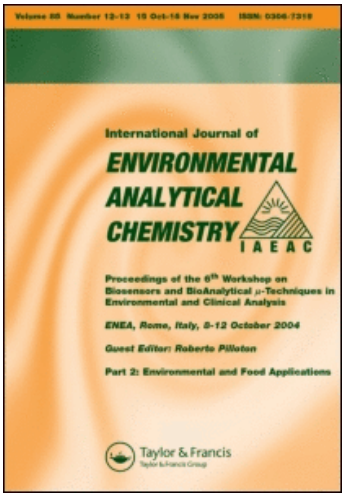

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DEVELOPMENT OF AN AUTOMATED MONITORING SYSTEM FOR VARIOUS GAS-PHASE ORGANIC CARBONYLS IN AMBIENT AIR

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An automated monitoring system for various C_1 to C_5 gas-phase organic carbonyls in ambient air is described. The system consists of a parallel plate diffusion scrubber (PPDS), which is coupled with a high-performance liquid chromatography–ultraviolet (HPLC–UV) system using an automated injection valve. Compared with an annular diffusion scrubber (DS) employed so far for gas-phase carbonyl monitoring, PPDS shows an improved collection efficiency for formaldehyde, acetaldehyde, propionaldehyde, and acetone with >97% at an airflow rate of 0.5 L/min. High gas–liquid concentration ratios of PPDS and an optimised HPLC–UV system allow limits of detection (LOD) in a range of 80–500 pptv. A low liquid hold-up volume of the PPDS results in a short response time of about 10 min. Additionally, the optimised analysis time for 13 carbonyl compounds containing calibration standard enables brief measurement intervals of 25 min. The developed PPDS–HPLC system shows its reliability from urban site monitoring in Seoul, South Korea.

Keywords: Parallel plate diffusion scrubber; Porous membrane; Carbonyl gas; Automated air monitoring; HPLC; DNPH

INTRODUCTION

Sources of carbonyl gases in ambient air can be as various as their adverse impacts on human health and their role in tropospheric chemistry. Besides, low-molecular-mass carbonyl gases are among the most abundant volatile organic compounds (VOCs) in the atmosphere. This led in the past 10 years to increasing concern on ascertaining organic carbonyls in indoor and outdoor air. Based on governmental ambient air-monitoring programmes, there is a comprehensive pool of data for abundant carbonyls, formaldehyde, acetaldehyde, and acetone. However, with regard to other low-molecular-mass carbonyls, there is still a significant lack of data, though some sporadic monitoring with a larger variety of carbonyl species has been carried out [1–8].

In the last two decades, the majority of organic carbonyl monitoring in ambient air has been performed using impinger or adsorbent cartridge sampling followed

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by high-performance liquid chromatography analysis with UV detection. Nowadays, standard methods, ISO 16000-3 and US EPA TO-11A represent well-characterized and reliable tools for indoor or outdoor air analysis [9–12]. These standard methods are based on sample collection with a 2,4-dinitrophenylhydrazine (DNPH) silicagel cartridge, subsequent extraction of the hydrazone products with acetonitrile (ACN), and final quantification using HPLC with UV detection at 360 nm. Sampling of several less abundant carbonyls (e.g. acrolein, glutaraldehyde, and dialdehydes) based on the cartridge method has encountered stability problems with the DNPH hydrazones [11]. Modifications in analytical procedure in terms of the type of adsorbents, the derivatization reagent, as well as the utilization of other analytical measurement principles have been reported in recent years [1,3,4,13–17]. Owing to interference, ozone has to be removed by employing a KI denuder or scrubber upstream to the carbonyl collection.

Utilizing an automated multi-port sampler, numerous short-term (2–3 h) samples can be collected automatically, and prolonged monitoring can be carried out over several days. None the less, the subsequent sample work-up and the HPLC measurement have to be carried out offline. These steps are time-consuming, cost-intensive, and prone to cross-contaminations and systematic errors. Compared with this standardized procedure, an automated monitoring system has significant advantages. It allows the automated, continuous sampling of numerous gas-phase carbonyl species followed by online analysis. Providing a time resolution of just several minutes, short-term variations regarding the kind of carbonyl species and their concentration can be detected over a monitoring period of several days.

