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Determination of aldehydes in rainwater using micro-solid-phase extraction and high-performance liquid chromatography

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ABSTRACT

A simple and rapid extraction procedure was developed for determining aldehydes in rainwater samples. This extraction technique involved the use of micro-solid-phase extraction in which the sorbent was held within a polypropylene membrane envelope, followed by high-performance liquid chromatographic analysis. Aldehydes such as formaldehyde, acetaldehyde, propionaldehyde and valeraldehyde were used as model compounds. Extraction conditions were optimized. The method linearity ranged between 0.5 and 50 $\mu g\,l^{-1}$ with the correlation coefficient of 0.987–0.999. The relative standard deviations (RSDs) of the method ranged from 7 to 12%. Method detection limits were in the range of 0.07–0.15 $\mu g\,l^{-1}$, which is lower than those previously reported for solid-phase microextraction combined with gas chromatography–mass spectrometric techniques. The proposed extraction technique was used for determination of aldehydes in rainwater samples to demonstrate the applicability of the method.

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1. Introduction

Carbonyl compounds are known to have toxic and carcinogenic properties and hence have received regulatory attention as toxic contaminants in Clean Air Act Amendments, USEPA [1]. Carbonyls are present in the atmosphere as a primary source of pollutants from industrial processes and vehicular exhaust, and furthermore produced as secondary pollutants from photooxidation of atmospheric hydrocarbons [2–6]. In urban air, the dominant carbonyls are formaldehyde and acetaldehyde which originate from both primary and secondary sources. These aldehydes play a major role in urban photochemical smog, in the production of free radicals in atmosphere and are the precursors to formation of tropospheric ozone [7]. Aldehydes are water-soluble and hence wet deposition is an important removal mechanism for these compounds that can influence ecosystem health. Rainfall thus causes a large net flux of the water-soluble compounds from the atmosphere to the receiving ecosystems [8–10]. There remains a need to develop simple analytical methods to monitor the trace levels of aldehydes in the rainwater in order to quantify the wet deposition of these compounds.

The main analytical challenges involved in the determination of aldehydes in the rainwater are that (i) they are present in trace levels and (ii) they are easily volatile, (iii) they lack chromophores for UV measurements, (iv) lower molecular weight aldehydes being highly polar in nature are difficult to retain by reversed-phase HPLC columns, and (v) they are highly reactive, leading to poor precision and quantification. However, derivatization of aldehdyes with suitable reagents will provide stable products with chromophores which can be used for HPLC–UV analysis [11]. Many derivatization reagents such as 2,4 dinitrophenylhydrazine (2,4-DNPH), dansyloxyamine and *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) have been used for quantification of aldehydes based on HPLC measurements together with ultraviolet detection (UV) [1,3–5,11,12–23] and fluorescence detection [12,21,23]. In recent years, the DNPH–HPLC–UV method has been most widely used as a standard method for determination of aldehydes in environmental samples [24]. The DNPH–HPLC–UV method is selective and has an absorbance maximum at 360 nm; the interferences are greatly reduced at this wavelength.

Indeed, there are GC methods are available for analysis of aldehydes analysis with derivatization [12,25,26]. *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBOA) is commonly used as

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a derivatization agent (formation of corresponding oximes) in gas chromatography. The PFBHA-oxime derivatives, which are extremely volatile due to their high fluorine atom content, are amenable to GC analysis and detection by electron capture detection [12] and MS-olfactometry [24]. Although these methods provide good reproducibility, however, they are relatively less sensitive than the DNPH–HPLC–UV method.

Aldehydes are present in atmospheric samples in trace levels, so preconcentration is required in most cases. The traditional methods of extraction involve the use of cartridges and tubes [1,2,14,16,21,23] packed with silica gel coated with 24-DNPH. Recently, solid-phase microextraction (SPME) has been introduced for the detection of carbonyls in air and water samples [27] together with GC–MS. It is a simple, solvent-free method. However, the derivatized hydrazones may decompose at high temperatures in the injector port and the method is less reproducible than the HPLC methods.

