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On-line analysis of carbonyl compounds with derivatization in aqueous extracts of atmospheric particulate PM_{10} by in-tube solid-phase microextraction coupled to capillary liquid chromatography

M.C. Prieto-Blanco[a], P. López-Mahía[a], P. Campíns-Falcó[b,*]

[a] Departamento de Química Analítica, Facultade de Ciencias, Universidade da Coruña, Campus da Zapateira, E-15071 A Coruña, Spain
[b] Departament de Química Analítica, Facultat de Química, Universitat de Valencia, C/Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

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ABSTRACT

A new device for carbonyl compounds based on coupling on-line and miniaturizing both, sample pretreatment and chromatographic separation, is reported. Two capillary columns, a GC capillary column (95% methyl–5% phenyl substituted backbone, 70 cm × 0.32 mm i.d., 3 μm film thickness) in the injection valve for in-tube solid-phase microextraction (IT-SPME) and a Zorbax SB C18 (150 mm × 0.5 mm i.d., 5 μm particle diameter) LC capillary column were employed. Different combinations of IT-SPME and derivatization using 2,4-dinitrophenylhydrazine (DNPH) were examined for mixtures containing 15 carbonyl compounds (aliphatic, aromatic and unsaturated aldehydes and ketones). A screening analysis of aqueous extracts of atmospheric particulate PM_{10} was carried out. Moreover, the possibility of coupling IT-SPME and conventional liquid chromatography is also tested. Derivatization solution and IT-SPME coupled to capillary liquid chromatography provided the best results for achieving the highest sensitivity for carbonyl compounds in atmospheric particulate analysis. Detection limits (LODs) using a photodiode array detector (DAD) were ranged from 30 to 198 ng L^{-1}, improving markedly those LODs reported by conventional SPME–LC–DAD.

1. Introduction

Carbonyl compounds are organic compounds formed mainly in several oxidative processes (photochemical oxidation [1], lipid peroxidation [2] or chemical oxidation [3]). For this reason, they are detected in numerous matrices such as atmosphere (air and particulate matter) [4], treated water (disinfection using ozone) [5], biological fluids (urine, plasma, and serum) [2], food (wine and beer) [3] and emissions of industrial and treatment plants [6].

Gas chromatography (GC) and high performance liquid chromatography (HPLC) are the most widely employed separation techniques for the analysis of carbonyl compounds. With respect to sample treatment, solid-phase extraction (SPE) and solid-phase microextraction (SPME) are frequently used combined with a derivatization step due to the polarity and reactivity of these compounds.

The application of miniaturized techniques for both preparation and separation of the sample, for the estimation of carbonyl compounds is currently being of interest in order to achieve an increase of selectivity and sensitivity and low wastes, in order to develop cost-effective methods. Time-consuming pretreatment procedures are needed in order to achieve suitable sensitivity for non-miniaturized techniques [4]. On the other hand, on-line coupling of sample preparation in the chromatographic system allows an improvement in the repeatability, analysis time and cost.

Miniaturized sample preparation using SPME and GC with different detectors (electron capture, flame ionization detector) or coupled to mass spectrometry detector has been successful employed. The analytes are extracted by headspace and on fiber-derivatizated frequently using O-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine (PFBHA) as derivatizing agent and divinylbenzene–polydimethylsiloxane (DVB–PDMS) as the most adequate fiber [5–10]. In addition, a needle device packed with a polymer-coated filament for the determination of four volatile carbonyl compounds in gaseous samples has been proposed by Saito et al. [10]. The extraction and derivatization were carried out simultaneously using 2,4-dinitrophenylhydrazine (DNPH).

When HPLC is used for chromatographic separation, a minor number of studies have evaluated the miniaturized techniques of sample preparation [1–11]. Salt-assisted liquid–liquid microextraction after DNPH derivatization provides a good sensitivity for seven aldehydes and ketones and the method was applied to environmental samples and pharmaceutical formulation [1]. Polymer

* Corresponding author. Tel.: +34 96 3543002; fax: +34 96 3544436.
E-mail address: pilar.campins@uv.es (P. Campíns-Falcó).

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monolith microextraction with DNPH derivatization allowed the determination of hexanal and heptanal in plasma [2] and low-aliphatic aldehydes in human saliva [11]. Either in both cases the on-line coupling of microextraction techniques in chromatographic system was realized.

