of PFBHA derivatives of unsaturated aldehydes and benzaldehyde is acceptable by using the headspace SPME with magnetic stirring/without salt addition and the addition of salt makes the SPME procedure more complicated, salt addition was not considered for subsequent experiments.

Figs. 3 and 4 show the SPME absorption–time profiles for the derivatives of the tested carbonyl

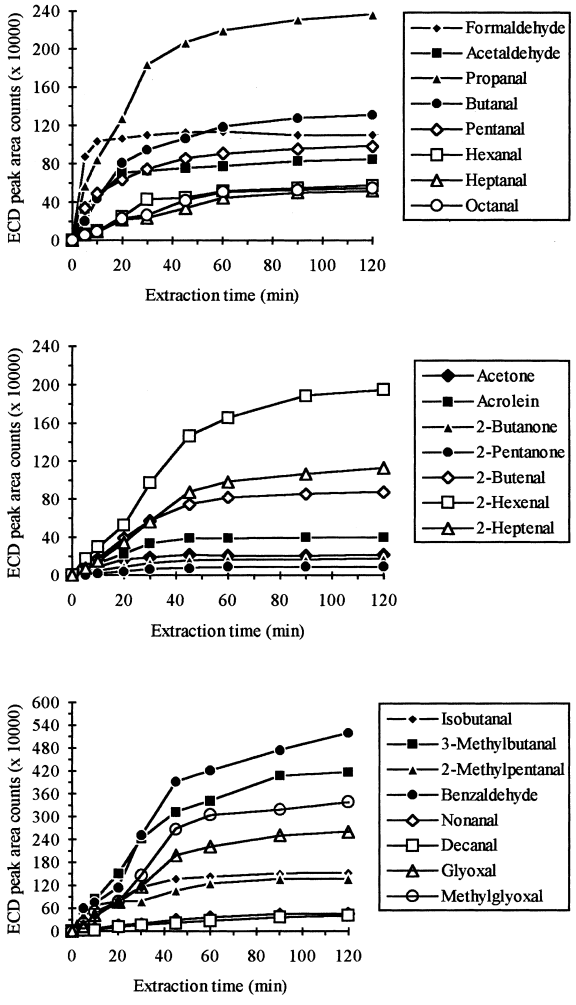

Fig. 3. Absorption–time profiles for PFBHA derivatives of carbonyl compounds in water using liquid SPME. Sample volume was 4 ml. Spiking level was 5 μg/l. The sample was agitated by magnetic stirring.

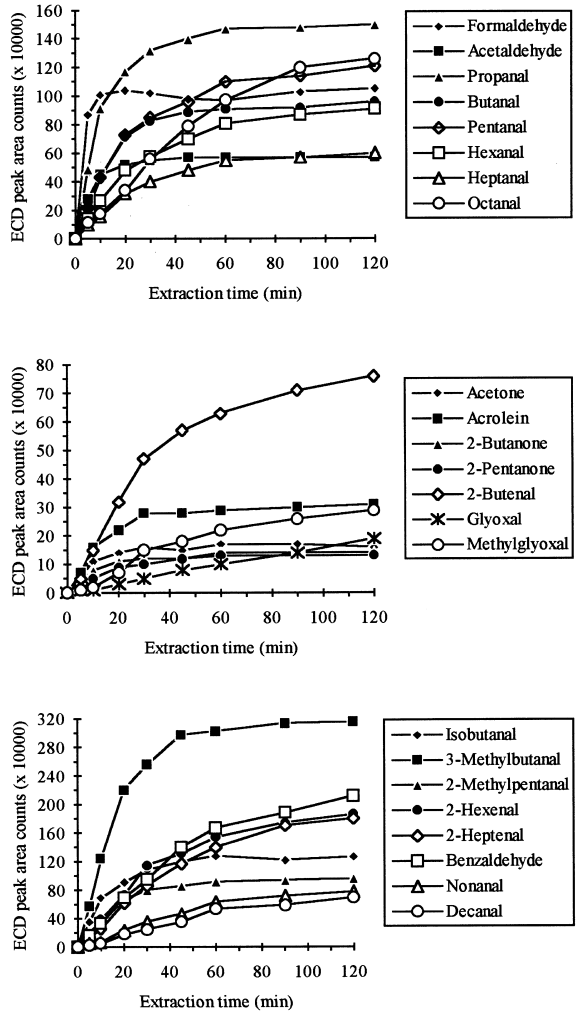

Fig. 4. Absorption–time profiles for PFBHA derivatives of carbonyl compounds in water using headspace SPME. Sample volume was 4 ml. Spiking level was 5 μg/l. The sample was agitated by magnetic stirring.

