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Improved solid-phase extraction/micellar procedure for the derivatization/preconcentration of benzaldehyde and methyl derivatives from water samples

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ABSTRACT

A simple, rapid and sensitive method has been developed for the determination of aromatic low-molecular mass aldehydes (LMMAs) such as benzaldehyde (BA) and methyl derivatives in water samples through the use of liquid chromatography–diode array detection (LC–DAD). The method is based on the continuous *in situ* derivatization of the aldehydes with 2,4-dinitrophenylhydrazine (DNPH) on a LiChrolut EN solid-phase extraction (SPE) column in the presence of sodium dodecyl sulfate (SDS) micelles. After elution, hydrazones were successfully separated on a RP-C_{18} column using a linear gradient mobile phase of acetonitrile (ACN)–water at 75–95% ACN for 10 min. Linearity was established over the concentration range 0.4–200 $\mu g\,L^{-1}$ and limits of detection (LODs) from 120 to 200 $ng\,L^{-1}$; the inter-day precision expressed as the relative standard deviation (RSD) of the aldehydes ranged from 3.0% to 3.5%. The method was successfully applied to the analysis of aromatic and aliphatic LMMAs in water samples with average recoveries ranging between 93.6% and 99.5%. The proposed method surpasses other chromatographic alternatives in terms of LODs, sample requirements for analysis and cost.

1. Introduction

Aldehydes are one of the most important classes of organic compounds that are known for toxicity and carcinogenic properties, hence the increased interest in their analysis in recent years. These carbonyl compounds are present in the atmosphere as a primary source of pollutants derived from industrial processes and vehicular exhaust, and are produced furthermore as secondary pollutants of the photooxidation of atmospheric hydrocarbons [1–4]. Because aldehydes are water soluble, they are deposited on the ground and the sea surface as rain, which constitutes an important removal mechanism for these compounds that can influence ecosystem health [5–7]. The presence of these compounds has been reported in natural waters due to the photochemical degradation of dissolved oxygen matter [8,9] and more recently in drinking waters as disinfection by-products produced primarily from organic matter present in water after treatment with ozone [5,10–12]. In addition, various aldehydes are also recognized as potential indicators of lipid oxidation in food [13,14] and as diagnostic markers of cancer status [15–17]. In view of the widespread presence of these compounds, accurate aldehyde measurements are important both on order to study the formation mechanism of aldehydes and to evaluate their implications for human health.

The direct determination of LMMAs is complicated due to their high polarity, chemical instability, volatility and the absence of a chromophore or fluorophore group in their chemical structure. In view of all these worrying peculiarities, derivatization reactions are required prior to their detection by chromatographic techniques. Although a variety of derivatizing reagents have been reported for this purpose, 2,3,4,5,6-(pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) [18–25] and DNPH [26–39] are the most widespread choices for gas chromatography (GC) and LC analysis, respectively. Both derivatizing reagents are included in the U.S. Environmental Protection Agency (EPA) Methods 556.1 and 8315A for the determination of free carbonyl compounds in various matrices [40,41]. Over recent years, LC-DNPH methods are increasingly being viewed as a useful alternative to GC-PFBHA ones for the determination of these aldehydes in liquid samples, particularly in waters [34–39]. Aromatic LMMAs have scarcely been determined in water samples even though interest in the analysis of aldehydes has increased significantly in recent years because human are becoming more and more exposed to contaminated waters. To our knowledge, no reference has been reported for the determination of aromatic aldehydes in water samples by LC using DNPH. Recently, the analysis of BA in spiked water samples has been the subject of two sporadic studies [34,37].