DNPH derivatization and extraction of derivatives by SPE is a simple treatment widely used previously to LC separation [4,12]. Baños and Silva [13,14] employed mini-columns of SPE in a continuous flow system for the determination of carbonyl compounds in water samples. Moreover, DNPH derivatization and concentration was carried out in the SPE cartridge.

In-tube solid-phase microextraction (IT-SPME), also called as capillary microextraction (CME) [15], is a miniaturized technique which the extracting phase is into the capillary tube accomplishing a greater protection and lower number of the breakages during this use. Moreover the capillary tube facilitates, in contrast with conventional fiber SPME, that on-line coupling to HPLC can be realized easily and a higher sample capacity is achieved.

In the microextraction techniques, the volume of extractant phase is very small in relation to the sample volume [16]. In some configurations of IT-SPME in which the capillary is inserted in the injection valve, the *sample*/*phase extractant* relation can be increased because of higher sample volumes than in IT-SPME configurations as the draw/eject systems are passed through the capillary.

Capillary HPLC involves the miniaturization of chromatographic system using columns of internal diameter of 500 μm or lower. Thus, all the components of chromatographic system (pump, connecting tubes, injector, detector cell volume and geometry) ought be adapted and reduced. In comparison with conventional HPLC, capillary HPLC uses lower sample sizes and flow rates. Therefore it consumes a low volume of solvents. Another advantage is the improvement of the sensitivity since the chromatographic dilution is reduced [17,18].

The objective of this work was to evaluate the capacity of the miniaturized techniques such as IT-SPME and capillary HPLC for the screening analysis of carbonyl compounds shown in Fig. 1. We

