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Optimization of two-stage thermal desorption combined with pentafluorophenyl hydrazine derivatization-gas chromatography/mass spectrometry analytical method of atmospheric carbonyl compounds

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ABSTRACT

The detection method of carbonyl compounds (CCs) in the atmosphere has been a challenging problem because of its low concentration and strong volatility and reactivity. Based on the existing thermal desorption (TD) technology, the TD instrument was combined with gas chromatography/mass spectrometry (GC/MS), and pentafluorophenyl hydrazine (PFPH) was used as derivatization reagent to establish a simple, high sensitivity, good stability and simultaneous detection of 13 atmospheric carbonyl compounds, namely PFPH derivation-two-stage TD-GC/MS analysis method. The main factors affecting the TD conditions were discussed, including desorption temperature, desorption time and carrier gas flow rate. The results showed that when the tube desorption flow rate and time were 10 mL min^{-1} and 8 min, and the trap desorption flow rate and time were 5 mL min^{-1} and 8 min, the recoveries of various CCs PFPH-derivatives were relatively high. The collection efficiencies of all detected carbonyls by this method were above 85 %. The method detection limits (MDLs) of the tested carbonyls were in the range of 0.44–1.23 ng cartridge^{-1}. Compared with the method of PFPH-solvent desorption-GC/MS, the two-stage TD-GC/MS method showed lower MDLs and more carbonyls detected at low concentrations. In brief, the two stage TD-GC/MS analysis method is of great significance for the detection of trace CCs in the time-varying atmospheric environment, and is worthy of popularization and application in atmospheric samples.

1. Introduction

Carbonyl compounds (CCs) are important species of oxygenated volatile organic compounds (OVOCs). CCs have a high reactivity in the atmosphere and can be oxidized by OH free radicals to give rise to secondary pollutants such as O_3 and secondary organic aerosols [1]. Carbonyls not only play an important role in atmospheric chemistry, but are also associated with adverse effects on human health. Long-term exposure to high concentrations of CCs can irritate the skin, eyes and nasopharyngeal membranes and increase the risk of cancer, as shown by numerous studies [2,3]. The field observations of carbonyl compounds were most concentrated in the developed areas of China, including the North China Plain (the average concentrations of formaldehyde, acetaldehyde and acetone vary in the range of 1.86–44.90, 1.99–20.80 and 6.14–28.70 μg m^{-3}), Yangtze River Delta (2.67–31.87, 0.32–30.92 and 6.44–18.40 μg m^{-3}) and Pearl River Delta region (2.57–66.97, 1.55–23.15 and 0.70–15.61 μg m^{-3}) [4–9]. The main research results on carbonyl compounds in China in the last two decades were reviewed by [10]. The presence of carbonyls in the environment is thus of great concern.

However, it is a challenging task to determine trace levels of carbonyls due to their high volatility, polarity and reactivity in the complex environmental air matrix. In particular, the wide range of concentrations in atmospheric air required the development of more sophisticated detection technology [11,12]. The most common analytical method for airborne carbonyls was collected onto silica gel cartridges coated with a derivative agent (2, 4-dinitrophenyl hydrazine, DNPH) to form a stable derivative and was analyzed using high-pressure liquid

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chromatography/ultraviolet detection (HPLC/UV) [13,14]. However, the extraction efficiency of DNPH-HPLC was relatively lower due to significant experimental deviations, especially for heavier CCs, resulting in the questionable reliability of measurement results [15]. The use of pentafluorophenyl hydrazine (PFPH) as a derivative reagent for GC or GC/MS (gas chromatography/mass spectrometry) analysis has received much attention since the initial report by Cecinato et al., [16]. Compared with HPLC/UV method, GC/MS can be superior in terms of chromatographic separation, detection limit and identifying unknown carbonyls by using MS detection. The derivatives formed by the reaction of PFPH with CCs are more suitable for gas chromatography analysis than DNPH derivatives [15,17–19]. However, the pretreatment of these methods mostly depends on complex solvent extraction technology, which is not only time-consuming, labor-intensive, large amount of organic solvents, but also only a few eluents are analyzed, which will reduce the sensitivity of low concentration target samples [20–24]. Therefore, it is necessary to seek a simple, efficient, solvent-free and automation compatible ideal sample pretreatment technology.

Thermal desorption (TD) is another common sample pretreatment technique, which transfers the target compounds adsorbed on the adsorbent directly to the analytical system by heating and carrier gas purging. Compared with the solvent elution method, thermal desorption has the advantages of environmental protection, no pollution, high automation and fast desorption speed. It can be directly combined with certain analytical instruments, and all target compounds after desorption can be transferred to the analytical system for analysis, greatly improving the detection limit of the method [25–28]. Chien and Yin. (2009) used mixed sorbent (Tenax TA and Tenax TA coated with PFPH) and TD-GC/MS analysis for simultaneous determination of airborne carbonyls and aromatic hydrocarbons, which is a simple and feasible method. However, the method detection limit (MDLs) of formaldehyde was much higher and the value reached 25.4 ng cartridge^{-1}. To describe the basic methodological methods available in CCs analysis, Kim et al., [29] investigated the experimental compatibility and differences between HPLC and GC methods. The results confirm that TD-GC/MS is beneficial for obtaining the maximum recovery rate of heavier CCs.

In principle, there are two methods of thermal desorption: one-step thermal desorption and two-step thermal desorption. One-step thermal desorption is the process of desorbing the target compound from the adsorbent and blowing it directly into the GC column by the carrier gas. However, the injection time is often long, and it is easy to produce different degrees of peak expansion, and it is difficult to be used in capillary column analysis. In order to solve this problem, a cold trap system is added after the first step thermal desorption to enrich the target compounds, which improves the chromatographic separation efficiency and has higher sensitivity [30,31]. In this study, we established a two-step thermal desorption method combined with GC/MS, using PFPH as the derivative reagent, namely PFPH derivation-two-stage TD-GC/MS analysis method. The method has high sensitivity, good stability, low method detection limit (MDLs), and can simultaneously detect 13 carbonyl compounds (C1-C10) in the atmosphere. It not only improves the non-online detection method, but also is a starter for the future online measurement of CCs in the atmosphere.

