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Determination of carbonyl compounds in particulate matter $PM_{2.5}$ by in-tube solid-phase microextraction coupled to capillary liquid chromatography/mass spectrometry

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ABSTRACT

In this paper, a new procedure based on in-tube solid phase microextraction (IT-SPME)-capillary liquid chromatography hyphenated to mass spectrometry detection by using microelectrospray ionisation (CapLC–MS), has been reported. The device was proposed to quantify 12 carbonyl compounds (10 aliphatic aldehydes, an unsaturated aldehyde and a ketone) derivatized with 2,4-dinitrophenylhidrazine (DNPH) reagent in aqueous extracts of $PM_{2.5}$. This methodology involves the on-line preconcentration of DNPH-carbonyl compounds derivatives coupled to the CapLC–MS system, efficiently providing appropriate sensitivity for the determination of the target analytes. Detection limits for the analytes ranged between 0.9 and 8.2 ng L^{-1}. These values represent a remarkable improvement over the existing methods since $PM_{2.5}$ analysis can be carried out avoiding off-line preconcentration steps. The procedure is also proved useful for analysing water samples. Under the optimised conditions, IT-SPME-CapLC–MS shows satisfactory recovery values (80–90%) for spiked samples.

1. Introduction

Carbonyl compounds are organic pollutants of concern from both environmental and human health aspects. The potential carcinogenic effects of these compounds have been pointed out by the International Agency of Research on Cancer, and 10 of these compounds have been included as possible carcinogenic substances [1,2]. These compounds are detected in several matrices such as air samples [3], water samples [4], biological samples [5], food samples [6] and industrial samples [7].

The determination of carbonyl compounds in atmospheric samples has gained interest since they play an important role as intermediary products in secondary reactions, which involves pollutants such as ozone, hydrocarbons or volatile organic compounds. Carbonyl compounds have been determined in outdoor air [8–13], indoor air [14], cigarette smoke [2,12,15] and automobile exhaust [6,10]. Besides, there is an increasing interest in determining carbonyl compounds in particulate matter (PM) due to its health adverse impact [3,16,17]. Particulate matter is a complex mixture of a wide range of inorganic and organic compounds, which contribute to adverse health and environmental effects. These effects depend on PM chemical composition. Particularly, carbonyl compounds are important contributors to the water soluble fraction of fine PM [2,3,18,19]. Therefore, the determination of these pollutants is of high importance in order to identify the potential harmful effects caused by PM [20]. PM_{10} (PM with an aerodynamic diameter $d_p < 10$ μm) has been traditionally used to measure human exposure to particulate matter. Nevertheless, the exposure to $PM_{2.5}$ (PM with an aerodynamic diameter $d_p < 2.5$ μm) has been associated with an increase in the health adverse effects caused by PM [21,22]. The concentrations of pollutants, such as carbonyl compounds are typically of trace level, being the concentrations in $PM_{2.5}$ are lower than those in PM_{10}. Therefore, the development of more sensitive and reliable methods is mandatory to identify this source of pollutants in PM.

HPLC–MS after 2,4-dinitrophenylhydrazine (DNPH) derivatization is one of the most reliable methods for quantification of various carbonyl compounds at trace level [18,19]. Kolliker et al. [8] and Grosjean et al. [9] analysed carbonyl compounds in ambient air using mass detection with APCI ionisation source. Other papers approached the quantitative analysis using APCI for air and automobile exhaust samples by using internal isotope labelled standards [10,11]. Zweiner et al. [23] and Baños and Silva [24] determined carbonyl compounds using ESI-MS–MS combined with solid-phase extraction (SPE) in water samples treated by chlorination. However, literature on measuring carbonyl compounds in PM is still scarce.