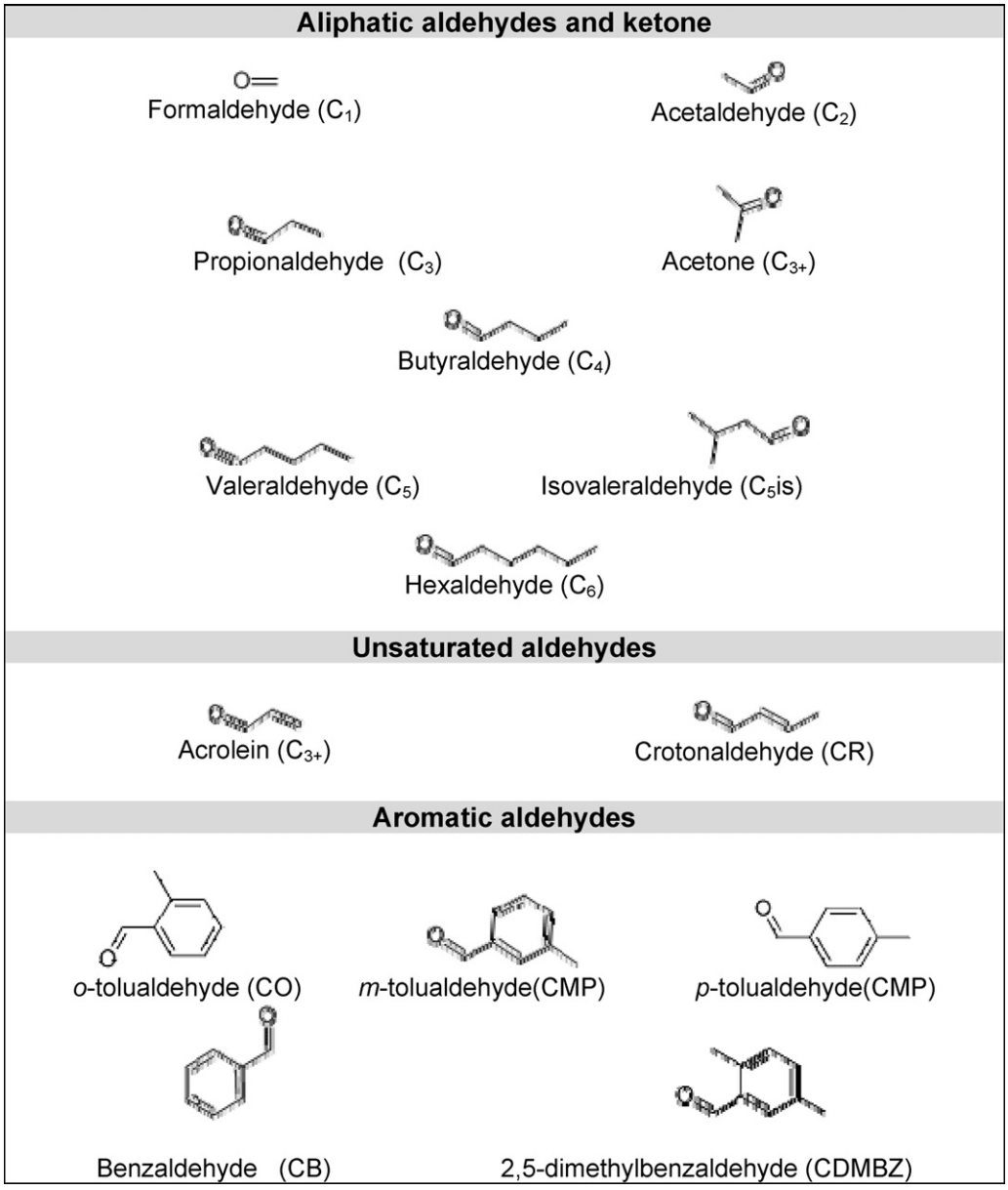

Fig. 1. Structures, names and abbreviations of carbonyl compounds studied.

placed particular emphasis on the improvement of detection limits due to the characteristics of these techniques above mentioned. The analysis of aqueous extracts of atmospheric particulate matter (PM_{10}), which contained different groups of carbonyl compounds was carried out. Although IT-SPME has demonstrated its versatility for extraction polar and non-polar compounds, in this case, it was necessary the simultaneous extraction of the carbonyl compounds with different functionalities (aliphatic, aromatic and unsaturated) and polarities. Moreover, different combinations of microextraction and derivatization were tested and evaluated.

2. Experimental

2.1. Reagents

Acetonitrile of HPLC grade (Scharlau, Barcelona, Spain) was used and water was deionized and filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain). 2,4-Dinitrophenylhydrazine (DNPH) (50% in water) was obtained from Fluka (Steinheim, Germany).

Two derivatized carbonyl compounds mixtures with DNPH in acetonitrile, DCC8315-1JM and DCC8315-2JM from Chem-Service (West Chester, USA) (100 μg/mL of each derivatized carbonyl), were used. DCC8315-1JM contained the following 12 derivatized carbonyl compounds: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, crotonaldehyde, valeraldehyde, cyclohexanone, hexaldehyde, heptaldehyde, octyl aldehyde, nonanal and decyl aldehyde. DCC8315-2JM contained the following 15 derivatized carbonyl compounds: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, butyraldehyde, crotonaldehyde, valeraldehyde, isovaleraldehyde, hexaldehyde, benzaldehyde, 2,5-dimethylbenzaldehyde, *o*-tolualdehyde, *m*-tolualdehyde and *p*-tolualdehyde. Individual carbonyl compounds were obtained from Sigma–Aldrich (Madrid, Spain).

2.2. Chromatographic systems

2.2.1. In-tube SPME/capillary LC

A LC capillary pump (Agilent 1100 Series, Waldbronn, Germany) equipped with a high-pressure six-port injection valve (Rheodyne model 7725), a degasser 1100 and an interface 35900E was used. An UV photodiode array detector (DAD, Hewlett-Packard, 1040M Series II) coupled to a data system (Agilent, HPLC ChemStation) for data acquisition and calculation and equipped with a 80nL flow cell was used. All components of the system were linked with fused silica tubing (220 mm × 50 μm i.d. supplied by Agilent) except to the tubing between analytical column and detector (200 mm × 25 μm i.d. Agilent). The signal was registered in the DAD detector and it was monitored at 365 nm. The corresponding spectra were saved. A spectra library of the pure compounds was performed.

