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Determination of airborne carbonyls via pentafluorophenylhydrazine derivatisation by GC–MS and its comparison with HPLC method

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ABSTRACT

The classical analytical method for gaseous carbonyl measurements based on solid sorbent coated with 2,4-dinitrophenylhydrazine (DNPH) and analysis by HPLC/UV suffers from limited resolution of carbonyls with similar molecular structures and high molecular weights. In this paper, we report the development of a sensitive and reliable analytical method for simultaneous determination of 21 airborne carbonyls within the C_1–C_9 range. Carbonyls were collected on a sampling tube filled with 100 mg Tenax TA (60–80 mesh) sorbent coated with 1 μmol pentafluorophenyl hydrazine (PFPH), followed by solvent desorption and analysis by gas chromatography (GC)/mass spectrometry (MS). Common carbonyl gases including formaldehyde, acetaldehyde, butyraldehyde, hexaldehyde and benzaldehyde at ppbv levels were collected with efficiency greater than 90% onto sampling tubes at a flow rate of 100 mL min^{-1}. The limits of detection (LODs, signal/noise = 3) of the tested carbonyls were in the range of 0.08–0.20 ppbv for a sampled volume of 24.0 L. These limits are less than or comparable with those that can be obtained using the DNPH–HPLC method. The method has been field-tested both in ambient air of York and in diluted cigarette smoke. Comparing field tests with the classical DNPH–HPLC method, good agreement was displayed between the two methods for the same carbonyls, but with more carbonyl species detected by the PFPH–GC/MS method. The PFPH–GC/MS method provides better molecular separation for carbonyls with similar structures, is highly sensitivity and gives confirmation of identification by structures when detected using MS.

1. Introduction

Carbonyl compounds are the almost obligatory intermediates of the photooxidation of hydrocarbons and offer important mechanistic insights into the oxidation processes of the atmosphere [1]. Photolysis can yield carbonyl-produced free radicals which can react rapidly and serve as intermediates in the formation of ozone and peroxyacylnitrates (PANs). As such this group of compounds play a crucial role in the formation of photochemical smog [2,3]. In addition, some carbonyl compounds such as formaldehyde, acetaldehyde, and acrolein are known to have various direct adverse effects on human health [4]. This combination of impacts makes measurement of airborne carbonyls in both ambient and indoor environments of great interest.

The most commonly used method for analysis of airborne carbonyls is via collection of analytes on solid sorbents coated with a suitable derivatization agent, commonly, 2,4-dinitrophenylhydrazine (DNPH), followed by solvent desorption and liquid injection for analysis by HPLC. This DNPH/HPLC method is currently the standard analytical method for atmospheric carbonyls recognized by the EU and US EPA due to its acceptable reproducibility and specificity. However, HPLC co-elutions of larger carbonyl compounds occur due a combination of increasing possible isomers and limited HPLC peak capacity. A result is that typically only lightweight carbonyls (C_1–C_5) can be reliably determined. To compensate for limited column resolution, HPLC combined with mass spectrometry has been used for the structural elucidation and identification of DNPH derivatives of higher carbonyls [5,6]. HPLC/MS/MS methods have been shown to differentiate between aldehydes and ketones, straight-chain and branched structures, and unsaturated and aromatic carbonyls [5,7]. The above HPLC methods have all been based on the same pre-processing including sampling and solvent desorption, which are, however, time-consuming and manually intensive. In addition the methodology is prone to artefact formation and has long integration periods for sampling to compensate for limitations in intrinsic sensitivity. The relatively high-cost of HPLC/MS/MS instrumentation has also been a factor in relatively limited take-up of this methodology.

To improve time resolution of measurements some high time resolution on-line GC/MS–FID techniques have been developed to

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allow near real-time measurements of carbonyls and other OVOCs simultaneously in ambient air by agencies such as NOAA, NASA and NCAS [8–10]. These instruments are equipped with automatic sampling systems and multiple detectors (quadrupole ion trap mass spectrometer (ITMS) and FID). Reductive gas detection (RGD) has also been used with GC to detect atmospheric carbonyls in near real time and this has been used in the projects such as TRACE-P, ABLE and PEM-West: B [11]. However, formaldehyde cannot be detected using on-line GC/MS–FID because it does not produce unique ions in the MS. An automated sampling and analysis HPLC system was recently developed based on DNPH derivitization [12]. But the complicated designation would prevent the common use of automatic system and many improvements should be made for it.

GC/MS coupled with on-sorbent derivatization can be used to determine airborne C_1–C_{11} carbonyls including formaldehyde and some di-carbonyls and is superior in terms of chromatographic separation and detection sensitivity compared with HPLC methods [13–16]. Pentafluorophenyl hydrazine (PFPH) has been proved to be an effective derivatising agent for GC analysis [17,18]. The five fluorine atoms in PFPH make the carbonyl-PFPH derivatives more thermally stable and more volatile than the DNPH derivatives. Ho and Yu [15] recently developed an approach to collect carbonyls onto PFPH-coated solid sorbents followed by in-injection port thermal desorption-GC/MS analysis of PFPH derivatives. The in-injection port thermal desorption of the sampling tube eliminated solvent and lowered background carbonyls in the lab. Thermal desorption can however lead to a loss of compounds due to lower than optimal desorption efficiency. Additionally, the thermal desorption apparatus is not commonly installed on most general GC/MS systems. Li et al. [13] developed a GC/MS method for simultaneous determination of 20 carbonyl compounds using PFPH-coated tube. However, in the study, the preparation of sampling tube was complex and cumbersome and formaldehyde was found not to be completely separated from PFPH during GC analysis. There remains therefore a requirement to develop a convenient and feasible analytical method based on standard GC/MS instrumentation, which can be used in ordinary laboratories.

This paper reports a novel GC/MS method to analyse airborne carbonyls based on their PFPH derivatives. The method involves preparing simple sampling tubes packed with PFPH-coated Tenax TA, using sampling tubes as collection substrate and then GC/MS analysis by liquid injection. The method was found appropriate for the determination of 23 carbonyl compounds in the range of C_1–C_9. The method was applied to determine those carbonyls in ambient air and in a strong emission source (cigarette smoke). We complete this paper by comparing to DNPH–HPLC/MS method for identification and quantification of carbonyls.