Another rapid and straightforward method with the use of a continuous solid-phase extraction (SPE) system has been developed for *in situ* derivatization and preconcentration of carbonyls in aqueous samples. Briefly, 2,4-DNPH, the derivatizing agent, is adsorbed on a C_{18} cartridge and then samples are continuously aspirated into the flow system, where the derivatization and preconcentration of the analytes take place simultaneously [8]. In this procedure, the C_{18} cartridge is used for single use and moderately large amounts of sample and solvents are required.

In this work, a micro-solid-phase extraction (μ-SPE) [28,29,30] approach has been developed for determination of aldehydes present in trace levels in the aqueous phase. The sorbent in the μ-SPE devices was coated with 2,4-DNPH and then used for the extraction of aldehydes from rainwater samples. The use of 2,4-DNPH for aldehyde determination is well known, but applying it together with μ-SPE has not been achieved previously. Various extraction parameters such as the nature of sorbent material, the sample volume and extraction time were optimized to obtain maximum extraction efficiency. The applicability of the proposed method for routine analysis was evaluated using freshly collected rainwater samples.

2. Experimental

2.1. Reagents and materials

Analytical grade 2,4-DNPH was obtained from Alltech (Nicholasville, KY, USA). HPLC-grade organic solvents were purchased from Merck (Darmstadt, Germany). Nanopure water was obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA). Formaldehyde (37% w/w aq. solution, 7-8% methanol), acetaldehyde (98.5%), propionaldehyde (97%) and valeraldehyde were purchased from Supelco (Bellefonte, PA, USA). A stock solution (1000 mg l^{-1}) of all the four aldehydes was prepared and stored at 4 °C in bottles wrapped with aluminum foil. 2,4-DNPH solution was prepared by dissolving 2 mg of 2,4-DNPH in 20 ml of acetonitrile (100 mg l^{-1}). Few drops of HCl were added to the resulting solution. Commercial sorbents i.e. C_2 (Si–C_2H_5), C_8 (Si–C_8H_{17}), C_{18} (Si–$C_{18}H_{37}$), Hayesep-A (divinylbenzene-ethyleneglycodimethylacrylate), Hayesep-B (divinylbenzene polyethyeneimine), and Porapak-R (divinylbenzene-vinyl pyrrolidinone) were purchased from Alltech. Q3/2 Accurel 2E HF (R/P) polypropylene sheets (157 μm thickness, 0.2 μm pore size) were purchased from Membrana (Wuppertal, Germany).

2.2. Rainwater samples

Rainwater samples were collected on the roof top of the tallest building in the Faculty of Engineering at the National University of Singapore from February to June 2009 using an automated, wet-only rainwater sampler and analyzed on the same day. A sample volume of 5 ml was sufficient for the determination of aldehydes. However, adequate amounts of rainwater were collected for the routine determination of other parameters. The pH of rainwater varied from 3.85 to 5.44 (mean 4.45). The conductivity of rainwater was in the range of 20.91–54.54 μcm S^{-1} (mean 36.31 μcm S^{-1}).

The concentration of total dissolved solids was in the range of 11.35–29.43 mg l^{-1} (mean 19.80 mg l^{-1}).

2.3. Preparation of μ-SPE device

A porous polypropylene membrane sheet was used to contain the sorbent. To prepare the former, polypropylene sheets were cut into dimensions of ~1.8 cm × 1.2 cm, and folded into half along the longer axis. The edges of the flaps were then heat-sealed. One of the two open ends of each piece was then heat-sealed, leaving one opening. A glass pipette with a cut-off tip was used to introduce sorbent materials via the remaining open end, which was then heat-sealed to secure the contents. Each device was packed with 20 mg of sorbent. The device was then conditioned by using ultrasonication with methanol followed by water for 10 min.