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In the present work, a rapid and sensitive method for the determination of aromatic LMMAs by LC-DAD is developed based on the combination of an efficient SPE system with a SDS micellar medium for the *in situ* derivatization of aldehydes with DNPH. In previous works [35,36], we have determined aliphatic LMMAs at microgram-per-litre levels in waters after their *in situ* derivatization/preconcentration with DNPH using a continuous-flow SPE approach by LC with UV [35] and mass spectrometric (MS) [36] detection. In this work, a micellar medium for improving the efficiency of the DNPH derivatization process is presented and the SPE approach is extended to the analysis of aromatic LMMAs in water samples. To our knowledge, this study constitutes the first report on the enhancing effect of micelles on the DNPH derivatization of aldehydes. BA, 3-methylbenzaldehyde (3-MBA) and 2,5-dimethylbenzaldehyde (2,5-DMBA) have been selected in this study because they are included as target analytes in the list provided by EPA Methods 556.1 and 8315A [40,41] for the determination of carbonyl compounds in air and water samples.

2. Materials and methods

2.1. Standards and solutions

All solvents and reagents were of analytical grade and used without further purification. Water was purified using an Elix-3 electrodeionization station coupled with a Milli-Q Simplicity water purification system (Millipore Ibérica S.A., Madrid, Spain). BA (≥99.0% purity), 3-MBA (≥97% purity), 2,5-DMBA (≥99% purity) and 2-methyl-1-nitronaphthalene (≥99% purity), as an internal standard (IS), were supplied by Aldrich (Sigma–Aldrich Química, Madrid, Spain). Formaldehyde (C1, 37% w/v solution in water) and acetaldehyde (C2, ≥99.5% purity) were supplied by Sigma (Sigma–Aldrich Química), whereas propionaldehyde (C3, ≥96% purity), butyraldehyde (C4, ≥99% purity) and valeraldehyde (C5, ≥97% purity) were acquired from Fluka (Sigma–Aldrich Química). Standard stock solutions of each carbonyl compound and the IS with a concentration of 4000 μg mL^{-1} were prepared by dissolving an appropriate amount in chromatographic grade methanol (Romil Chemicals, Cambridge, UK); standard mixtures of the analytes were prepared daily by dilution of the corresponding stock solutions with purified water as required. Stock DNPH (≥99% purity, Fluka, Sigma–Aldrich Química, Madrid, Spain) solution, 60 mmol L^{-1}, was made by dissolving 594.4 mg of the derivatizing reagent in 50 mL of concentrated hydrochloric acid:water:ACN solution (2:5:1). A solution containing 0.25 mg mL^{-1} (1.25 mmol L^{-1}) DNPH was prepared by appropriate dilution of the stock solution with purified water. All standard, DNPH and IS solutions were stored at 4 °C. LiChrolut EN (particle size 40–120 μm, surface area ~1200 m^2 g^{-1}) was provided by Merck (Darmstadt, Germany). SDS, polyethylene glycol tert-octylphenyl ether (Triton X-100), and polyoxyethylene (23) lauryl ether (Brij 35) were purchased from Fluka whereas cetyl trimethylammonium bromide (CTAB) was supplied by Sigma. Other solvents and chemicals were purchased from Romil Chemicals and Merck.