2. Experimental

2.1. Chemical reagents

Hexane as solvent was from Fisher, UK (HPLC grade). All organic carbonyls (25 species) and Tenax TA (60/80 mesh) were purchased from Sigma–Aldrich (Gillingham, UK), including formaldehyde (37% in water), acetaldehyde (99.5%), propionaldehyde (97%), acetone (99.5%), acrolein (95%), crotonaldehyde (99.5%), n-butyraldehyde (98%), ethyl methyl ketone (99%), methacrolein (95%), methyl vinyl ketone (99%), crotonaldehyde (99.5%), valeraldehyde (99%), caproaldehyde (98%), 2-furaldehyde (98%), 2-hexen-1-al (98%), benzaldehyde (99%), heptaldehyde (95%), *o*-tolualdehyde (98%), *m*-tolualdehyde (99.1%), *p*-tolualdehyde (98.6%), octylaldehyde (99%), hexyl methyl ketone (99%), 2,5-dimethylbenzaldehyde (98.2%), and glyoxal (40% in water), pentafluorophenyl hydrazine (PFPH) (97%). Standard solutions containing 15 species of carbonyl-DNPH hydrazones (15 μg/mL), 2,4-dinitrophenylhenylhydrazine (DNPH)-coated silica cartridges and potassium iodide (KI) ozone scrubbers were purchased from Supelco (USA). Standard gas containing 0.5 ppm acetaldehyde, butyraldehyde and caproaldehyde was purchased from the Apel-Riemer Environmental Inc. (Boulder, USA).

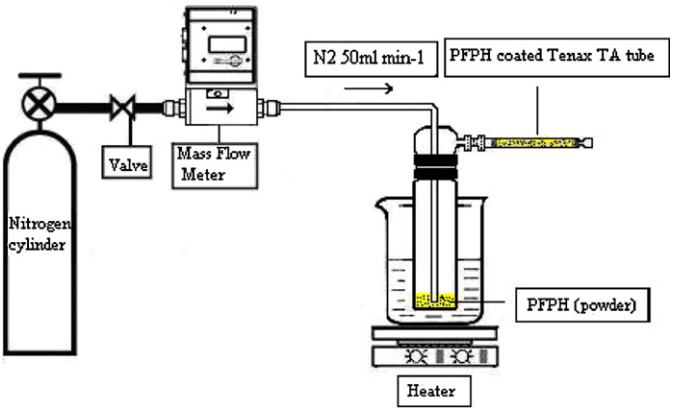

Fig. 1. Schematic diagram of the apparatus to prepare PFPH coated Tenax TA tube.

2.2. Preparation of sampling tubes and standard gases

The sampling tubes were fabricated from Gerstel glass liners with a taper one end (6.0 cm length, 4 mm i.d. and 6 mm o.d.). Before use, Tenax TA was placed in a furnace at 275 °C overnight to remove impurities. Each sampling tube was packed with about 100 mg of Tenax TA and both ends of the tube were plugged with glass wool that had been prebaked at 550 °C overnight. Coating was achieved by connecting each sampling tube with a bubble bottle containing a known amount of PFPH (Fig. 1). The bubble bottle was heated by a water bath at 50 °C and PFPH was vaporized. The PFPH vapour slowly passed through the sample tube and was absorbed by Tenax TA under a gentle flow of nitrogen (20 mL min^{-1}). The coating time for each sampling tube was 20 min. Under such conditions each sampling tube could be coated with about 1 μmol PFPH. To avoid the interference from the ubiquitous presence of formaldehyde and acetone in the laboratory air, all processes were carried out in a fume hood. The PFPH-coated sampling tubes were then stored in a test tube sealed with Teflon cap and wrapped in an aluminium foil. To avoid the contamination during storage, the storage tube was filled with nitrogen. The glass sampling tubes could be reused and directly recoated by PFPH after they had been eluted by solvent and then heated at 275 °C overnight. Gloves must be worn and the tubes must be handled only with cleaned forceps to minimize contamination during the whole process.

To validate and optimise the method, a multicomponent gas standard containing 10 ppb of formaldehyde, acetaldehyde, butyraldehyde, heptaldehyde, and benzaldehyde were prepared by the dilution a multicomponent compressed gas standard containing 0.5 ppm of acetaldehyde, butyraldehyde, heptaldehyde (Apel-Reimer Environmental, USA) and vaporization of formaldehyde and benzaldehyde in methanol in a 100-L Tedlar bag (SKC Limited, UK). The bag was cleaned by filling it with high-purity nitrogen gas and evacuating it with a pump at least three times before use. The bag was first filled with 2.0 L multicomponent standard gas and then filled to 50 L by high purity nitrogen gas. Then a 10 μL of methanol solution containing 4.16×10^{-2} mol L^{-1} of formaldehyde and benzaldehyde was injected into the bag by a syringe and vaporization of methanol solution was assisted by gently heating the bag with a hairdryer as Ho and Yu conducted in the study [15]. The bag was also gently shaken to facilitate the

uniform distribution of carbonyls in the bag. At last, the standard gas was diluted to 100 L by nitrogen and the concentrations of carbonyl compounds were all 10 ppb in the 100-L Tedlar bag. The flow rates of gases were exactly controlled by a mass flow controller (MKS Instruments, UK).

2.3. Sample collection and analysis by the PFPH method

Test air samples including ambient air and cigarette smoke were collected in the packed sampling tubes using a sampling pump (KNF, Germany). The collection efficiency for various carbonyls was obtained by passing the test atmospheres of standard gas mixtures through two identical sampling tubes connected in series. The collection efficiency was calculated as a % using $100 \times (1 - A_b/A_f)$, where A_f and A_b are the amounts of a carbonyl collected on the front and the back sampling tubes, respectively. Ambient samples were taken at a roadside location of the University of York. A KI ozone scrubber was placed upstream of the sampling tube to minimize ozone interference during ambient sampling. Each ambient sample was collected at a flow rate of 100 mL min^{-1} for 4 h. At least one field blank sample was collected for each set of samples. The blank sample was handled the same as the other samples with the exception of drawing air through it. Cigarette smoke was prepared by collecting a burning cigarette to the inlet of a Teflon bag and the smoke was drawn into the bag at a rate of 0.4 L min^{-1}. After tobacco combusting, the cigarette smoke in Teflon bag was diluted by nitrogen to 100 L and the diluted cigarette smoke was collected at a flow rate of 50 mL min^{-1} for 20 min. One brand cigarette (Regal, Imperial Tobacco), which is commonly consumed in UK, was tested in this study. To eliminate the influence of particle in smoke, a filter was collected on the upstream of the sampling tube. The flow rate was exactly controlled by mass flow controller. After sampling, all samples were resealed in a Teflon bag, stored in a desiccator and analyzed at least three day later but within one week to obtain a stable yield of carbonyl derivatives with coated PFPH [15].