It might be assumed that C_1–C_{14} carbonyls are present in the gas phase and, hence, are not considerably partitioned to particulate matter (PM) [6]. In any case, the application of a diffusion-based sampler for an automated monitoring system will prevent the sampling of particulate organic carbonyls. Installing a PM sampler downstream from the gas-phase sampler also allows PM carbonyls to be collected without any sampling artefacts due to gas-phase species.

A limited number of monitoring systems for versatile water-soluble air pollutants employing diffusion denuders (DN) and DS have been tested so far. In particular, the annular type DN and DS have shown appropriate collection efficiencies as a function of the monitored airflow rates [18–23]. Based on high-concentration factors and optimized analytical conditions, these systems are suitable to monitor air pollutants continuously in the ppbv and sub-ppbv concentration range. Regarding the monitoring of organic carbonyls, just one annular DS, fitted with a porous PTFE membrane tube, has been reported [20]. Also, this DS was only employed for formaldehyde and acetaldehyde, the most abundant carbonyls in urban ambient air.

This work presents an automated ambient air monitoring system for various short-chain organic carbonyls (C_1 to C_5). A planar high-efficiency diffusion scrubber (HEDS), equipped with a microporous, hydrophobic PTFE membrane, is employed and operated with an acidified DNPH solution in acetonitrile (ACN). The planar HEDS is coupled with a HPLC–UV system to separate and quantify the carbonyl hydrazone reaction products. Exemplary for the low-molecular-mass organic carbonyls, the system had been tested and validated with various C_1 to C_5 gas-phase carbonyls (formaldehyde, acetaldehyde, propionaldehyde, acetone, *n*-butyraldehyde, and *n*-valeraldehyde).

EXPERIMENTAL

Parallel Plate Diffusion Scrubber

The parallel plate diffusion scrubber (PPDS) employed in this work was designed for easy manufacturing and use, but also with regard to a quantitative collection at high sample gas flow rates as well as a fast response time. The construction details and materials used are illustrated in Fig. 1. The commercially available PTFE membrane (F02UP00010, 70 μm thickness, 0.22 μm pore size, 0.8 fractional surface porosity, Osmonics, USA) used here has an effective air–liquid contact surface of *ca.* 145 mm × 15 mm. The hold-up volume for air was *ca.* 2500 μL and for DNPH scrubbing solution *ca.* 400 μL. PEEK was chosen for the guard plates instead of acryl, because of its chemical stability to the DNPH scrubbing solution. PPDS is now available from Lab-solution Co. (Seoul: www.lab-solution.com).

Reagents

HPLC-grade acetonitrile (ACN, J.T. Baker, USA) was used for the preparation of eluent, standards, and scrubbing solutions. The DNPH scrubbing solution was prepared by dissolving 0.33 g of purified DNPH in 1600 mL of acetonitrile. To this solution, 16.7 mL of phosphoric acid was added. The DNPH was recrystallized twice in HPLC-grade acetonitrile and dried in a vacuum desiccator over night. A commercially available stock solution containing 13 carbonyl compounds from C_1 to C_8 (1 μg/mL for each analyte as DNPH derivate, Supelco, USA) was serially diluted with acetonitrile to obtain the calibration standard solutions of lower concentrations.

PPDS–HPLC System

Schematics of the PPDS–HPLC system are shown in Fig. 2. Different gas samples can alternately be introduced at the bottom of the PPDS using a manual switching valve