2.2. Derivatization/preconcentration of aldehydes

A schematic diagram of the setup of the continuous-flow SPE system used in this study for the *in situ* DNPH derivatization/preconcentration of aldehydes is given in Fig. 1. Initially, the laboratory-made sorption column (PTFE, 3 mm ID, 1.0 cm long) packed with 25 mg of LiChrolut EN sorbent material and located in the loop of the injection valve IV_1 (Rheodyne, Cotati, CA, USA) was conditioned with 1.0 mL of ACN and then 1.0 mL of purified water both delivered at a flow rate of 0.5 mL min^{-1} using a Minipuls-3 peristaltic pump (Gilson, Middleton, WI, USA) fitted with poly(vinylchloride) tubes. After conditioning, the SPE column was impregnated with 2.0 mL of 0.25 mg mL^{-1} DNPH solution at 1.0 mL min^{-1}. Then, a volume of 25 mL of standard solution or water sample with a concentration between 0.5 and 250 μg L^{-1} of aldehydes and 400 μg L^{-1} of IS in a 50 mmol L^{-1} SDS and 1.0 mol L^{-1} hydrochloric acid medium was continuously loaded into the system at 1.0 mL min^{-1} using the selecting valve (Rheodyne). The aldehydes were derivatized *in situ* with DNPH on the LiChrolut EN column and the sample matrix was sent to waste. Simultaneously, the loop of injection valve IV_2 (Rheodyne) was filled with the eluent by using a syringe. Prior to elution, by switching IV_1, residual aqueous solution inside the column and the connectors were flushed by passing an air stream through the carrier line of IV_2 at 0.5 mL min^{-1} for 2 min. In the elution step, IV_2 was switched and 100 μL of ACN, carried by an air stream at 0.5 mL min^{-1}, were passed through the column (upstream through the sample) to elute derivatives. The extract was collected in an eppendorf vial and 20 μL aliquot was injected into the LC. LiChrolut EN columns prepared sequentially provided analytical signals with similar DNPH derivative peak areas, which confirmed their high reproducibility. Under these experimental conditions, the SPE column was serviceable for about 6 months.

2.3. LC analysis

The LC system (Varian, Palo Alto, CA, USA) included a Varian 230 multisolvent pump and a Varian 335 DAD. A Rheodyne Model 7215 manual injection valve with a 20 μL sample loop was used for sample injection. Separations were performed on the Microsorb-MV 100-5 analytical column, 250 mm × 4.6 mm id, stainless steel tube packed with octadecylsilane and 5 μm particle sizes. The DAD was operated at 380 nm. DNPH-aldehydes were chromatographically separated with this LC system by using a linear ACN-water gradient 75–95% ACN in ca. 10 min circulated at 1.0 mL min^{-1}. Under these conditions, all derivatives were eluted within about 9 min. Chromatographic data (retention times and peak areas) were processed with a 6.41 Varian Star Chromatography Workstation interfaced to a PC compatible computer.

3. Results and discussion

3.1. Optimization of the in situ derivatization/preconcentration of aldehydes

The optimization of the continuous-flow SPE system used in this work for the cleanup, derivatization and preconcentration of aromatic LMMAs is based on one reported elsewhere by us for aliphatic LMMAs [35]. However, and because aromatic LMMAs have a smaller polarity and volatility than aliphatic ones, some variables have been re-optimized. So, the acidity of the aqueous sample, adjusted with hydrochloric acid, was studied in the 0.5–3.0 mol L^{-1} range. All aromatic LMMAs behaved similarly: the analytical signal showed a peak at about 1.0 mol L^{-1} hydrochloric acid over the range studied (see Fig. 2A), and therefore this concentration was selected as optimal. By comparing to aliphatic LMMAs, they require less acidity for DNPH derivatization (pH 1.5) [35]. This behaviour can be ascribed to the different charge distribution in the carbonyl group when comparing both types of LMMAs [42]. In fact, the C=O bond in aromatic LMMAs has a higher dipole moment and as a result, higher acidity is required for the protonation of carbonyl oxygen prior to the nucleophilic attack of the amine group of DNPH to form the corresponding hydrazone. The amount of DNPH was studied in the range of 0.1–1.0 mg by passing 2.0 mL of derivatizing reagent solution through the SPE system at a rate of 1.0 mL min^{-1}. Maximum analytical signals were obtained for DNPH amounts of

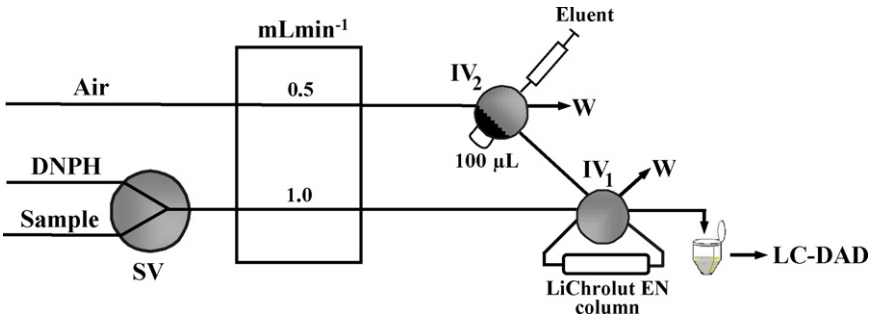

Fig. 1. Continuous-flow SPE system developed for the determination of aromatic LMMAs in water samples. IV, injection valve; SV, selection valve; W, waste.