2.4. Extraction procedure

Ultrapure water (5 ml) spiked such that 20 μg l^{-1} of a mixture of aldehydes was obtained, and then equilibrated for 1 min using magnetic stirring at 105 rad s^{-1}. Prior to extraction, the sorbent in the μ-SPE device was loaded with 2,4-DNPH for 20 min. For aldehyde extraction, two μ-SPE devices were introduced into the sample vial and allowed to tumble freely with stirring at 105 rad s^{-1}, for 20 min. After that, the devices were removed from sample vials and then placed in microcentrifuge tubes and 100 μl of acetonitrile was added. Desorption was carried out via ultrasonication for 5 min. Finally, 50 μl was injected into the HPLC. The μ-SPE devices were tested for carryover effect by re-desorbing the devices again with the same solvent. No contamination was observed. Thus, we were able to reuse each μ-SPE device for up to 15 times.

2.5. HPLC conditions

Analyses were performed using Waters HPLC 15 μ binary pump system, with a manual injection port. A Nova-Pak Waters C_{18} column (3.9 μm, 150 mm) was used for the separation of the aldehydes at room temperature. The detection wavelength was set at 360 nm, and optimal separation was achieved with a binary mobile phase at a flow rate of 1 ml min^{-1} of acetonitrile (solvent A) and water (solvent B). A gradient elution was used: starting with acetonitrile:water at 37:63 from 0 to 10 min, and to 60:40 up to 20 min, before returning to the original ratio to re-equilibrate the system.

3. Results and discussion

Optimum extraction conditions were investigated to evaluate the different factors that affect the extraction efficiency of the technique. Since μ-SPE is an equilibrium-driven process, the efficiency is dependent on the partitioning of the analyte between the aqueous phase and the sorbent. Optimization was carried out by triplicate analysis. The parameters investigated were the nature of sorbent material, the extraction and desorption time, desorption solvent, and the sample volume. To evaluate the applicability of the method, repeatability, linearity, limits of detection and enrichment factors were measured under the optimized extraction conditions. A blank (in triplicate) analysis was carried out with empty polypropylene envelope (coated with 2,4-DNPH) to ensure that the

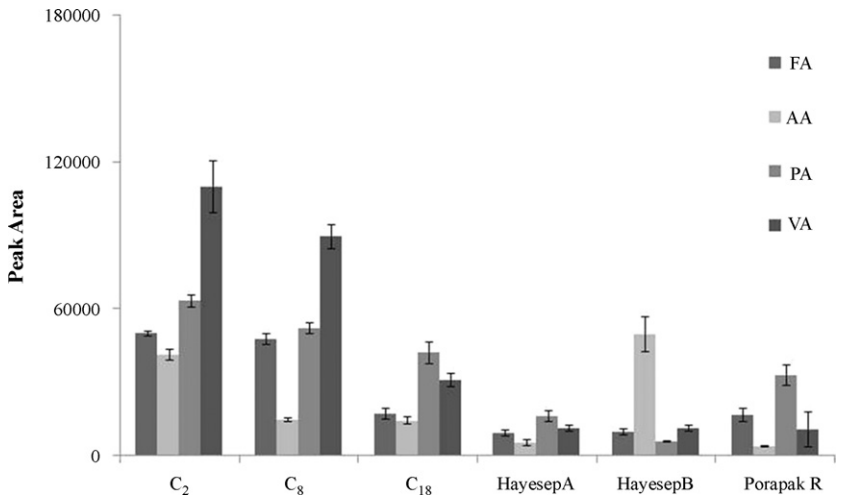

Fig. 1. Effect of different packing sorbents in the extraction efficiency of μ-SPE device. 20 mg of sorbent material was packed in the device; coated with 2,4-DNPH and analytes were extracted from spiked water samples (50 $\mu g\,l^{-1}$) and desorbed in 100 μl of acetonitrile; injected in HPLC acetonitrile:water: 37:63; 1 ml/min). Peak identification: FA, formaldehyde; AA, acetaldehyde; PA, propionaldehyde; VA, valeraldehyde.

extraction was due to the derivatized sorbent, and the membrane envelope itself played no role.