The hydrazones formed by carbonyl reaction with PFPH were eluted slowly from the Tenax-TA with 8.0 mL hexane and the hexane extracts were concentrated to 1.0 mL by a centrifugal evaporator (V-10 1.6 Evaporator, Biotage, Sweden) under the condition of 100 Pa vacuum and 20 °C. Separation and detection of PFPH derivatives with carbonyls was performed on a GC–TOF/MS incorporating an Agilent 6890N GC (USA) and a Leco Pegasus III reflection time-of-flight MS (USA) equipped with an HP5 column (30 m × 33 mm × 0.25 μm, length × internal diameter × film thickness). The GC oven temperature program was initially set at 70 °C, programmed at a rate of 8–150 °C min^{-1} and then at a rate of 6–210 °C min^{-1}, and held at the final temperature of 210 °C min^{-1} for 5 min. The injector was set in the splitless mode. The inlet temperature was 275 °C and the GC/MS transfer line temperature was 290 °C. Solvent delay was set at 6.5 min for MS detector to avoid the possible damage to MS detector due to the high level of PFPH in solvent. The mass spectrometer was operated in a scan mode with a mass range of 50–500 Da to identify the most abundant ions and the molecular ion of each compound. The three most abundant ion fragments of each derivative were chosen as selective ion monitoring (SIM) ions for quantification of the parent carbonyl (Table 1).

2.4. Calibration of the PFPH method

Calibration curves were established by analyzing known concentrations of the PFPH-carbonyl derivatives prepared in hexane solutions. A set of the PFPH-carbonyl derivative standards at six concentration levels were prepared in hexane by mixing carbonyls with PFPH at least 10 times more abundant than the total moles of carbonyls in the highest concentration calibration standard. Concentrations of individual carbonyls ranged from 4.0 to 14.0 μmol L^{-1} (4.0, 6.0, 8.0, 10.0, 12.0, 14.0 μmol L^{-1}, respectively). The calibration mixtures included 21 species of carbonyl compounds. The mixtures of the calibration standards and PFPH in hexane were allowed to stand at room temperature overnight to ensure complete reactions. Kinetics experiments from this work and also work done by other work [19] show that the derivatization reactions in the liquid phase can be completed in 2 h.

Table 1
GC retention times and characteristic mass fragments of carbonyl-PFPH derivatives.

No.	Carbonyls	R.T. (min)	Base ion	MW	SIM ions
1	Formaldehyde	4.82	155	210	155,182,210
2	Acetaldehyde	6.15, 6.58[a]	182	224	155,182,117
3	Acetone	7.2	238	238	155,183,236
4	Propionaldehyde	7.51	183	238	183,155,210
5	Acrolein	7.95	236	236	155,183,236
6	Butyraldehyde	8.53	252	252	155,183,252
7	Ethyl methyl ketone	8.94	183	252	183,224,252
8	Methacrolein	9.06	183	250	155,183,250
9	Methyl vinyl ketone	9.05	155	250	155,182,250
10	Crotonaldehyde	10.14	250	250	250,182,155
11	Valeraldehyde	10.75	224	266	183,224,155
12	Caproaldehyde	11.96	183	280	155,183,280
13	Furfural	13.0, 13.6	276	276	94, 117,155
14	Hexenal	13.1, 13.5	278	278	155,182,278
15	Heptaldehyde	13.72	168	295	105,168,210
16	Methyl hexyl ketone	14.50	238	308	196,238,308
17	Octyl aldehyde	15.86	183	308	69,155,183
18	Benzaldehyde	16.51	286	286	155,183,286
19	4-Fluorobenzaldeh	16.54	183	304	155,183,304
20	*m*-Tolualdehyde	18.20	183	300	117,155,183
21	*o*-Tolualdehyde	18.25	183	300	155,183, 300
22	*p*-Tolualdehyde	18.38	183	300	118,155,300
23	2,4-Bimethylbenzaldehyde	19.62	314	314	155,182,314
24	Glyoxal	22.93	155	418	117,155,182

[a] Two peaks/isomers are formed due to non-symmetric carbonyls.

2.5. Sample collection and analysis using a DNPH method

Air samples were collected at a flow rate of 1 L min^{-1} through DNPH-coated silica cartridges (Supelco) with a KI ozone scrubber (Supelco) placed upstream. After sample collection, each cartridge was eluted with acetonitrile and the final volume of the eluent was 5.0 mL. Calibration standards were prepared by diluting 1.0 mL of 15 μg carbonyl-DNPH hydrazones (Supelco) in an acetonitrile solution. Concentrations of individual carbonyls in the calibration standards ranged from 0.25 to 2.0 μg mL^{-1}. The DNPH-carbonyl derivatives were separated and analyzed by a LC–MS/MS equipped with a HCT Plus ion trap mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany) and a Supelcosil C_{18} column with 5 μm particle size (25 cm × 4.6 mm). Acetonitrile and water were used as mobile phases according to the following gradient procedure: 0–30 min from 40% to 80% acetonitrile, and 60% to 20% water, hold for 6 min and return to starting condition in 4 min. The flow rate of mobile phase was 0.8 mL min^{-1} and the injection volume was 20 μL. The mass spectrometer with atmospheric pressure chemical ionization (APCI) in the negative mode was used to qualify the different carbonyl DNPHs by their quasi-molecular ions. For MS detection, APCI interface conditions were nebulizer pressure of 40 psi with 5 L min^{-1} of 300 °C N_2 and 350 °C vaporizer temperature. The corona discharge was set to 10 μA for negative ion generation. The ramp range for capillary was 1500–4500 V opposite in polarity to the ions generated. The mass/charge scan range examined was 50–500 Da.

2.6. Field sample collection for method comparison

Two side-by-side sampling trains, one employing a PFPH sampling tube and the other using a DNPH cartridge, were used to

Table 2
Linear regression parameters for calibration curves and minimum detection limits.