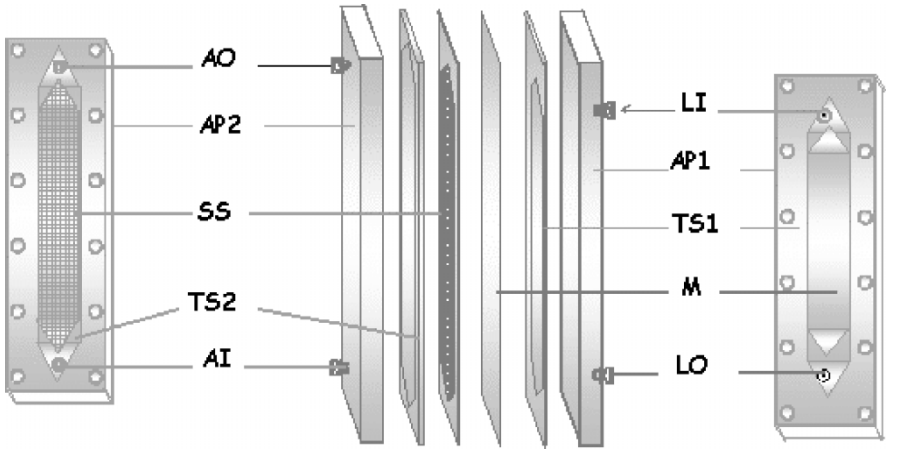

FIGURE 1 Schematic diagram of the parallel plate diffusion scrubber (PPDS): AI, air inlet; AP1, AP2, peek guard plate; TS1, liquid channel (0.2 mm thick); SS, stainless steel screen; TS2, air channel (1 mm thick); LI, liquid inlet; LO, liquid outlet; M, membrane (PTFE).

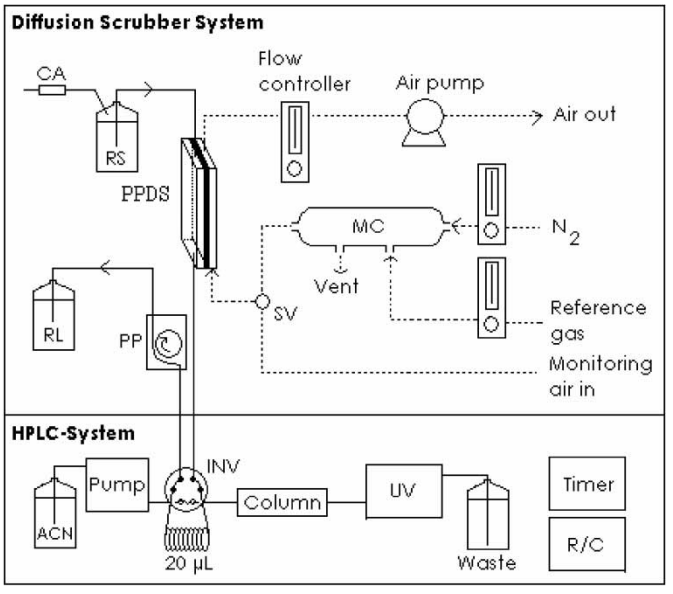

FIGURE 2 Automated monitoring system for gas-phase organic carbonyls in ambient air: CA, DNPH-cartridge; PPDS, parallel plate diffusion scrubber; INV, automated injection valve with sample loop (mode: loading loop); MC, mixing chamber; SV, switching valve; R/C, recorder/computer; RL, reservoir loaded scrubbing solution; RS, reservoir scrubbing solution; UV, UV detector; Vent, ventilation (out).

SV. The sample gas flow rate was controlled using a needle-valve flow controller (Cole-Parmer, USA) placed between PPDS and the air. The flow rate was set at 0.5 L/min, unless stated otherwise. DNPH scrubbing solution contained in a brown glass reservoir RS was aspirated through PPDS into an HPLC injection valve INV at a flow rate of 40 µL/min using a peristaltic pump PP (Minipuls 3, Gilson, Villiers, France). The DNPH reservoir was positioned 30–60 cm higher than PPDS to maintain the solution under a low positive pressure (otherwise, aspiration of air bubbles through the membrane pores of PPDS may have occurred). The reservoir had a DNPH cartridge air vent CA to prevent DNPH solution from airborne contamination. The HPLC injection valve was a six-port, three-way valve with a 20-µL sample loop. All instrument manipulations for the continuous sampling and analysis were carried out using a programmable timer (Model XT, Chrontrol, USA).