3.1. Effect of sorbent material

The selection of a sorbent is important as it determines the selectivity of the analytes. To examine the selection of the best solvent for the extraction of the target aldehydes, the μ-SPE was packed with 20 mg of different sorbents (C_2, C_8, C_{18}, Hayesep-A and Hayesep-B and Porapak-R). The silica-based sorbent, C_{18} is the most hydrophobic, followed by C_8 and C_2. Hayesep-A and Porapak-R which are of intermediate polarity, and Hayesep-B, which has the highest polarity. Based on the peak area analysis, C_2 was found to be the most effective sorbent, followed by C_8 and C_{18}. Poor extraction efficiency was observed for Hayesep-A, Hayesep-B, and Porapak-R (Fig. 1). The 2,4-DNPH coated on C_2 showed better performance than the rest of the sorbents. This could be due to the moderate polarity of the C_2 which could interact with the polar derivatization agent 2,4-DNPH and aldehydes. In addition, both C_2 and the aldehydes used have relatively short carbon chains, which promote the interactions between the sorbent and analytes.

3.2. Derivatization approach

Two derivatization approaches were considered. The use of pre-2,4-DNPH-loaded μ-SPE devices for aldehyde extraction was compared with that in which the analytes were derivatized first and then extracted by μ-SPE. For the former, the C_2 μ-SPE device was loaded by immersing in a solution of 2,4-DNPH (100 $mg\,l^{-1}$) and introduced into the spiked mixture of aldehydes for extraction. For the after-extraction procedure, 2,4-DNPH was added (500 $\mu g\,l^{-1}$) in excess to the acidified spiked mixtures of aldehydes to form 2,4-dinitrophenylhydrazones. The μ-SPE device with C_2 sorbent was then introduced for extraction. The results are shown in Fig. 2. The use of a pre-loaded μ-SPE device gave higher LC peak areas, especially for formaldehyde and valeraldehyde as compared to extraction after derivatization. This difference could be due to the selective derivatization of 2,4-DNPH with certain aldehydes, and also perhaps that the excess of 2,4-DNPH in the sample solution interfered with the extraction. Based on these observations, μ-SPE devices were loaded with 2,4-DNPH prior to extraction.

3.3. Effect of desorption solvents

The analytes were desorbed in a suitable organic solvent after extraction via ultrasonication. Factors such as analyte solubility, solvent polarity, reactivity of solvents with the derivatizing agent affect the desorption process. Since the hydrazones are polar, they desorb better in solvents such as methanol and acetonitrile, as compared to non-polar solvents such as hexane. Acetone was not used, as it would react with 2,4-DNPH to form hydrazones. Acetonitrile gave better peak area compared to the other solvents, and hence it was chosen as the desorption solvent for subsequent experiments (Fig. 3).

3.4. Effect of desorption volume

The volume of the solvent to be used to achieve maximum extraction efficiency was also investigated. Desorption experiments were carried out in the range of 100–250 μl acetonitrile to minimize the consumption of the solvent and to determine if desorption occurred to a greater extent with increasing volume. Less than 100 μl was not sufficient to immerse the μ-SPE devices during

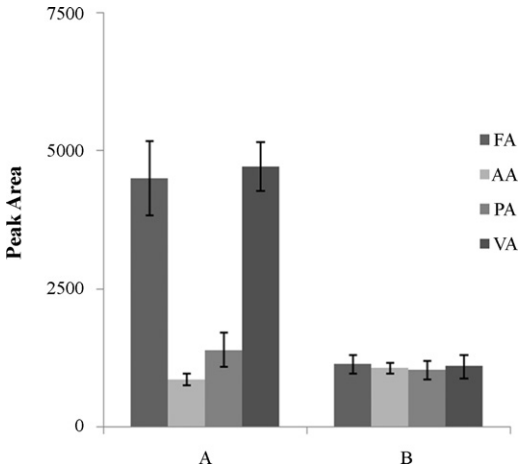

Fig. 2. Comparison of different derivatization setup. (A) μ-SPE device is loaded with 2,4-DNPH and then used for extraction; (B) analytes are derivatized before extraction using μ-SPE as described in the text. Peak identification: FA, formaldehyde; AA, acetaldehyde; PA, propionaldehyde; VA, valeraldehyde.