No.	Carbonyls	Slope ($\times 10^6$)	Intercept	R^2	MLD (ppb)			RSD[c] (%, $n=5$)	Recovery (%, $n=6$)
					GC/MS[a]	GC/MS[b]	HPLC/MS[a]		
1	Formaldehyde	38.94	125	0.995	0.08	0.26	0.21	5.6	93.1 ± 3.4
2	Acetaldehyde	12.85	102	0.996	0.15	0.10	0.18	6.4	98.2 ± 2.3
3	Butyraldehyde	7.189	84	0.993	0.16	0.10	0.14	7.3	96.4 ± 4.4
4	Caproaldehyde	5.734	44	0.995	0.15	–[d]	–	6.9	96.4 ± 3.3
5	Benzaldehyde	7.895	57	0.998	0.11	0.06	0.14	7.8	94.5 ± 2.5
6	Acetone	9.856	96	0.992	0.14	–	–	5.3	–
7	Propionaldehyde	9.432	95	0.993	0.14	0.04	0.12	5.9	–
8	Acrolein	8.738	90	0.995	0.15	0.10	–	6.7	–
9	Methyl ethyl ketone	7.439	85	0.994	0.17	0.06	–	5.7	–
10	Methacrolein	7.893	88	0.992	0.16	–	–	5.4	–
11	Methyl vinyl ketone	7.684	76	0.994	0.16	–	–	5.3	–
12	Crotonaldehyde	6.943	86	0.994	0.18	–	0.23	4.7	–
13	Valeraldehyde	5.459	84	0.995	0.15	–	0.10	4.5	–
14	Furfural	4.659	65	0.991	0.17	0.04	–	7.5	–
15	Hexenal	4.636	52	0.992	0.17	–	–	7.7	–
16	Heptaldehyde	2.734	54	0.995	0.14	0.08	–	6.4	–
17	Methyl hexyl ketone	3.657	55	0.989	0.21	–	–	6.5	–
18	Octyl aldehyde	5.764	56	0.992	0.19	0.10	–	4.5	–
19	4-Fluorobenzaldeh	5.767	55	0.993	0.21	–	–	5.6	–
20	*m*-Tolualdehyde	2.565	52	0.985	0.24	0.05	–	10.6	–
21	*o*-Tolualdehyde	4.766	62	0.978	0.21	–	–	7.8	–
22	*p*-Tolualdehyde	5.728	52	0.994	0.22	–	–	6.8	–
23	2,4-Bimethylbenzaldehyde	1.563	76	0.996	0.20	–	–	4.7	–
24	Glyoxal	2.763	54	0.997	0.18	0.12	–	7.9	–

MLD (method limit of detection) GC/MS: assumes a sampled air volume of 24 L, i.e., 4-h sampling at 0.1 L min^{-1}; HPLC/MS: assumes a sampled air volume of 60 L, i.e., 1-h sampling at 1 L min^{-1}.
[a] This study.
[b] Ho and Yu [15].
[c] Relative standard division.
[d] No data obtained.

collect ambient air and cigarette smoke. The PFPH sampling train was operated at 100 mL min^{-1}, whereas the DNPH sampling train was operated at 1 L min^{-1}. The ambient sampling site was at roadside site on the campus of University of York. The university is located at a suburban site on the eastern side of York and away from commercial and industrial centres in the city. Four sets of samples were taken at this location; each sample was collected for 4 h. The samples were taken daily from 7:00 to 19:00 from March 2 to 3, 2010. To eliminate the influence of particles, a filter was located upstream of the sampling tubes. For diluted cigarette smoke sample, each DNPH sample was collected for 40 min, whereas each PFPH sample was collected for 20 min to avoid breakthrough. Field blanks were taken for each sampling event. The DNPH samples were stored in a refrigerator at <4 °C before analysis.

3. Results and discussion

3.1. Calibration and method evaluation including laboratory blank

Table 2 lists the calibration and method performance parameters, including the calibration slopes, correlation coefficient (R^2), method precision (relative standard deviations, RSDs), the limits of detection (LODs), for pentafluorophenyl hydrazones of the 23 carbonyl compounds.

The calibration curves were established by plotting the average peak area ($n=5$) of the quantification ion (m/z 155) for a given carbonyl versus the carbonyl concentration in the standard solutions. The m/z 155 ion originates from the PFPH moiety and is the base peak in the EI mass spectra of all the PFPH derivatives. Correlation coefficients (R^2) ranging from 0.975 to 0.997 were obtained for 21 carbonyl compounds, indicating that the calibration curves can be directly used to quantify the concentration of carbonyl-PFPH hydrazones. The limits of detections (LODs) for this method were calculated by using 3 times of ratio of signal to noise (S/N). The LODs in nanomoles per sample tube are translated into mixing ratios in the sub-ppb range for a sample volume of 24 L, which corresponds to sampling for 4 h at a flow rate of 100 mL min^{-1}. If the sampled air volume is increased or decreased, the LODs in ppbv would be proportionally lower or higher. Compared with the LODs reported by Ho and Yu [15], the LODs of the carbonyls with higher molecular weight were higher since their SIM signals were lower in this study. This arises through the use of a ToF MS detector which does not convey any addition sensitivity when limited ions are used for quantification – in contrast for example to quadrupole MS.

The calibration curves in the DNPH method were established by plotting peak areas of MS signals versus the carbonyl concentration in the standard solutions. Table 2 also lists the LODs of the DNPH method expressed in ppbv. The LODs in ppbv are calculated by assuming a sampled air volume of 240 L, which corresponds to sampling at a flow rate of 1 L min^{-1} for 4 h. It can be seen from Table 2 that the LODs of PFPH method are comparable with those given by the DNPH method even though the sample volume in PFPH method is much lower than that in DNPH method. The two methods had similar method precision. Method precision was assessed by analyzing five replicate standard gas samples collected simultaneously under the identical sampling conditions. The relative standard deviations of the measured carbonyls ranged from 0.7 to 7.5% in the PFPH method, which indicated that the steps of coating PFPH, sampling, and analysis were generally reproducible.

To evaluate the feasibility of this method, standard calibration gases containing formaldehyde, acetaldehyde, butyraldehyde, hexanaldehyde, benzaldehyde at 10.0 ppbv were collected by the PFPH-coated sampling tubes and then determined by this GC/MS method under typical sampling and analysis conditions. It was found that the recovery values varied from 92.1 ± 3.4% for formaldehyde to 98.5 ± 2.5% for benzaldehyde.

Table 3
Background levels (ng tube^{-1}) of carbonyls in blank samples coated by PFPH gas and PFPH solution.

Blank samples	Coating method	Formaldehyde	Acetaldehyde	Acetone
Ambient air	Gas	2.6 ± 2.1 (n = 6)[a]	–[b]	–
	Solution	5.8 ± 4.9 (n = 4)	7.5 ± 4.1	15.3 ± 7.4
Cigarette smoke	Gas	3.8 ± 3.2 (n = 6)	6.4 ± 3.1	11.4 ± 6.3
	Solution	5.8 ± 4.9 (n = 4)	15.7 ± 7.4	24.3 ± 9.6

[a] n, number of blank samples.
[b] Under method limit of detection.

In this study, the Tenax-TA sorbent was coated by PFPH gas in a sealed system, which can greatly reduce the contamination from carbonyls in laboratory air. Unlike a PFPH solution coating method, PFPH gas has less chance to react with carbonyls in laboratory air during coating time. From the comparison of background levels of carbonyls in blank samples by two coating method (Table 3), it can be observed that the PFPH gas coating method can be less contaminated by ambient air. Compared with other reported coating methods [13,15], the method in this study is more convenient to conduct without repacking of tubes and is less polluted by ambient air during the procedure.

