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Determination of Airborne Carbonyls: Comparison of a Thermal Desorption/GC Method with the Standard DNPH/HPLC Method

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The standard method for the determination of gaseous carbonyls is to collect carbonyls onto 2,4-dinitrophenyl hydrazine (DNPH) coated solid sorbent followed by solvent extraction of the solid sorbent and analysis of the derivatives using high-pressure liquid chromatography (HPLC). This paper describes a newly developed approach that involves collection of the carbonyls onto pentafluorophenyl hydrazine (PFPH) coated solid sorbents followed by thermal desorption and gas chromatographic (GC) analysis of the PFPH derivatives with mass spectrometric (MS) detection. Sampling tubes loaded with 510 nmol of PFPH on Tenax sorbent effectively collect gaseous carbonyls, including formaldehyde, acetaldehyde, propanal, butanal, heptanal, octanal, acrolein, 2-furfural, benzaldehyde, *p*-tolualdehyde, glyoxal, and methylglyoxal, at a flow rate of at least up to 100 mL/min. All of the tested carbonyls are shown to have method detection limits (MDLs) of sub-nanomoles per sampling tube, corresponding to air concentrations of <0.3 ppbv for a sampled volume of 24 L. These limits are 2−12 times lower than those that can be obtained using the DNPH/HPLC method. The improvement of MDLs is especially pronounced for carbonyls larger than formaldehyde and acetaldehyde. The PFPH/GC method also offers better peak separation and more sensitive and specific detection through the use of MS detection. Comparison studies on ambient samples and kitchen exhaust samples have demonstrated that the two methods do not yield systematic differences in concentrations of the carbonyls that are above their respective MDLs in both methods, including formaldehyde, acetaldehyde, acrolein, and butanal. The lower MDLs afforded by the PFPH/GC method also enable the determination of a few more carbonyls in both applications.

Introduction

Measurement of airborne carbonyls in both ambient and indoor environments is of great interest because of their ubiquitous presence and because a few compounds in this family (e.g., formaldehyde, acetaldehyde, and acrolein) are known to have various adverse effects on human health (*1*, *2*). In addition, by their photolysis reactions, some carbonyls are important in initiating and sustaining the photochemical radical pool necessary to produce tropospheric ozone (*3*).

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The standard method for their determination is to collect air onto a solid sorbent cartridge coated with 2,4-dinitrophenyl hydrazine (DNPH), followed by solvent desorption of the cartridge and liquid injection of the eluent into a high-pressure liquid chromatograph (HPLC) for analysis (*4*). This method has been widely used for measurements of airborne carbonyls in ambient samples as well as source samples for more than three decades (e.g., refs *5*−*12*). Recently, we have demonstrated the feasibility of a new approach for the determination of airborne carbonyls (*10*). In this approach, carbonyls are collected onto a solid sorbent tube packed with a derivatization agent that reacts with carbonyls to form thermostable derivatives suitable for subsequent analysis by a gas chromatography/mass spectrometer (GC/MS). Thermal desorption (TD) is used to transfer the derivatives from the sampling tube to the GC/MS for analysis. The standard DNPH/HPLC method and our TD-GC/MS method have similar sampling strategies; however, the latter method offers several apparent advantages. First, the use of GC provides better separation for derivatives of similar carbonyls (e.g., acetone, propanal, and acrolein) than does HPLC. Second, lower detection limits can be achieved through the use of TD, which utilizes the entire sample in the analysis. Third, the use of MS allows easier identification of unknown carbonyls. A different version of the TD-GC/MS approach without using any derivatization agent was reported by Possanzini et al. (*13*), in which the gaseous carbonyls collected onto a carbon sampling tube were thermally desorbed onto a GC/MS for detection. This version of the TD-GC/MS approach was limited to quantification of carbonyls larger than propanal and acetone.

A derivatization agent, *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA), has been tested to be suitable for the TD-GC/MS approach (*13*). Our previous work has shown that principal factors affecting the collection efficiency of the PFBHA sampling tubes are the PFBHA coating amount and the sampling flow rate. At a flow rate of 20 mL/min and 127 nmol of PFBHA coating per sampling tube, carbonyls are collected with $>90\%$ efficiency. Increases in the sampling flow rate beyond 20 mL/min lead to deterioration in the collection efficiency. A higher amount of the PFBHA coating could compensate for the loss of collection efficiencies at sampling flow rates >20 mL/min, but this option is not feasible because of the following reason. The entire excessive reagent PFBHA elutes between the derivatives of formaldehyde and acetaldehyde on a GC column of a nonpolar stationary phase (e.g., 95% dimethylsiloxane/5% phenylmethylsiloxane). This limits the amount of PFBHA coating in two respects in order not to compromise the analysis of the two most important carbonyls, formaldehyde and acetaldehyde. First, too much PFBHA reagent leads to the instrument aborting the analysis due to saturation of the mass spectrometric (MS) detector. This could be circumvented by turning off the MS detector during the elution of the excessive PFBHA. However, it is not feasible to extend the MS detector off-mode beyond the elution of PFBHA because of the desire to analyze formaldehyde, the PFBHA derivative of which elutes earlier than does PFBHA. Second, a large PFBHA peak makes the earlier-eluting acetaldehyde−PFBHA isomer peak appear as a shoulder peak of PFBHA, thereby affecting the accurate quantification of acetaldehyde.

A second derivatization agent, namely, 2,3,4,5,6-pentafluorophenyl hydrazine (PFPH), has been subsequently tested. Cecinato et al. (*14*, *15*) have demonstrated that this reagent reacts with carbonyls to form hydrozone derivatives suitable for GC analysis. PFPH differs from DNPH only in the

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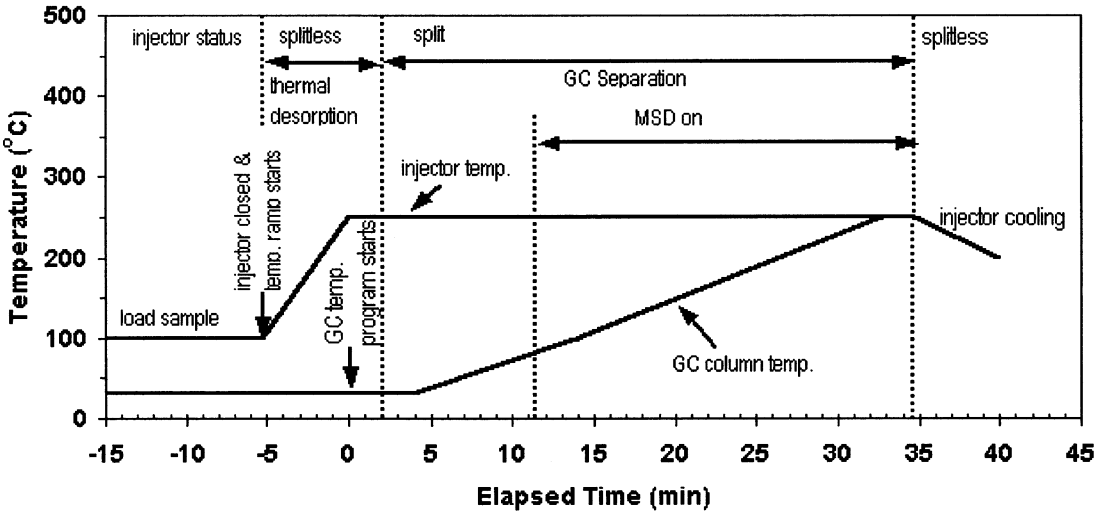