2. Experimental section

2.1. Materials and regents

Hexane was purchased from Merck Corporation, Germany (GC Grade). Standard mixtures of 13 carbonyls (1000 μg·mL^{-1}), was bought from AccuStandard Inc., USA, including formaldehyde, acetaldehyde, propanal, butanal, crotonaldehyde, pentanal, hexanal, cyclohexanone, heptanal, octanal, benzaldehyde, nonanal and decanal. Pentafluorophenyl hydrazine (PFPH, 97 %), employed as a derivative agent, was from Sigma-Aldrich, Germany and used without further purification. Tenax TA (60/80 mesh) was from Supelco Corporation, USA. Stock standard mixtures of carbonyl-PFPH derivatives at 50 μg mL^{-1} were prepared by mixing the standard mixtures of 13 carbonyls (1000 μg mL^{-1}) with PFPH of 5 times more than the total moles of carbonyls in hexane. The stock standard mixtures were left to react at the room temperature for 12 h in the dark to ensure complete reaction.

2.2. Preparation of PFPH sampling cartridge

The glass sampling cartridges were fabricated from Agilent glass liner with a taper one end (7.85 cm length, 4.0 mm i.d., and 6.3 mm o.d.). The length and outside diameter can match up with the thermal desorption oven, which was a component of the developed thermal desorbed and used to heat the sampling cartridges. Tenax TA was used as the solid sorbent. For each sampling cartridges, 50 mg of Tenax TA was packed with the aid of a micro funnel. Both ends of the cartridge were plugged with glass wool of salinization. The sampling cartridge of Tenax TA has been successfully applied to collect VOCs for TD, which has been proved to show excellent thermal stability, great adsorption capacity and high desorption efficiency [23,32]. In order to remove the impurities adsorbed on the sorbent, Tenax TA cartridges were preconditioned twice at 300℃ under the high-purity nitrogen flow of 100 mL· min^{-1} for 1 h before initial use.

In this study, we used the vapor coating technique to coat Tenax TA cartridges with the derivative agent, PFPH. A schematic diagram of the coating set-up was shown in **Figure S1** [18]. A bubble bottle was kept in a water-bath. The inlet of bottle was linked to a high-purity nitrogen cylinder through a mass flow controller and the outlet was connected to a Tenax TA cartridge. About 50 mg of the PFPH powder was placed in the bottom of a bubble bottle. The bubble bottle was heated at 50 ℃ and PFPH was vaporized. The PFPH vapor slowly passed through the Tenax TA cartridge and was absorbed by Tenax TA under a gentle flow of nitrogen (40 mL·min^{-1}). The coating time for each sampling cartridge was 5 min. Under such conditions each sampling cartridge could be coated with about 500 nmol PFPH. To avoid the interference from the ubiquitous presence of formaldehyde and other carbonyls in the laboratory, all processes were carried out in a fume hood. The sampling cartridges were then wrapped in aluminum foil, sealed in Teflon bags and stored in refrigerator at 4 ℃ until use. The sampling cartridges can be reused and directly recoated by PFPH after re-conditioned following the method described above. The vapor coating method not only avoided the problem of impurities in PFPH and reduced the background of the sampling cartridge, but also improved the coating efficiency greatly.

2.3. Thermal desorption (TD)-GC/MS system and sample analysis

The two stage TD-GC/MS system includes a thermal desorption oven to heat the sampling cartridges, a cold trap for refocusing the PFPH-derivatives, a 6-port switching valve to inject samples, the gas control system and the GC/MS system. The schematic (Fig. S2**a**) showed the two-stage thermal desorption unit coupled with 6890 N GC/5975 MS (Agilent Corporation, USA) for the analysis of airborne carbonyls. The thermal desorption unit was designed with two-stage desorption: the sampling cartridge was firstly heated in a flow of helium and the target compounds released into a cold trap for refocusing (cartridge desorption or primary desorption); then the cold trap was rapidly heated to 300 ℃ and the target compounds were quickly transported to the GC column for subsequent analysis (trap desorption or secondary desorption). The thermal desorption oven was designed to a tubular copper with heat blocks and used to heat the sampling cartridges. The cold trap consisted of a stainless tube, the Peltier refrigeration system and the electronic heating system. The stainless tube clinging to the Peltier refrigeration system can obtain low temperature (-20 ℃) of the trap for refocusing target compounds during cartridge desorption, while it touched the electronic heating system to be promptly heated to 300 ℃ for trap desorption. The 6-port switching valve (VICI Valco Instruments Co. Inc., USA), with two positions (A and B), played an important role in switchover between the cartridge desorption and trap desorption. Split was not applied during injection, which allowed all desorbed compounds to be transported into GC column for analysis. During the cartridge desorption, helium flow through the sampling cartridge was controlled by a mass flow controller. While, in the trap desorption, the helium flow through the cold trap was offered and controlled by GC injector and represented the column flow (Fig. S2**a**). The injector was set in the pulsed split less mode. During the trap desorption, the higher pulsed column flow could ensure sufficient desorption of samples. In addition, this design lowered the costs of the instrument. The temperature of 6-port switching valve was kept at 200 ℃ and the transfer lines were fixed at 180 ℃ to prevent condensation of the target compounds. By heating the trap to 200 °C for 10 min, the accumulated PFPH derivatives were transferred via the heated transfer line (with a capillary column in it) to the GC system.

An analyzing cycle began by placing a sampling cartridge into thermal desorption oven. The sampling cartridge was conditioned by helium flow (10 mL·min^{-1}) for 2 min with the valve switched to position A (Fig. S2**b-i**). Cartridge desorption started with the valve switched to position B and the sampling cartridge was heated in the helium flow of 10 mL·min^{-1}. The PFPH derivatives were desorbed from the Tenax TA and re-focused onto the cold trap at −20 ℃ (Fig. S2**b-ii**). The trap desorption began with the valve switched to position A and the cold trap heated to 300 ℃ promptly and the GC run was started. The PHPH derivatives were transferred via a heated transfer line (200 °C) to the GC/MS system. The helium flow of 5 mL·min^{-1} from the GC injector back flushed the re-focused PFPH derivatives into the column of GC for 8 min (Fig. S2**b-iii**). Then, the cold trap was purged at the flow rate of 10 mL·min^{-1} for 10 min with the valve switched to position B (Fig. S2**b-iv**). Finally, the thermal desorption oven and cold trap were cooled for next analysis.