3.2. GC and MS characteristics of PFPH-carbonyl derivatives

A GC chromatogram of standard carbonyl-PFPH derivatives is shown in Fig. 2. The GC retention times for 21 tested carbonyls are listed in Table 1. An HPLC/MS chromatogram for the standard mixture of DNPH derivatives is also shown in the figure for comparison. In the GC chromatogram, two peaks are attributed to the same parent carbonyl (e.g., acetaldehyde, valeraldehyde, hexyl methyl ketone, and octylaldehyde) in some instances. Such double peaks are a result of two isomers formed between PFPH and any nonsymmetric carbonyls (Fig. 3). Similar multiple peaks corresponding to a single parent carbonyl have also been known to exist for the PFBHA and DNPH derivatives of carbonyls [14,20]. It is clear that the PFPH derivatives of the carbonyl compounds typically present in the atmosphere are well resolved by the GC column and that the method takes advantage of the better peak capacity available in GC compared to normal HPLC. Most notably, a baseline separation is achieved for acetone and acrolein, two carbonyls of very similar molecular weights. In the HPLC/MS chromatogram the DNPH derivatives of these two carbonyls are mixed and cannot be separated (Fig. 2). The inability to provide good separation for acetone and acrolein of the DNPH/HPLC

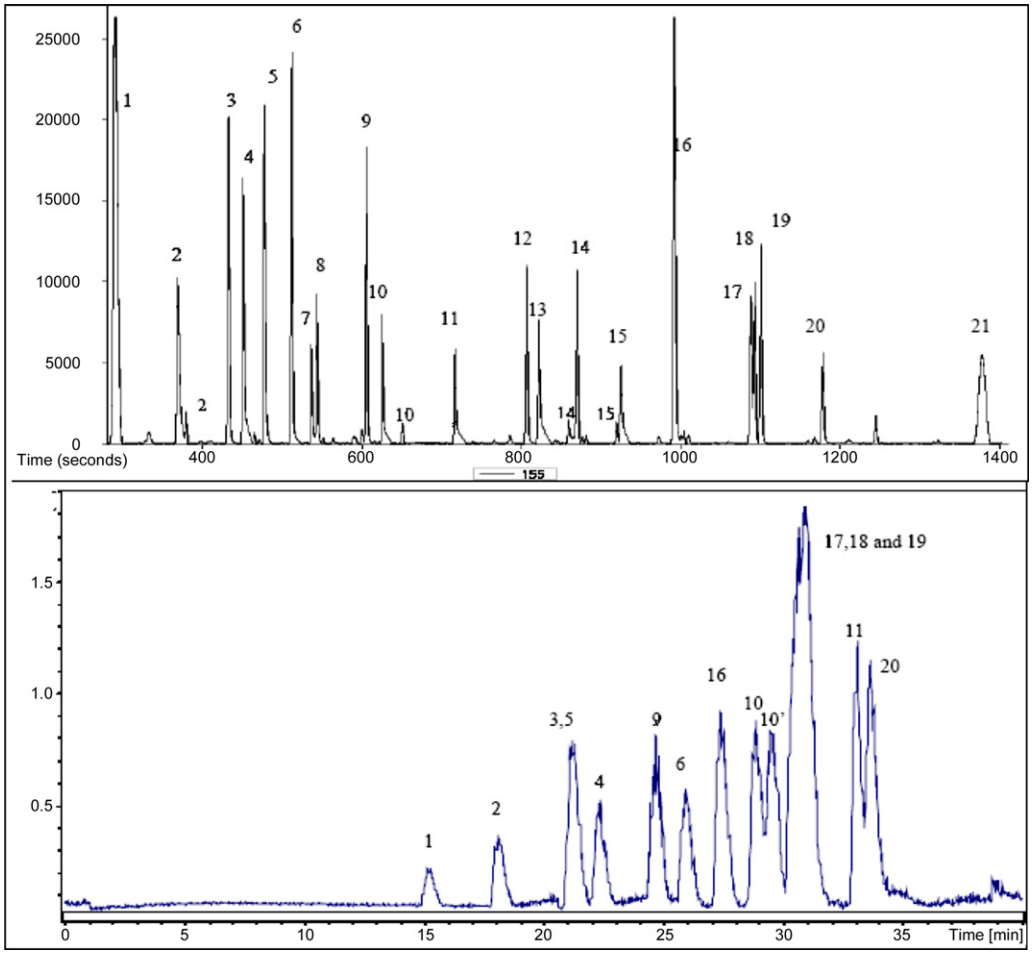

Fig. 2. Chromatograms of the standard mixture of carbonyl-PFPH derivatives and carbonyl-DNPH derivatives containing the following carbonyls. Peak 1, formaldehyde; 2, acetaldehyde; 3, acetone; 4, propionaldehyde; 5, acrolein; 6, butyraldehyde; 7, methyl ethyl ketone; 8, methacrolein; 9, crotonaldehyde; 10, valeraldehyde; 10′, isovaleraldehyde; 11, caproaldehyde; 12,furfural; 13, heptaldehyde; 14, methyl hexyl ketone; 15, octylaldehyde; 16, benzaldehyde; 17, *o*-tolualdehyde; 18, *m*-tolualdehyde; 19, *p*-tolualdehyde; 20, 2,5-dimethylbenzaldehyde; and 21, glyoxal.

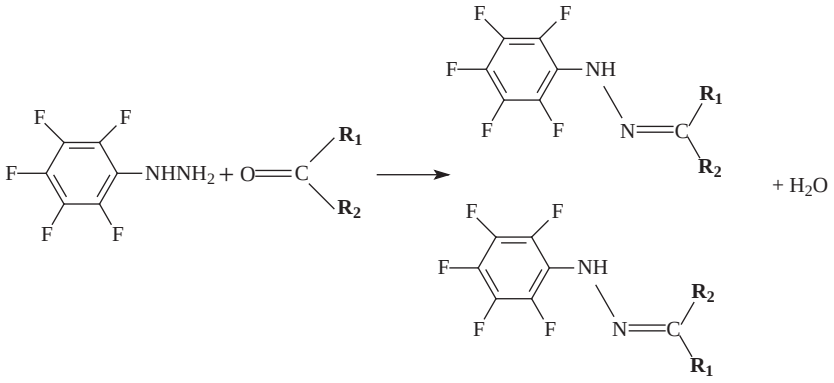

Fig. 3. Derivatization reaction of carbonyls with PFPH to form their corresponding isomers.

method is particularly a problem for ambient samples, in which acetone is normally present at much higher levels than acrolein [21]. As a result, small amounts of acrolein can potentially go undetected even though this is a key carbonyl from a health perspective. In the diluted cigarette smoke sample shown in Fig. 4, acrolein is unambiguously detected in the GC chromatogram; however, its presence cannot be detected in the HPLC chromatogram. Similar phenomena occur with *o*-tolualdehyde, *m*-tolualdehyde,