The DNPH scrubber solutions were analysed using an HPLC system consisting of a pump (Alltech 301, Deerfield, IL, USA), a column heater (Alltech 330), and a variable-wavelength UV detector (Linear Instrument Model 200, USA). The chromatographic separation was made on a Symmetry Shield RP-18 column with a polar embedded phase (Waters, USA; 4.6 × 250 mm, 5-µm particles) by isocratic elution with 65% v/v CAN in water at a flow rate of 1.0 mL/min. The column temperature was adjusted to $35 \pm 1^{\circ}$C. UV detector was carried out at a wavelength of 360 nm.

Generation of Standard Gases

Two methods have been employed for the generation of mixed standard gases. The tests to determine the experimental collection efficiency of the HEDS–HPLC system had

been performed with a gas mixture containing acetone and the three aldehydes formaldehyde, acetaldehyde, and *n*-butyraldehyde in pure nitrogen. This test gas mixture was generated utilizing a gas/liquid separator system with Gore-Tex^{TM} membrane (thermostated at $28 \pm 1^{\circ}C$). The source solution contained 4.7 mg of formaldehyde, 9.5 mg of acetaldehyde, 6.9 mg of *n*-butyraldehyde, and 10.3 mg of acetone in 1 L of ultrapure water. The primary source gas was further diluted with pure nitrogen in a 1-L glass mixing chamber under constant gas flows. The resulting gas concentrations of the analytes were determined for acetone with 170 ± 8 ppbv, formaldehyde with 88 ± 5 ppbv, acetaldehyde with 170 ± 8 ppbv, and *n*-butyraldehyde with 110 ± 6 ppbv (sampling on DNPH silicagel cartridges and HPLC–UV analysis). Frequent checks over a period of several weeks indicated no measurable change in gas concentrations generated by this gas source. The certified standard gas mixtures for the validation of the monitoring system had been prepared by diluting a reference gas mixture (Scott Speciality Gases, Plumsteadville, PA, USA), consisting of 1.0 ppmv of each acetaldehyde, propionaldehyde, *n*-butyraldehyde, and *n*-valeraldehyde in nitrogen gas, with pure nitrogen gas in a 1-L glass mixing chamber.

RESULTS AND DISCUSSION

HPLC Analysis

The analysis conditions such as column temperature, eluent composition, injection volume, and eluent flow rate, etc. had been optimized to shorten the total analysis time. A brief analysis time allows shorter intervals between consecutive samplings and hence a better time resolution. Additionally, it was essential to obtain proper separation of particular peak doublets as well as to improve the overall sensitivity of the monitoring system. Figure 3 depicts the ruggedness of the resolution of the acrolein/acetone double peak and the peak height of benzaldehyde.

Under the optimized conditions, the resolution of acrolein and acetone peaks was 0.82, sufficient for separate quantification. Though the eluent composition has a significant influence on the resolution, the drop in resolution with 33% at an eluent composition of 70:30 ACN/H_2O (v/v) still allows adequate separation and quantification. The analytical method can therefore be regarded as stable even considering more rugged analytical conditions for field measurements.

The resulting standard separation conditions led to a selective and reproducible HPLC method for the 13 carbonyl compounds in the standard calibration mixture, with *n*-hexanaldehyde (C_6) eluting last of all at 22.4 min (Fig. 4). The intensive peak tailing of unreacted DNPH in the PPDS scrubbing solution can have adverse effects on the quantification of early eluting peaks such as formaldehyde. The DNPH concentration in the scrubbing solution had been optimised therefore to reduce the peak tailing as much as possible, taking into consideration that a very low DNPH concentration has a negative effect on the collection efficiency of the PPDS.