FIGURE 1. Sequence of events of the GC injector, column oven, and MSD during thermal desorption and GC/MS analysis.

substituents of the benzene moiety, the former with five fluorine substituents and the latter with two nitro groups. The five fluorine atoms in PFPH make its hydrozone derivatives more thermally stable and more volatile than the hydrozone derivatives of DNPH. GC analysis of the DNP hydrozones was attempted in a number of studies in the 1970s (e.g., refs *16* and *17*), but problems caused by their thermal decomposition during the GC analysis may well explain the lack of subsequent applications after publication of these studies. PFPH elutes before any of its carbonyl derivatives on a nonpolar stationary phase GC column (*14*). As a result, switch-on of the MS detector can be delayed until after the elution of PFPH to avoid saturation of the MS detector. This can be achieved through setting the duration of the "solvent delay" in the GC/MS operation software sufficiently long until PFPH has exited the MS detector. The concepts behind solvent delay and reagent delay needed here are the same; that is, for the protection of the MS detector, its switch-on is delayed until the unwanted excessive components in a sample mixture have eluted from the MS detector. The use of reagent delay allows a higher amount of PFPH coating on each sampling tube in comparison with the PFBHA method. This in turn makes possible more efficient collection of carbonyls at a higher sampling flow rate than with PFBHA. Consequently, PFPH sampling tubes can collect more air in a given time period, which translates into improved detection limits in air concentrations. An additional advantage of PFPH is that it is 10 times cheaper than PFBHA. As a result, PFPH is selected for further work.

The objectives of this work are to present the PFPH/TD-GC/MS method and to compare the performance of this newly developed method with that of the standard DNPH/HPLC method for the determination of gaseous carbonyls.

Experimental Section

Preparation of PFPH Sampling Tubes. The sampling tubes were fabricated from Pyrex glass tubes (7.8 cm length, 4 mm i.d., and 6 mm o.d.). The length and the outside diameter were identical to those of an HP 5890 GC injector liner. This design allows thermal desorption to take place inside the GC injector by exchanging the GC injector inlet with the sampling tube. Each sampling tube was packed with ~50 mg of Tenax TA (60/80 mesh, Alltech, Deerfield, IL) that was precoated with ~510 nmol of PFPH (Acros, Geel, Belgium). The PFPH reagent was used as purchased without further purification. Coating was achieved by mixing Tenax TA with a known amount of PFPH in hexane (HPLC/GC grade, Mallinckrodt Laboratory Chemicals, Phillipsburg, NJ). The detailed coating procedure was the same as the one described in our previous study for the coating of Tenax TA with PFBHA (*13*). The sampling tubes were then stored in test tubes capped and sealed with Teflon tape. The glass sampling tubes could be reused, although the Tenax solid sorbent had to be removed, recoated with PFPH, and repacked before the next use.

Sample Collection and Analysis by the PFPH Method. Air samples were collected at a flow rate of ~100 mL/min using a personal sampling pump (Gelair II, Sensidyne, Clearwater, FL). The exact flow rate was recorded for each sample. Sampling duration varied from 15 min for source samples to 4 h for ambient samples. An ozone scrubber was placed upstream of the sampling tube to minimize ozone interference during ambient sampling. The ozone trap was made of a coiled stainless steel tube (1 m, $^3/_8$ in. o.d., and $^1/_4$ in. i.d.) coated with potassium iodide (*18*, *19*). After sample collection, each tube was stored in a desiccator at room temperature for 3 days. Before analysis, 1 nmol of the PFPH derivative of 4-fluorobenzaldehyde in a hexane solution, acting as an internal standard, was spiked onto each sampling tube.

Each analysis was started by exchanging the sampling tube with the injector liner in an HP 5890 GC/5972 mass spectrometry detector (MSD) system. The TD step was an integrated part of the analysis. It took place in the injector port. Figure 1 illustrates the sequence of the time events of the GC injector, the column oven, and the MSD during one cycle of analysis. The injector temperature was first lowered to 100 °C to allow handling by hand of the sampling tube and the injector port. Once the sampling tube was in place inside the injector port, the injector port was quickly closed with a septum cap. The temperature of the injector was raised to 250 °C by setting the injector temperature at 250 °C. The injector was kept at this temperature until the end of the analysis. Approximately 5.3 min elapsed before the injector port reached 250 °C from 100 °C. During this injector temperature ramping step, TD had started, although the GC analysis had not commenced. PFPH and its carbonyl derivatives released from the injector port were focused at the head of the GC column, which was kept at 30 °C. The GC oven temperature program was manually started as soon as the injector temperature reached 250 °C. PFPH and its derivatives were subsequently separated on the column and detected by the MSD as the column temperature program progressed. The injector was set in the splitless mode for the first 2 min in the GC temperature program, switched to the split mode at 2 min, and returned to the splitless mode at the end of the GC run. The GC oven program was initially

TABLE 1. GC Retention Times and Characteristic Mass Fragment Ions of the PFPH−Carbonyl Derivatives

carbonyl	retention time (min)	MW[a]	base peak ion	SIM ions
formaldehyde	11.73	210	155	155, 182, 210
acetaldehyde	13.12, 13.30	224	155	155, 182, 224
propanal	14.57, 14.81	238	183	155, 182, 238
acrolein	15.01	236	155	155, 182, 236
2-butanone	15.56	252	155	155, 182, 252
n-butanal	16.09, 16.34	252	183	155, 183,196
2-furfural	20.00, 20.46	276	276	155, 182, 276
n-heptanal	20.58, 20.92	294	224	155, 182, 224
n-octanal	21.94, 22.29	308	224	155, 182, 224
4-fluorobenzaldehyde[b]	22.86	304	183	304
benzaldehyde	22.86	286	286	286
p-tolualdehyde	24.31	300	300	155, 183, 300
glyoxal	27.77	418	182	155, 182, 236
methylglyoxal	28.28	432	182	155, 182, 250