compounds using liquid SPME and headspace SPME, respectively. As shown by other researchers using SPME [17,25], the equilibration times generally increased with increasing molecular mass of the analytes, especially using headspace SPME. The PFBHA derivative of formaldehyde reached an absorption equilibrium in 10 min. For the derivatives of C_2–C_6 carbonyl compounds, absorption equilibrium was reached in 20 to 60 min, while for the derivatives of C_7–C_{10} aliphatic aldehydes, benzaldehyde, glyoxal and methylglyoxal, equilibrium was not reached within 120 min. Since the extraction with SPME is based on an equilibrium between the analyte concentrations in the liquid, headspace, and fiber coating solid phases, it is not necessary to reach an absorption equilibrium for quantitative analysis if the absorption time and mixing conditions are held constant throughout the experiment [18,26]. Thus, a 30-min extraction time was employed because this yielded sufficient extraction (most analytes reaching greater than 80% of their final equilibrium value by 30 min) and acceptable precision data (see R.S.D. values shown in Tables 1 and 2, and also allowed the sample extraction to be run in approximately the same time as required for the GC analysis.

To determine if any of the analytes remained on the fiber after 5 min desorption at a temperature of 250°C, tests of carryover with samples containing analytes at concentration of 100 μg/l were performed. The results show that after 5 min of desorption, complete desorption was achieved for all analytes, except for the derivatives of formaldehyde, glyoxal and methylglyoxal, for which less than 1% of carryover was observed.

Table 1
Precision achieved with PFBHA derivatization–liquid SPME–GC–ECD method for the tested carbonyl compounds spiked in different water matrix[a]

Compound	Bidistilled water R.S.D. (%)	Ozonated drinking water		Rain water	
		Relative recovery[b] (%)	R.S.D. (%)	Relative recovery[b] (%)	R.S.D. (%)
Formaldehyde	15.1	113	16.4	104	14.7
Acetaldehyde	8.2	103	9.3	98	10.6
Acetone	14.2	94	15.2	105	16.3
Propanal	6.9	101	7.7	93	6.8
Propenal	10.5	89	9.1	87	9.2
Isobutanal	8.7	95	7.3	103	7.9
2-Butanone	12.1	110	10.2	106	8.8
Butanal	7.0	101	8.1	96	6.3
2-Pentanone	9.6	93	10.8	107	11.8
3-Methylbutanal	6.6	97	7.3	92	8.6
2-Butenal	9.9	87	13.2	89	16.3
Pentanal	6.3	96	7.4	93	7.9
2-Methylpentanal	7.4	96	7.0	98	8.1
Hexanal	7.3	92	9.1	104	8.8
2-Hexenal	8.8	89	10.8	90	7.3
Heptanal	7.9	103	8.5	96	9.9
2-Heptenal	8.3	92	9.7	89	11.5
Octanal	12.4	93	13.2	94	11.3
Benzaldehyde	8.4	105	10.3	98	9.2
Nonanal	11.3	93	13.9	108	12.7
Decanal	13.4	97	14.3	101	12.1
Glyoxal	10.5	103	11.7	95	14.1
Methylglyoxal	17.3	108	16.9	116	15.3

[a] Sample volume was 4 ml. Spiking level was 5 μg/l. The sampling time was 30 min with magnetic stirring. Number of determinations was seven for each type of water sample.
[b] Relative recoveries for spiked ozonated drinking water and rain water were calculated relative to the spiked bidistilled water after blank correction.

Table 2
Precision achieved with PFBHA derivatization–headspace SPME–GC–ECD method for the tested carbonyl compounds spiked in different water matrix[a]