Table 1
Characteristic parameters of the calibration equations and analytical figures of merit for the determination of aromatic and aliphatic LMMAs.

Aldehyde	Calibration equation[a]	r	Linear range[b] ($(g L^{-1})$)	LOD (μg/L)	RSD (%)
BA	$S=(0.181\pm0.003)C+(0.8\pm0.3)$	0.9993	0.4–200	0.12	3.3
3-MBA	$S=(0.153\pm0.001)C-(0.1\pm0.1)$	0.9994	0.5–200	0.15	3.0
2,5-DMBA	$S=(0.108\pm0.001)C+(0.4\pm0.2)$	0.9991	0.7–200	0.20	3.5
C2	$S=(0.225\pm0.003)C+(0.3\pm0.2)$	0.9990	0.3–200	0.10	9.1
C3	$S=(0.194\pm0.004)C-(0.3\pm0.2)$	0.9987	0.4–200	0.12	9.0
C4	$S=(0.124\pm0.004)C+(1.4\pm0.2)$	0.9982	0.6–200	0.18	8.6
C5	$S=(0.122\pm0.004)C+(2.1\pm0.2)$	0.9979	0.6–200	0.18	8.3

[a] S, analyte to the IS peak area; C, analyte concentration ($(g L^{-1})$).
[b] Sample volume, 25 mL.

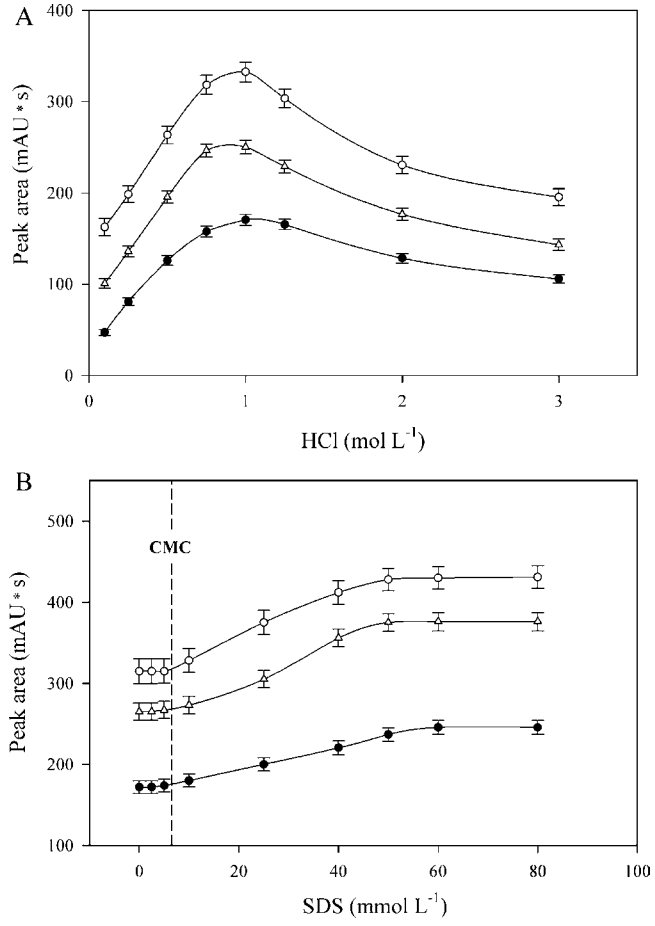

Fig. 2. Effect of (A) acidity of the sample solution and (B) SDS concentration on the derivatization of aromatic LMMAs. BA (○), 3-MBA (△) and 2,5-DMBA (●) at 50 μg L^{-1}. Sample volume, 10 mL. Other conditions as described in Section 2. Each data point represents an average of three individual runs and error bars indicate SD.