The analytical column employed was a capillary column Zorbax SB C_{18} (150 mm × 0.5 mm i.d., 5 μm particle diameter) (Agilent). A GC TRB-5 capillary column of 70 cm and coated with 95% dimethyl–5% diphenylpolysiloxane (Teknokroma, Barcelona, Spain) with 0.32 mm of internal diameter and 3 μm of coating thickness was used for IT-SPME. The flow rate was 20 μL min^{-1} and the mobile phase was a (60–40%) acetonitrile–water mixture.

2.2.2. In-tube SPME/conventional LC

The HPLC system consisted of a pump (Agilent 1100 Series) equipped with a high-pressure six port valve (Rheodyne model 7725) and an UV detector (Hewlett-Packard 9153C),. The signal was monitored at 365 nm.

The chromatographic separation was carried out in a conventional column Lichrospher RP-18 (125 mm × 4.0 mm i.d., 5 μm particle diameter) (Merck, Darmstadt, Germany) using gradient elution at flow rate of 1 mL min^{-1}. Initially, the eluent was a mixture of water:acetonitrile (60%:40%), then the percentage of acetonitrile was increased up to 50% at 3 min, followed to linearly elution up to 60% at 14 min and up to 100% at 16 min. The content of 100% acetonitrile was maintained constant until 18 min. Finally a gradient elution was required to reach the initial conditions from 18 to 21 min.

2.3. Sampling, extraction and derivatization procedures for particulate samples

2.3.1. Sampling

PM_{10} (atmospheric particulate matter with an aerodynamic diameter less than 10 μm) samples were collected over 24 h period one site of semi-urban typology in A Coruña-Galicia (Northwestern Spain), by EN-12341 reference high volume sampler (Digitel) on 15 cm diameter QF20 Schleicher and Schuell quartz fiber filters. The filters were pre-baked at 400 °C overnight before use in order to remove organic compounds and they were stored in baked aluminium foil. Subsequently, sampling filters were conditioned at 20 ± 1 °C and 50 ± 5% relative humidity during 48 h according to the EN-12341 gravimetric determination of particulate matter.

2.3.2. Extraction of carbonyl compounds from the particulate matter

A preliminary extraction of carbonyl compounds from solid sample was carried out according to Prieto-Blanco et al. [4]. An eighth portion of PM10 samples was twice ultrasonically extracted with 10 mL milli-Q water at ambient temperature in 15 min. The two portions of extract were diluted to 25 mL.

2.3.3. In-tube SPME/capillary LC procedure

In-tube SPME device was simply configured replacing the stainless steal injection loop of the six port valve of the chromatograph (see Section 2.2) by a piece of commercial GC capillary column. An aliquot of carbonyl compounds extracted by ultrasonic bath, DNPH acidic solution and 50 μL of water were loaded in capillary column using different options of IT-SPME. The acidic solution of DNPH is prepared according to Zwiener [12] (HCl:water:acetonitrile in the ratio 2:5:1, v/v, respectively) at concentration of 3885 μM for conventional LC (see Section 2.2.2) and 215 μM for capillary LC (see Section 2.2.1). Three options combining derivatization and extraction were tested:

Option 1. Solution derivatization and concentration in IT-SPME: 10 mL of carbonyl standards or sample aqueous extracts obtained according to Section 2.3.2 were derivatizated using 500 μL of DNPH during 5 min. Next, in the load position of the six-port valve, between 2 and 4 mL of solutions were passed manually through the capillary, which replace the injection loop, at flow-rate of 250 mL min^{-1} using a manual syringe. After, 50 μL of water is processed for cleaning and for replacing the derivatized mixture in the GC capillary. Finally, desorption of derivatives is performed in dynamic mode (flowing the mobile phase) by rotation the valve to the injection position.

Option 2. Extraction of carbonyl compounds and derivatization in IT-SPME: 2 mL of standards or sample extracts was passed through the capillary. Next, 500 μL of DNPH was flushed into the capillary for derivatizing of extracted carbonyl compounds. After 5 min, cleaning and desorption were performed like option 1.