Recently, an in-tube solid phase microextraction (IT-SPME) and capillary liquid chromatography using diode array detection has

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been proposed for the screening of carbonyl compounds in aqueous extracts of PM_{10} [25]. IT-SPME methodology permits a dynamic and solventless extraction, compatible with aqueous and organic sample solvents. In addition, IT-SPME allows concentration and clean-up of samples and high sample/extractant ratios as well as direct coupling with the LC system. Detection limits (LODs) ranged from 30 to 198 ng L^{-1} in Ref. [25]. Nevertheless, an increase in the sensitivity is still required for the analysis of fine PM ($PM_{2.5}$) in order to permit in-depth toxicology and health effect studies and also for improving the knowledge of the chemical identification of the particle- and gas-phase chemical composition [26]. Zhu et al. [27] reported a good relationship between time averaged concentrations of $PM_{2.5}$ mass and two gas-phase carbonyl compounds (formaldehyde and acrolein) at an international airport.

In the present work, the potential of IT-SPME coupled to Cap-LC–MS detection for quantifying carbonyl compounds in $PM_{2.5}$ has been demonstrated. The proposed procedure has also been applied for determining the target analytes in water samples.

2. Experimental section

2.1. Reagents and standard solutions

A mixture of carbonyl compounds derivatizated with DNPH in acetonitrile DCC8315-1JM ChemService (West Chester, USA) (100 mg mL^{-1} of each derivatized carbonyl) was used. DCC8315-1JM contained the following 12 carbonyl compounds: formaldehyde (C_1), acetaldehyde (C_2), propionaldehyde (C_3), butyraldehyde (C_4), crotonaldehyde (C_R), valeraldehyde (C_5), cyclohexanone (CH), hexaldehyde (C_6), heptaldehyde (C_7), octylaldehyde (C_8), nonanaldehyde (C_9) and decylaldehyde (C_{10}). 2,4-Dinitrophenylhydrazine (DNPH) (50% in water) was obtained from Fluka (Steinheim, Germany).

Acetonitrile of HPLC grade (Romil, Barcelona, Spain) was used and water was deionised and filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain).

2.2. Apparatus and chromatographic conditions

The chromatographic system consisted of a capillary pump (Agilent 1100 Series, Waldbronn, Germany) and a high-pressure six-port injection valve (7725 Reodhyne) with an internal loop of 2 μL for direct injection. The mass spectrometer was an Agilent G6140A quadrupole system equipped with atmospheric pressure ionisation microelectrospray source (API–ESI).

For IT-SPME the injection loop of the six-port valve was replaced by a section of a GC TRB-35 capillary column of 43 cm in length and 0.32 mm i.d., coated with 35% diphenyl-65% polydimethylsiloxane (PDMS) (3 μm coating thickness). Capillary connections were facilitated by the use of a 2.5 cm sleeve of 1/16″polyetheretherketone (PEEK) tubing at each end of the capillary. A PEEK tubing internal diameter of 535 μm i.d. was suitable to accommodate the capillary used. Fig. 1 shows a schematic diagram of the equipment. 2 mL of the derivatized extract were passed manually through the capillary using a syringe. Then, 34 μL of water were passed through the capillary column in order to clean and replace the derivatized solution. Finally, dynamic desorption with the mobile phase was performed by rotating the valve to the injection position, so, the analytes were eluted from the extractive phase and transferred to the analytical column for separation and detection (see Fig. 1).

For the separation of the carbonyl compounds, an Agilent Zorbax C_{18} (RP-SiO_2) capillary column (150 mm × 0.5 mm i.d., 5 μm) was used. The mobile phase was a binary mixture of acetonitrile and water in gradient elution mode. The initial composition of the mobile phase was water:acetonitrile 55:45 (v/v) at 10 μL/min. The acetonitrile content was increased to 65% at 15 min with a flow rate of 15 μL/min; then, acetonitrile was increased up to 100% at 25 min, maintaining a constant flow rate of 15 μL/min. Finally, both acetonitrile content and flow rate were decreased to 45% and 10 μL/min, respectively, and maintained until 35 min. The solvents were filtered through 0.45 μm nylon membranes and degassed with helium before use.

The operating parameters for the MS detector in negative ion mode were: drying gas temperature: 325 °C, nebuliser pressure 12 psi, fragmentor voltage 70 V and capillary voltage 3.00 kV. Previously, the full scan mode (SCAN) in a mass range from m/z 50 to 600 was used to identify the analytes by matching the retention times with the standards. The single ion monitoring (SIM) according to Table 1 was used to quantify the analytes with external calibration.