ca. 0.5 mg for all aldehydes and afterwards they remained practically constant. This amount of DNPH provided a DNPH to aldehydes molar ratio higher 30,000 for the lower concentrations in the linear ranges shown in Table 1. Other SPE variables studied were the organic solvent used as eluent and its volume, the flow-rate of the air stream used as carrier for the eluent and the amount of LiChrolut EN sorbent for which the following conditions were selected: eluent, 100 μL of ACN flowing at 0.5 mL min^{-1} by using an air stream; and sorbent material, 25 mg.

At this point and with the aim of increasing the sensitivity of the proposed method further experiments were carried out, such as the evaluation of the possible influence of surfactants on the derivatization of aromatic LMMAs and the determination of the breakthrough volume, which is simply a measure of the sample that may be passed through the sorbent before the aldehyde is no longer derivatized with DNPH. In the first instance, anionic (SDS), cationic (CTAB) and non-ionic (Triton X-100 and Brij 35) surfactants at concentrations below and above their respective critical micelle concentration (CMC) were added to the sample solution. From the results found, it can be concluded that nonionic micelles practically did not affect the peak area corresponding to each aldehyde derivative, whereas cationic micelles strongly interfered with the determination of aromatic LMMAs due to the presence of interfering peaks that co-eluted with those of BA and 3-MBA derivatives. Only SDS at concentrations higher than its CMC proved to be suitable to increase the sensitivity for the determination of aromatic LMMAs: the peak areas increased about 30–40% in the presence of this micellar medium at SDS concentrations over 50 mmol L^{-1} (see Fig. 2B), and therefore this concentration was chosen as the optimum. This influence can be ascribed to interactions between the benzene ring of the aromatic LMMAs and the micellar core, which could favour the protonation of carbonyl oxygen (rate-determining step for the formation of the hydrazones [42]) with the subsequent increase in the derivatization efficiency. Finally, the breakthrough volume was evaluated in order to attain the greatest enrichment factor. This study was carried out by adding 250 ng of each aldehyde in variable volumes of purified water, from 5 to 50 mL, in a 50 mmol L^{-1} SDS and 1.0 mol L^{-1} hydrochloric acid. Sample volumes up to 25 mL can be used with negligible changes