Compound	Bidistilled water R.S.D. (%)	Ozonated drinking water		Rain water	
		Relative recovery[b] (%)	R.S.D. (%)	Relative recovery[b] (%)	R.S.D. (%)
Formaldehyde	16.1	96	16.8	112	18.1
Acetaldehyde	8.9	104	10.7	98	9.2
Acetone	12.8	113	10.6	110	13.0
Propanal	7.8	93	9.2	94	8.1
Propenal	10.1	95	12.8	89	14.0
Isobutanal	6.7	98	7.3	97	7.9
2-Butanone	9.8	107	13.8	107	10.2
Butanal	6.5	97	7.3	95	6.1
2-Pentanone	9.7	93	8.7	98	8.3
3-Methylbutanal	7.9	113	8.3	102	6.8
2-Butenal	8.6	88	10.7	93	13.0
Pentanal	7.3	108	10.1	98	7.9
2-Methylpentanal	5.7	91	7.4	93	7.1
Hexanal	8.9	96	8.8	104	9.8
2-Hexenal	10.4	90	9.7	94	8.7
Heptanal	6.7	101	7.3	96	6.5
2-Heptenal	7.8	93	9.3	103	8.6
Octanal	12.9	110	10.7	109	10.1
Benzaldehyde	11.5	87	9.0	85	11.3
Nonanal	15.3	104	13.7	95	13.6
Decanal	16.8	95	15.1	94	13.7
Glyoxal	20.6	114	18.8	109	21.1
Methylglyoxal	17.7	118	20.3	121	16.8

[a] Sample volume was 4 ml. Spiking level was 5 μg/l. Sampling time was 30 min with magnetic stirring. Number of determinations was seven for each type of water sample.
[b] Relative recoveries for spiked ozonated drinking water and rain water were calculated relative to the spiked bidistilled water after blank correction.

3.2. Precision, linearity and limits of detection

The precision of the proposed SPME techniques was assessed by spiking of bidistilled water, ozonated drinking water, and rain water with 5 μg/l of each of the tested carbonyl compounds and then analyzing each type of aqueous matrix seven times. Results are reported in Tables 1 and 2. Comparison of the data obtained show that the R.S.D. values of liquid SPME from different spiked water matrix were similar and in the range of 6.3–17.3%. The same results were also obtained for headspace SPME; R.S.D. values from different spiked water matrix ranged from 5.7 to 21.1%. The data of relative recovery (%) listed in Tables 1 and 2 from spiked ozonated drinking water and rain water were calculated by normalizing to the results obtained from spiked bidistilled water after correcting for the data obtained from unspiked water samples. For liquid or headspace SPME, the relative recoveries from spiked ozonated drinking water and rain water were in the range of 85–121%.

Table 3 shows the slopes, correlation coefficients, linear ranges, and limits of detection (LODs) for the tested carbonyl compounds determined by the proposed PFBHA derivatization–SPME techniques. For liquid SPME, all tested carbonyl compounds showed linearity in the range of 0.1–100 μg/l with correlation coefficients better than 0.98, the only exceptions being 2-butanone and 2-pentanone (0.5–100 μg/l), benzaldehyde, glyoxal and methylglyoxal (0.1–50 μg/l). For headspace SPME, most carbonyl compounds showed excellent linearity in the concentration range from 0.1 to 100 μg/l, except for

Table 3
Calibration data and limits of detection (LODs) for the analysis of tested carbonyl compounds in water with PFBHA derivatization and liquid or headspace SPME–GC–ECD

Compound	Liquid SPME–GC–ECD				Headspace SPME–GC–ECD			
	Slope ($\cdot 10^{-5}$) (area counts/μg/l)	R^2	Linear range (μg/l)	LOD (μg/l)	Slope ($\cdot 10^{-5}$) (area counts/μg/l)	R^2	Linear range (μg/l)	LOD (μg/l)
Formaldehyde	1.404	0.989	0.1–100	0.015	1.382	0.998	0.1–100	0.02
Acetaldehyde	0.802	0.993	0.1–100	0.02	0.647	0.990	0.1–100	0.03
Acetone	0.344	0.994	0.1–100	0.08	0.316	0.988	0.1–100	0.10
Propanal	2.062	0.988	0.1–100	0.008	1.711	0.992	0.1–100	0.01
Propenal	0.307	0.998	0.1–100	0.10	0.289	0.998	0.5–100	0.12
Isobutanal	1.549	0.994	0.1–100	0.015	1.362	0.997	0.1–100	0.01
2-Butanone	0.219	0.988	0.5–100	0.12	0.209	0.995	0.5–100	0.13
Butanal	1.440	0.993	0.1–100	0.015	1.212	0.999	0.1–100	0.02
2-Pentanone	0.163	0.996	0.5–100	0.20	0.199	0.991	0.5–100	0.18
3-Methylbutanal	3.039	0.995	0.1–100	0.008	3.385	0.994	0.1–100	0.006
2-Butenal	0.702	0.996	0.1–100	0.03	0.609	0.992	0.1–100	0.04
Pentanal	0.882	0.998	0.1–100	0.02	1.062	0.989	0.1–100	0.02
2-Methylpentanal	1.247	0.997	0.1–100	0.02	1.437	0.997	0.1–100	0.01
Hexanal	0.693	0.995	0.1–100	0.035	0.807	0.994	0.1–100	0.025
2-Hexenal	1.093	0.986	0.1–100	0.02	1.285	0.986	0.1–100	0.015
Heptanal	0.413	0.995	0.1–100	0.045	0.505	0.999	0.1–100	0.04
2-Heptenal	0.698	0.982	0.1–100	0.03	1.098	0.985	0.1–100	0.02
Octanal	0.301	0.998	0.1–100	0.06	0.631	0.990	0.1–100	0.03
Benzaldehyde	2.990	0.995	0.1–50	0.008	1.076	0.990	0.1–50	0.02
Nonanal	0.354	0.995	0.1–100	0.07	0.472	0.990	0.1–100	0.05
Decanal	0.301	0.996	0.1–100	0.08	0.332	0.997	0.1–100	0.07
Glyoxal	2.680	0.999	0.1–50	0.01	0.043	0.988	0.5–50	0.5
Methylglyoxal	2.916	0.999	0.1–50	0.01	0.102	0.984	0.5–50	0.3