Option 3. Simultaneous derivatization/extraction in IT-SPME: 500 μL of DNPH was flushed into the capillary and after, 2 mL of standards or sample extracts were processed in order to achieve simultaneously derivatization and extraction of carbonyl com-

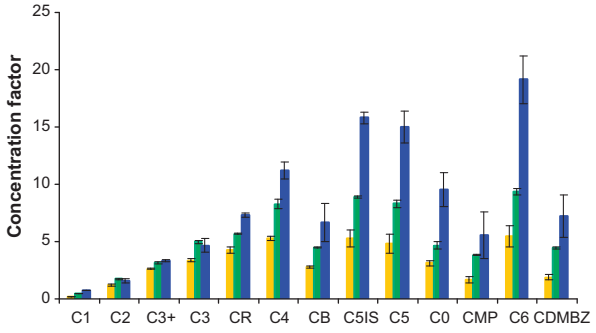

Fig. 2. Effect of sample volume on concentration factor of derivatized carbonyl compounds using IT-SPME and capillary LC. Yellow bar: 1 mL ($n=4$), green line: 2 mL ($n=2$), blue line: 4 mL ($n=4$). The derivatives are shown according their elution order (see Fig. 3). Derivatization yield 100% (for more details see option 1 in Section 2.3.3), yellow, green and blue corresponds to first, second and third ones, for each carbonyl compound, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

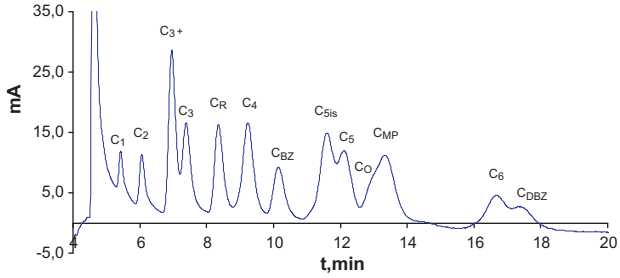

Fig. 3. Formaldehyde (C_1) (1.4 ng mL^{-1}), acetaldehyde (C_2) (2.0 ng mL^{-1}), acetone + acrolein (C_{3+}) (2.4 + 2.4 ng mL^{-1}), propionaldehyde (C_3) (2.4 ng mL^{-1}), butyraldehyde (C_4) (2.9 ng mL^{-1}), crotonaldehyde (CR) (2.8 ng mL^{-1}), valeraldehyde (C_5) (3.2 ng mL^{-1}), isovaleraldehyde (C_{5IS}) (3.2 ng mL^{-1}), hexaldehyde (C_6) (3.6 ng mL^{-1}), benzaldehyde (C_{BZ}) (C_5) (3.7 ng mL^{-1}), 2,5-dimethylbenzaldehyde (C_{DBZ}) (C_5) (4.3 ng mL^{-1}), *o*-tolualdehyde (C_5) (4.0 ng mL^{-1}) (C_O), *m*-tolualdehyde, *p*-tolualdehyde (C_{MP}) (4.0 + 4.0 ng mL^{-1}) (for more details see option 1 in Section 2.3.3).

pounds. After 5 min, cleaning and desorption were performed like option 1.

3. Results and discussion

3.1. Study of the IT-SPME in standards

The factor of concentration for each DNPH derivative using a capillary coated with 95% dimethyl–5% diphenylpolysiloxane was evaluated. An aqueous solution containing 7 aliphatic aldehyde derivatives from formaldehyde C_1 to hexaldehyde C_6 and one isomer of C_5 (isovaleraldehyde), one ketone derivative (acetone), 2 unsaturated aldehyde derivative (acrolein and crotonaldehyde) and 5 aromatic aldehydes derivatives (benzaldehyde, 2,5-dimethylbenzaldehyde, *o*-tolualdehyde, *m*-tolualdehyde, and *p*-tolualdehyde) at 50 ng mL^{-1} concentration was passed through the capillary at different volumes (1000 μL, 2000 μL, and 4000 μL). The analytical response of more polar aldehydes (C_1, C_2, and C_3) and also acetone (C_{3+}) and acrolein (C_{3+}) remains constant from 2 mL. For aliphatics (C_4, C_5, C_{5is}, and C_6), unsaturated (C_R), and aromatic aldehyde derivatives, the sensitivity was increased with the higher volume tested (see Fig. 1). Concentration factors for each volume tested are calculated from the obtained area with respect to the area value achieved using the capillary as loop injection (volume 60 μL). Considering the type of carbonyl compound, the highest concentration factors were obtained for aliphatic aldehydes with the higher alkyl chain (C_5 and C_6) as can be seen in Fig. 2. If the 15 carbonyl compounds tested are considered, a sample volume of 4 mL provides the better average concentration factor, as can be seen in Fig. 2. Higher concentration factors achieved for the aldehydes with higher alkyl chain and lower polarity are due possibly the low polarity of the stationary phase of the GC capillary. If the objective was improving aromatic aldehydes response, then a higher percentage of diphenylpolysiloxane in the stationary phase could increase probably their concentration factor by means of π–π interactions. The stationary phase used provides a good compromise for selected compounds which have a wide range of polarities.