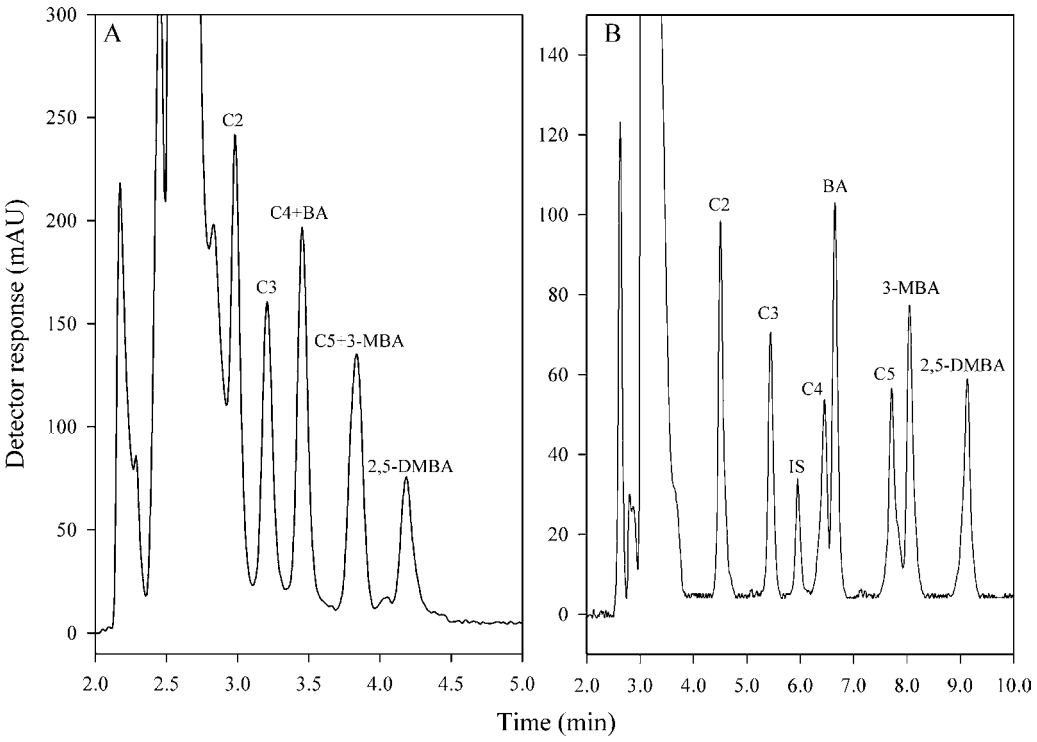

Fig. 3. Chromatograms for aromatic and aliphatic LMMAs using (A) an isocratic mobile phase of ACN-water (95:5 v/v), and (B) a linear gradient elution of ACN in water from 75 to 95% in ACN. Aldehyde concentration, 50 $\mu g\,L^{-1}$. Sample volume, 25 mL. Other conditions as described in Section 2.

in chromatographic signals, although only a decrease of ca. 15% was observed for the corresponding peak areas at higher sample volumes (up to 50 mL). In any case, a sample volume of 25 mL flowing at 1.0 mL min^{-1} was selected for further experiments, which provided a preconcentration factor of 250 for aromatic LMMAs, allowing their detection in water samples at ng L^{-1} levels.

3.2. Chromatographic optimization

The composition of the mobile phase and its flow rate were optimized in order to provide the most suitable conditions for LC determination of aromatic LMMA-DNPD derivatives. Because DNPH derivatives of aliphatic LMMAs were efficiently separated in a C_{18} column using gradient elution with ACN in water [36,38,41], this mobile phase composition was also assayed in this study. Thus and based on experimental results, an isocratic mobile phase of ACN-water (95:5 v/v) circulating at 1.0 mL min^{-1} was used to separate DNPH-aldehydes in ca. 5 min using a 5-μm analytical reversed-phase C_{18} column (25 cm × 4.6 mm). As can be seen in Fig. 3A, the elution order for DNPH derivatives of the aromatic LMMAs was consistent with the polar character of these compounds. With a view to applying the proposed method to the determination of these aromatic LMMAs in water samples, and bearing in mind the possible presence in these samples of aliphatic ones, some experiments were carried out to evaluate the possible effect of these aliphatic aldehydes on the chromatographic separation. Thus, mixtures of the most common aliphatic LMMAs found in waters (C1–C5 aldehydes) and the aromatic LMMAs were analyzed under optimum conditions and some of the peaks observed in the chromatogram co-eluted with those of aromatic aldehydes (see Fig. 3A). However, by using a linear gradient elution of ACN in water (75–95% in ACN for 10 min), all peaks were practically separated to the baseline (see Fig. 3B) with the exception of C1, which co-eluted with the excess of DNPH.