2.3. Sampling and sample preparation

PM_{10} and $PM_{2.5}$ samples were collected over 24 h period one site of semi-urban typology in A Coruña-Galicia (North-western

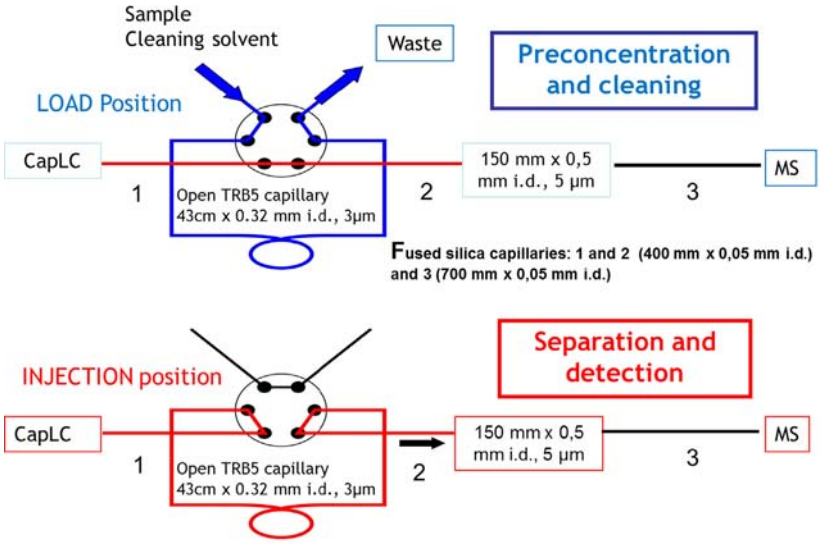

Fig. 1. Scheme and dimensions of IT-SPME-CapLC–MS device. In the load position, analytes are preconcentrated and cleaned. Separation and detection is carried out in the injection position.

Table 1
Precursor ions for carbonyl DNPH-compounds $[M–H]^-$ and figures of merit using the IT-SPME-CapLC–MS method.

Compound/identification	$[M–H]^-$ (m/z)	Sensitivity $b \pm s_b$ (ng L^{-1})	R^2	Linear range (ng L^{-1})	LOD[a] (ng L^{-1})	LOD[b] (pg m^{-3})	LOD[c] (pg m^{-3})
Formaldehyde/1	209	791 ± 18	0.9969	27–2143	8.2	25.0	8.0
Acetaldehyde/2	223	2160 ± 25	0.9997	9.2–983	2.7	10.0	2.2
Propionaldehyde/3	237	4917 ± 140	0.9984	3.1–1219	0.9	3.0	0.7
Crotonaldehyde/4	251	5785 ± 150	0.9986	8.4–1429	2.5	1.0	0.2
Butyraldehyde/5	249	5763 ± 120	0.9999	4.6–1400	1.4	3.0	0.7
Valeraldehyde/6	265	6177 ± 200	0.9979	6.6–1617	2.0	9.5	2.2
Cyclohexanone/7	277	2312 ± 120	0.9974	27–1763	8.1	1.5	0.4
Hexaldehyde/8	279	5205 ± 70	0.9996	4.5–1786	1.3	2.0	0.5
Heptaladehyde/9	293	4084 ± 50	0.9987	6–1940	1.8	1.5	0.4
Octaldehyde/10	307	2217 ± 80	0.9974	15.5–2098	4.4	2.0	0.5
Nonanaldehyde/11	321	1549 ± 60	0.9968	12.7–2206	3.8	5.0	1.2
Decanaldehyde/12	335	1172 ± 40	0.9980	17.7–2322	5.3	4.5	1.0

[a] Aqueous standards and water samples.
[b] PM_{10}.
[c] $PM_{2.5}$.

Spain), by EN-12341 reference high volume sampler (DHA-80 Digitel) on 15 cm diameter QF20 Schleicher and Schuell quartz fibre 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. Finally, sampling filters were conditioned at 20 ± 1 °C and $50 \pm 5\%$ relative humidity during 48 h, according to the EN-12341 gravimetric determination of particulate matter.

