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Optimization of solid-phase extraction method for analysis of low-ppb amounts of aldehydes-ozonation by-products

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Abstract

Ozonation is commonly used in drinking water treatment technology. Ozone reacts with natural organic substances present in water to produce a number of by-products. Aldehydes are the important class of ozonation byproducts due to their health effects. The determination of aldehydes in water by conventional analytical techniques is difficult because they are polar, unstable and exist at low concentration. A modern method for the determination of aldehydes in drinking water applies derivatization with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBOA) and liquid–liquid extraction (LLE). The objective of this study was to improve the method by application of solid-phase derivatization and extraction. C_{18}, C_{18}polar plus and Phenyl Baker SPE sorbents were used for simultaneous derivatization and enrichment of aldehydes. Detection limits with GC–electron-capture detection technique were in the low ppt range.

Keywords: Ozonation; Water analysis; Derivatization, GC; Extraction methods; Aldehydes

1. Introduction

Ozone produces a variety of by-products which are more polar, more oxidized, more hydrophilic and more biodegradable than their precursors. Carboxylic acids and aldehydes represent the most important classes of ozonation by-products [1,2]. Aldehydes are major disinfection by-products formed as a result of oxidation of organic contaminants in waters. The formation of aldehydes after ozonation is important due to their health effects. Many of them have been shown to cause cancer or to be suspected carcinogens [3–13].

Analysis of aldehydes in water is very difficult due to low concentrations (ng–μg/l) and high polarity [14–19]. There are colorimetric and chromatographic methods of aldehyde determination. The MBTH method adapted from Mattews and Howell [20] is used in Hach test procedure. Numerous substances (eg. ammonium, bicarbonate, calcium, carbonate, aniline, chloride, copper, iron, manganese, nitrate, nitrite, and other aldehydes) can interfere with the results.

Aldehydes can be determined chromatographically after prior derivatization: with DNPH (2,4-dinitrophenylhydrazine) by HPLC or with PFBOA by GC.

Possanzini and DiPalo [21] have described a method of olefinic aldehyde determination in ambient air by passing the matrix through the DNPH-coated C_{18} cartridges. Another method of analysis for aldehydes and other carbonyl compounds was originally described by Yamada and Somiya [14] and

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improved by Glaze et al. [19]. The method is based on the PFBOA-derivatization in aqueous phase and appears to be satisfactory and sensitive enough to detect aldehydes in water in ppb quantities [14,15,18,19]. The derivatizing reagent reacts with carbonyls to form the corresponding oximes. With most of the aldehydes, two geometric isomers are formed (*E* and *Z*), except for symmetrical carbonyls (e.g. formaldehyde) [19].

Growing popularity of the solid-phase extraction (SPE) technique for determination of organic micropollutants can be recently observed [22–24]. Chemically bonded silicas, usually with C_8 and C_{18} organic groups, are the most commonly used materials for SPE.

We have designed a similar (to Possanzini and DiPalo [21]) setup with PFBOA as impregnating reagent for determination of aldehydes-ozonation by-products from water. By using Baker sorbents and a room temperature for derivatization, acceptable recovery and shortening of analysis time have been obtained.

2. Experimental

2.1. Chemicals

Analytical standards used in the experiments were obtained from Aldrich-Chemie (Steinheim, Germany), and BDH (Poole, UK; AnalaR and GPR grades). Aldehyde solutions were prepared in methanol from pure compounds and then diluted with bidistilled water to prepare standard solutions (0.1–5 μg/l). The derivatizing agent: O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBOA) was obtained from Aldrich and prepared gravimetrically as an aqueous solution in bidistilled water. *n*-Hexane (Merck, Darmstadt, Germany) was used as a solvent for extraction. The 500-mg C_{18}, C_{18} polar plus and phenyl silica SPE cartridges were obtained from J.T. Baker.