HEDS–HPLC Validation

The HEDS–HPLC system was validated with regard to the overall linearity and precision. A reference gas mixture containing the C_2 to C_5 carbonyl compounds

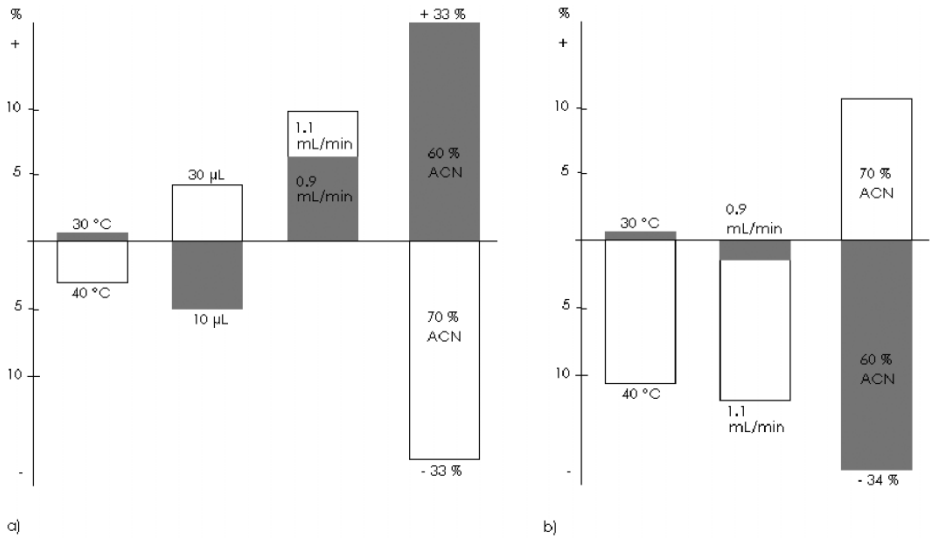

FIGURE 3 (a) Resolution of the acrolein/acetone double peak and (b) the peak height of benzaldehyde as a function of various chromatographic parameters (basis: standard method with 35°C column temperature; 20 µL injection volume; 1.0 mL/min eluent flow rate and eluent mixture ACN/H_2O, 65:35, v/v).

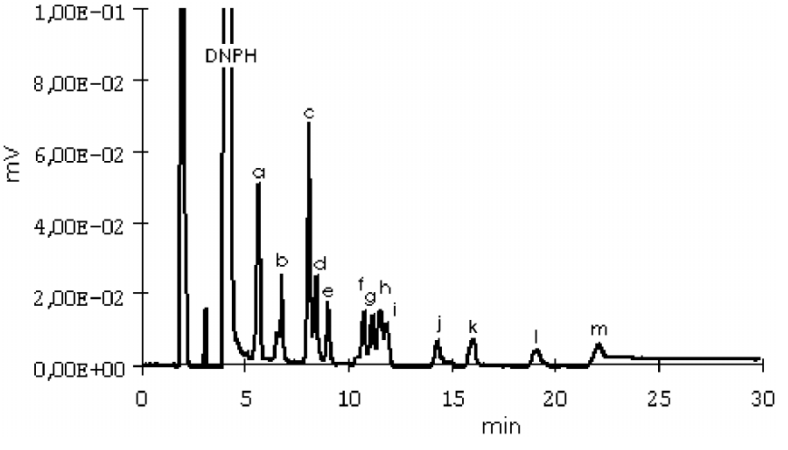

FIGURE 4 Chromatogram of the scrubbing solution spiked with the mixed calibration standard 100 ng/mL for each carbonyl compound). Hydrazone peaks: a, formaldehyde; b, acetaldehyde; c, acrolein; d, acetone; e, propionaldehyde; f, crotonaldehyde; g, methacrolein; h, 2-butanone; i, *n*-butyraldehyde; j, benzaldehyde; k, *n*-valeraldehyde; l, *m*-tolualdehyde; m, *n*-hexaldehyde.

acetaldehyde, propionaldehyde, *n*-butyraldehyde, and *n*-valeraldehyde in pure nitrogen was used. Five concentration levels of this gas mixture within a range of 4–36 ppbv for each carbonyl compound had been measured under repeatable conditions. For quantification purposes, the calibration functions based on peak areas showed a regression coefficient, R^2, of >0.9991, an excellent linearity for the four analytes investigated (Table I). For both the low concentration at 4 ppbv and the highest concentration level at 36 ppbv, the relative standard deviations of the peak areas were within 7 and