Separation and detection of PFPH derivatives of carbonyls were performed on GC/MS equipped with an HP-5MSI column (5 % phenyl Methyl Siloxane, 30 m × 250 μm × 0.2 μm film thickness). The GC oven temperature program was initially maintained at 40 ℃ for 8 min, then programmed to 150 ℃ at a rate of 4 ℃ min^{-1} and held for 5 min, and finally raised to 250 ℃ at a rate of 6 ℃ min^{-1}. Helium was used as the carrier gas, running at the constant flow of 1.0 mL·min^{-1}. The injector was set in the pulsed split less mode: the pulsed pressure and the holding time were 35 psi and 8 min, respectively. The GC/MS interface temperature was 290 ℃. The MSD electron ionization (EI) energy was set at 70 eV. The mass spectrometer was operated in a selective ion monitoring (SIM) mode. The three most abundant ion fragments of each derivative, reported in previous study [19], were chosen as SIM ions for identification and quantification of the parent carbonyls. Solvent delay was set at 21 min to avoid the possible damage to MS detector due to the high level of PFPH in sampling cartridges.

2.4. *Optimization of thermal desorption condition*

The conditions of cartridge desorption and trap desorption were optimized to achieve the maximal recovery and low detection limits. The bank sampling cartridges without the PFPH coating were spiked with 3 μL of 10 μg·mL^{-1} standard mixtures of carbonyl-PFPH derivatives, which were acquired by diluting the stock standard mixtures (50 μg·mL^{-1}) with hexane, and analyzed. Three replicates were run for each of the data points. In order to obtain the profile of recoveries versus the flow rate of cartridge desorption for the carbonyl-PFPH derivatives coated onto the sampling cartridge, varying helium flow rates from 5 mL·min^{-1} to 50 mL·min^{-1} were chosen for the test. Selection of optimum cartridge desorption time were performed by heating the sampling cartridges from 30 ℃ at a ramp rate of 30 ℃ min^{-1} for different time between 5 min and 15 min (the maximum ramp temperature 240 ℃). For the optimization of trap desorption, the effects of flow rate and time on the trap desorption were studied according to the following design: when a certain flow rate between 1 mL·min^{-1} and 15 mL·min^{-1} was selected for trap desorption, the desorption time would vary from 2 to 12 min. In the study, the GC area counts, which represented the absolute recoveries, were investigated.

2.5. *Calibration*

Calibration curves were established by analyzing sampling cartridges spiked with known amounts of carbonyl-PFPH derivatives. Carbonyl-PFPH derivative standards at five concentration levels in the range of 1–30 μg·mL^{-1} were obtained by diluting the stock standard solution (50 μg·mL^{-1}) with hexane. 5 μL of each standard were spiked into a calibration sampling cartridge that contained 50 mg of un-coated Tenax TA. The calibration sampling cartridges were analyzed to obtain calibration data after they were stored at room temperature overnight. The calibration curves were established by plotting the peak area of the quantification ions of a given carbonyl versus its loading amount.

3. Results and discussion

3.1. *Thermal desorption*

The flow rate was a key factor during cartridge desorption, since it must be high enough to allow complete desorption of target compounds and to prevent compound condensation in the transfer line, but not too high to ensure the capture the efficiency of the cold trap. Fig. 1 showed the peak area at different cartridge desorbing flow rate for carbonyl-PFPH derivatives coated onto the sampling cartridges. With cartridge desorbing flow rate increasing, there was a sharp drop in the recovery for PFPH derivative of formaldehyde. For the PFPH-derivatives of carbonyls with lower molecular mass, such as acetaldehyde and propanal, the recoveries increased at first and then decreased slowly with the flow rate increasing. For the derivatives of carbonyl compounds with higher molecular mass, the recoveries increased at first and then remain unchanged with the flow rate increasing. Therefore, during cartridge desorption, obtaining a high recovery does not only need a high desorption efficiency of the sampling cartridge but also requires a good trapping efficiency of the cold trap. When the cartridge desorbing flow rate was low, the trapping efficiency of the cold trap was better. But the PFPH-derivatives cannot to desorb from the adsorbent completely, especially for the derivatives with higher molecular mass. At the higher flow rate, the desorption efficiencies of all tested compounds were higher, but the trapping efficiency of cold trap reduced, especially for the derivatives with lower molecular mass. Thus, the cartridge desorbing flow rate of 10 mL min^{-1} was employed in subsequent study because the higher recoveries and acceptable precision (RSD < 15 %, n = 3) for all tested carbonyl-PFPH derivatives.

The relative of peak area versus cartridge desorbing time for carbonyl-PFPH derivatives coated onto the sampling cartridges was shown in the Fig. 2. At 5 min, the sampling cartridges were heated to 180 ℃. The recoveries of all the carbonyl-PFPH derivatives were very low, especially for the derivatives of benzaldehyde, nonanal and decanal, which just started to be desorbed from the sorbent. At 7 min, the sampling cartridges were heated to 240 ℃, and the recoveries for all tested derivatives showed a significant increase. It demonstrated that the temperature had an important effect on desorption efficiency. In addition, the desorption equilibration times increased with increasing molecular mass of the analytes. The PFPH-formaldehyde derivative can reach the adsorption equilibrium in 6 min. For other derivatives of C_2-C_6 carbonyl compounds, the desorption equilibration was reached in 7 or 8 min, while for the derivatives of C_7-C_{10} carbonyls, equilibrium was reached within 10 min. There was no significant change in the recoveries for most tested derivatives after desorption equilibration, but the recovery for formaldehyde-PFPH derivative decreased intensively. It showed that the cold trap (-20 ℃) was valid to trap all tested carbonyl-PFPH derivatives at the cartridge desorbing flow rate of 10 mL·min^{-1} except for the derivative of formaldehyde. Taking into account the time