Water volume was 4 ml. Sampling time was 30 min with magnetic stirring. R^2 was the linear correlation coefficient. Eight plots with different concentrations (0.1–100 μg/l) of each compound were used.

propenal, 2-butanone and 2-pentanone (0.5–100 μg/l), benzaldehyde (0.1–50 μg/l), glyoxal and methylglyoxal (0.5–50 μg/l). The relatively short linear range for the analysis of glyoxal and methylglyoxal using liquid SPME may be caused by higher electronegativity and extractability of the PEBHA derivatives of these two compounds. For headspace SPME, the PFBHA derivatives of glyoxal and methylglyoxal showed a very low extractability due to their low volatility. Thus, the relatively short linear range for the analysis of these two compounds may be caused by competitive adsorption on the SPME fiber by other PFBHA derivatives under high concentrations. The LODs in Table 3 were estimated by comparing the GC–ECD area counts of a sample spiked at 0.5 μg/l level to a peak threshold of 3000, which was arbitrarily chosen according to the instrument's noise. For most carbonyl compounds tested in this study, the LODs by liquid SPME and headsapace SPME were similar and ranged from 0.006 to 0.2 μg/l, with the exception of glyoxal and methylglyoxal, for which the LODs by headspace SPME (0.3 and 0.5 μg/l, respectively) were much higher than those obtained by liquid SPME (0.01 μg/l). These LODs were achieved using only 4 ml of water sample and generally one to two orders of magnitude lower than those obtained via PFBHA derivatization–LLE method [6].

3.3. Comparison of SPME with LLE

The reliability of SPME–GC–ECD techniques for the determination of carbonyl compounds in water was checked by the analysis of an ozonated drinking water and by comparison with the conventional LLE–GC–ECD method. The concentrations of carbonyl compounds determined in an ozonated drink-

Table 4
Carbonyl compounds in an ozonated drinking water sample determined by PFBHA derivatization and SPME or LLE methods

No.	Compound	Liquid SPME–GC–ECD		Headspace SPME–GC–ECD		LLE–GC–ECD	
		Concentration (μg/l)	R.S.D. (%)	Concentration (μg/l)	R.S.D. (%)	Concentration (μg/l)	R.S.D. (%)
1	Formaldehyde	9.72	16.5	9.28	14.1	11.0	2.7
2	Acetaldehyde	4.30	9.6	5.19	8.2	4.4	4.3
3	Acetone	2.71	17.2	2.33	15.1	3.1	7.1
4	Propanal	0.44	8.3	0.51	9.2	0.6	6.3
6	Isobutanal	0.24	8.1	0.32	7.4	ND	
7	2-Butanone	0.39	12.5	0.48	14.1	0.6	5.6
8	Butanal	0.42	7.7	0.33	9.8	0.5	8.6
10	3-Methylbutanal	0.11	10.9	0.07	9.2	ND	
12	Pentanal	0.34	8.3	0.22	6.1	ND	
14	Hexanal	0.27	7.9	0.36	8.7	ND	
16	Heptanal	0.39	8.7	0.58	7.2	0.6	8.2
18	Octanal	0.26	16.8	0.41	14.7	ND	
19	Benzaldehyde	0.036	11.2	0.03	17.4	ND	
20	Nonanal	0.98	14.3	1.36	13.7	1.4	6.5
21	Decanal	2.63	11.2	3.13	10.9	2.6	7.2
22	Glyoxal	2.45	10.9	3.1	13.6	3.5	6.7
23	Methylglyoxal	0.38	17.3	0.4	24.1	ND	