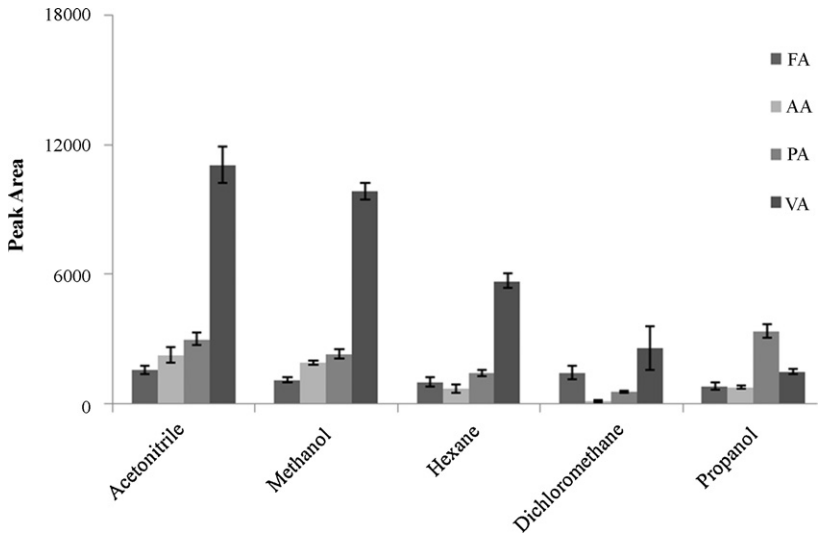

Fig. 3. Comparison of different desorption solvents. After extraction, analytes were desorbed using ultrasonication with in 100 μl of different solvents. Peak identification: FA, formaldehyde; AA, acetaldehyde; PA, propionaldehyde; VA, valeraldehyde.

ultrasonication which led to poor precision of the analysis. Higher volume of acetonitrile (<200 μl) caused a decrease in the peak area resulting from dilution of the analyte. Thus, 100 μl was chosen for subsequent desorption.

3.5. Effect of desorption time

The desorption (ultrasonication) time was investigated for a range of 3–20 min with 100 μl acetonitrile. Optimum desorption was achieved at 5 min. As desorption time increased beyond 5 min, the peak areas for the aldehydes decreased. Since it is an equilibrium-driven process, re-adsorption of the analytes to the sorbent may be one of the reasons for the decrease in peak area observed, when desorption time was increased. Five minutes were chosen as the optimum time for desorption, as the peak areas for three of the aldehydes used in the study were highest at 5 min. After the first desorption, the μ-SPE was further desorbed in acetonitrile and checked for carryover effect. No analytes were detected, suggesting that the μ-SPE device could be reused after conditioning with water and methanol by ultrasonication.

3.6. Derivatization time

The time that is required to load the 2,4-DNPH onto the μ-SPE sorbent also plays an important role in the extraction process. Aldehydes have no optical detectability, so their derivatization is a very important step from an analytical point of view. The μ-SPE device with the sorbent was placed in a solution of (100 $\mu g\,l^{-1}$ in 3 ml) of 2,4-DNPH solution and ultrasonicated between 5 and 30 min. A 20 min loading gave higher peak areas with no significant further improvement with longer times. Thus, 20 min was used as the most suitable loading time for the 2,4-DNPH. As earlier, the key challenge involved in the aldehyde analysis deals with derivatization with 2,4-DNPH to form stable analytes with chromophores for UV analysis. Based on the literature reports, the C_2 (SiC_2H_5) bonding is not stable at low pH (below 2 and above 13). Therefore, to avoid the complications, we did not evaluate the sample pH.