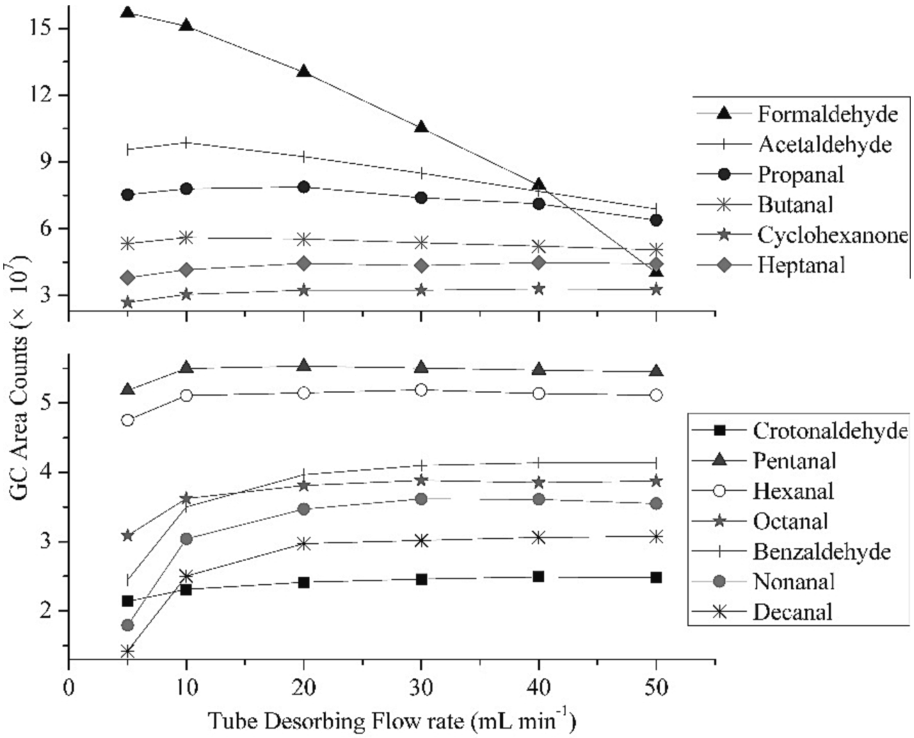

Fig. 1. Peak area versus different cartridge desorbing flow rate for carbonyl-PFPH derivatives coated onto the sampling cartridges.

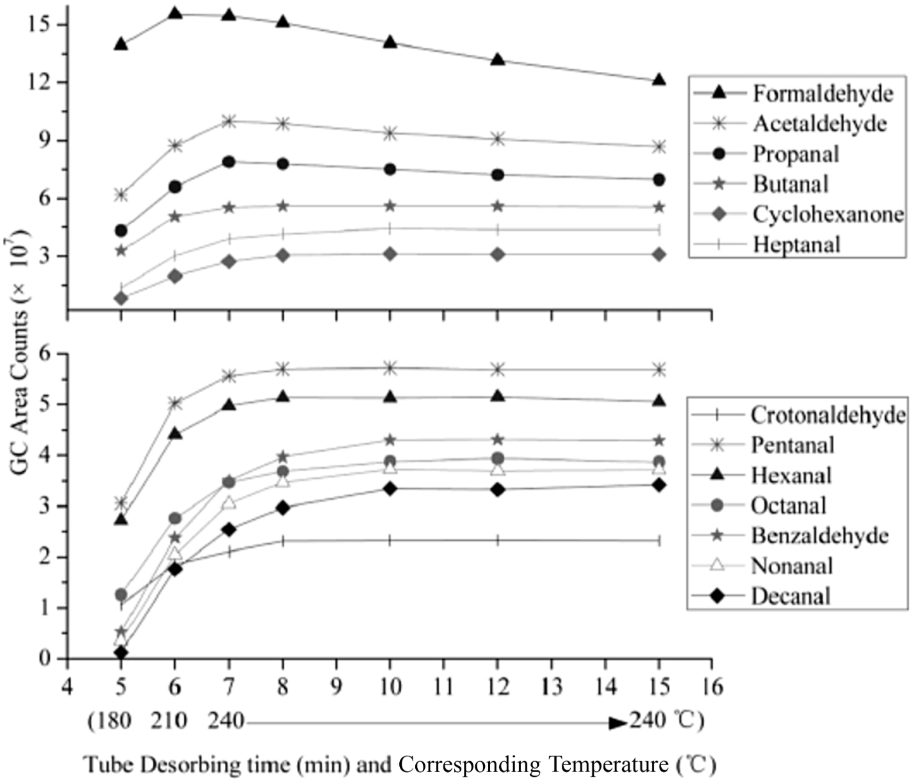

Fig. 2. Peak area versus different cartridge desorbing time for carbonyl-PFPH derivatives coated onto the sampling cartridges.

of the whole analysis and the recoveries of all the carbonyl-PFPH derivatives, the desorbing time of 8 min was chosen as the optimal for cartridge desorption.

Results from the test on trap desorbing flow rate and time (Fig. 3) showed that the higher desorbing flow rate and the longer desorbing time, the higher recovery was achieved. At 1 mL·min^{-1}, the derivatives of octanal, benzaldehyde, nonanal and decanal were not desorbed completely for 12 min. At the moderate flow rate of 5 mL·min^{-1} and 10 mL·min^{-1}, it took about 8 min for all the derivatives to reach the desorption equilibration and have the maximal recovery. It only took

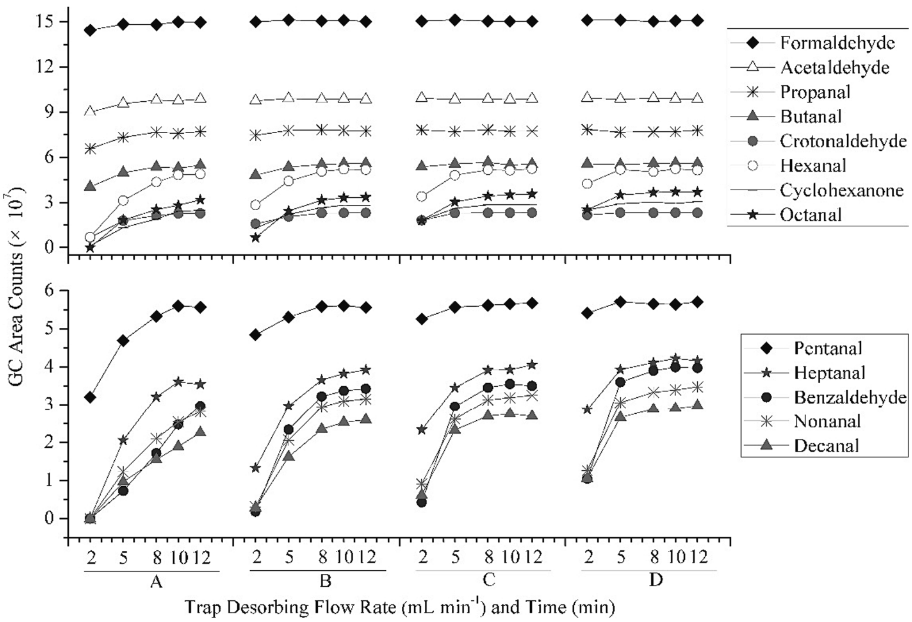

Fig. 3. The profiles of peak area versus trap desorbing flow rate and time for carbonyl-PFPH derivatives coated onto the sampling cartridges. A, B, C and D represent the different trap desorbing flow rate: 1 mL min^{-1}, 5 mL min^{-1}, 10 mL min^{-1} and 15 mL min^{-1}. The numbers of X axis represent the different desorbing time at different desorbing flow rate.