[a] Molecular weight of the PFPH−carbonyl derivatives. [b] Internal standard used in the analysis.

set at 30 °C, held at this temperature for 4 min, programmed at a rate of 7 °C/min to 100 °C and and at a rate of 8 °C/min to 250 °C, and then held at the final temperature of 250 °C for 2 min. A solvent delay time was set at 11.3 min to allow the elution of the PFPH reagent before the MSD was turned on. An HP-5MS column (5% diphenyl/95% diethyl polysiloxane, 30 m × 0.25 mm i.d. × 0.25-μm film thickness) was used in this study. The carrier gas was helium held at a constant pressure of 8 psi. The MSD electron ionization (EI) energy was set at 70 eV, and the GC/MS interface temperature was set at 280 °C. 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). The only exceptions were benzaldehyde and 4-fluorobenzaldehyde. Their PFPH derivatives coelute. Consequently, only their respective molecular ions, which were also the base peak ions, were used for their quantification.

Calibration in the PFPH Method. Calibration curves were established by analyzing sampling tubes spiked with known amounts of the PFPH−carbonyl derivatives prepared in hexane solutions. The calibration sample tubes were packed with the same amount of Tenax TA, but without the PFPH coating. A set of the PFPH−carbonyl derivative standards at five concentration levels was prepared in hexane by mixing carbonyls with PFPH of at least 10 times more than the total moles of carbonyls in the highest concentration calibration standard. Concentrations of individual carbonyls ranged from 0.1 to 1.25 mmol/L. The internal standard, 4-fluorobenzaldehyde, in each calibration mixture was at a concentration of 0.5 mmol/L. The calibration mixtures included formaldehyde, glyoxal, and methylglyoxal from Sigma (St. Louis, MO); acetaldehyde, acrolein, 2-furfural, butanal, 2-butanone, heptanal, octanal, benzaldehyde, and *p*-tolualdehyde from Aldrich (Milwaukee, WI); and propanal from Riedel-deHaen (Hannover, Germany). The mixtures of the calibration standards and PFPH in hexane were allowed to stand at room temperature overnight for both convenience and also to ensure complete reactions. Kinetics experiments from this work and also work done by Cecinato et al. (*14*) show that the derivatization reactions in the liquid phase went to completion in 2 h. Two microliters of each liquid standard was spiked onto a calibration sampling tube. The calibration sample tubes were stored at room temperature overnight before their TD-GC/MS analysis.

Sample Collection and Analysis by the DNPH Method. Air samples were collected at a flow rate of 1 L/min through DNPH-coated silica cartridges (Waters, Milford, MA) with an ozone scrubber (Waters) placed upstream. After sample collection, each cartridge was eluted with 3 mL of acetonitrile. The final volume of the eluent was made to be 5.0 mL in a volumetric flask. Calibration standards were prepared by mixing carbonyl standard mixtures in acetonitrile with 1 mL of ~12 mmol/L DNPH in an acidic aqueous solution. The final volume of each calibration mixture was made to be 5.0 mL. Concentrations of individual carbonyls in the calibration standards ranged from ~0.7 to 28 μM. The DNPH−carbonyl derivatives were analyzed by injecting 20 μL of the samples to an HP1100 HPLC equipped with a photodiode array detector. The column for separation of the hydrazones was a 4.6 × 150 mm Hypersil ODS 5 μm reversed-phase column (Alltech). The mobile phase consisted of two solvent mixtures: mixture A, 60:30:10 (v/v) of water/acetonitrile/tetrahydrofuran; mixture B, 40:60 (v/v) of water/acetonitrile. The gradient program was 100% A for 1 min, followed by a linear gradient from 100% A to 100% B in 10 min. The flow rate was 1.5 mL/min for the first 15 min, increased to 1.7 mL/min in 2 min, and maintained at this flow until the end of the analysis. Absorbance at 420 nm was used for quantification of glyoxal and methylglyoxal, whereas absorbance at 360 nm was used for quantification of the other carbonyls.

Determination of Collection Efficiency. Collection efficiencies of the PFPH sampling tubes were determined by passing test atmospheres or ambient and kitchen exhaust air through two identical sampling tubes connected in series. The collection efficiency was calculated as 100% $(1 - A_b/A_f)$, where A_f and A_b are the amounts of a carbonyl collected on the front and back sampling tubes, respectively (*7*). The test atmospheres containing carbonyls at ppbv levels were prepared in a Tedlar bag through liquid injection and subsequent vaporization, the details of which have been given in the previous study by Ho and Yu (*13*).

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 set up in an ambient environment and in a location where kitchen exhaust air was sampled. The PFPH sampling train was operated at 100 mL/min, whereas the DNPH sampling train was operated at 1 L/min. The ambient sampling site was on the rooftop of an 11-story building on the campus of the Hong Kong University Science and Technology. The university is located at a coastal site on the eastern side of Hong Kong and away from commercial and industrial centers in the city. Six sets of samples were taken at this location in a 24-h period; each sample was collected for 4 h. The kitchen exhaust samples were taken from an exhaust duct of a demonstration kitchen built in a cooking utensil supplier company. The cooking fuel was natural gas. Two dishes, fried rice noodles with sliced beef and fried shrimp with pepper and salt, were cooked, each on a separate sampling day.

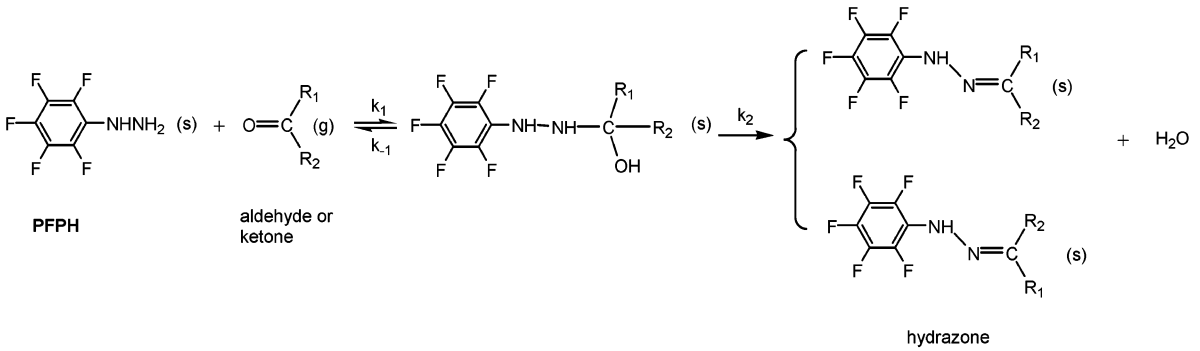

FIGURE 2. Derivatization reaction scheme of gaseous carbonyls with PFPH on the sorbent (s, surface; g, gaseous state).