3.7. Effect of sample extraction volume and extraction time

The influence of the sample volume was also investigated by carrying out the extraction over a range of extraction volumes from 5 to 15 ml (with extraction time of 20 min). The volume affects the equilibrium and hence the optimum extraction efficiency. A sample volume of 5 ml gave the highest peak areas, which means that the greatest amount of target analytes was extracted. Thus, only 5 ml of the sample is sufficient for optimum extraction. It is conceivable that larger sample volume would require longer extraction time or larger amounts of the sorbent.

As mass transfer is a time dependent process, the extraction time was also varied to determine if it had any effect on the extraction efficiency. Extraction time was varied between 5 and 25 min.

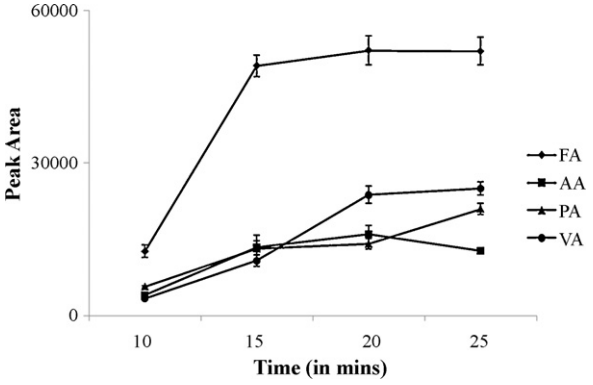

Fig. 4. Influence of extraction time. Peak identification: FA, formaldehyde; AA, acetaldehyde; PA, propionaldehyde; VA, valeraldehyde.

Table 1
Linearity range of calibration plots, LODs, LOQs and precision (%RSDs) of μ-SPE.

Target analytes	RSD (%) $n=6$	Regression equation	Linearity range ($\mu g\,l^{-1}$)	LODs ($\mu g\,l^{-1}$)	LOQs ($\mu g\,l^{-1}$)	Coefficient of determination (r^2)
Formaldehyde	11.8	$y = 268.69(\pm 7.5)x + 1427.6(\pm 10.5)$	0.5–50	0.15	0.5	0.993
Acetaldehyde	7.9	$y = 374.71(\pm 5.5)x + 1511(\pm 9.0)$	0.5–50	0.027	0.09	0.998
Propionaldehyde	12.0	$y = 236.25(\pm 9.8)x + 1886.9(\pm 10.9)$	0.5–50	0.11	0.36	0.999
Valeraldehyde	9.0	$y = 303.31(\pm 5.6)x + 1751.6(\pm 7.5)$	0.5–50	0.070	0.23	0.987

As the extraction time was increased from 5 to 20 min, the peak areas increased until maximum efficiency was achieved at 20 min (Fig. 4). The peak areas slowly decreased when the extraction time increased from 20 to 25 min. This could be due to the rate of desorption of analytes compared to adsorption occurring after 20 min. The most suitable extraction time, from the results, appear to be 20 min.

3.8. Quantitative information

To assess the practical applicability of the proposed μ-SPE method, the optimized extraction conditions were adopted to evaluate performance characteristics such as reproducibility, linearity, limits of detection (LODs) and limits of quantification (LOQs). Linearity was investigated by plotting the HPLC peak areas of the individual aldehydes with spiked ultrapure water concentrations. The linearity was investigated over a range of 0.5–50 $\mu g\,l^{-1}$ and least squares linear regression was used to analyze the linearity. The correlation coefficients were determined to be better than 0.987 which are acceptable for trace analysis. Thus, a proportional relationship can be approximated between the amount of analytes extracted and the concentration of the sample. The relative standard deviations were calculated and were between 9 and 12%. The LODs were determined by progressively decreasing the concentration of the aldehydes spiked in the nanopure water until distinct responses were still clearly observed at a signal to noise ratio of 3. The LODs ranged from 0.06 to 0.11 $\mu g\,l^{-1}$. The method is thus suitable for the determination of aldehydes in genuine environmental water samples (Table 1). The data obtained from this work were compared with the LODs of other common methods employed as summarized in Table 2 [31]. It was found that the LODs obtained from μ-SPE are lower than the other routine methods.