Concentrations determined using liquid or headspace SPME were based on the external standard method. Concentrations determined using LLE were based on the internal standard method. R.S.D. values were obtained from four determinations for each method. ND, not detectable.

ing water using SPME from liquid or from headspace, and LLE are reported in Table 4, while Fig. 5 shows the typical chromatograms obtained by liquid SPME (top) and headspace SPME (bottom). The concentrations obtained with liquid SPME were comparable with those obtained with headspace SPME. The advantage in the use of headspace SPME is that much cleaner extracts can be obtained, as evidenced by comparing the chromatograms in Fig. 5. The data in Table 4 show that for all carbonyl compounds determined both by SPME techniques and the LLE method, the concentrations obtained with SPME were in good agreement with those obtained by LLE. The LODs with LLE–GC–ECD for the tested carbonyl compounds are between 0.5 to 1.0 μg/l. Therefore, some carbonyl compounds such as pentanal, hexanal, heptanal, octanal, benzaldehyde, methylglyoxal, detected by SPME–GC–ECD methods at concentrations less than 0.5 μg/l, were not detected with the LLE method.

R.S.D. data in Table 4 show that the precision of the SPME methods was not as good as that obtained with the LLE method. For the SPME techniques, 10 of 17 detected compounds had R.S.D. values exceeding 10%, whereas for the LLE technique, all detected compounds gave an R.S.D. of less than 9%. The SPME sampling was performed under nonequilibrium conditions (30 min extraction time) for most of the analytes tested in this study. Under nonequilibrium conditions, the variations of the mixing conditions could have a significant influence on the precision of the SPME method. In fact, we found that the mixing conditions, especially the position of the SPME fiber in the sample vial and the stirring conditions, were difficult to keep constant throughout the experiment. This may be the main contributing factor to the relatively poor precision obtained by SPME methods in this study. This problem could be reduced by sampling under equilibrium conditions, by automating the whole process, or by using internal standard (I.S.). Using an I.S., such as 4-fluorobenzaldehyde, we observed that the precision of SPME techniques could be improved significantly. Before derivatization, 4-fluorobenzaldehyde, was added to the spiked bidistilled water samples at 10 μg/l, and then derivatized with PFBHA and analyzed using SPME as described in Section 2.3. Table 5 summarizes the R.S.D. data calculated from seven