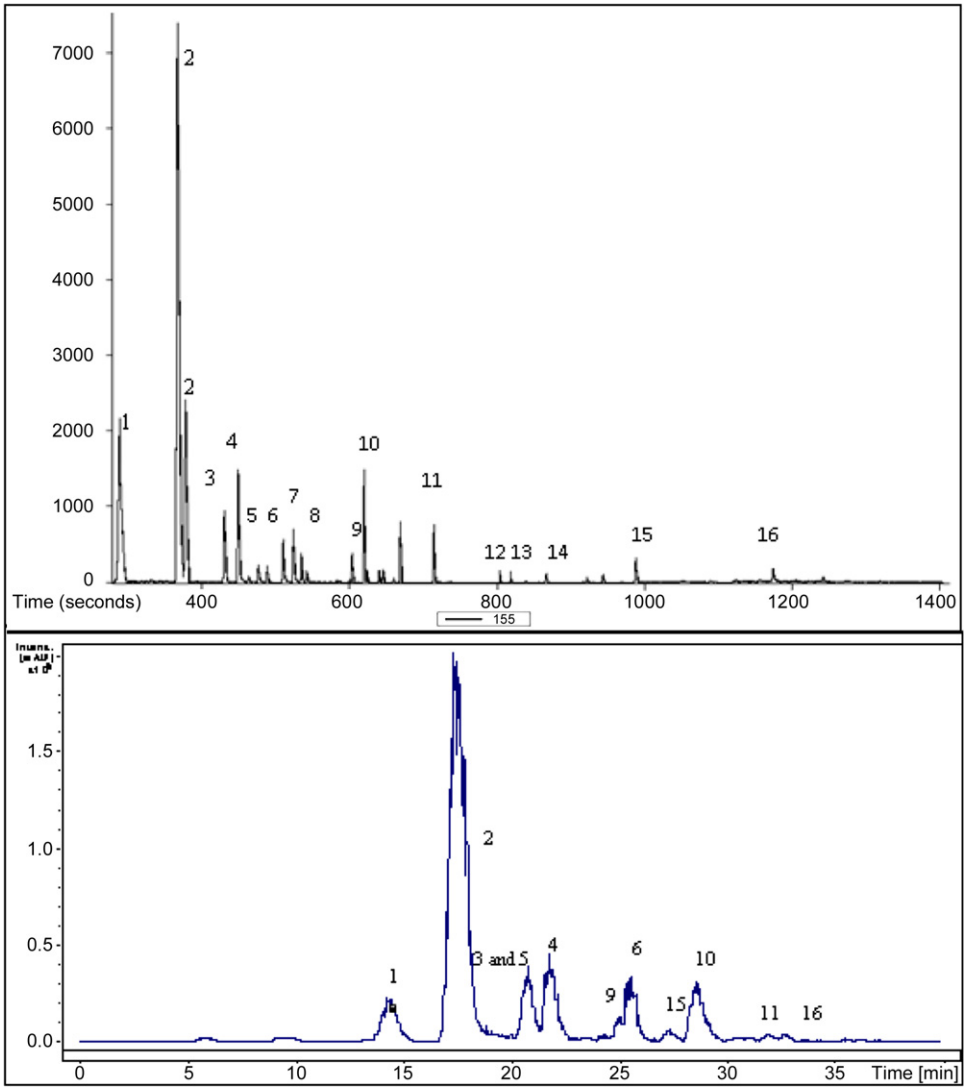

Fig. 4. Chromatograms of carbonyl-PFPH derivatives (top, GC–MS) and carbonyl-DNPH derivatives (bottom, HPLC–MS) in cigarette smoke. 1, formaldehyde; 2, acetaldehyde; 3, acetone; 4, propionaldehyde; 5, acrolein; 6, butyraldehyde; 7, methyl ethyl ketone; 8, methacrolein; 9, crotonaldehyde; 10, valeraldehyde; 11, caproaldehyde; 12, furfural; 13, heptaldehyde; 14, methyl hexyl ketone; 15, benzaldehyde; and 16, 2,5-dimethylbenzaldehyde.