Each DNPH sample was collected for 30 min, whereas each PFPH sample was collected for 15 min to avoid breakthrough. Eight PFPH samples and four DNPH samples were taken from the kitchen exhaust. Field blanks were taken for each sampling event. The DNPH samples were stored in a refrigerator at <4 °C before analysis. The PFPH sampling tubes were stored at room temperature in a desiccator for 3 days before analysis.

Results and Discussion

Reaction Kinetics. We suggest a two-step reaction mechanism for the reaction of gaseous carbonyls with PFPH immobilized on the Tenax solid sorbent particles on the basis of observations made in this reaction system and in a similar reaction system previously studied (*13*) (Figure 2). In our previous study that used PFBHA sorbent tubes, we observed that the PFBHA derivative yields increase with postcollection storage times up to 5 days (*13*). We have shown that this slow rise in derivatization yield can be explained only if the reaction consists of multiple steps and if the formation rate of the hydrazones is limited by the later step. A similar storage effect on the PFPH derivative yields was also observed when the postcollection storage time varied from 0 to 4 days (Figure 3). The maximum derivative yields were reached after the sampling tubes were stored for 2−3 days after collection. The yields stayed relatively constant afterward, indicating that they were stable after their formation. On the basis of the kinetic data, a storage time of 3 days was adopted for all samples.

GC and MS Characteristics of the PFPH−Carbonyl Derivatives. Three example EI mass spectra of the PFPH−carbonyl derivatives are given in Figure 4. A number of ion fragments are common 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 $[C_5F_5NH]^+$, $[C_5F_5NH_2]^{+\cdot}$, respectively. The 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 two dicarbonyls, glyoxal and methylglyoxal, show reduced molecular ion intensity, with relative abundances of 10 and 7%, respectively. The presence of a strong molecular ion is particularly useful 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, with the exception of the derivatives of *n*-heptanal and *n*-octanal. The two derivatives have a common base peak ion at *m*/*z* 224, corresponding to the loss of neutral fragments $(CH_2)_5$ and $(CH_2)_6$ from the respective molecular ions.

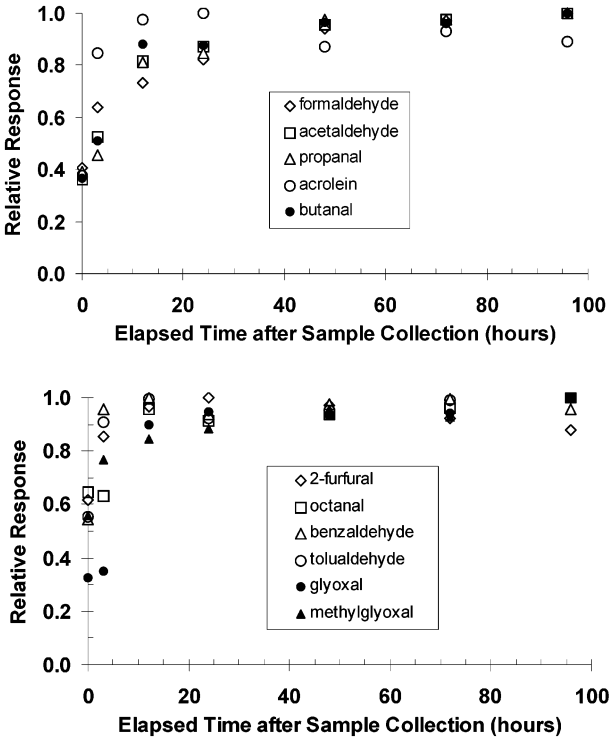

FIGURE 3. Kinetics of the gas−solid-phase reaction between PFPH and the carbonyls.

Example GC chromatograms for an ambient sample and a kitchen exhaust sample are shown in Figures 5 and 6. HPLC chromatograms for the respective collocated DNPH cartridge samples are also shown in the figures for comparison. The GC retention times for 14 tested carbonyls are listed in Table 1. In some instances, two peaks are attributed to the same parent carbonyl (e.g., acetaldehyde and propanal). Such double peaks are a result of two isomers formed between PFPH and any nonsymmetric carbonyls (Figure 2). Similar multiple peaks corresponding to a single parent carbonyl have also been known to exist for the PFBHA derivatives of carbonyls (*20*). It is clear that the PFPH derivatives of the carbonyl compounds typically present in the atmosphere are well resolved by the GC column. Most notably, a baseline separation is achieved for acetone, propanal, and acrolein, three carbonyls of similar molecular weights. As seen in the HPLC chromatogram for the kitchen sample, in which acrolein, acetone, and propanal are present at comparable levels, the separation of the DNPH derivatives of these three carbonyls is acceptable, but a baseline separation is not achieved (Figure 6). The inability to provide good separation for acetone and acrolein of the DNPH/HPLC method is particularly a problem for ambient samples, in which acetone is normally present at much higher levels than acrolein (*21*).