5 min for all the derivatives to reach the desorption equilibration at 15 mL·min^{-1}. Besides, the high trap desorbing flow rate did not only burden the flow controlling system of GC injector, but also affect the GC peak resolution and the vacuum degree of the MSD, with the result in discounting the separation and analysis of GC/MS. Therefore, desorbing flow rate 5 mL·min^{-1} and desorbing time of 8 min were selected for trap desorption.

3.2. Calibration and method detection limits (MDLs)

The GC chromatogram (SIM ions) for a standard mixture of the 13 carbonyl-PFPH derivatives and ambient samples were shown in Figs. 4 and 5, respectively. In order to evaluate the proposed method, some parameters, including the calibration slopes, correlation coefficient (R^2), method precision (relative standard deviations, RSDs) and the limits of detection for the 13 carbonyl compounds, were determined and the results were listed in Table 1.

Linearity was investigated over a loading amount range of 5–150 ng cartridge^{-1}. Good linearities with correlation coefficients (R^2) ranging from 0.990 to 0.999 were obtained for the 13 carbonyl compounds. Method precision was assessed by analyzing six parallel ambient samples collected simultaneously under the same sampling conditions. The sampling duration was 3 h and the sampling flow rate was 50 mL·min^{-1}. The relative standard deviations of all the carbonyl compounds were below 13 %. This indicated that the steps of coating PFPH, sampling, thermal desorbing and analysis were reproducible.

The method detection limits (MDLs) was determined by using replicate analyses of seven calibration sampling cartridges coated with the lowest amount of the carbonyl-PFPH derivatives, which was described in detail in 40 CFR Part 136B (Code of Federal Regulation,

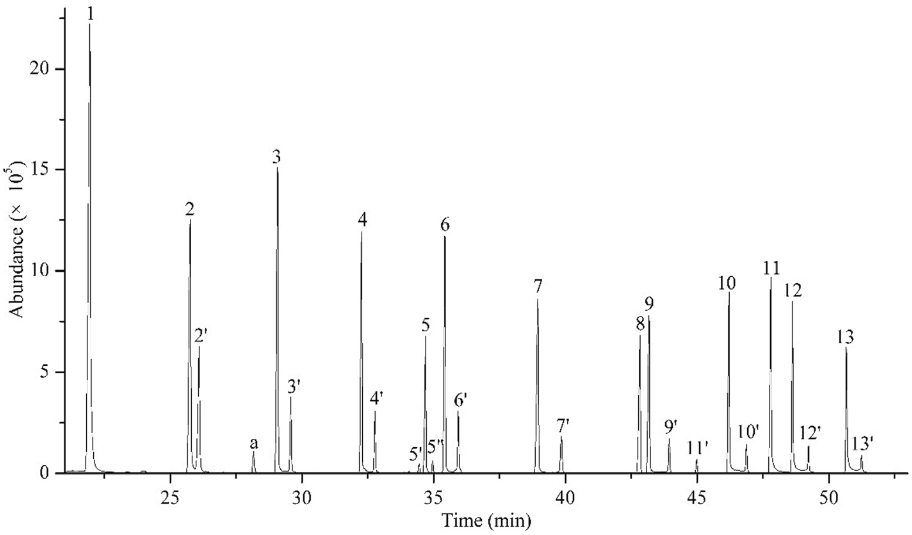

Fig. 4. Chromatograms of standard mixture of PFPH derivatives (SIM mode). 1: Formaldehyde; 2, 2′: acetaldehyde; 3, 3′: propanal; 4, 4′: butanal; 5, 5′,5′′: Crotonaldehyde; 6, 6′: pentanal; 7, 7′: hexanal; 8: cyclohexanone; 9, 9′: heptanal; 10, 10′: octanal; 11, 11′: benzaldehyde; 12, 12′: nonanal; 13, 13′: decanal; a: acetone, not detected in this study.

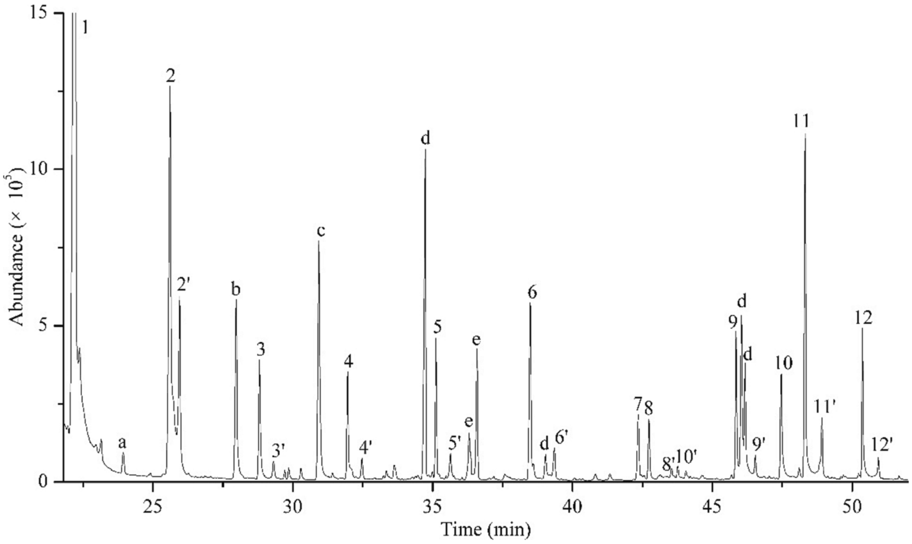

Fig. 5. An example chromatogram for ambient sample (SIM mode). 1: Formaldehyde; 2, 2′: acetaldehyde; 3, 3′: propanal; 4, 4′: butanal; 5, 5′: pentanal; 6, 6′: hexanal; 7: cyclohexanone; 8, 8′: heptanal; 9, 9′: octanal; 10, 10′: benzaldehyde; 11, 11′: nonanal; 12, 12′: decanal; b and c: acetone and butanone, respectively, not detected in this study; a, d, e: unknown compounds present in both blank and sample.

Table 1
Analytical parameters for calibration curves and method evaluation in this study and comparison with other studies of MDLs.