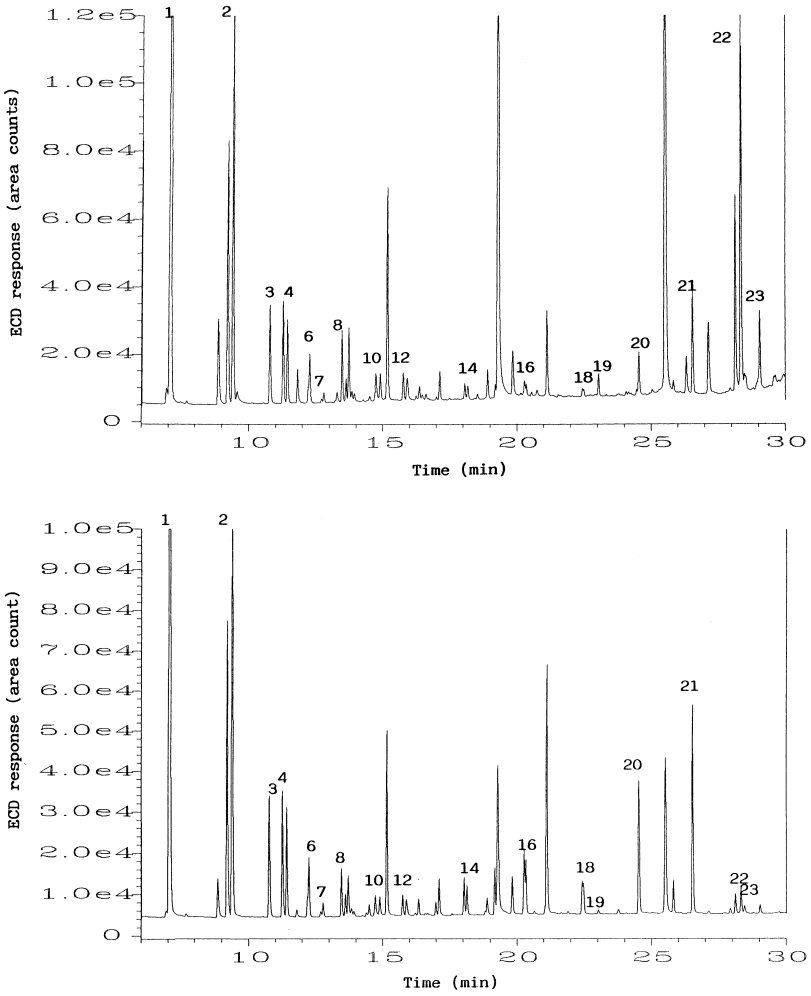

Fig. 5. Typical GC–ECD chromatograms of an ozonated drinking water sample after PFBHA derivatization and liquid (top) or headspace (bottom) SPME. Numbered peaks are identified in Table 4.

consecutive determinations using an internal standard and liquid or headspace SPME technique. By comparing the data in Tables 1, 2 and 5, the precision of the SPME techniques using the I.S. method was much better than the SPME techniques based on the external standard method. Using the I.S., all analytes had R.S.D. values of less than 10%, with the exception of the formaldehyde (13.1% for liquid SPME and 14.8% for headspace SPME), acetone (12.8% for liquid SPME and 14.1% for headspace SPME), and methylglyoxal (12.2% for headspace SPME), whereas using the external standard method, 9 and 10 compounds exhibited R.S.D. values exceeding 10% when using liquid SPME and headspace SPME, respectively.

The PFBHA derivatization–liquid or headspace SPME–GC–ECD procedure may be easily performed automatically by a simple modification of a conventional GC autosampler, as other papers described [21,27]. This automated system will further improve the precision of the method and will also make the method simple, rapid, and ideal for routine analysis of carbonyl compounds in different environmental water samples. For this purpose, after about 280 extractions (including ~180 extractions performed in spiked bidistilled water samples and

Table 5
Precision achieved with PFBHA derivatization–liquid or headspace SPME–GC–ECD and using the internal standard method for the tested carbonyl compounds spiked in bidistilled water

Compound	R.S.D. (%)	
	Liquid SPME–GC–ECD	Headspace SPME–GC–ECD
Formaldehyde	13.1	14.8
Acetaldehyde	7.7	9.1
Acetone	12.8	14.1
Propanal	6.5	7.8
Propenal	8.6	7.9
Isobutanal	6.7	5.4
2-Butanone	9.2	7.8
Butanal	6.4	7.7
2-Pentanone	9.3	9.8
3-Methylbutanal	5.8	5.4
2-Butenal	8.3	7.9
Pentanal	7.3	6.1
2-Methylpentanal	5.7	7.3
Hexanal	5.9	6.2
2-Hexenal	7.4	6.7
Heptanal	6.7	7.2
2-Heptenal	5.3	5.9
Octanal	9.2	8.9
Benzaldehyde	6.6	9.1
Nonanal	8.9	7.2
Decanal	7.4	8.3
Glyoxal	6.7	8.9
Methylglyoxal	9.8	12.2

Spiking level was 5 μg/l. R.S.D. values were based on seven determinations for each method using 4-fluorobenzaldehyde as internal standard.

~100 extractions performed in real water samples), the extraction efficiency and precision of the SPME fiber were evaluated by carrying out repeated analyses of an ozonated drinking water spiked at 5 μg/l of each tested carbonyl compound. The obtained relative recoveries and precisions compared well with those reported in Tables 1 and 2. Thus, it appeared that the SPME fiber could be used for more than 280 extractions.

4. Conclusions

The results of this study demonstrate that the PFBHA derivatization–liquid or headspace SPME–GC–ECD procedure produced acceptable precision data for the quantitative analysis of carbonyl compounds in environmental water samples. The high sensitivity achieved using only 4 ml water sample makes this method attractive for the trace determination of carbonyl compounds in different natural waters, especially when the sample volume is limited as in the case of rain and cloud water samples. For water samples containing relatively high levels of carbonyl compounds, a smaller sample volume or a much shorter sampling time may be used for quantitative analysis. Furthermore, the potential of automation of the entire analysis makes the proposed method well suited for routine analysis of carbonyl compounds in aqueous samples.

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