A preliminary extraction of carbonyl compounds from quartz fibre filter was carried out according to Prieto-Blanco et al. [3,25]. Field blanks were also prepared and processed in order to assure the suitable blanks following the previously described procedure [3,25]. An eighth of PM_{10} samples were ultrasonically extracted with milli-Q water (10 mL) twice at ambient temperature in 15 min. The two extracted portions were diluted to 25 mL. Analytes derivatization was performed by mixing 10 mL of extract with 500 μL of acidic DNPH (4.1 mM) during 5 min. It should be noted that PM_{10} extracts were diluted 10 times before addition of the derivatizing agent. Meanwhile, $PM_{2.5}$ extracts were directly derivatized due to the low concentration level of carbonyl compounds in these samples. Sample pools of four sampling months (from March 2011 to July 2011) were analysed. Each sample was analysed by triplicate.

Two wastewater samples collected at different sampling points of the Comunidad Valenciana coast (Spain) were directly analysed (without filtration). After the arrival to the laboratory, water samples were stored in the dark in brown glass flasks at 4 °C until analysis. Each sample was analysed by triplicate at room temperature.

3. Results and discussion

3.1. MS conditions

Initially, MS conditions were optimised by direct injection of 2 μL of a mixture of the target analytes. The analytical responses showed remarkable differences as function of the analyte structure. The analytical signal for compounds up to C_6 was one order of magnitude higher than those achieved for semivolatile compounds (C_7–C_{10}). This effect was also observed by other authors [13,23], who proposed the use of ammonium acetate as a modifier to increase the response of C_7–C_{10} carbonyl-DNPH compounds. Nevertheless, under our experimental conditions, the addition of ammonium acetate did not markedly improve the sensitivity of semivolatile compounds. Therefore, acetonitrile:water (50:50, v/v) was chosen as analyte solvent in the optimised procedure.

Next, capillary and fragmentor voltages were studied. The best results were obtained by using 3.00 kV and 70 V as capillary and fragmentor voltage, respectively. Table 1 shows the m/z values selected for each carbonyl compounds under these conditions. MS detection was performed in SIM mode using a time programme: analysis time *versus* m/z values. It should be noted that some analytes eluted at the same retention time. Therefore, data acquisition was carried out using two signals, each of them monitoring a set of target compounds during a time interval. Signal 1 and signal 2 measured analytes 1–8 and 9–12, respectively (see Table 1). By using these two signals, the sensitivity was also markedly improved.

3.2. Study of TRB-35 as adsorbent phase for carbonyl compounds in IT-SPME system

Preconcentration of carbonyl-DNPH compounds was carried out using 35% diphenyl-65% polydimethylsiloxane (PDMS) as adsorbent phase (43 cm) (see Fig. 1). The percentage of phenylpolisiloxane monomer affects the partitioning coefficient of the analytes in the adsorbent phase and then, the concentration factor reached. In this work, we modified the length and nature of the capillary previously reported for IT-SPME-CapLC–DAD [25]. A shorter capillary (43 cm *versus* 70 cm), and a greater phenylpolisiloxane monomer contained in the stationary phase (35% *versus* 5%) than those previously established [25] were selected for the coupling IT-SPME-CapLC–MS. We selected TRB-35 due to the higher polarity difference of the carbonyl assayed in this work.

Moreover, the concentration factor depends on the sample volume processed. Fig. 2 shows the analytical response as a function of the processed sample volume (500–2000 μL). As expected, the extraction efficiency for the most polar compounds (formaldehyde and acetaldehyde) was not improved with an increase on the sample volume due to the weaker interaction of these compounds with the adsorbent phase. Based on these results, a volume of 2000 μL was selected for further studies. Comparing these results with the results obtained with TRB-5 [25], it was evident that an increase on the percentage of phenylpolisiloxane monomer improved the adsorption of most of the derivatized carbonyl compounds assayed. As an illustrative example, the concentration factors achieved with TRB-35 for C1, C2, C3, C4, CR, C5 and C6 were 10, 18, 36, 57, 39, 40 and 50, respectively. In contrast, concentration factors with TRB-5 capillary column were below 20 for those analytes.

Fig. 3 depicts the chromatograms obtained for a mixture of the carbonyl-DNPH compounds in the range from 71 to 232 ng L^{-1}. It should be noted that the use of the two signals solved the problem with overlapped peaks, allowing the quantification of the target analytes.