3.9. Preliminary studies of rainwater samples

To evaluate the suitability of the proposed method, genuine rainwater samples were spiked and recoveries were calculated. The percentage recoveries of aldehydes at 10 $\mu g\,l^{-1}$ spiked in rainwater samples ranged from 83.8 to 105.9% which indicates no matrix interferences (Table 3).

Genuine rainwater samples were extracted using the optimized extraction conditions of μ-SPE. Aldehydes were detected in the samples (Fig. 5). The concentrations found in the samples are summarized in Table 4. The concentration of aldehydes, particularly formaldehyde, measured in rainwater samples throughout the world were compared, and are summarized in Table 5. The results obtained in the present study are quite comparable with the data obtained in other countries. The abundance of aldehydes measured in the present study was found to be in the following order: formalde-

Table 2
The LODs and upper concentration limits for three solid-phase microextraction (SPME) techniques (HS-SPME-OFD, headspace SPME with on fiber derivatization; D-HS-SPME, direct derivatization headspace SPME; D-L-SPME, direct derivatization liquid phase SPME) under selected extraction conditions as reported [31].

Analyte	HS-SPME-OFD ($\mu g\,l^{-1}$)	D-HS-SPME ($\mu g\,l^{-1}$)	D-L-SPME ($\mu g\,l^{-1}$)
Formaldehyde	53–220	108–150	55–250
Acetaldehyde	3.7–350	11–200	1.0–350
Propionaldehyde	3.0–400	0.5–220	0.8–350
Valeraldehyde	0.8–450	0.3–300	1.3–400

Table 3
Percentage recoveries of carbonyls at 10 $\mu g\,l^{-1}$ spiked in to rainwater samples.

Aldehydes	Concentration detected in rainwater ($\mu g\,l^{-1}$)	Amount detected (n = 6) ($\mu g\,l^{-1}$)	Percentage recovery
Formaldehyde	4.4	14.25 ± 1.5	96.5 ± 10.5
Acetaldehyde	ND	8.53 ± 0.6	85.3 ± 7.0
Propionaldehyde	ND	10.6 ± 1.2	106.7 ± 11.3
Valeraldehyde	ND	9.16 ± 0.8	91.6 ± 8.7

ND: not detected.