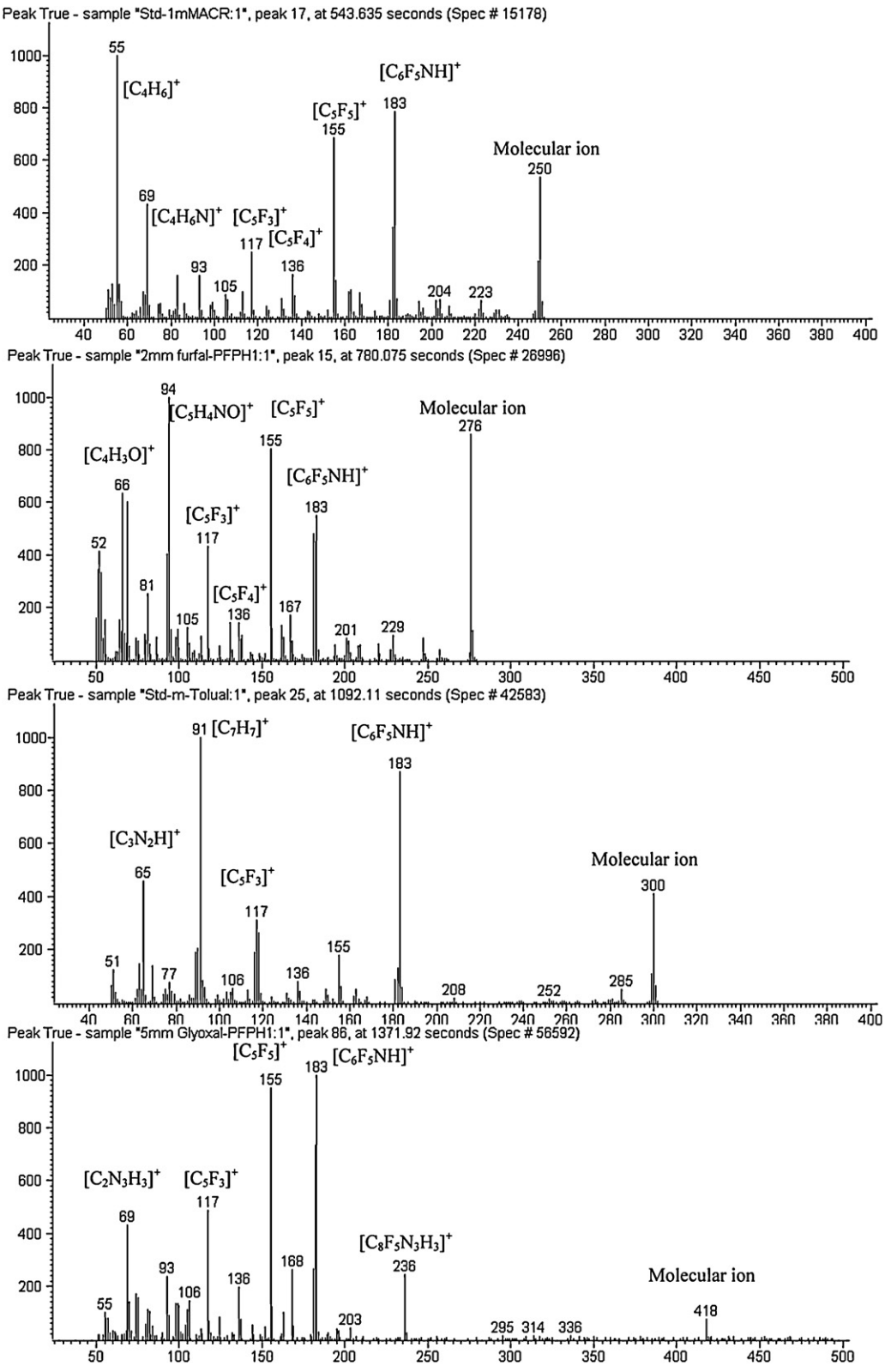

Fig. 5. EI mass spectra of the PFPH derivatives of methacrolein, furfural, *m*-tolualdehyde, and glyoxal.

and *p*-tolualdehyde. The three isomers were mixed and could not be separated by the HPLC method but a baseline separation was achieved by GC/MS. Additionally, as seen in the HPLC chromatogram, partial co-elutions of the DNPH derivatives of other carbonyls occur such as valeraldehyde and isovaleraldehyde, hexaldehyde and dimethylbenzaldehyde, whereas their PFPH derivatives were clearly separated from each other on the GC column. The PFPH/GC method we conclude provides superior separation for those carbonyls, especially those with high molecular weights.

Four example EI mass spectra of the PFPH carbonyl derivatives are given in Fig. 5. A number of ion fragments are common

Table 4
Carbonyl collection efficiencies using PFPH sampling tubes under various collection conditions.

	Standard gas					Ambient air	Cigarette smoke	
Flow rate (mL min^{-1})	50	100	250	500	1000	100	50	100
Sampling period (min)	240	240	240	120	120	240	30	20
Carbonyl levels (ppb)	10	0.2–3.0	3–800					
Sampling times (n)	6	6	6	6	6	12	5	5
Formaldehyde (%)	95 ± 2	93 ± 3	80 ± 4	53 ± 6	32 ± 4	96 ± 2	98 ± 2	81 ± 5
Acetaldehyde (%)	96 ± 3	94 ± 2	81 ± 6	60 ± 5	35 ± 5	97 ± 3	94 ± 4	72 ± 8
Butyraldehyde (%)	97 ± 3	93 ± 3	86 ± 5	54 ± 3	28 ± 8	97 ± 5	95 ± 3	89 ± 3
Caproaldehyde (%)	97 ± 2	94 ± 2	82 ± 4	55 ± 6	33 ± 6	98 ± 5	97 ± 4	91 ± 3
Benzaldehyde (%)	98 ± 3	95 ± 1	88 ± 2	61 ± 4	33 ± 4	98 ± 3	95 ± 3	92 ± 5
Acetone (%)	–[a]	–	–	–	–	95 ± 3	95 ± 2	92 ± 2
Propionaldehyde (%)	–	–	–	–	–	96 ± 2	96 ± 3	93 ± 2
Acrolein (%)	–	–	–	–	–	–	97 ± 1	94 ± 3
Ethyl methyl ketone (%)	–	–	–	–	–	–	99 ± 1	98 ± 2
Methacrolein (%)	–	–	–	–	–	–	99 ± 1	99 ± 1
Crotonaldehyde (%)	–	–	–	–	–	–	100	100
Valeraldehyde (%)	–	–	–	–	–	–	100	100
Hexenal (%)	–	–	–	–	–	–	100	100
Furfural (%)	–	–	–	–	–	–	100	100
Isovaldehyde (%)	–	–	–	–	–	–	100	100

[a] No data can be obtained.

to PFPH and its derivatives as a result of the common moiety C_6F_5NH imparted by the derivatization agent PFPH. The common ions with relative abundance exceeding 10% include ions at m/z, 117, 155, 182, and 183. They are postulated to be $[C_5F_3]^+$, $[C_5F_5]^+$, and $[C_5F_5NH]^+$, $[C_5F_5NH_2]^+$, respectively. For some carbonyls such as caproaldehyde, n-heptanal, and n-octanal, their derivatives have a common base peak ion at m/z 224, corresponding to the loss of neutral fragments $(CH_2)_4$, $(CH_2)_5$ and $(CH_2)_6$ from the respective molecular ions. Those common ions can be used to isolate carbonyls from other classes of compounds that coexist in the samples. Molecular ions are abundant, with their relative abundance ranging from 27 to 100% for the derivatives of monocarbonyls. The dicarbonyls, such as glyoxal show reduced molecular ion intensity, with relative abundances of 10%. The presence of a strong molecular ion is particularly useful in the identification of unknown carbonyls. Additionally, as shown in Fig. 5, some ions involving particular carbonyls such as $[CH_3CCHCH_2]^+$ (m/z 55) for methacrolein $[C_5H_4NO]^+$ (m/z 94) for furfural $[C_7H_7]^+$ (m/z 91) for tolualdehyde $[C_2N_3H_3]^+$ (m/z 69) for glyoxal, have relative abundances exceeding 50%. Those strong common ions are also important in the identification of unknown carbonyls. Table 1 lists the base peak ion fragment and the three most abundant ion fragments for each tested PFPH derivative. The base peak ion is either the molecular ion or one of the common ion fragments.