TABLE I Overall linearity and repeatability for some carbonyl compounds

Carbonyl compound	*Calibration (Range: 4–36 ppbv, 5 levels, n = 2)*			*Repeatability of peak area (n = 4)*	
	Function[a]	R^2	*RSD* (%, 4 ppbv)	*RSD* (%, 36 ppbv)	*Overall RSD* (%)
Acetaldehyde	$y = 65\,892x + 3635$	0.999	10.8	9.0	9.9
Propionaldehyde	$y = 74\,817x - 34\,852$	0.999	13.7	6.9	10.3
n-Butyraldehyde	$y = 57\,787x - 26\,280$	0.999	9.8	8.2	9.0
n-Valeraldehyde	$y = 41\,126x - 80\,559$	0.999	12.8	11.2	12.0

[a]y denotes the peak area of the carbonyl DNPH derivative, and x denotes the gas concentration (ppbv).

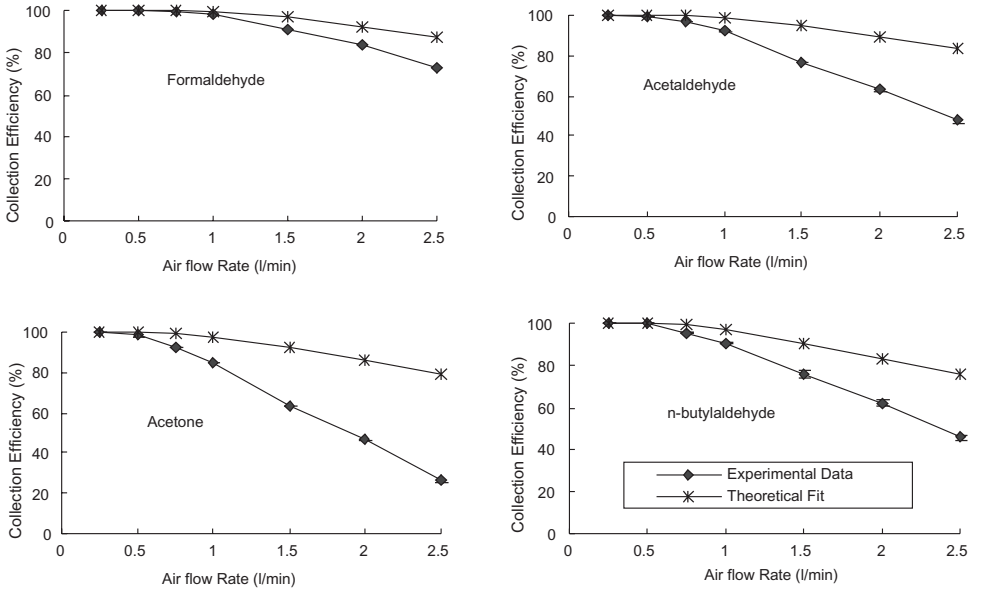

FIGURE 5 Theoretical and empirical collection efficiencies for formaldehyde, acetaldehyde, *n*-butyraldehyde, and acetone as a function of the air sampling flow rate.

14% and indicated a good repeatability. Interferences caused by O_3 and NO_2, which occur in the manual method using a DNPH silicagel cartridge, have been found in previous work to be negligible [19]. The effect of particulate carbonyl collection has not been tested, but this is highly unlikely because PPDS, a diffusion-based sampler, preferentially collects gaseous species. In addition, low-molecular-mass carbonyl compounds are likely to exist in gaseous form under ambient conditions.

Collection Efficiency

The collection efficiency of PPDS is shown in Fig. 5 for four carbonyl gases, formaldehyde, acetaldehyde, *n*-butyraldehyde, and acetone, at various air sampling flow rates. The solid line shows the experimental collection efficiency of the PPDS, and the dashed line shows the theoretical collection efficiency. The experimental collection efficiencies (f) had been determined by analyses of the scrubbing solutions of two

PPDSs connected in series. The collection efficiency, f_{exp}, is calculated using the following equation:

$$f_{exp}(\%) = (1 - C_2/C_1) \times 100,$$

where C_1 and C_2 denote the concentrations of the individual carbonyl gas collected by the first and second PPDS, respectively.