2.2. Aqueous-phase derivatization with PFBOA

Aqueous-phase derivatization of aldehydes consists of the following steps: (1) PFBOA solution is added to the analyzed water, (2) the mixture is heated to 45°C for 2 h, (3) the aqueous phase is extracted with *n*-hexane.

Water samples were collected in glass vials with glass caps and acidified with concentrated sulfuric acid (to pH 2). A 1-ml volume of a 1 mg/ml aqueous PFBOA–HCl solution was added to 50 ml of water in glass vial and the mixture was heated at 45°C for 2 h. After derivatization the sample was allowed to cool to room temperature for 15 min. The derivatives were extracted with 2 ml of *n*-hexane. The extract volume was reduced to 1 ml and analysed by GC–electron-capture detection (ECD).

2.3. Solid-phase derivatization with PFBOA

The derivatization in SPE bed consists of three steps: (1) the sorption of appropriate amount of PFBOA on the SPE bed, (2) the reaction between the reagent and the analytes in aqueous phase passing through the bed, (3) the elution of the oximes from the SPE bed with *n*-hexane.

Solid-phase extraction was carried out with J.T. Baker SPE-12G system. J.T. Baker SPE cartridges were used throughout. Prior to their initial use, columns were cleaned by passing through 3 ml of methanol. Subsequently, 2 ml of a 1 mg/ml aqueous PFBOA–HCl solution were added as derivatization reagent. Then 6 ml of bidistilled, acidified water (pH 2) was passed through. 50 ml of water sample of pH 2 was spiked with standard solution of aldehydes and then forced through the bed at a sample flow-rate of 2 ml/min. The column was then washed with bidistilled water and air was blown through the column for 10 min to dry the bed. A 2-ml volume of *n*-hexane was used for elution. The extract volume was reduced to 1 ml and analysed by GC–ECD.

2.4. LLE and SPE results

The recovery of LLE method is reported in literature as 80–98% [15,18]. However the exact values are extremely difficult to find (particularly for low ppb concentration) since it is impossible to determine directly underivatized aldehydes at low ppb amounts. That is why we have assumed a LLE recovery as 100% and the results of SPE are always presented in relation to LLE. Thus recovery values higher than 100% mean that SPE recovery is better

than LLE recovery and vice versa. Two factors determine the recovery of aldehydes in both methods: (1) completeness of the derivatization reaction, (2) degree of the extraction

2.5. GC-ECD analysis of PFBOA–oximes

Extracts were analysed by using GC 6000 and GC 8000 series (Fisons Instruments) equipped with ^{63}Ni electron capture detector. The analytical column was a DB-5 (J and W) fused-silica capillary column (30 m×0.32 mm, 0.25 μm film) and the confirmation column was a Rtx-1301 (Restek) fused-silica capillary column (30 m×0.32 mm, 0.5 μm film). Helium and nitrogen were used as a carrier gas and a detector make-up gas. The temperature program for GC was as follow: 80°C isothermal for 4 min, increase to 240°C at 5°C/min, then increase to 270°C at 20°C/min, hold at 270°C for 5 min. Chrom-Card system for collection and processing the chromatographic data was used. Table 1 lists the retention times and method detection limits for the aldehydes in form of PFBOA–oximes, Fig. 1 presents their chromatograms.

Table 1
Retention times and method detection limits for the derivatized aldehydes

Compounds (oximes of aldehydes)	t_R (min)		Method detection limit (μg/l)
	DB-5 column	Rtx-1301 column	
Formaldehyde (HCH–PFBO)	5.75	7.18	0.01
Acetaldehyde	8.30	9.85	0.005
(*E*/*Z*-CH_3CH–PFBO)	8.50	10.10	
Propanal	10.77	12.30	0.007
(*E*/*Z*-C_2H_5CH–PFBO)	10.97	12.52	
Hexanal	18.50	19.97	0.01
(*E*/*Z*-$C_5H_{11}CH$–PFBO)	18.65	20.12	
Heptanal	20.96	22.40	0.01
(*E*/*Z*-$C_6H_{13}CH$–PFBO)	21.05	22.50	
Octanal	23.33	24.73	0.01
(*E*/*Z*-$C_7H_{15}CH$–PFBO)	23.40	24.82	
Benzaldehyde (C_6H_5CH–PFBO)	23.94	25.86	0.02
Nonanal (*E*/*Z*-$C_8H_{17}CH$–PFBO)	25.65[a]	27.04[a]	0.02
Decanal (*E*/*Z*-$C_9H_{19}CH$–PFBO)	27.82[a]	29.18[a]	0.006
Glyoxal (*E*/*Z*-PFBO–HCCH–PFBO)	29.60 29.80	31.72 31.90	0.006