Carbonyl	Slope (*10–6)	R2a	Linear range (ng cartridge-1)	Method detection limits (MDLs)					Method precision (RSD in %, n = 6)
				ngcartridge-1b	nmolcartridge-1b	µg m-3b	ngcartridge-1c	nmolcartridge-1d	
Formaldehyde	5.04	0.996	5–150	0.87	0.029	0.097	9.3	0.26	9.7
Acetaldehyde	3.29	0.998	5–150	0.52	0.012	0.058	7.1	0.097	7.8
Propanal	2.6	0.997	5–150	0.46	0.008	0.051	3.7	0.042	6.9
Butanal	1.87	0.997	5–150	0.51	0.007	0.057	6.1	0.096	10.2
Crotonaldehyde	0.77	0.998	5–150	1.23	0.018	0.137	4.8	e	bd[f]
Pentanal	1.9	0.997	5–150	0.50	0.006	0.056	4.1	e	11.2
Hexanal	1.71	0.998	5–150	0.44	0.004	0.049	5.6	e	7.9
Cyclohexanone	1.02	0.995	5–150	0.65	0.007	0.072	7.3	e	12.6
Heptanal	1.39	0.994	5–150	0.76	0.007	0.084	8.9	0.074	10.3
Octanal	1.23	0.990	5–150	0.56	0.004	0.062	6.3	0.095	8.3
Benzaldehyde	1.32	0.997	5–150	0.73	0.007	0.081	6.4	0.062	8.8
Nonanal	1.16	0.992	5–150	0.82	0.006	0.091	7.8	e	7.0
Decanal	0.99	0.999	5–150	1.02	0.007	0.113	8.5	e	7.4

[a] Correlation coefficient, the calibration curves being calibrated to pass through the original point.
[b] This study, assuming a sampling volume of 9 L, which corresponds to sampling for 3 h at a flow rate of 50 mL min^{-1}.
[c] PFPH-solvent desorption-GC/MS method [28]. [d] PFPH-in-injection port TD-GC/MS method [19].
[e] No data obtained. [f] Below detection limit.

2001). Compute the MDLs (the MDLs based on spiked samples) as follows:

$$MDLs = t(n-1, 1-\alpha = 0.99)Ss.$$

Where:

$MDLs$ = the method detection limit based on spiked samples.

t ($n - 1$, $1 - \alpha = 0.99$) = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom.

Ss = sample standard deviation of the replicate spiked sample analyses.

In this study, when n = 7, the MDLs = 3.143 Ss.

The MDLs of the proposed method were in the range of 0.44–1.23 ng cartridge^{-1} or 0.004–0.029 nmol cartridge^{-1} for various carbonyls. These values were about one order of magnitude better than PFPH-solvent desorption-GC/MS method described by Li et al., [19], in which the MDLs were in the range of 3.7–9.3 ng cartridge^{-1} for 20 carbonyl compounds. Compared with the MDLs of PFPH-in-injection port TD-GC/MS method reported by Ho and Yu. [18], the MDLs in the present method were lower because the two-stage desorption improved the GC peak of the tested compounds and obtained higher sensitivity. When the sampling volume was 9 L, the proposed method can be applied for the determination of below µg m-3 level ambient simple.

In this study, the vapor coating technique was used to coat Tenax TA with PFPH, which can greatly reduce the inherent impurities in the PFPH reagent and the contamination from laboratory air. In the vapor coating process, PFPH was evaporated more easily than other impurities with the higher molecular mass and purer PFPH gas would be coated onto the sampling cartridges. In addition, PFPH gas has less chance to react with carbonyls in laboratory air. Compared with solvent coating method, background levels of carbonyls in blank samples by PFPH vapor coating were much lower (Table S1). Besides, the coating method in this study is more convenient to conduct without repacking of cartridges.

3.3. *PFPH coating amount and sampling flow rate*

As PFPH can be thermally desorbed and transferred onto the GC column, too much PFPH coating could overload the GC column, cause baseline increase, and lower GC peak resolution. In particular, a big

PFPH peak could make the quantification of formaldehyde, which elutes right after PFPH in the GC analysis, inaccurate or even impossible. On the other hand, a higher PFPH coating amount is expected to facilitate the vapor–solid derivatization reaction from a reaction kinetics point of view [19]. Experiments were carried out to determine the suitable PFPH coating amount that balances adequate collection of carbonyls and their subsequent GC analysis. Three PFPH coating amounts (200, 500 and 800 nmol) were tested on the collection of carbonyls in the ambient air. Samples were collected for 3 h at a flow rate of 50 mL·min^{-1}. The collection efficiencies of carbonyl compounds collected at three different PFPH coating amounts were shown in Table 2. It is obvious that the more PFPH coating, the better collection efficiency was achieved. However, the collection efficiency was not improved much when the coated amount was increased from 500 nmol to 800 nmol PFPH per 50 mg Tenax TA. In addition, PFPH coating amount of 800 nmol was observed to compromise the separation of PFPH and the formaldehyde-PFPH derivative peaks. Consequently, the PFPH coating amount of 500 nmol per cartridge was used in the subsequent sampling.

Sampling flow rate was considered as the key parameters to affect the collection efficiency. The optimal sampling flow rate for the collection of carbonyls was evaluated for three levels, 25, 50 and 100 mL·min^{-1}. Samples (in a cartridge that contained 50 mg of PFPH-coated Tenax TA) were taken in the ambient air with different flow rates. The sampling times varied such that the sampling volumes were equal (9 L). Results from the test on sampling flow rate were shown in Table 2. The collection efficiency dropped as the sampling flow rate increased. At the lowest flow rate of 25 mL·min^{-1}, at least 97 % collection efficiencies were achieved for all tested carbonyls. At an intermediate flow rate of 50 mL·min^{-1}, collection efficiencies of acetaldehyde, cyclohexanone and octanal decreased to 86–90 %, while the collection efficiencies for the other carbonyls remained better than 90 %. At the highest flow rate of 100 mL·min^{-1}, the collection efficiency of every tested carbonyl dropped to below 80 %. The progressively less efficient collection of carbonyls at higher flow rates may be due to kinetic limitation, which is same as the conclusions of previous reports [18]. In addition, at the flow rate of 25 mL·min^{-1}, it allowed longer sampling periods meet the analytical requirement and the sampling time resolution decreased. As a result, the sampling flow rate was set at 50 mL·min^{-1} for subsequent testing.