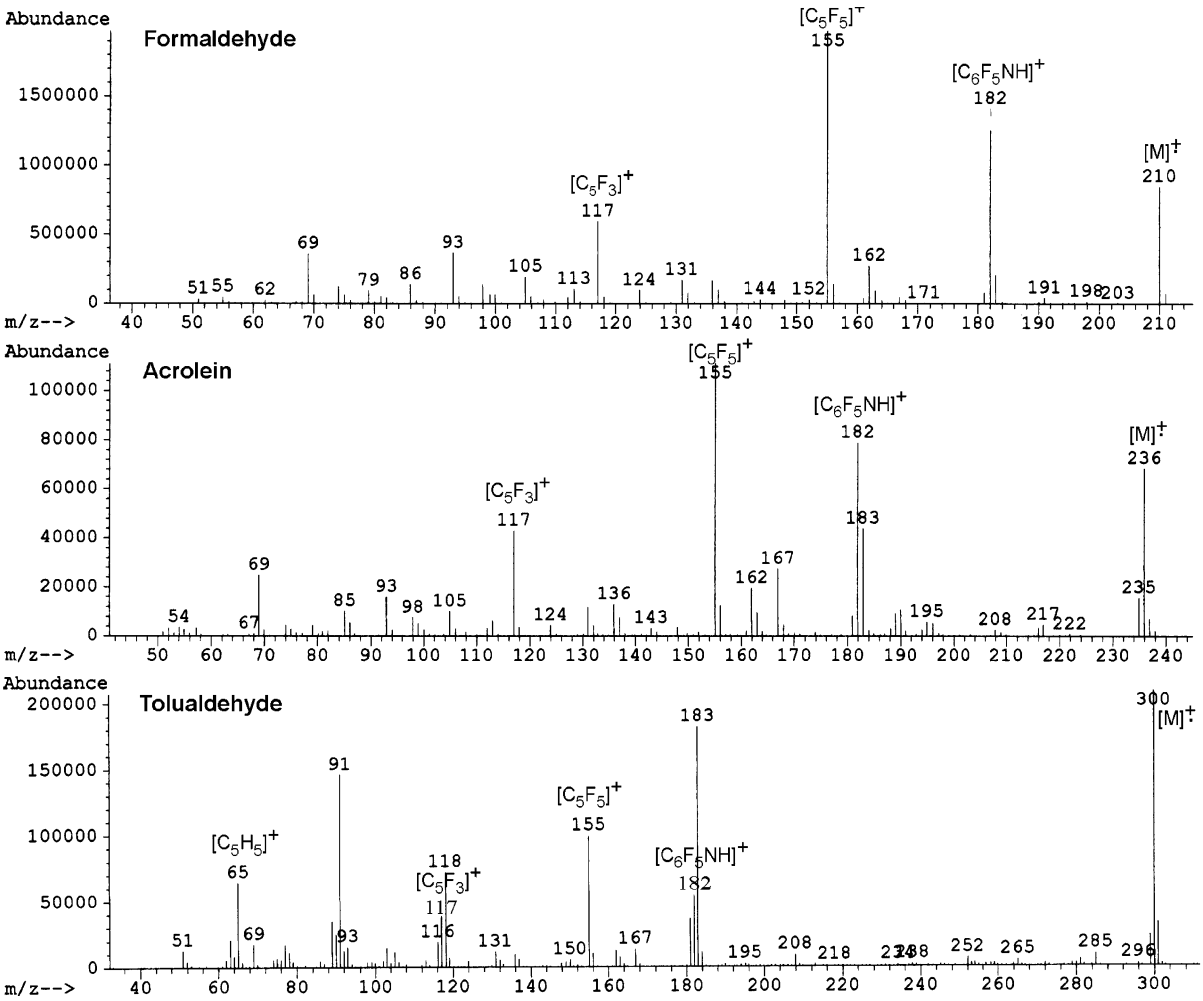

FIGURE 4. EI mass spectra of the PFPH derivatives of formaldehyde, acrolein, and *p*-tolualdehyde.

As a result, small amounts of acrolein could go undetected. In the ambient sample shown in Figure 5, acrolein is unambiguously detected in the GC chromatogram; however, its presence cannot be detected in the HPLC chromatogram.

The PFPH/GC method also provides superior separation for 2-furfural, acrolein, and propanal. Although 2-furfural is not detected in either the ambient or the kitchen exhaust samples collected in this work, its presence has been reported in source samples of some common combustion processes, for example, automobile combustion (*11*) and incense burning (*18*). Our analysis of standard mixtures containing all three carbonyls shows that the DNPH derivative of 2-furfual partially coelutes with acrolein and propanal, whereas the PFPH derivative of 2-furfural is clearly separated from the three C_3-carbonyls on the GC column.

Calibration and Minimum Detection Limits (MDLs). The calibration curves in the PFPH method are established by plotting the ratio of the sum of the SIM ion peak areas between a given carbonyl and 4-fluorobenzladehyde versus the nanomoles of the carbonyl compound on the calibration sample tubes. Table 2 lists the calibration slopes, intercepts, coefficients of determination (R^2), and MDLs for the 13 tested carbonyls. R^2 values >0.991 have been achieved for all of the carbonyls, indicating that the liquid spiking step and the subsequent TD step are quantitative. The MDL for each carbonyl is defined as the amount of a carbonyl that generates an analytical signal equal to the sum of the mean blank signal plus 3 times the standard deviation of the blank signals (*22*, *23*). The blank signals are taken as those of the blank sampling tubes. No peak is detected for heptanal, octanal, 2-furfural, tolualdehyde, or methylglyoxal in the blank tubes. For these compounds, the mean blank signal is approximated with the calibration line intercept and the blank signal standard deviation is approximated with the standard error for the *y* estimate, *y* being the ratio of the SIM ion peak area ratio between the carbonyl derivative and the internal standard (*24*). All of the carbonyls have MDLs at sub-nanomole levels, ranging from tens to a few hundred picomoles per sampling tube. The MDLs in nanomoles per sample tube are translated into mixing ratios in the sub-ppbv range for a sample volume of 24 L, which corresponds to sampling for 4 h at a flow rate of 100 mL/min. When the sampled air volume is increased or decreased, the MDLs in ppbv would be proportionally lower or higher.

The calibration curves in the DNPH method are established by plotting peak areas of UV absorbance at 360 or 420 nm versus the carbonyl concentrations in the standard solutions. Table 2 also lists the MDLs of the DNPH method expressed in nanomoles of a carbonyl per cartridge and in ppbv. The MDLs 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 for 4 h. These MDL values by the two different methods correspond to sampling for the same duration under their respective typical sampling and analysis conditions as described under Experimental Section. It can be seen from Table 2 that the PFPH method offers a MDL in ppbv that is 2−15 times lower than that given by the DNPH method. In particular, the two dicarbonyls (i.e., glyoxal and methylglyoxal) and the two aromatic aldehydes (i.e., benzaldehyde and *p*-tolualdehyde) have much improved MDLs