[a] The *E*- and *Z*-PFBO isomers co-elute from the column.

2.6. Evaluation of reagent water

We have found it extremely difficult to obtain a satisfactory laboratory reagent water for preparing standards of aldehydes. Therefore, determination of aldehydes in reagent water is very important. The chromatogram data of formaldehyde, acetaldehyde and glyoxal identified in organic pure, bidistilled and distilled waters are presented in Fig. 2. We observed high background of aldehydes in laboratory reagent water. Even organic pure water is polluted with formaldehyde and acetaldehyde (Table 2). Thus our results confirm the observation of Sclimenti et al. [18]. The reason for this phenomenon is not obvious. Sclimenti et al. suggest that formaldehyde and acetaldehyde are air pollutants.

3. Results and discussion

The objective of this study was to develop the SPE technique as an alternative to the aldehyde determination. The effect of amount of derivatizing agent (PFBOA) on the results of aldehyde recovery in SPE method was investigated first. A 2-mg amount of PFBOA appeared to be a sufficient dose to obtain acceptable yield of derivatization process. Possazini and DiPalo used 4 mg DNPH/cartridge for determination of aldehydes [21]. The results show that there is no need to increase PFBOA amount over 2 mg on the cartridge.

Table 3 shows the correlation coefficients and slopes of calibration curves for derivatives of aldehydes determinated by LLE and SPE (C_{18} sorbent). It is noted that linearity for LLE and SPE method is high (about 0.99) for concentration range 0.1–5 μg/l and detection by SPE is better in this range of concentration.

Higher "slope value" means better detectability of the PFBOA derivative. The slopes are exceptionally high for acetaldehyde and propanal and generally are higher for SPE method.

C_{18}, C_{18} polar plus and Phenyl Baker sorbents were used for enrichment of aldehydes by solid phase extraction. The comparison of those different