The theoretical collection efficiencies for a parallel plate diffusion scrubber as a function of axial position, in which only one side is a perfect sink, can be estimated from the following equation [24]:

$$f_{ideal}(\%) = (1 - 0.896 \exp(-1.22\alpha DL/Q)) \times 100$$

here, D is the diffusion coefficient of the gas, L is the length of the scrubber, and Q is the volumetric flow rate. The parameter α is given by:

$$\alpha = 2b/a,$$

where a and b are the short and long dimensions of the active cross-section of the scrubber, respectively. The following diffusion coefficients are used: formaldehyde $0.171 \times 10^{-4}\,m^2/s$ at 25°C [20]; acetaldehyde $0.15 \times 10^{-4}\,m^2/s$ at 25°C [20]; *n*-butyraldehyde $0.117 \times 10^{-4}\,m^2/s$, and acetone $0.131 \times 10^{-4}\,m^2/s$, as computed according to Graham's law.

As shown in Fig. 5, the experimental collection efficiencies are generally lower than the theoretical efficiencies, especially at high airflow rates and for acetone and butylaldehyde. Lower experimental collection efficiencies may be explained on the basis of the fact that the membrane porosity is not considered in theoretical calculations. The experimental collection efficiencies of the four carbonyl gases are almost quantitative at airflow rates up to 0.5 L/min. At a sampling flow rate of 0.5 L/min, this results in an HEDS concentration factor of nearly 12 500, providing a scrubbing solution flow rate of 40 μL/min. For higher airflow rates, the efficiencies tend to be lower, especially for acetone and *n*-butyraldehyde, which have the lowest gas diffusion coefficient of the four analytes. Also, acetone might be more deactivated for the acid-catalysed derivatization reaction with DNPH, which affects longer reaction times and, hence, a stronger back-diffusion into the gas phase [15]. In any case, our empirical results and theoretical considerations confirm the improvement in collection efficiencies applying a parallel plate DS compared with the annular DS employed for carbonyl monitoring [20]. In comparison with the annular DS used previously, the PPDS hold-up volume for the DNPH scrubbing solution is just about 400 μL. Provided that the flow rate is 40 μL/min and that there is no significant influence from diffusive mixing, this causes a rapid response time of nearly 10 min.

Limits of Detection

The LOD of the HPLC–UV analysis method was ascertained for each carbonyl compound by evaluating the chromatogram of a DNPH scrubbing solution, spiked at a low concentration with a 13-compound mixed calibration standard solution.

TABLE II Limits of detection (LOD) for some carbonyl compounds

Carbonyl compound	*HPLC/UV instrumental LOD*[a] (ng/mL)	*Overall method LOD*[b] (ng/mL)	*Resulting LOD* (pptv)[c]
Acetaldehyde	1.7	1.7	75
Propionaldehyde	2.7	2.9	100
n-Butyraldehyde	5.6	7.1	195
n-Valeraldehyde	6.7	17.9	470

[a]Peak height signal-to-noise ratio of 3. [b]Without DNPH purification. [c]Computed from overall method LOD assuming a PPDS concentration factor of 12 500.

Providing a peak height signal-to-noise ratio (S/N) of 3, the extrapolated instrumental limits of detection lay within a few nanograms per litre for the four carbonyls considered (Table II). The overall method LOD for acetaldehyde, propionaldehyde, *n*-butyraldehyde, and *n*-valeraldehyde were determined by repeated measurements of the 4 ppbv reference gas generated, as mentioned in the Experimental section. The instrumental LOD for *n*-butyraldehyde and *n*-valeraldehyde tend to be higher as a result of lower response factors and peak broadening. Also, the collection efficiencies of *n*-butyraldehyde and *n*-valeraldehyde do not seem to be more quantitative as a result of the higher overall method LOD compared with the instrumental LOD. In general, to ensure a low overall method LOD, it is essential to keep the hydrazone blank values low by purifying the DNPH and preventing any contamination of the scrubbing solution within a monitoring run.