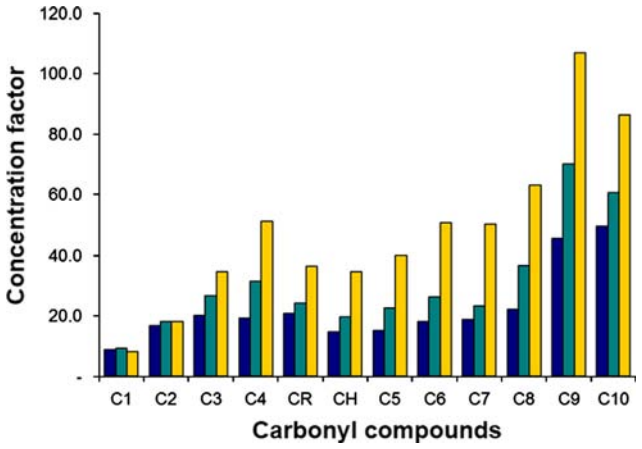

Fig. 2. Effect of sample volume on concentration factor of carbonyl-DNPH compounds using IT-SPME-CapLC–MS. Blue bar: 0.5 mL ($n=2$), green bar: 1 mL and yellow bar: 2 mL. The analytes are shown according to their elution order.

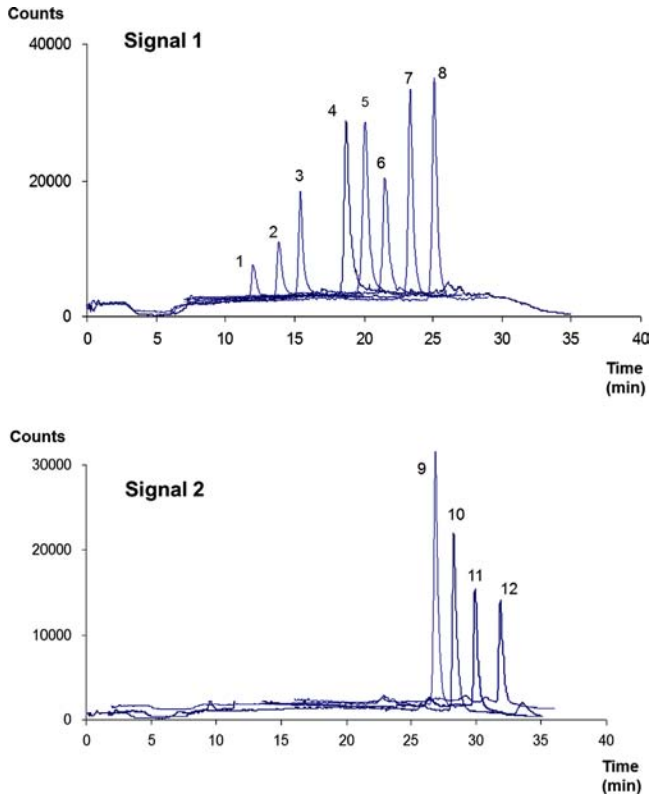

Fig. 3. Chromatograms obtained from a standard mixture of the 12 carbonyl-DNPH compounds. (1) Formaldehyde, (2) acetaldehyde, (3) propionaldehyde, (4) crotonaldehyde, (5) butyraldehyde, (6) valeraldehyde, (7) cyclohexanone, (8) hexaldehyde, (9) heptaldehyde, (10) octylaldehyde, (11) nonanaldehyde and (12) decylaldehyde. The concentration is in the range of 71–232 ng L^{-1}.