The effect of the composition and volume of washing solvent after the concentration step was examined using water and acetonitrile. 60 μL of water was selected since acetonitrile or a greater volume of water (120 μL) diminished the achieved sensitivity.

A suitable chromatographic separation was performed in 19 min using an isocratic elution as can be seen in Fig. 3. For resolving acetone and acrolein the use of ternary mixtures and gradient elution was necessary [4], but for screening purposes the separation achieved is sufficient and the analysis time and wastes were improved using isocratic elution. As expected, the spectra obtained were similar for all the carbonyl compounds derivatized. Nevertheless, several spectral differences were detected in carbonyl compounds with different functionalities. Derivatives from aliphatic, unsaturated, aromatic carbonyl compounds showed an absorption maximum to 360, 370 and 380 nm, respectively. These differences facilitate the screening analysis.

The possibility of derivatization with DNPH into the capillary was evaluated taking valeraldehyde as the model compound. Other authors Zhang et al. [2] analyzed hexanal and pentanal using DNPH simultaneously with polymer monolith microextraction but derivatization/extraction was performed off-line of the chromatographic system.

The combination of microextraction and derivatization in the GC capillary support offers two options (analyte extraction followed by derivatization or extraction simultaneously with derivatization). The latter option was selected since a lower amount of DNPH is needed for obtaining similar yields and the separation of more volatile carbonyl compounds was also improved (experimental results are not shown). Several parameters were evaluated for optimizing IT-SPME supported derivatization as can be seen in Table 1. A multi-step procedure improved the obtained yields. As it can be seen in Table 1, in each cycle, firstly DNPH solution is passing once through the capillary column for the adsorption of derivatizing agent and after the solution of carbonyl compound for its extraction/derivatization. This operation mode may be comparable with the cycles of absorption/desorption in automated IT-SPME. Their efficiency is increased with an increase in the number of cycles. The response factor of valeraldehyde used as model carbonyl compound was 24 times lower than that achieved by solution derivatization and concentration by IT-SPME. For this procedure extraction and derivatization yields cannot be calculated independently as for solution derivatization followed by IT-SPME–capillary LC. Solution derivatization yields were near 100% for all carbonyl compounds and the extraction yields can be seen in Fig. 2 for several tested volumes.

Table 1
Variables studied and optimum value for derivatization/extraction of carbonyl compounds by IT-SPME. For more details see option 3 in Section 2.3.3.

Variable	Range studied	Optimum value
[DNPH]	43–430 μmol/L	215 μmol/L
Multi-step procedure	1–20 cycles	20 cycles
Volume of each cycle	50–250 μL	100 μL valeraldehyde50 μL DNPH
Total DNPH volume	50–1000 μL	1 mL
Total sample volume	100–4000 μL	2 mL
Derivatization time	0–5 min	5 min

Table 2
Some figures of merit of the solution derivatization and IT-SPME–capillary LC method. For more details see option 1 in Section 2.3.3.