3.4. Comparison with solvent desorption

Four groups of the ambient samples were collected and each group included six parallel samples. Three samples were analyzed with the proposed method and the other three samples with solvent desorption method reported by Li et al., [19]. Table 4 presents mean concentrations of the tested carbonyls in the ambient samples using both methods. Compared with the solvent desorption, there were more carbonyls detected in the ambient air by the thermal desorption. The main reason might be that the thermal desorption method allowed the whole sample to be analyzed and obtained lower limit of detection for all tested compounds. From the data in Table 4, the concentrations of carbonyls obtained by thermal desorption were not significantly different to those by solvent desorption. Especially for higher concentration carbonyls, such as formaldehyde and acetaldehyde, good agreement existed between the two detection methods and the deviations between the two methods were in the range of 2.3–6.0 % and 2.7–5.2 %, respectively. For lower concentration carbonyls such as octanal and benzaldehyde, the deviations were in the range of 7.5–14.2 % and 7.5–13.6 %, respectively. But for all the carbonyls detected by the two methods, the deviations were below 15 % and the results were acceptable. Because of the lower MDLs, the determination of low concentration carbonyls in air samples was much more precise by the proposed method in this study.

3.5. Field study

Field samples were collected using a 9-channal carbonyl autosampler on the roof of a 6-storey building in Shanghai University of Baoshan District in Shanghai, China. A total of 36 carbonyl samples including three parallel samples. There was no breakthrough during 3 h sampling. All the target carbonyls were detected for all samples, except for crotonaldehyde. The GC chromatogram of ambient samples was shown in Fig. 5. Mean concentrations of individual carbonyl on different daytime were listed in Table 3. Formaldehyde and acetaldehyde were the two most abundant carbonyls in the ambient air. Their concentrations were from 6.64 ± 1.36 to 12.07 ± 0.53 and 3.99 ± 0.57 to 7.27 ± 0.41 μg·m^{-3}, respectively. Besides, the concentrations of nonanal were 2.40 ± 0.49 to 3.50 ± 0.24 μg·m^{-3} and higher in the semi-volatile aldehydes, which were very close to the previous studies [23]. Diurnal variations of low molecular weight (LMW) carbonyl compounds were shown in Fig. 6. Formaldehyde and acetaldehyde concentrations have obvious diurnal variations during 7:00–10:00 and 16:00–19:00 (the rush hours in Shanghai) on day 1 to 3, which implied that vehicular exhaust was the most important source at this time.

4. Conclusions

This work presented a sensitive and reliable analytical method for the determination carbonyl compounds in ambient air. The proposed method incorporated the collection of carbonyls via the on-sorbent derivatization with PFPH, and an analysis was performed using a two-step thermal desorption system coupled with GC/MS. Good linearity,

Table 2
Carbonyl collection efficiencies in the ambient air under various conditions.

	Collection efficiency (%)				
PFPH coating amount (nmol)	200	500	800	500	500
Sampling flow rate (mL min^{-1})	50	50	50	25	100
Sampling time (h)	3	3	3	6	1.5
Formaldehyde	62.3 ± 5.5[a]	90.1 ± 3.5	-[c]	98.3 ± 1.4	65.7 ± 6.2
Acetaldehyde	63.7 ± 4.4	87.5 ± 2.5	96.4 ± 1.2	97.8 ± 2.2	68.6 ± 6.2
Propanal	69.9 ± 6.2	94.6 ± 2.5	96.8 ± 2.1	97.1 ± 2.0	78.9 ± 7.4
Butanal	73.1 ± 6.2	91.0 ± 4.3	97.5 ± 1.2	98.1 ± 2.4	73.9 ± 8.4
Crotonaldehyde	bd[b]	bd	bd	bd	bd
Pentanal	66.3 ± 7.1	93.7 ± 3.2	95.4 ± 1.2	99.1 ± 2.7	75.3 ± 7.2
Hexanal	70.7 ± 8.3	90.3 ± 3.4	97.6 ± 2.3	98.2 ± 3.6	78.5 ± 9.2
Cyclohexanone	75.2 ± 10.1	86.4 ± 2.6	98.0.2 ± 3.8	98.2 ± 2.4	72.8 ± 7.1
Heptanal	71.9 ± 7.8	90.5 ± 1.7	98.5 ± 2.4	97.3 ± 1.6	75.3 ± 6.4
Octanal	67.7 ± 9.3	89.2 ± 3.6	98.7 ± 1.2	98.3 ± 2.1	76.3 ± 8.1
Benzaldehyde	72.8 ± 6.5	91.9 ± 5.1	99.2 ± 1.1	99.3 ± 1.3	79.9 ± 6.4
Nonanal	64.7 ± 7.3	91.0 ± 4.4	96.4 ± 3.3	98.8 ± 2.7	74.8 ± 5.6
Decanal	66.0 ± 5.4	91.8 ± 3.5	97.78 ± 2.4	97.5 ± 2.4	73.3 ± 7.6

[a] The arithmetic mean ± standard deviation, n = 3; [b] Below detection limit; [c] Not quantified, because of the co-elution of formaldehyde-PFPH derivative and PFPH.

Table 3
Mean concentration of individual carbonyl compound on different daytime in Shanghai urban ambient air (μg m^{-3}).

Carbonyl	Day1		Day2		Day3	
	Range	Mean ± S.D[a]	Range	Mean ± S.D.	Range	Mean ± S.D.
Formaldehyde	11.49–12.67	12.07 ± 0.53	9.77–10.87	10.16 ± 0.49	5.29–8.13	6.64 ± 1.36
Acetaldehyde	6.75–7.68	7.27 ± 0.41	5.96–6.81	6.27 ± 0.38	3.39–4.65	3.99 ± 0.57
Propanal	2.30–2.61	2.45 ± 0.13	2.05–2.47	2.30 ± 0.18	1.26–2.01	1.67 ± 0.36
Butanal	1.54–2.19	1.82 ± 0.27	1.36–1.91	1.68 ± 0.23	1.11–1.49	1.31 ± 0.17
Crotonaldehyde	bd[b]	bd	bd	bd	bd	bd
Pentanal	1.81–2.11	1.98 ± 0.13	1.43–1.91	1.71 ± 0.20	0.99–1.29	1.14 ± 0.12
Hexanal	2.48–3.01	2.79 ± 0.23	2.31–2.89	2.64 ± 0.24	1.76–2.21	2.01 ± 0.19
Cyclohexanone	1.21–1.69	1.44 ± 0.20	1.02–1.47	1.28 ± 0.19	0.82–1.27	1.06 ± 0.19
Heptanal	1.23–1.97	1.67 ± 0.34	1.38–1.89	1.67 ± 0.22	1.05–1.21	1.09 ± 0.10
Octanal	1.34–1.88	1.51 ± 0.25	1.47–1.79	1.66 ± 0.14	1.29–1.75	1.52 ± 0.20
Benzaldehyde	1.79–2.29	2.03 ± 0.21	1.54–1.92	1.78 ± 0.17	1.19–1.49	1.35 ± 0.14
Nonanal	3.21–3.79	3.50 ± 0.24	2.79–3.21	3.00 ± 0.18	1.87–2.98	2.40 ± 0.49
Decanal	2.07–2.47	2.27 ± 0.17	1.83–2.21	2.06 ± 0.17	1.75–2.11	1.95 ± 0.15
Total carbonyls	38.26–42.54	40.85 ± 2.24	33.54–37.60	36.22 ± 1.88	21.77–30.59	26.12 ± 3.96

[a] The arithmetic mean ± standard deviation, n = 12; [b] Below detection limit.