Results of Urban Site Monitoring

The PPDS–HPLC system developed was employed with a 7-day monitoring at the campus of Yonsei University in Seoul, on January 2003. This urban site is surrounded by a green belt of plants and trees and is not directly influenced by motor-vehicle emissions or industrial activities. Figure 6 illustrates the results for the monitoring of formaldehyde, acetaldehyde, acetone, and *n*-butyraldehyde. The diurnal change with maximum concentrations reached at noontime and lows at night are observed for almost all monitoring days. On 14 January, there was a strong westerly wind, which prevented accumulation of air pollutants. The occasional over-scaling of the acetone peak mostly occurs at the time of organic solvent waste disposal outside the monitoring building. Though the PPDS/HPLC system usually runs stably and reliably, an appropriate overall calibration and periodical measurement of a control standard gas are necessary to obtain reliable and comparable results during long-term monitoring.

CONCLUSION

The PPDS–HPLC system developed is promising for automated, long-term monitoring of various C_1 to C_5 organic carbonyl compounds in ambient air. A planar diffusion scrubber allows quantitative sampling at an airflow rate of 0.5 L/min, resulting in an LOD range of 80–500 pptv for the organic carbonyls tested. The design of the PPDS can be adapted to improve the collection efficiencies for certain carbonyl compounds at higher airflow rates. This, and the employment of a low noise UV-detection

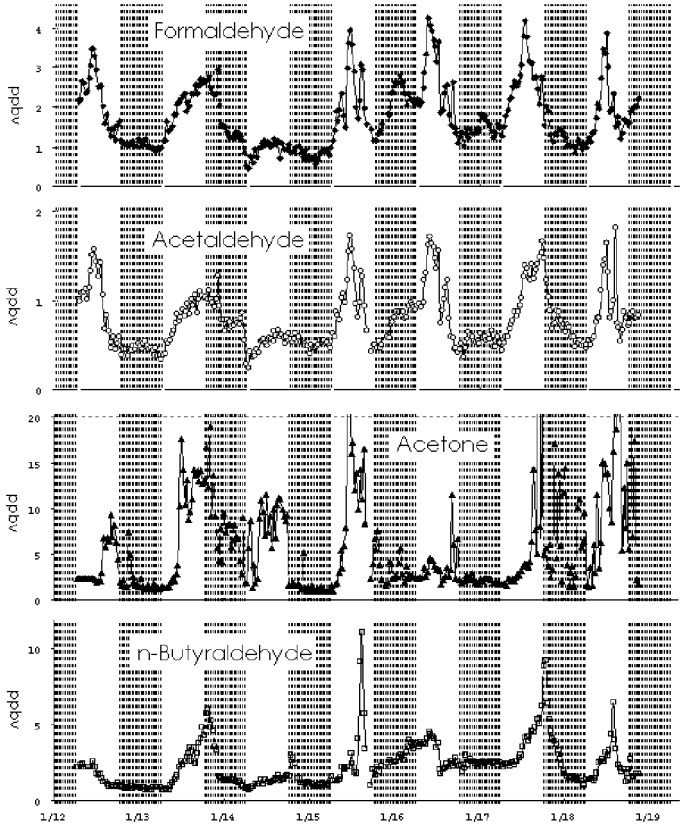

FIGURE 6 Ambient air concentrations (ppbv) of several gaseous carbonyls in Seoul during 12–18 January 2003. The shaded areas represent the night-time from 6 p.m. to 6 a.m.

system, will significantly increase the working range to lower gas concentrations and enable continuous monitoring of low-concentration secondary carbonyl compounds in ambient air. Furthermore, a better time resolution for the system should enable automated monitoring of short-term emission events of mal-odour carbonyls, such as those originating from industrial facilities. Future work in our group will also include additional validation activities of the PPDS–HPLC system at low analyte concentrations, the expansion of the carbonyl compound spectrum, as well as comparisons with reference methods.

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