Compound	Calibration equation ($y = b_0 + b_1x$)			Concentration interval (ng mL^{-1})	LOD (ng L^{-1})	LOQ (ng L^{-1})
	$b_0 \pm s_{b_0}$	$b_1 \pm s_{b_1}$	R^2			
Acetaldehyde	10 ± 20	36 ± 4	0.9908	0.15–9.8	75	153
Acetone + acrolein	5 ± 9	83.6 ± 0.8	0.9998	0.2–24	78	179
Propionaldehyde	10 ± 45	99 ± 6	0.9962	0.2–12.2	64	194
Crotonaldehyde	10 ± 45	130 ± 5	0.9983	0.2–14	68	196
Butyraldehyde	10 ± 50	166 ± 7	0.9969	0.14–14.3	38	143
Benzaldehyde	20 ± 30	67 ± 2	0.9976	0.4–18.5	132	440
Isovaleraldehyde	30 ± 80	185 ± 10	0.9946	0.09–16.2	30	87
Valeraldehyde	35 ± 150	177 ± 15	0.9926	0.2–16.2	66	185
o-Tolualdehyde	20 ± 50	56 ± 4	0.9911	0.3–21.3	91	302
p,m-Tolualdehyde	54 ± 20	54 ± 1	0.9997	0.7–40	198	739
Hexaldehyde	−12.0 ± 12.5	139 ± 10	0.9900	0.5–17.9	126	462
2,5-Dimethylbenzaldehyde	−27 ± 6.0	59.5 ± 0.5	0.9999	0.4–21.3	108	362

Table 3
Interassay precision (for more details see option 1 in Section 2.3.3).

Compound	Concentration (μg/L)	RSD (%) $n = 3$	Concentration (μg/L)	RSD (%) $n = 3$
Acetaldehyde	1.0	7	2.9	1
Acetone + acrolein	2.4	1	7.2	2
Propionaldehyde	1.2	1	3.7	4
Crotonaldehyde	1.4	2	4.2	4
Butyraldehyde	1.4	0.5	4.3	4
Benzaldehyde	1.8	13	5.6	8
Isovaleraldehyde	1.6	1	4.9	2.5
Valeraldehyde	1.6	1	4.9	1
o-Tolualdehyde	2.0	4.5	6.0	4
p,m-Tolualdehyde	2.0	11	6.0	1
Hexaldehyde	1.8	5	5.4	1
2,5-Dimethylbenzaldehyde	2.1	7.5	6.4	1

From this study we selected solution derivatization followed by IT-SPME coupled on-line with capillary liquid chromatography as the best option for carbonyl screening analysis due to sensitivity is improved in reference to IT-SPME supported derivatization.

3.2. Analytical performance

Table 2 summarizes the calibration equations and LODs and LOQs which were calculated according to Miller and Miller [19] and from standards solutions providing S/N ratios of 3 and 10, respectively. Solution derivatization followed of IT-SPME provides low LODs, ranged from 30 to 198 ng L^{-1}. Table 3 shows inter-assay precision, suitable % RSDs values were obtained independently of the concentration tested. No carryover was observed after dynamic desorption. Blanks were processed between samples and standards for testing carryover.

In Table 4, LODs are compared with those obtained by SPE–HPLC [4], SPE–LC–MS–MS [12] and SPME–GC [5,9]. LODs are 2–197 times lower than the methods which use the formation of 2,4-dinitrophenylhydrazone derivatives in solution and SPE off-line [4,12] or continuous derivatization/SPE followed liquid chromatography [13]. Also, LODs are 0.5–147 times lower than GC in which the derivatization is performed with PFBHA in solution followed headspace or liquid-phase SPME. The LODs obtained in this work are comparable (ng L^{-1}) with those obtained by Baños and Silva [14] for aliphatic compounds using SPE/LC–MS–MS. According these authors, which previously has been used a DAD-detector; the MS–MS detection system is more sensitive for these compounds than UV detection The present paper shows the great potential of IT-SPME for the concentration of carbonyl compound derivatives.

3.3. Application to real samples

Fig. 4 shows the results obtained for a sample by the optimized procedure. Six compounds were screened: formaldehyde, acetaldehyde, acetone, propionaldehyde and isovaleraldehyde when solution derivatization and IT-SPME were used. Only formaldehyde, acetone and propionaldehyde were screened by performing simultaneously derivatization and preconcentration by IT-SPME (see Fig. 4). This option could be suitable when only the more abundant carbonyl compounds be of interest, which can be found in the PM_{10} in concentration levels of ng m^{-3}.

IT-SPME coupled to conventional liquid chromatography was also tested for screening analysis of carbonyl compounds. The influence of volume of the sample processed was the same than that discussed previously for IT-SPME coupled to capillary LC. If concentration factors are calculated as the relation between response by IT-SPME and direct injection (loop of 20 μL), the greatest concentration factor (137) was achieved for decylaldehyde using a sample volume of 5000 μL.