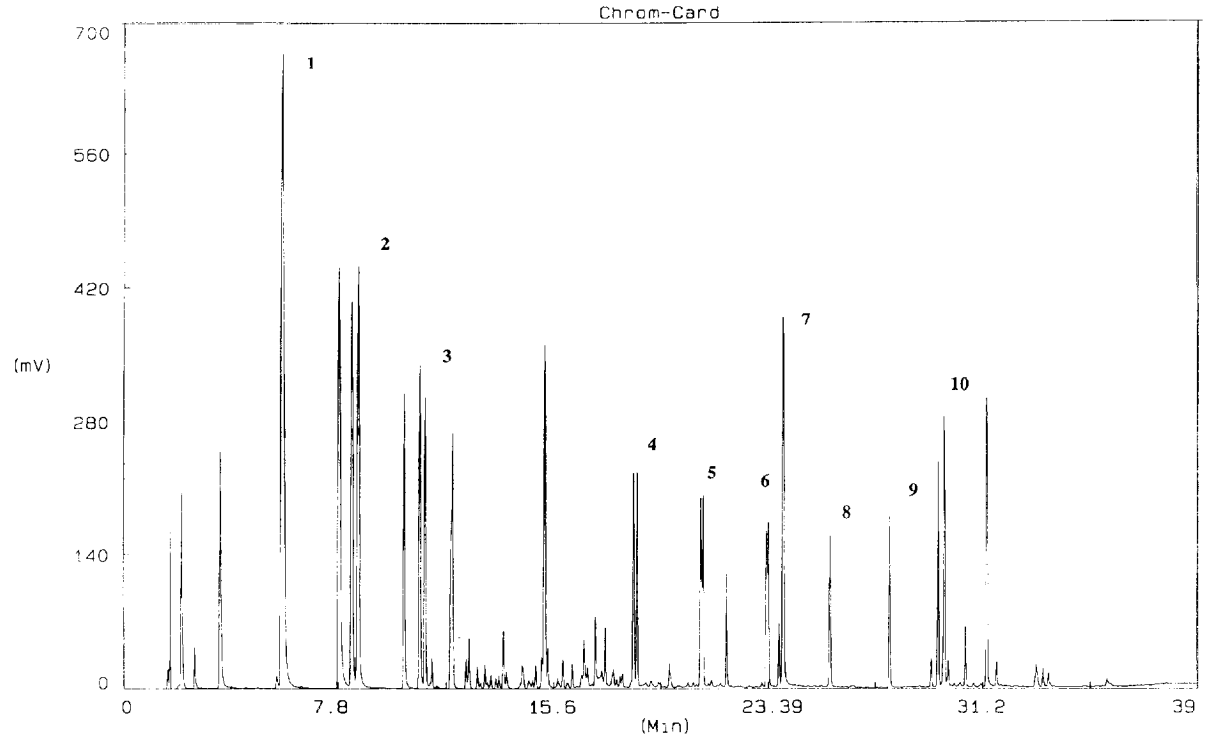

Fig. 1. Chromatogram of aldehydes in form of PFBOA–oximes. 1=formaldehyde, 2=acetaldehyde, 3=propanal, 4=hexanal, 5=heptanal, 6=octanol, 7=benzaldehyde, 8=nonanal, 9=decanal, 10=glyoxal.

types of sorbents is shown in Table 4. Higher recoveries are obtained for C_{18} sorbent for propanal, octanal, nonanal and decanal. However for formaldehyde, acetaldehyde, hexanal, and heptanal C_{18} polar plus sorbent is better. Phenyl sorbent appears to be less useful for determination of aldehydes by SPE method.

Table 4 should not be understood straightforward. The data presented in Table 4 are relative to the recoveries observed in LLE. The results for acetaldehyde, propanal, nonanal and decanal (higher than 100%) mean that the recovery in SPE method is higher than that in LLE method.

The SPE method for determination of aldehydes can compete with LLE method. The derivatization in water (LLE method) proceeds for 2 h at 45°C. In SPE method the reaction of derivatization runs directly in the sorbent bed at ambient temperature. The whole SPE process takes about half of the time of the LLE process.

Generally, higher recoveries of aldehydes are obtained in the new SPE method compared to the LLE method. Surprisingly high results were obtained for acetaldehyde and propanal. They mean that the recovery of acetaldehyde and propanal in the LLE method is lower than stated before [15,18]. Authors must add here that the direct calculation of recovery for aldehydes, especially for first members of homologous series is very difficult due to volatility of acetaldehyde and propanal. The best aldehyde recovery by SPE was achieved for acetaldehyde, propanal, nonanal and decanal comparing to LLE result. In general, recovery rates are satisfactory.