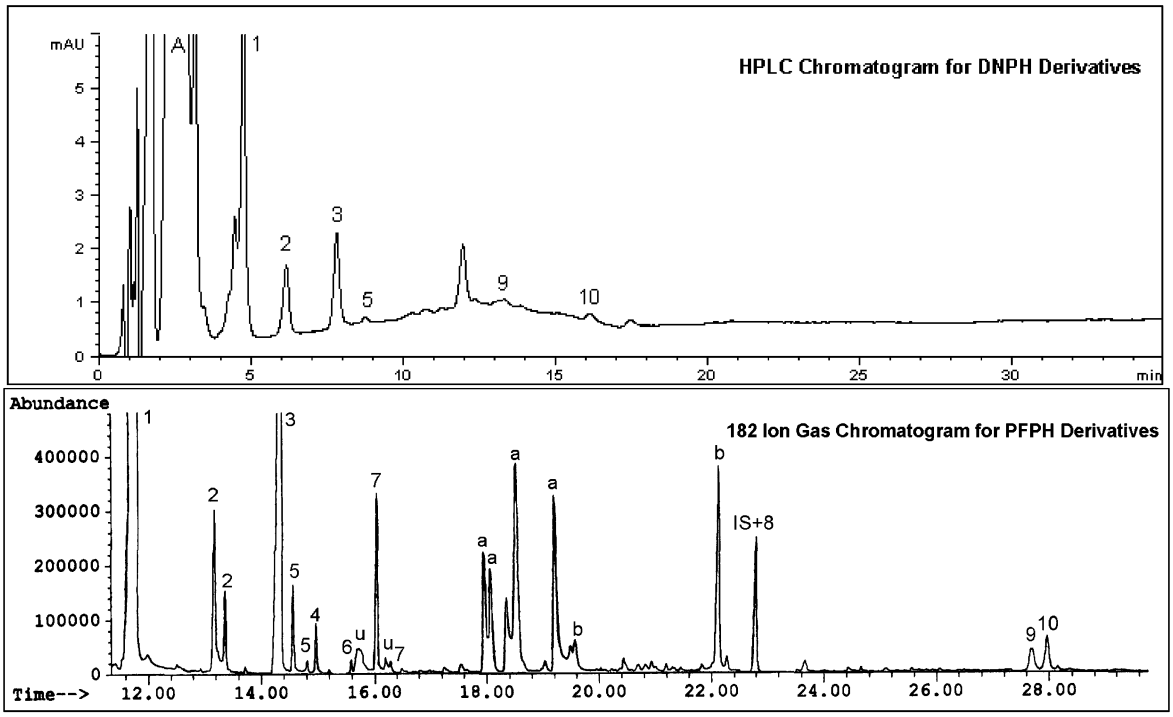

FIGURE 5. Chromatograms of two collocated ambient samples: (a) HPLC chromatogram using the DNPH method; (b) gas chromatogram using the PFPH method. Peaks: 1, formaldehyde; 2, acetaldehyde; 3, acetone; 4, acrolein; 5, propanal; 6, 2-butanone; 7, *n*-butanal; 8, benzaldehyde; 9, glyoxal; 10, methylglyoxal; A, DNPH; IS, 4-fluorobenzaldehyde; a, C6 saturated carbonyls; b, pentafluorobenzaldehyde; u, unknown compounds present in both blank and sample.

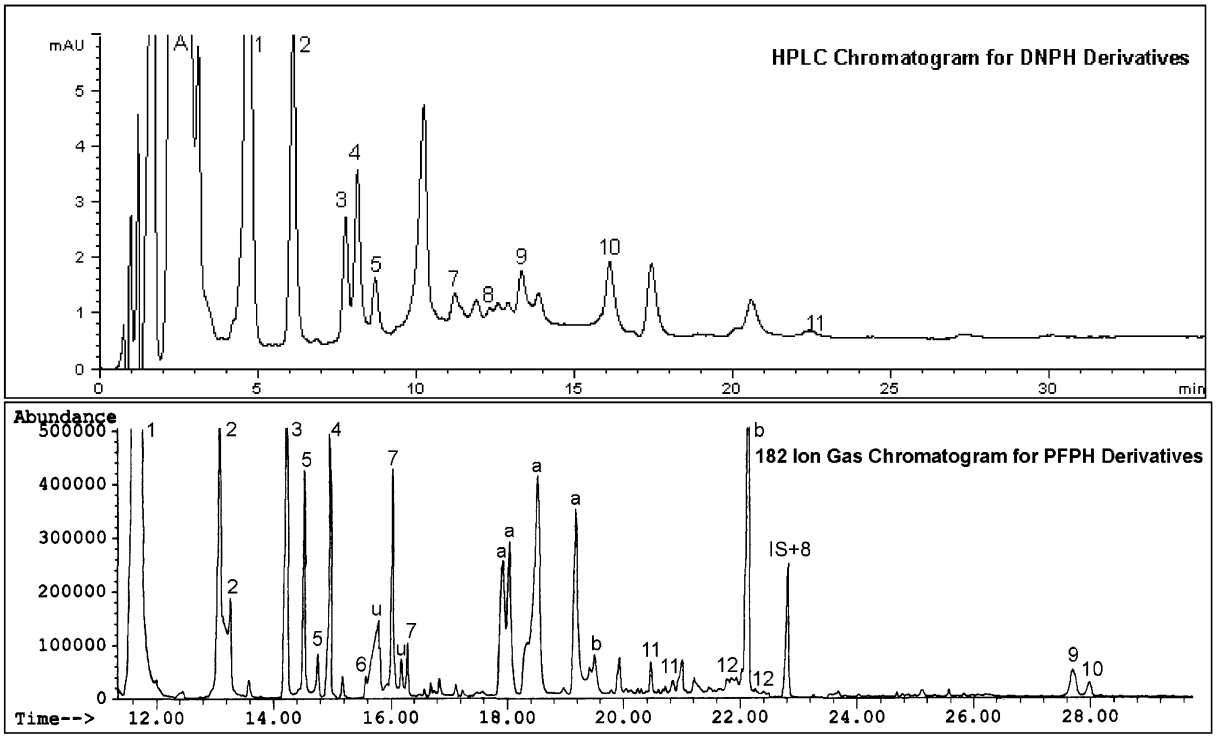

FIGURE 6. Chromatograms of two collocated kitchen exhaust samples: (a) HPLC chromatogram using the DNPH method; (b) gas chromatogram using the PFPH method. Peaks: 1, formaldehyde; 2, acetaldehyde; 3, acetone; 4, acrolein; 5, propanal; 6, 2-butanone; 7, *n*-butanal; 8, benzaldehyde; 9, glyoxal; 10, methylglyoxal; 11, *n*-heptanal; 12, *n*-octanal; A, DNPH; IS, 4-fluorobenzaldehyde; a, C6 saturated carbonyls; b, pentafluorobenzaldehyde; u, unknown compounds present in both blank and sample.

by the PFPH method. The improved MDL of carbonyls larger than acetaldehyde is especially advantageous for ambient samples, which usually have these carbonyls at levels typically <1 ppbv. To achieve similar levels of sensitivity using the DNPH method, one has to take samples of longer duration, consequently, at the cost of time resolution. As a result, the PFPH method will enable us to characterize the ambient concentrations of carbonyls larger than acetaldehyde and their temporal variations at a better time resolution.