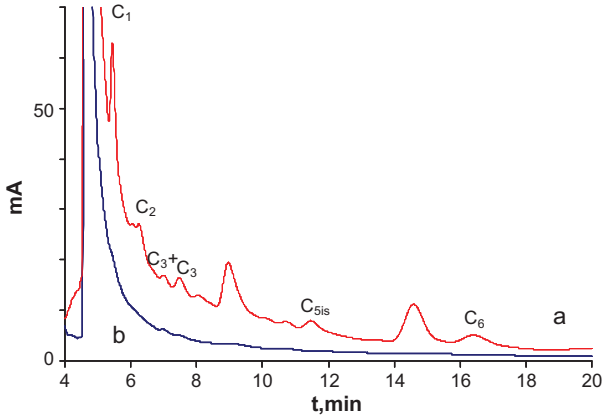

Fig. 4. PM_{10} aqueous extract (a) derivatized in solution and preconcentred on line by IT-SPME and (b) derivatized and preconcentred in IT-SPME (see also Fig. 3) (for more details see option 1 in Section 2.3.3).

Table 4
Comparison of LODs (ng mL^{-1}) obtained by IT-SPME–capillary LC with SPE–HPLC and SPME–GC and different combinations of derivatization.

Compound	D–SPE–HPLC [4]	D–SPE–LC–MS–MS [12]	D/SPE–HPLC [13]	D/SPE–LC–MS–MS [14]	D–IT-SPME– capLC (this work)	D–HS-SPME–D–L–SPME– GC–MS [9]	D–HS-SPME–GC [5]
Acetaldehyde	3.3	0.18	0.3	0.018	0.075	11–1.1	0.04
Acetone + acrolein	2.6 + 2.4		–	+0.006	0.077		–
Propionaldehyde	4.1	0.17	0.3	0.012	0.064	0.5–0.8	0.15
Crotonaldehyde	2.9			0.023	0.068	1.1–0.2	–
Butyraldehyde	4.0	0.23	0.6	0.018	0.038	1.2–0.9	0.05
Benzaldehyde	6.1			–	0.132	0.5–0.6	–
Isovaleraldehyde	5.9		–	–	0.030		0.07
Valeraldehyde	10.1	0.19	1.0	0.017	0.066	0.3–1.3	–
o-Tolualdehyde	7.3			–	0.091	5.5–4.2	–
p,m-Tolualdehyde	–			–	0.198	0.2–0.6	–
Hexaldehyde	3.5	0.24	1.0	0.024	0.125	0.3–0.5	0.18
2,5-Dimethylbenzaldehyde	4.7				0.108	0.7–0.3	–

The same approaches assayed with capillary LC were tested using acidic DNPH (3885 μM), which must be 18 times more concentrated than that used in capillary LC, for a PM_{10} sample. As for capillary LC, solution derivatization and IT-SPME provided the better average sensibility for the carbonyl compounds found in the PM_{10} extract, especially for C_6–C_8 carbonyl compounds. Gradient elution instead of isocratic elution was needed to achieve the chromatographic separation of the carbonyl compounds. Besides minor consumption of derivatizing agent and isocratic elution, capillary LC provided better sensitivity and low amount of wastes.

4. Conclusions

A wide range of carbonyl derivatives (aliphatic, aromatic, and unsaturated) with different functionalities are extracted and concentrated by IT-SPME. The optimum sample volume and the composition and volume of the washing solvent were optimized for screening analysis. The best concentration factors were achieved for aliphatic aldehydes with a longer alkyl chain. For the more polar carbonyl compound (C_1–C_3), the concentration factor does not increase from 2 mL sample volume and for the other carbonyl compounds tested 4 mL allowed a higher concentration factor.

The present paper proved that IT-SPME combined with derivatization can be coupled to capillary LC as well as conventional LC for the screening analysis of carbonyl compounds.

Solution derivatization and IT-SPME provided an optimized screening analysis of aliphatic, aromatic and unsaturated carbonyl compounds. Excellent limits of detection at the ppt (ng L^{-1}) level were obtained. Simultaneous derivatization and concentration by IT-SPME based on derivatization–extraction in multiple steps could permit to quantify only the more abundant carbonyl compounds in aqueous extracts of PM_{10}.

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