Table 4
Comparison of Thermal desorption and solvent desorption.

Carbonyl	Thermal desorption (μg m^{-3})				*Solvent desorption (μg m^{-3})				Deviation of the two methods (%)
	07:00–10:00	10:00–13:00	13:00–16:00	16:00–19:00	07:00–10:00	10:00–13:00	13:00–16:00	16:00–19:00	
Formaldehyde	8.11 ± 0.37[a]	6.15 ± 0.28	5.37 ± 0.31	7.23 ± 0.29	7.86 ± 0.30	6.53 ± 0.26	5.25 ± 0.24	6.99 ± 0.29	2.3–6.0
Acetaldehyde	4.75 ± 0.19	4.12 ± 0.20	3.43 ± 0.17	4.46 ± 0.19	4.55 ± 0.21	3.91 ± 0.16	3.54 ± 0.17	4.34 ± 0.2	2.7–5.2
Propanal	1.82 ± 0.11	1.27 ± 0.08	1.42 ± 0.09	1.99 ± 0.08	1.97 ± 0.09	1.39 ± 0.10	1.30 ± 0.07	1.86 ± 0.06	6.8–9.1
Butanal	1.49 ± 0.09	1.26 ± 0.06	1.03 ± 0.07	1.21 ± 0.06	1.37 ± 0.08	1.11 ± 0.06	bd	1.30 ± 0.1	7.2–12.7
Crotonaldehyde	bdb	bd	bd	bd	bd	bd	bd	bd	NAd
Pentanal	1.34 ± 0.07	1.15 ± 0.08	1.07 ± 0.06	1.28 ± 0.05	1.26 ± 0.07	bd	0.95c	1.17 ± 0.08	6.6–11.9
Hexanal	2.31 ± 0.11	1.78 ± 0.0.07	1.67 ± 0.09	2.21 ± 0.10	2.19 ± 0.12	1.90 ± 0.11	1.81 ± 0.13	2.06 ± 0.11	5.3–8.1
Cyclohexanone	0.84 ± 0.04	0.70 ± 0.03	0.61 ± 0.03	0.81 ± 0.04	bd	bd	bd	bd	NA
Heptanal	0.81 ± 0.05	0.68 ± 0.02	0.57 ± 0.04	0.76 ± 0.05	bd	bd	bd	bd	NA
Octanal	1.67 ± 0.09	1.43 ± 0.09	1.27 ± 0.06	1.58 ± 0.07	1.55 ± 0.07	1.24 ± 0.09	1.11 ± 0.08	1.46 ± 0.10	7.5–14.2
Benzaldehyde	1.52 ± 0.08	1.26 ± 0.08	1.18 ± 0.07	1.44 ± 0.08	1.41 ± 0.09	1.12 ± 0.10	1.03 ± 0.09	1.29 ± 0.08	7.5–13.6
Nonanal	2.47 ± 0.12	2.25 ± 0.11	1.99 ± 0.10	2.23 ± 0.12	2.35 ± 0.13	2.10 ± 0.12	1.83 ± 0.11	2.07 ± 0.12	5.0–8.4
Decanal	1.11 ± 0.80	0.87 ± 0.07	0.75 ± 0.06	0.98 ± 0.07	0.97c	bd	bd	bd	13.5

*[19].

[a] The arithmetic mean ± standard deviation, n = 3; [b] Below detection limit; [c] Only one sample; [d] Not applied.

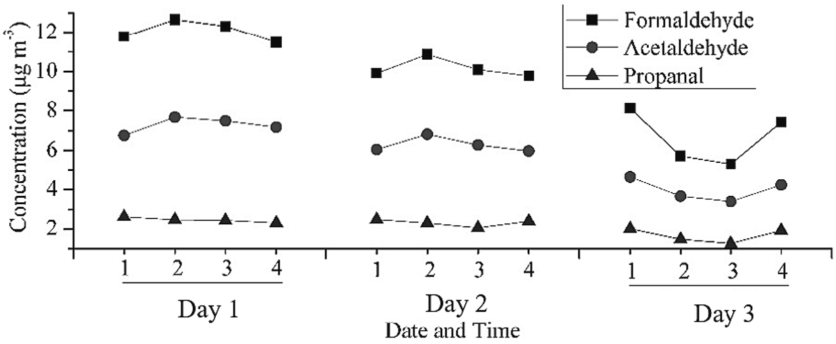

Fig. 6. Diurnal variations of low molecular weight (LMW) carbonyl compounds on different daytime in Shanghai urban ambient air. 1: 7:00–10:00; 2: 10:00–13:00; 3: 13:00–16:00; 4: 16:00–19:00.

detection sensitivity and reproducibility were obtained. It had number of distinct advantages over the traditional on-sorbent derivatization and solvent desorption method (PFPH-solvent desorption-GC/MS). The detection sensitivity was improved with the use of TD, which allowed the whole sample to be analyzed. This method eliminated the use of solvents and the complex sample pre-treatment step. Comparing with the PFPH-solvent desorption-GC/MS method, the results showed good agreement between the two methods and the TD-GC/MS method was found to be a better analytical method for determination of lower concentration carbonyls. In this work, the background carbonyl levels in the sampling cartridge were lowered distinctly through the PFPH vapor coating method. In addition, the developed thermal desorbed reasonably utilized the flow controlling system of GC injector. It did not only make it compatible with GC/MS perfectly, but also reduced the design cost of the instrument. What is more, the development of two step thermal desorption method (PFPH-TD-GC/MS) created significant conditions for on-line measurement of carbonyl compounds.

CRediT authorship contribution statement

Yu Peng: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Xinxin Feng:** Methodology, Formal analysis, Investigation, Writing – review & editing, Visualization. **Yanli Feng:** Conceptualization, Writing – review & editing, Funding acquisition, Supervision, Project administration. **Li Li:** Investigation, Writing – review & editing. **Yingjun Chen:** Investigation, Writing – review & editing. **Jianzhen Yu:** Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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