3.3. Analytical parameters

Some figures of merit, such as the equation of the calibration curve, linear range, limits of detection (LOD) and limits of quantification (LOQ) are shown in Table 1. The following criteria for linearity range were applied: linear regression through zero with a correlation coefficient better than 0.99 and bias from the calibration line less than 15% for all individual calibration points. LOD and LOQ were calculated according to Miller and Miller [28] based on the linear regression parameters (regression standard deviation Sy/x). In addition, these parameters were experimentally verified in samples as the concentration of analyte required to generate a signal-to-noise ratio of 3 and 10 for LOD and LOQ, respectively. The LOD values ranged from 0.9 to 8.2 ng L^{-1}. Comparing these results with previously reported values [23–25], the coupling IT-SPME-CapLC–MS improved the LODs in a factor between 30 and 100. By way of example, the LODs achieved with IT-SPME-CapLC–DAD for acetaldehyde, propionaldehyde, crotonaldehyde, butyraldehyde and hexaldehyde were 75, 64, 68, 38 and 126 ng L^{-1}, respectively [25]. In this work LOD for acetaldehyde, propionaldehyde, crotonaldehyde, butyraldehyde and hexaldehyde were 2.7, 0.9, 2.5, 1.4 and 1.3 ng L^{-1}, respectively. This improved LODs allowed the determination of the target analytes in the $PM_{2.5}$ water-soluble fraction and in water samples, without the need of including laborious evaporation steps before the chromatographic separation and detection. On other hand, the proposed method provided wider linear ranges between nanograms per liter and micrograms per liter than those previously published. Table 2 shows the inter-assay precision. The % RSD values were higher than those obtained in [25]. In order to assess the acceptability of the precision characteristics of the proposed procedure, the reproducibility standard deviation (RSD_R) using the Horwitz equation [29,30] was calculated. Taking into account that reproducibility (R) can be estimated from repeatability (r) by using $r=0.66\,R$ [31], RSD_r was 30%. In addition, Horrat value ($RSD_{r,\ measured}/RSD_{r,\ Horwitz\ predicted}$) was 0.8 lower than 1.5 which is the threshold limit. These results indicated satisfactory precision for the proposed method.

3.4. Application to real samples

Blanks were processed using ultra-pure water and filters blank. Ultrapure water was extracted, derivatized and concentrated by IT-SPME in order to control procedure blanks ($n=4$). Formaldehyde, acetaldehyde, octanaldehyde, nonanaldehyde and decanaldehyde at concentrations of (3 ± 1), (0.7 ± 0.25), (0.2 ± 0.1), (0.5 ± 0.2) and (1.3 ± 0.6) ng mL^{-1} respectively, were found in blanks. These values were in accordance with those found in treatments, which include derivatization using DNPH and cleaning of glass material [27]. Other compounds such as butiryraldehyde and crotonaldehyde at (0.09 ± 0.05) and (0.02 ± 0.007) ng mL^{-1}, respectively, were also quantified. Similar concentration levels were found in filter blanks from C_2 to C_5 and C_{10}, and two to three times higher than procedure blank for C_7 to C_9.

The proposed method was applied to analyse water soluble fractions of PM_{10} and $PM_{2.5}$ and water samples. Validation of the proposed method was carried out by a confirmation study, measuring the PM_{10} extracts with the proposed procedure and with the previously developed method [3]. In a first step, the samples were extracted and derivatized in solution according the procedure described in [25]. In two PM_{10} samples collected in two sites with industrial and urban typologies, C_1–C_4 were detected.

Table 2
Interassay precision.

Compound	Concentration (ng mL^{-1})	Precision % RSD ($n=4$)
Formaldehyde	5.0	25
Acetaldehyde	1.0	18.0
Propionaldehyde	1.2	10.0
Crotonaldehyde	1.4	14.0
Butyraldehyde	1.4	5.0
Cyclohexanone	1.6	9.0
Valeraldehyde	1.8	11.0
Hexaldehyde	1.7	8.5
Heptaladehyde	1.9	5.5
Octaldehyde	2.1	10.0
Nonanaldehyde	2.2	8.0
Decanaldehyde	2.3	18.0