3.3. Analytical performance characteristics

The performance and reliability of the proposed method were assessed by determining the regression equation, linear range, LOD and precision expressed as RSD for the aromatic LMMAs studied. For this purpose, 50–200 μL of working standard solutions containing analytes at variable concentrations were spiked to 25 mL of uncontaminated water in the 0.4–200 $\mu g\,L^{-1}$ interval plus the IS (400 $\mu g\,L^{-1}$) and treated as described in Section 2. Calibration curves were obtained by plotting the analyte to the IS peak area against the analyte concentration. Table 1 gives the linear ranges and the least-squares parameters of the working curves. Calibration curves showed a wider linear range (from 0.4 to 200 $\mu g\,L^{-1}$) with adequate linearity (correlation coefficients greater than 0.9991). LOD, defined as the lowest concentration of the analyte in a sample that provides a chromatographic signal three times higher than background noise [43], ranged from 0.12 to 0.20 $\mu g\,L^{-1}$. The precision of the method expressed as the RSD was obtained by analyzing 6 samples per run of 25 mL of uncontaminated water samples spiked with 20 $\mu g\,L^{-1}$ of each aldehyde on three different days (inter-day precision). The average RSD found was ca. 3.3%, which demonstrates the excellent reproducibility of the method proposed. Finally, the RSDs of the retention times were within 1.5%, which indicates the good robustness of the method proposed.

At this point, it may be interesting to compare the analytical features of the proposed method for the *in situ* DNPH derivatization/preconcentration of aromatic LMMAs with reported chromatographic alternatives for the determination of these carbonyl compounds in water samples. As stated above and to our knowledge, no reference exists on LC determination of aromatic LMMAs in water samples using DNPH as derivatizing agent; however, the analysis of BA in spiked water samples has been the subject of two recent sporadic works focused on the evaluation of salt-assisted liquid–liquid microextraction [34] and headspace in-drop derivatization [37] techniques for the determination of carbonyl

Table 2
Results for the determination of aldehydes in water samples.

Water sample	Aldehyde	Content[a] (μg/L)	Added (μg/L)	Average recovery (%)
Tap	C2	1.2 ± 0.1	5, 10	94.9
	C3	ND	10, 25, 50	99.5
	C4	ND	10, 25, 50	95.7
	C5	ND	10, 25, 50	98.8
	BA	ND	10, 25, 50	97.6
	3-MBA	ND	10, 25, 50	99.2
	2,5-DMBA	ND	10, 25, 50	98.8
Stream	C2	4.2 ± 0.3	5, 10	95.9
	C3	ND	10, 25, 50	99.4
	C4	ND	10, 25, 50	95.2
	C5	ND	10, 25, 50	98.5
	BA	3.2 ± 0.1	5, 10	96.3
	3-MBA	ND	10, 25, 50	99.3
	2,5-DMBA	ND	10, 25, 50	98.7
Indoor swimming pool	C2	24 ± 2	10, 25	94.9
	C3	ND	10, 25, 50	99.5
	C4	17 ± 1	10, 25	94.0
	C5	ND	10, 25, 50	98.2
	BA	11 ± 1	10, 25	97.6
	3-MBA	ND	10, 25, 50	98.9
	2,5-DMBA	0.9 ± 0.1	5, 10	97.9
Outdoor swimming pool	C2	9.8 ± 0.7	5, 10	93.6
	C3	ND	10, 25, 50	99.4
	C4	ND	10, 25, 50	94.8
	C5	ND	10, 25, 50	98.3
	BA	3.2 ± 0.2	5, 10	97.4
	3-MBA	ND	10, 25, 50	98.8
	2,5-DMBA	ND	10, 25, 50	98.4

ND, No detection
[a] ±SD (n = 3)

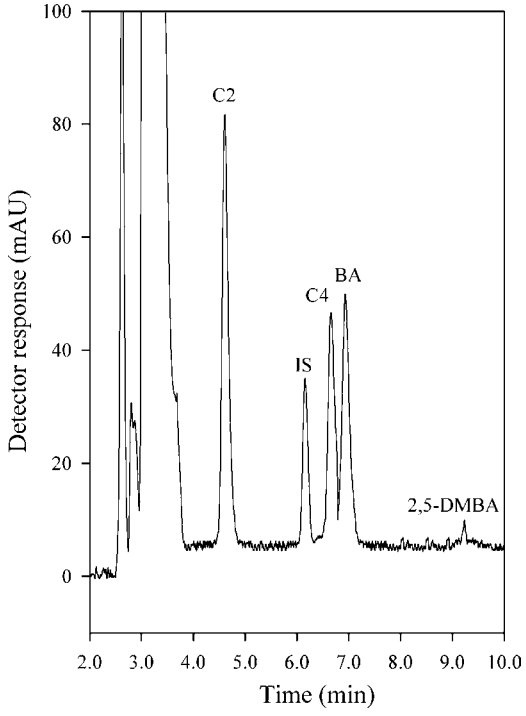

Fig. 4. Chromatogram of indoor swimming pool water sample (see Table 2). Peak identification as stated in Fig. 3. For experimental conditions see Section 2.