The two methods had similar method precision. Three replicate samples were collected from test atmospheres to obtain carbonyl loadings >3 times MDLs on the PFPH

TABLE 2. Linear Regression Parameters for Calibration Curves and Minimum Detection Limits

	PFPH method						DNPH method		
					MDL		MDL		
carbonyl	slope	intercept	R^2	loading range (nmol/tube)	nmol/tube	ppbv[a]	nmol/cartridge	ppbv[b]	MDL ratio[c]
formaldehyde	5.04	−0.481	0.991	0.5−2.5	0.26	0.26	5.7	0.58	2.2
acetaldehyde	3.12	0.240	0.999	0.5−2.5	0.097	0.10	5.7	0.58	6.0
propanal	2.78	−0.091	0.998	0.2−1.0	0.042	0.04	2.1	0.21	5.0
acrolein	1.22	−0.099	0.991	0.2−1.0	0.10	0.10	6.1	0.62	6.2
2-butanone	2.48	0.024	0.997	0.2−1.0	0.059	0.06	—[d]	—	
n-butanal	3.20	−0.094	0.992	0.2−1.0	0.096	0.10	3.0	0.31	3.2
2-furfural	2.84	−0.084	0.999	0.2−1.0	0.035	0.04	3.1	0.32	9.1
n-heptanal	2.30	−0.008	0.995	0.2−1.0	0.074	0.08	4.0	0.40	5.0
n-octanal	2.01	−0.045	0.993	0.2−1.0	0.095	0.10	4.4	0.45	4.7
benzaldehyde	0.82	0.057	0.997	0.2−1.0	0.062	0.06	3.8	0.39	6.3
tolualdehyde	1.90	−0.048	0.998	0.2−1.0	0.046	0.05	7.2	0.73	16
glyoxal	0.31	−0.044	0.997	0.4−2.0	0.12	0.12	14.4	1.47	12
methylglyoxal	0.49	−0.029	0.993	0.4−2.0	0.18	0.18	12.5	1.27	7.0

[a] Assume a sampled air volume of 24 L, i.e., 4-h sampling at 0.1 L/min. [b] Assume a sampled air volume of 240 L, i.e., 4-h sampling at 1 L/min. [c] Ratio of the MDLs by the DNPH and PFPH methods. [d] 2-Butanone was not included in the DNPH/HPLC analysis.

TABLE 3. Carbonyl Collection Efficiencies of the PFPH Sampling Tubes under Various Collection Conditions

	test atmospheres			ambient air	kitchen exhaust
flow rate (mL/min)	54	118	224	101	100
sampling duration (min)	80	40	20	120	30
PFPH/carbonyl molar ratio	2.8:1	2.8:1	2.8:1	29−60:1	8:1
carbonyl levels (ppbv)	5−10	5−10	5−10	0.3−8.9	1.6−120
formaldehyde (%)	96 ± 1[a]	85 ± 1	41 ± 5	99 ± 2	94
acetaldehyde (%)	93 ± 2	75 ± 2	32 ± 5	90 ± 3	93
propanal (%)	91 ± 3	88 ± 1	32 ± 6	100 ± 0	100
butanal (%)	99 ± 5	86 ± 4	32 ± 10	91 ± 4	100
acrolein (%)	99 ± 1	84 ± 1	62 ± 5	100 ± 0	92
2-furfural (%)	96 ± 2	97 ± 1	68 ± 2	—[b]	—
octanal (%)	98 ± 2	96 ± 1	76 ± 4	—	100
benzaldehyde (%)	100 ± 0.3	93 ± 2	82 ± 1	100 ± 0	100
tolualdehyde (%)	100 ± 0	100 ± 0	88 ± 3	100 ± 0	—
glyoxal (%)	93 ± 3	76 ± 4	42 ± 4	95 ± 3	97
methylglyoxal (%)	97 ± 1	91 ± 3	81 ± 3	89 ± 6	100

[a] The values, expressed as the arithmetic mean ± standard deviation, are obtained from three to four measurements. [b] Not available due to absence of the given carbonyl in the ambient or kitchen exhaust samples.

sampling tubes and the DNPH cartridges. The relative standard deviation for the individual carbonyls ranged from 0.7 to 7.5% in the PFPH method and from 1.6 to 7.7% in the DNPH method.

Collection Efficiency. Collection efficiencies of the DNPH cartridges are reported by their producer to be >95% for sampling flow rates up to 2 L/min (*25*). Using test atmospheres, we have confirmed that the DNPH cartridges have 95% collection efficiency for glyoxal and methylglyoxal, 99% collection efficiency for acetaldehyde, and 100% collection efficiency for formaldehyde, propanal, 2-furfural, benzaldehyde, and acetaldehyde at a flow rate of 1 L/min.

Table 3 lists the collection efficiencies of the PFPH sampling tubes for 11 carbonyls determined under various collection conditions. In all experiments, the PFPH coating was fixed to be 510 nmol per sampling tube, whereas the sampling duration and carbonyl source mixing ratios were varied to give different molar ratios of PFPH to carbonyl groups. The collection efficiencies at three sampling flow rates, 54, 102, and 224 mL/min, were compared at the same PFPH/carbonyl ratio of 2.8 using the test atmospheres. At the lowest flow rate of 54 mL/min, >91% collection efficiencies were achieved for all of the carbonyls. The collection efficiency dropped as the flow rate increased, reflecting that retaining the carbonyls was kinetically limited. The drop was more pronounced for the smaller carbonyls. At the medium flow rate of 118 mL/min, collection efficiencies >84% were attained for all of the tested carbonyls except for acetaldehyde and glyoxal. The latter two carbonyls were collected at a collection efficiency of ∼75%. At the highest flow rate of 224 mL/min, only the few larger carbonyls were collected at >75% efficiency. As a result, the sampling flow rate was set at 100 mL/min for subsequent testing.

Sampling with greater excess of PFPH relative to carbonyls was conducted using the test atmospheres at a flow rate of 100 mL/min. Similar or a few percentages better collection efficiencies were obtained when sampled at a PFPH/carbonyl ratio of 10:1 in comparison with 2.8:1. We therefore conclude that sampling with PFPH in excess of total carbonyls by 1.8 times provides adequate collection of the carbonyls. That is, the PFPH sampling tubes prepared as described have a collection capacity of 180 nmol of carbonyls at a flow rate of 100 mL/min.