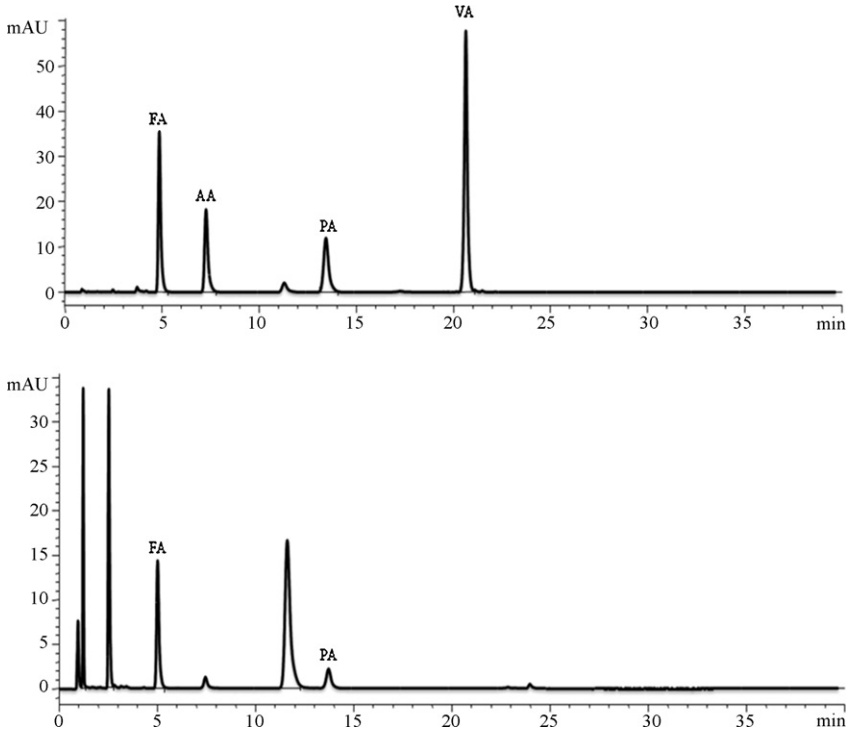

Fig. 5. Liquid chromatogram for (A) mixture of standards (50 $\mu g\,l^{-1}$) and (B) rainwater sample (samples/standard were extracted using μ-SPE device under optimized conditions and injected in HPLC (RP C_{18} column; acetonitrile:water: 37:63 (gradient),1 ml/min, VWD 360 nm). Peak identification: FA, formaldehyde; AA, acetaldehyde; PA, propionaldehyde; VA, valeraldehyde.

Table 4
Mean concentrations of each aldehyde ($\mu g\,l^{-1}$) detected in rainwater samples collected from University premises (roof top) using a rainwater sampler.

Sample	Formaldehyde	Acetaldehyde	Propionaldehyde	Valeraldehyde
6-February	89.18[a]	25.51	36.47	9.53
13-February	8.47[a]	ND	35.57	15.54
20-February	74.98[a]	6.53	20.66	ND
6-March	107.11[a]	7.16	38.76	10.51
17-March	111.48[a]	15.51	24.66	ND
27-March	43.73	29.76	33.96	ND
27-April	87.06[a]	ND	ND	ND
4-May	111.11[a]	19.43	ND	ND
11-May	111.73[a]	25.51	24.66	ND
26-May	50.9	ND	ND	ND
3-June	50.9	ND	ND	ND
17-June	127.56[a]	ND	ND	ND
Mean	81.18	18.49	30.67	11.86

ND: not detected.
[a] Values above calibration curve; samples diluted before injection.

Table 5
Concentrations of carbonyls reported throughout the world in rainwater samples.

Location	Period	Compound (s)	Concentration (μM/VWM)*	References
Rural				
Deuselbach, Germany	1975–1978	FA	4.7 ± 1.6	[33]
Mainz, Germany	1975–1978	FA	5.8 ± 2.8	[33]
Chaguaramas, Venenzuela	1990	FA	9.8	[34]
La, Paragua, Venenzuela	1990	FA	5.4	[34]
Agra, India	1995–1996	FA	4.4	[35]
Galicia, NW Spain	1995–1996	FA	0.69	[36]
		AA	0.13	
Urban				
Camarillo, California	1982	FA	2.0	[37]
Hannover, Germany	1988–1989	FA	2.55 (76.9 μg/L); 3.69 (111 μg/L)	[38]
		AA	0.32 (14.4 μg/L); 0.29 (12.0 μg/L)	
		PA	0.22 (13.2 μg/L); 0.08 (4.7 μg/L)	
Caracas	–	FA	4.8	[34]
Los Angeles, California	1985–1991	FA	3.2	[39]
		AA	0.2	
Los Angeles, California	1995	FA	2.7	[40]
		AA	0.3	
Yokohama, Japan	2003	FA	1.22 ± 1.41	[41]
		AA	0.10 ± 0.15	
Present study	February–June 2009	FA	2.706 (81.18 $\mu g\,l^{-1}$)	
		AA	0.42 (18.49 $\mu g\,l^{-1}$)	
		PA	0.53 (30.67 $\mu g\,l^{-1}$)	
		VA	0.14 (11.86 $\mu g\,l^{-1}$)	

* VWM: volume weighted mean.

hyde > acetaldehyde > propionaldehyde > valeraldehyde which are consistent with the studies reported in the literature [32].

4. Conclusion

The optimized μ-SPE technique used in tandem with HPLC is an efficient method that can be used for identification and quantification of aldehydes in water samples. The polypropylene membrane in the device eliminates interferences in the water samples. Reduced solvent consumption and time are the major advantages of μ-SPE. The μ-SPE device can be further used for targeting other common carbonyl compounds in air and water samples. This novel extraction technique can be successfully applied to the routine analysis of water samples.

Acknowledgments

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