compounds. In these studies, the lowest limit for the quantitative determination of BA was ca. 10 μg L^{-1}. In addition and by using other derivatizing reagents, a solid-phase microextraction method for trace analysis of aromatic aldehydes in aqueous solution has recently been reported by GC–MS [22]. In this method aldehydes were derivatized with PFBHA at 80 °C for 30 min and the LODs achieved ranged from 0.2 to 0.5 μg L^{-1}. Triazine-based hydrazine reagents have also been used for this purpose using LC-DAD, although with lower sensitivity: LODs ranged from 10 to 100 μg L^{-1} [44]. These results lead to the conclusion that the proposed method is a useful choice for the determination of these aldehydes in water samples as it provides higher sensitivity than existing LC [34,37,44] and GC [22] alternatives, even when using more expensive instrumentation such as GC–MS, and in all cases with simpler sample handling.

3.4. Determination of aromatic LMMAs in water samples

The performance of the proposed method in the analysis of aromatic LMMAs in waters was evaluated by analyzing different types of samples such as tap, stream and mineral waters as well as water samples from indoor and outdoor swimming pools. The detection and/or quantification of the C2 to C5 aliphatic LMMAs have also been carried out, for which the corresponding calibration plots were constructed under the experimental conditions described in Section 2 (see Table 1). C1 was not included in this study because of its DNPH-derivative co-eluted with the excess of the derivatizing reagent (see Section 3.2). Thus, volumes of 25 mL of water were analyzed, and the aldehydes found are listed in Table 2. The following conclusions can be drawn: (i) drinking and tap waters did not contain aromatic aldehydes (or they were below the LODs) and no aldehyde was detected in drinking water; (ii) C2 and BA were the most common aldehydes quantified in the analyzed water samples; (iii) as expected, a higher number of aldehydes were found in swimming pool waters taking into account the treatment of this class of water, and (iv) aldehyde concentrations were lower in outdoor swimming pool water samples owed probably to the volatility of these compounds. On the other hand, and in order to assess possible matrix effects, concentrations of aldehydes between 5 and

50 μg L^{-1} were spiked to the samples and the corresponding percentages of recovery determined. No matrix effect was observed in the determination of these aldehydes in this kind of water samples: the percentages of recovery ranged from 93.6% to 99.5%. Last, by way of example, Fig. 4 shows the chromatogram obtained in the analysis of indoor swimming pool water, where four aldehydes were quantified.

4. Concluding remarks

In this work, continuous-flow SPE combined with SDS micelles was found to be an effective tool for the *in situ* DNPH derivatization of aromatic LMMAs, which provided a rapid, simple and cost-effective way of measuring these aldehydes in water samples by LC-DAD with LODs at ng L^{-1} levels and good reproducibility. The obtained results warrant the following comments: (i) to our knowledge, this work constitutes the first report on the enhancing effect of micelles on DNPH derivatization of aldehydes; (ii) the method introduces LC with DNPH as a derivatizing reagent in the determination of aromatic aldehydes in water samples and, in general, also extends the scope of the determination of these aldehydes in this type of samples since very few papers have been published on this topic; and (iii) the proposed method has some advantages over EPA Method 8315A based on DNPH derivatization and LC-DAD, such as easier sample preparation, lower consumption of solvents and reagents, shorter analysis time, lower LODs (preconcentration factors up to 250 can be achieved) and better reproducibility.

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