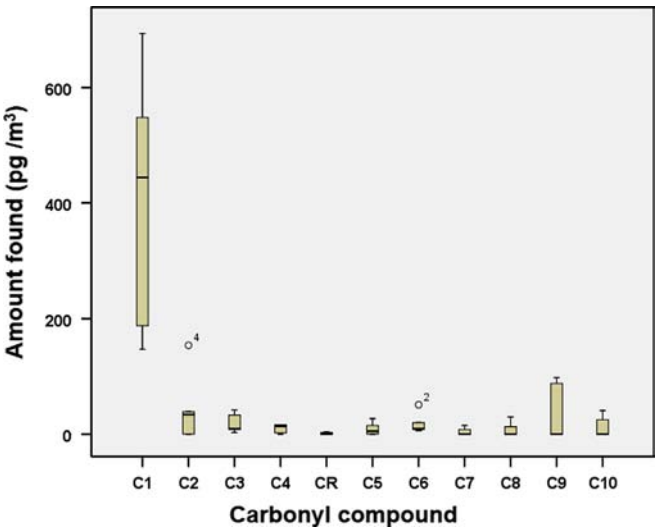

Fig. 4. Carbonyl-DNPH compounds detected in monthly sample pools of water soluble fraction of $PM_{2.5}$ from March (2011) to July (2011).

Formaldehyde was found at higher concentration levels of 20–30 ng m^{-3}, acetaldehyde at 10 ng m^{-3} and C_3–C_4 at 1 ng m^{-3}. Crotonaldehyde was only detected in urban sample close to its LOQ and C_6–C_8 were found in industrial sample at a concentration of about to 1 ng m^{-3}. These levels are in agreement with those obtained by off-line SPE and HPLC–DAD at the same sampling points [3].

The LOD reached by the proposed procedure allowed the determination of carbonyl compounds in water soluble fraction of $PM_{2.5}$. Fig. 4 shows the values obtained for monthly sample pools of this fraction. Formaldehyde, acetaldehyde, propionaldehyde, crontonaldehyde, butyraldehyde, hexaldehyde, heptalaldehyde, octaldehyde, nonanaldehyde and decanaldehyde were detected in samples collected in June and July. Although the total amount of carbonyl compounds detected were higher in July than in June. Formaldehyde and nonanaldehyde were the major compounds in those sample pools. In March, the highest content was found for acetaldehyde. While butyraldehyde and hexanaldehyde were the major carbonyl compounds in April.

Other environmental samples were also tested. In this case, two water samples were analysed. All the target analytes, except propanaldehyde and crotonaldehyde, were detected in both samples. In addition, butyraldehyde, cyclohexanone and valeraldehyde were found. The concentrations for butyraldehyde, cyclohexanone and valeraldehyde were 29 ± 4 ng L^{-1}, 38 ± 5 ng L^{-1} and 26.6 ± 0.8 ng L^{-1} for sample 1 and 53 ± 5 ng L^{-1}, 151 ± 29 ng L^{-1} and 69 ± 5 ng L^{-1} for sample 2.

The recovery study was carried out by spiking real water samples with the target analytes at concentration of 400 and 930 ng L^{-1}. IT-SPME-CapLC–MS results showed that the found concentrations agreed with the added concentrations with mean recoveries of $85 \pm 20\%$ ($n=24$) and $80 \pm 20\%$ ($n=24$) at 400 and 930 ng L^{-1}, respectively, and with relative standard deviation (RSD) lower than 25%.

4. Conclusions

Online IT-SPME-CapLC with MS detection has been applied for the first time to determine carbonyl compounds in $PM_{2.5}$ and water samples at nanograms per liter level. This methodology has been employed for the chromatographic separation and screening of ten aliphatic aldehydes from formaldehyde to decyladehyde, unsaturated aldehyde of four carbon atoms (crotonaldehyde) and a cyclic ketone (cyclohexanone). This combination provides a remarkable improvement of detection limits compared to existing methods (see Section 1). This improvement has allowed the screening and quantification of carbonyl compounds in water-soluble fractions of $PM_{2.5}$. Therefore, the proposed procedure avoided the additional evaporation step, usually needed for concentrating the obtained extract in order to reach nanograms per liter concentration levels. In the IT-SPME step, clean-up and preconcentration are carried out on-line. Therefore, the analysis time can be reduced to sampling and analytes extraction from the sampling filters. Thus, this coupling not only improves the sensitivity but also simplifies the sample pretreatment, as water soluble fraction of $PM_{2.5}$ can be directly processed into the chromatographic system. This procedure can be useful for increasing the knowledge about $PM_{2.5}$. The procedure can be also useful for analysing water samples as it is demonstrated.

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