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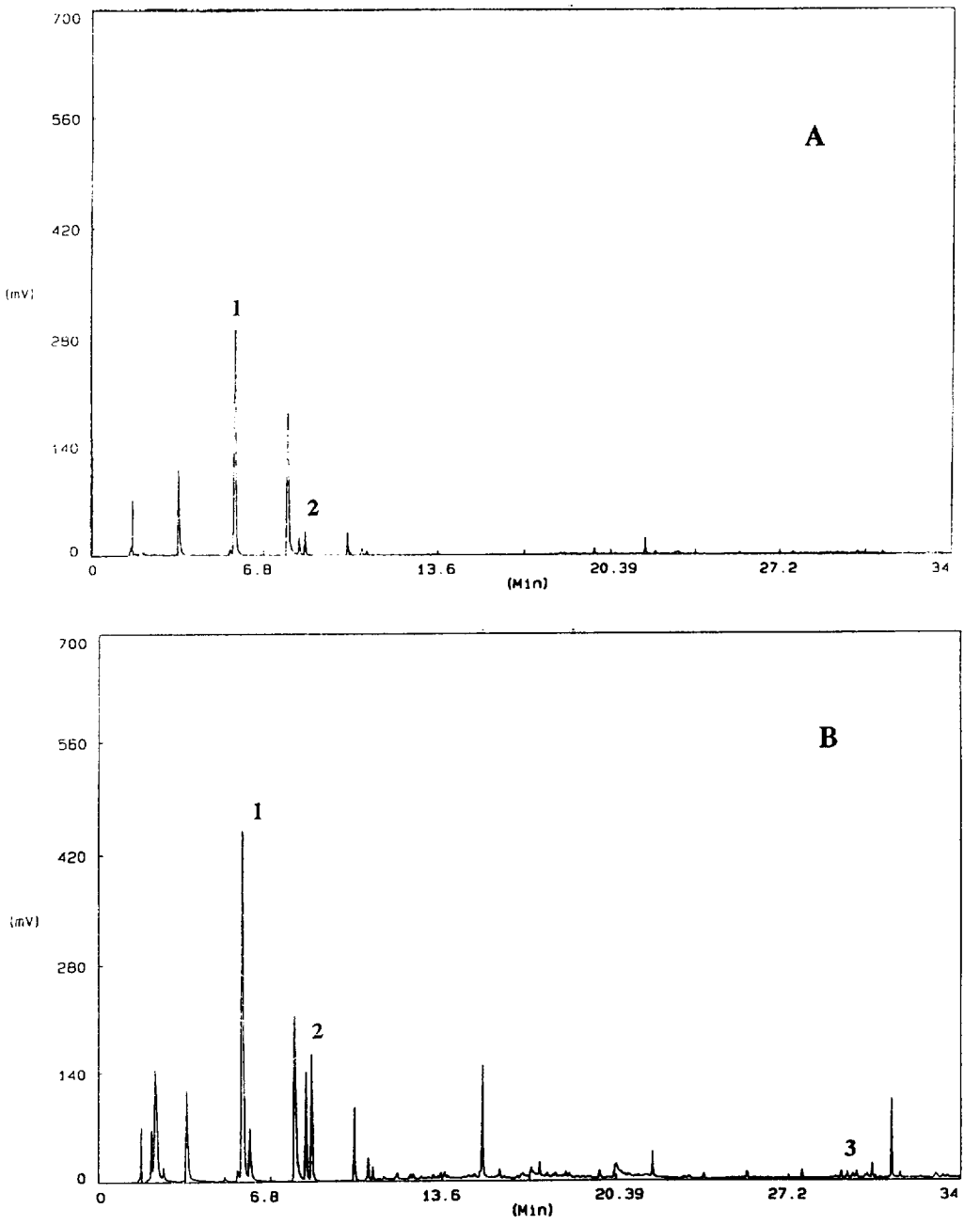

Fig. 2. Chromatogram of aldehydes identified in (A) organic pure water, (B) bidistilled water and (C) distilled water. 1=formaldehyde, 2=acetaldehyde, 3=glyoxal.