Collection efficiencies were also determined under field conditions. As seen from Table 3, they are generally better than those determined using the test atmospheres. The test atmospheres had a relative humidity (RH) of <1%, and the field samples were collected from atmospheres with RHs ranging from 63 to 85%. Different collection conditions such as higher RH and higher PFPH/carbonyl ratios encountered in the field samples than in the test atmospheres may explain the better collection efficiencies. Grosjean and co-workers

TABLE 4. Summary of the Carbonyl Mixing Ratios (in ppbv) in Collocated Kitchen Exhaust Samples and Ambient Samples Using the PFPH and DNPH Methods

formaldehyde		acetaldehyde		propanal		acrolein		butanal		benzaldehyde	glyoxal	methylglyoxal	heptanal	octanal
PFPH	DNPH	PFPH	DNPH	PFPH	DNPH	PFPH	DNPH	PFPH	DNPH	PFPH	PFPH	PFPH	PFPH	PFPH
Kitchen Exhaust														
119.1	130.2	48.8	56.9	8.19	10.9	53.4	55.8	9.09	9.81	2.82	22.8	8.68	4.27	4.32
73.2	76.0	38.3	37.9	7.52	9.01	28.0	32.4	8.89	9.47	2.44	6.74	6.27	2.81	2.70
32.7	34.4	35.0	38.9	3.24	3.37	9.5	9.8	3.17	2.78	0.58	3.50	0.89	2.80	1.71
28.3	29.2	24.7	24.8	2.28	2.07	5.4	5.1	2.89	2.38	1.10	4.03	2.00	1.73	1.09
Ambient Samples														
4.8	5.2	1.2	1.1	0.09	bd[a]	0.26	bd	0.31	bd	0.19	0.33	0.33	bd	bd
5.4	5.9	1.8	2.0	0.13	bd	0.18	bd	0.37	0.39	0.13	0.46	0.22	bd	bd
2.3	2.3	0.90	0.90	0.08	bd	0.13	bd	0.18	bd	0.09	0.20	0.15	bd	bd
1.2	1.0	0.62	0.66	0.05	bd	0.09	bd	0.16	bd	0.10	0.12	0.10	bd	bd
1.2	1.5	0.64	0.63	0.04	bd	0.09	bd	0.24	bd	0.06	0.23	0.15	bd	bd
4.2	4.6	1.6	1.6	0.12	bd	0.17	bd	0.18	bd	0.14	0.25	0.25	bd	bd

[a] Below detection limit.

have reported a humidity effect on the collection efficiencies by DNPH cartridges (*26*, *27*). Additional studies are under way in our laboratory to investigate the effects of various sampling parameters (e.g., humidity) on collection efficiencies of the PFPH sampling tubes, but the collection efficiencies determined here under the field conditions are believed to be suitable for correction of carbonyl concentrations in the field samples.

Field Measurement Comparison. Figures 5 and 6 show the HPLC chromatograms and the *m*/*z* 182 ion GC chromatograms of one pair of collocated ambient samples and one pair of collocated kitchen exhaust samples. More carbonyls peaks are detected by the PFPH/GC method for several reasons. First, the PFPH method offers low detection limits for all tested carbonyls. The level of some carbonyls (e.g., acrolein in the ambient samples) is high enough to be detected with the PFPH method, but they fall below the detection limit of the DNPH method. Second, more background contamination carbonyls are detected in the PFPH method, also because of the improved detection limits. For example, four peaks with a molecular weight matching that of a C_6 saturated carbonyl are present in both blank and sample tubes at similar levels. They are most likely from hexane solvent used to dissolve PFPH during coating. In addition, the same two peaks (labeled b in Figures 5 and 6) are present in every sample. Their EI mass spectra show strong ion fragments at *m*/*z* 117, 155, 182, and 376. The mass spectra information has led to an initial tentative identification and subsequent confirmation by an authentic standard as the PFPH derivative of pentafluorobenzaldehyde. This carbonyl compound is likely present as a contaminant in the PFPH reagent. The identification of this carbonyl impurity demonstrates the advantage of the PFPH method. This advantage is especially useful in analyzing unknown source samples. The background carbonyl contaminants do not interfere with the quantification of any target carbonyl compounds listed in Table 2 because they are resolved by the GC column from the target carbonyls.

Table 4 presents a summary of the carbonyl mixing ratios in the ambient samples and in the kitchen exhaust samples using both methods. For easy visual comparison, Figure 7 plots the concentrations of those carbonyls having concentrations above the detection limits in both methods. In the ambient samples, only formaldehyde and acetaldehyde are detected above the MDLs of the DNPH method in every sample. In the exhaust samples, formaldehyde, acetaldehyde, propanal, acrolein, and *n*-butanal are above the detection limits in both methods. The sampling duration for the kitchen exhaust samples in the PFPH method is only half that of the samples in the DNPH method. As a result, concentrations

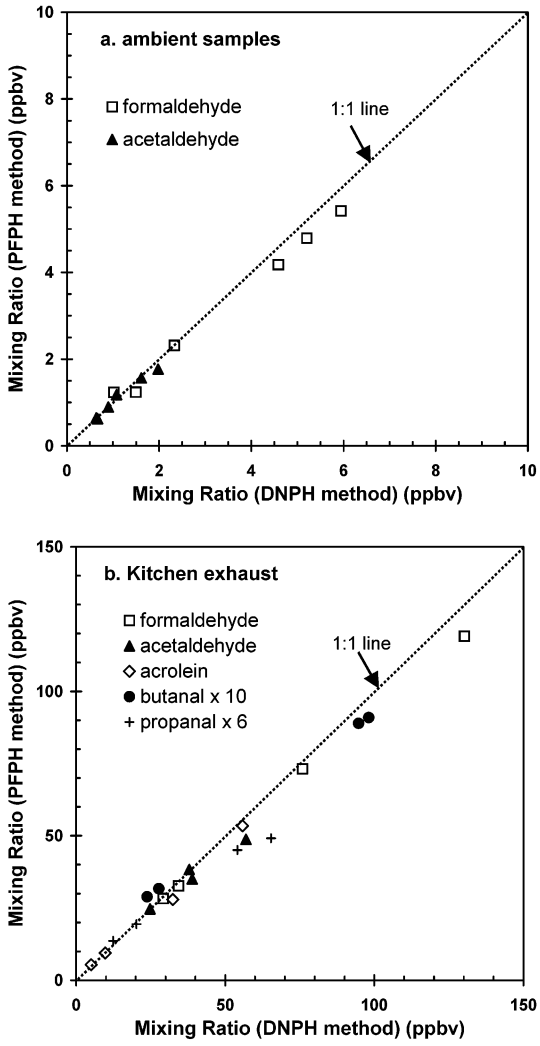

FIGURE 7. Comparison of carbonyl mixing ratios determined using the DNPH and PFPH methods: (a) ambient samples; (b) kitchen exhaust samples.

for the kitchen exhaust samples determined by the PFPH methods are the average values of two sequential samples that span the same duration as the collocated DNPH sample. In this way, a direct comparison of the two methods can be made.

As seen from Figure 7, the two methods generally give comparable concentrations. The difference in individual pairs

of measurement does not exceed 25%. A paired Student's *t* test indicates that the two methods give statistically the same concentrations for formaldehyde and acetaldehyde. Five more carbonyls, benzaldehyde, glyoxal, methylglyoxal, heptanal, and octanal, are also detected using the PFPH method. Table 3 lists their concentrations. These carbonyls are either not detected or fail under the detection limit in the DNPH method. This again demonstrates the advantages of the PFPH method.

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