3.3. Influence of sample flow rate on collection efficiency

Table 4 lists the collection efficiencies of the PFPH sampling tubes for 6 carbonyls determined under various collection conditions. In all experiments, the PFPH coating was fixed to be 1.0 μmol per sampling tube, whereas the sampling duration and carbonyl mixing ratios were varied. The collection efficiencies at five sampling flow rates, 50, 100, 250, 500 and 1000 mL min^{-1}, were compared using the test standard atmospheres. At the lowest flow rate of 50 mL min^{-1}, at least 96% collection efficiencies were achieved for all of the carbonyls. The collection efficiency dropped as the sampling flow rate increased. Low collection efficiency may be due to kinetic limitation or exhaustion of PFPH. But the high peaks of PFPH were still observed in the chromatograms of the samples with low collection efficiencies, which implied the exhaustion of PFPH was not the reason to low collection efficiency. Therefore, kinetic limitation is considered to be responsible for low collection efficiency in this study, which is same as the conclusions of previous reports [13,15]. At a moderate flow rate of 100 mL min^{-1}, collection efficiencies >94% were obtained for all of the tested carbonyls. At the highest flow rate of 1000 mL min^{-1}, the efficiency dropped to >28%. As a result, a sampling flow rate of 100 mL min^{-1} was used for subsequent testing in this study. Sampling with greater excess of PFPH relative to carbonyls was conducted using the test atmospheres at a flow rate of 100 mL min^{-1}. Collection efficiencies were also determined under field conditions. As seen from Table 4, they are generally better than those determined using the test standard gas. The field samples were collected from the atmosphere with high relative humidity, which has been reported previously to be favourable to improving collection efficiencies [22]. For diluted cigarette smoke, two flow rates were tested to determine the collection efficiency. Due to the higher carbonyl concentrations in cigarette smoke, 50 mL min^{-1} was chosen as the sampling rate and sampling period was reduced to 30 min to achieve high collection efficiency.

Based on this study, the sampling rate and time for ambient air containing tens of ppb carbonyls have been suggested to be 100–250 mL min^{-1} and 2–4 h while for some pollutant sources containing hundreds of ppb carbonyls to be 50–100 mL min^{-1} and 0.5–1.0 h, respectively, to achieve high collection efficiency by PFPH method.

3.4. Field measurement comparison

Cigarette smoke is considered as an important source for carbonyl compounds and especially acetaldehyde, however detailed carbonyl speciation of the source is still uncertain. In this study, one brand of cigarette consumed in UK has been tested, with its smoke drawn into a Teldar bag and diluted to 100 L by nitrogen. The carbonyls in the cigarette smoke were identified and their diluted concentrations in the Tedlar bag listed in Table 5. From the data in Table 5, the concentrations of carbonyls obtained by PFPH–GC/MS are not significantly different to those by DNPH–HPLC/MS, for the dominant carbonyls such as acetaldehyde, and formaldehyde with mean deviations of 7.4%, and 2.6% between the two methods. Fig. 4 shows the m/z 155 ion GC chromatogram and the HPLC chromatogram of one pair of diluted cigarette smoke samples. In the GC chromatogram, 16 carbonyl peaks are detected while 9 carbonyls are found in the HPLC chromatogram. More carbonyls peaks are detected by the PFPH–GC/MS for several reasons. First, more carbonyls with high molecular weight can be detected in the cigarette smoke by the PFPH–GC/MS method because of the high resolution and improved detection limits. Second, the PFPH–GC/MS method

Table 5
Summary of carbonyl mixing ratios (in ppb) in diluted cigarette smoke sample using the PFPH and DNPH methods.

Carbonyl(ppb) Brand of cigarette	PFPH–GC/MS Regal, imperial[a]	DNPH–HPLC/MS Regal, imperial
Formaldehyde	42.3 ± 2.5[b]	45.7 ± 4.3[c]
Acetaldehyde	662 ± 32.4	680 ± 21.4
Acetone	21.7 ± 2.4	–
Propionaldehyde	23.6 ± 3.4	–
Acrolein	31.4 ± 3.6	33.5 ± 4.2
Butyraldehyde	11.7 ± 2.1	14.6 ± 3.1
Methyl ethyl ketone	9.45 ± 0.8	–
Methacrolein	4.68 ± 0.2	–
Crotonaldehyde	5.2 ± 0.1	6.3 ± 0.2
Valeraldehyde	18.8 ± 0.2	18.6 ± 1.1
Caproaldehyde	9.1 ± 0.2	7.2 ± 0.4
Furfural	6.0 ± 0.1	–
Heptaldehyde	8.1 ± 0.3	–
Methyl hexyl ketone	6.7 ± 1.0	–
Benzaldehyde	7.4 ± 0.1	–
Bimethylbenzaldehyde	5.3 ± 0.3	3.1 ± 0.2

[a] Properties of cigarette: tar 10 mg, nicotine 0.9 mg, carbon monoxide 10 mg, weight 0.82 ± 0.02 g for each cigarette.
[b] $n = 3$, sampling times.
[c] $n = 3$, sampling times.

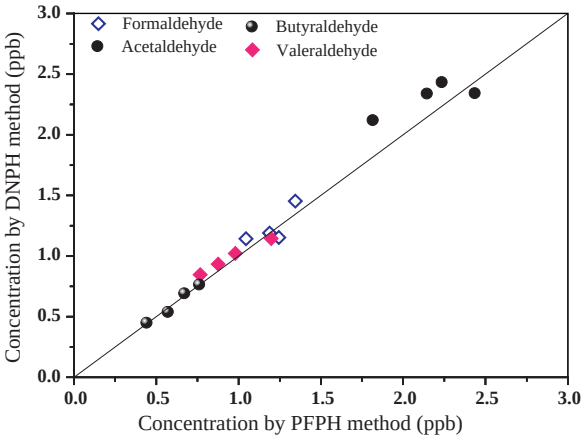

Fig. 6. Comparison of carbonyl mixing ratios (ppb) determined using the DNPH and PFPH methods in ambient samples.

provides better peak separation for carbonyls with similar structures; acetone and acrolein, crotonaldehyde and butyraldehyde can be baseline separated with the PFPH method, but they co-eluted by the DNPH method.

Fig. 6 shows the concentrations of four carbonyls above the detection limits in both methods in ambient air samples. Only formaldehyde, acetaldehyde, butyraldehyde, and valeraldehyde were detected by both PFPH and DNPH methods in York ambient air samples. As seen from Fig. 6, the two methods generally give comparable results and good agreement existed between the two methods.

4. Conclusions

This study demonstrates that sampling onto PFPH-coated Tenax TA solid sorbents with subsequent analysis by GC/MS is a sensitive and selective analytical method for the determination of carbonyl compounds in ambient air and source exhaust. Good linearity, reproducibility and recovery were obtained. Compared with DNPH–HPLC/MS method, the presented method has higher analytical resolution and lower LOD. Chromatographic separation is greatly enhanced through the use of capillary GC over HPLC. The LODs of all the 21 target carbonyls in the range of C_1–C_9 were at sub-ppb levels. Comparing ambient field tests with a classical DNPH–HPLC/UV method, the results showed good agreement between the methods. The PFPH method was found to be an improved method for determination of high molecular weight carbonyls and more carbonyl species could be uniquely determined in the cigarette smoke with this method. Better detection sensitivity was achieved since background carbonyl levels in the sampling tube were lowered through the PFPH gas coating method. The use of an MS detector facilitated the identification of unknown carbonyl species in complicated samples.

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