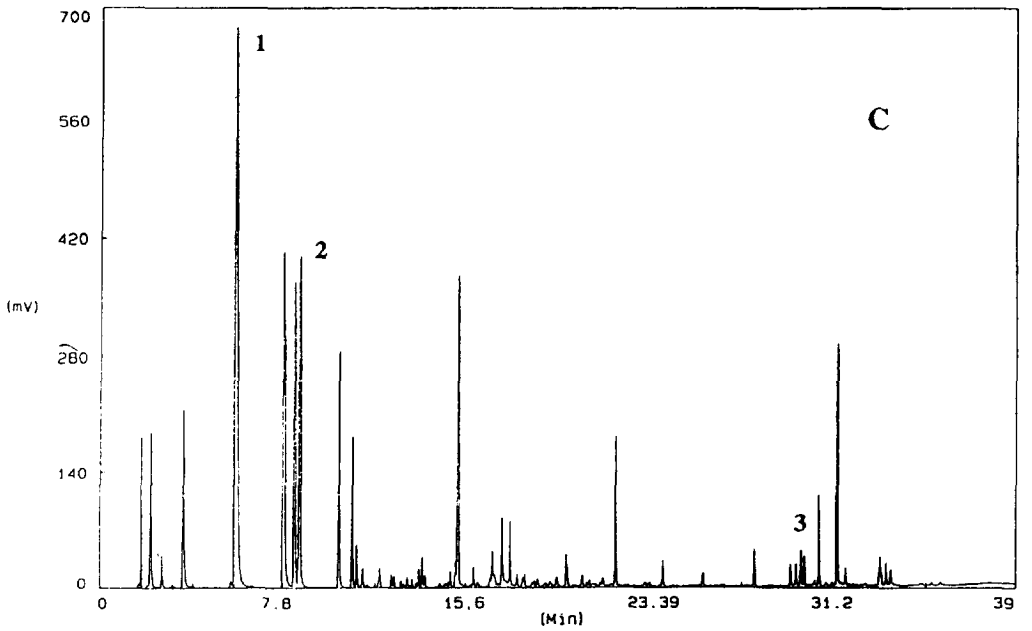

Fig. 2. (*continued*)

Table 2
Evaluation of aldehyde concentration in three laboratory waters

	Formaldehyde (μg/l)	Acetaldehyde (μg/l)	Glyoxal (μg/l)
Organic pure water	0.7	0.2	–
Bidistilled water	1.5	0.2	0.1
Distilled water	3.9	3.0	0.9

Table 3
Linearities and slopes of calibration curves for derivatives of aldehydes determined by LLE and SPE methods

Aldehyde	LLE		SPE	
	Slope (S.D.)	Linearity	Slope (S.D.)	Linearity
Formaldehyde	8.6 (1.3)	0.987	8.9 (1.4)	0.981
Acetaldehyde	6.4 (0.4)	0.993	12.2 (1.0)	0.976
Propanal	7.1 (0.6)	0.985	13.8 (1.0)	0.996
Hexanal	7.3 (0.7)	0.998	7.2 (0.6)	0.997
Heptanal	7.4 (0.5)	0.997	7.1 (0.5)	0.993
Octanal	8.2 (0.8)	0.997	8.1 (0.7)	0.985
Nonanal	6.1 (0.6)	0.996	8.4 (0.5)	0.979
Decanal	5.8 (0.4)	0.995	9.8	0.996

S.D.=standard deviation, n=4.

Table 4
Relative aldehyde recovery for various types of SPE cartridges

Compounds	Relative recovery (%) (S.D.)		
	C_{18}	C_{18} polar plus	Phenyl
Formaldehyde	63.4 (10.0)	82.3 (12.5)	47.6 (1.0)
Acetaldehyde	106.9 (7.0)	115.6 (9.9)	76.6 (1.0)
Propanal	214.1 (16.3)	198.5 (13.4)	167.5 (2.0)
Hexanal	45.8 (4.0)	73.3 (6.4)	16.4 (1.0)
Heptanal	56.2 (4.2)	65.6 (9.3)	26.9 (2.12)
Octanal	80.0 (7.1)	75.8 (13.7)	55.6 (5.8)
Nonanal	123.5 (7.8)	113.6 (12.7)	88.8 (2.3)
Decanal	143.1 (7.1)	125.4 (7.8)	115.6 (7.9)

S.D.=standard deviation, $n=4$.

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