Dynamic system for the calibration of semi-volatile carbonyl compounds in air

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Abstract

A dynamic calibration system designed for generating accurate and precise concentrations of semi-volatile carbonyls in the ppb (v/v) (ppbv)−ppt (v/v) (pptv) range has been developed and tested. Alkanals from C_6 to C_9 were used as test compounds. Diffusion rates of their vapours from capillary tubes were determined theoretically and with two methods whose accuracy was independently evaluated with liquid standard solutions. Methods selected for testing the calibration system were those commonly used for the selective quantification of carbonyls in air. One is based on the well-known reaction with 2,4-dinitrophenylhydrazine (DNPH), followed by the analysis of formed hydrazones by HPLC-UV. The other is based on the retention of carbonyls on graphitic carbon adsorbents, followed by MS detection of the sample injected into a capillary column by thermal desorption. A good consistency was found between the values of the diffusion rates determined by the two methods. The scatter between the two methods was in the range of ±10% when diffusion rates of ca. 1 ng/s were attained. Experimental values closely approached those calculated by applying the equation describing the diffusion of a vapour in equilibrium with the liquid through a capillary tube.   © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbonyl compounds are considered of primary interest in tropospheric chemistry as they are common products of the photochemical oxidation of hydrocarbons by OH radicals and ozone and they act as precursors of free radicals, ozone and peroxyacylnitrates in the atmosphere [1–3]. Carbonyls with carbon number lower than 5 are currently measured in many urban areas of the US whenever air quality standards for ozone are exceeded [4]. In the last few years, volatile carbonyls have been also monitored in Europe. In particular, regular samples are collected at the 10 stations belonging to the EMEP network [5].

Carbonyls with carbon number equal or larger than 5 are usually not included in these monitoring protocols, although several studies [6–11] have shown that semi-volatile alkanals and ketones from C_5 to C_{11} (particularly nonanal, decanal and 6-methyl-5-hepten-2-one) are quite common and abundant in the troposphere. The main reason for this choice relies on the fact that artificial formation of *n*-alkanals was observed when ozone-rich air was sampled through traps filled with Tenax adsorbents

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[12,13]. This, combined with difficulties in the identification of emission sources for semi-volatile carbonyls and photochemical pathways leading to their formation, supported the idea that these compounds were generated by ozone decomposition of airborne VOC or of the polymeric matrix of Tenax. The occurrence of sampling artifacts was strengthened by the fact that the detection and positive identification of semi-volatile compounds with DNPH-coated cartridges was highly uncertain due to the low sensitivity of HPLC-UV and the partial decomposition of hydrazones by ozone attack [14].

Only the development of efficient scrubbers for removing ozone from the air stream has made possible to assess the actual occurrence of semi-volatile carbonyls in air. Substantial amounts of *n*-alkanals were measured by Helmig and Greenberg [10] with Tenax traps equipped with ozone scrubbers based on potassium iodide. Levels measured were quite similar to those obtained by concentrating the air samples on inert materials (glass beads) kept at very low temperatures ($< -100°C$). Similar observations were reported by Ciccioli et al. [15] who found that the aerometric concentrations of *n*-alkanals and 6-methyl-5-heptene-2-one (6-MHO) measured with traps filled with graphitic carbons were only slightly higher than those collected on the same traps equipped with ozone scrubbers made by MnO_2 deposited on copper screens. It was found, however, that this type of scrubber was not ideal for the sampling of oxygenated compounds as it partly removed terpene compounds directly emitted from plants (linalol and 1,8-cineol) [16]. A large number of observations supporting the presence of substantial amounts of semi-volatile alkanals and 6-MHO were performed in the Mediterranean area [16–19]. Levels as high as 15 and 8 $\mu g/m^3$ were often reported for *n*-alkanals from hexanal to decanal and 6-MHO, respectively. These observations were particularly relevant as they were obtained by various groups using different trapping materials and ozone scrubbers, including traps coated with potassium iodide. Among the results obtained, it is worth to mention those collected in Burriana (Valencia, Spain) in 1996 [16,17], because some of the samples were collected by using a novel scrubber based on poly-

phenylenesulfide resin capable of removing ozone from the air stream without affecting reactive VOC of biogenic origin [20]. By fully preventing the decomposition of emitted compounds, Fruekilde et al. [21] were able to show that ozonolysis of waxes covering the leaf surface can act as a strong source for volatile and semi-volatile carbonyls in air in addition to direct emission [22,23].

The occurrence of semi-volatile carbonyls in air samples was also assessed with methods based on cartridges exploiting the reaction of carbonyls with DNPH [24]. Decomposition of DNPH-derivatives was prevented by using annular denuders coated with potassium iodide and positive identification performed by advanced MS techniques, the reliability of which has been recently confirmed [25,26]. The results obtained in the Los Angeles basin showed clearly that semi-volatile carbonyls could play an important role in driving the photochemical reactivity of polluted atmospheres. It was estimated that nonanal was the third most important carbonyl compound in the removal of OH radicals from the atmosphere, whereas *n*-alkanals from C_5 to C_{10} accounted for 25% of the total removal of this radical from the atmosphere [24].

Although the levels of semi-volatile carbonyls measured in the Los Angeles basin did not differ so much from those previously recorded in the Tiber valley [7,10] and in various Mediterranean sites [16–19], it is not possible to compare data obtained with different methods until a quality control is performed on the methods used. To achieve this goal, a dynamic calibration system capable of generating gaseous standard solutions of semi-volatile carbonyls was built in our laboratory within the frame of an European project called CATOME (Carbonyls in Tropospheric Oxidation Mechanisms). Due to the low volatility of compounds investigated, primary standards were generated by exploiting the diffusion of vapours through capillary tubes [27–29]. Alkanals from C_6 to C_9 were used as test compounds. Diffusion rates were theoretically estimated by using the equation describing the diffusion of a vapour through a capillary tube. Theoretical values were compared with those obtained by using the most common methods available today for determining semi-volatile carbonyls in air. Examples of cali-

bration curves obtained with our generation system are reported and results critically discussed in terms of accuracy and precision.

2. Experimental

2.1. Reagents and materials

High purity n-alkanals from C_6 to C_9 for generating gaseous standards by diffusion were purchased from Fluka (Sigma–Aldrich, Milan, Italy), whereas the corresponding dinitrophenylhydrazones were obtained from AccuStandard (New Haven, CT, USA). The latter compounds were supplied as acetonitrile solutions at concentrations of 1 mg/ml. Sep-Pak DNPH-silica cartridges used for the collection of alkanals in air were provided by Waters (Milford, MA, USA); methanol and acetonitrile of HPLC grade were purchased from BDH (Milan, Italy).

Carbon traps for the collection of semi-volatile carbonyls were prepared by using glass tubes (15 cm×0.3 cm I.D.) filled with 60 mg of Carbograph 1, 118 mg of Carbograph 2 and 115 mg of Carbograph 5. The retention features of these cartridges have been described in a recent publication [30]. The superior stability of carbon materials relatively to Tenax has been discussed, instead, in Ref. [31]. All graphitic carbon adsorbents used were supplied by Lara (Rome, Italy). They were provided in the particle range size of 20–40 mesh.

2.2. Diffusion tubes and dynamic calibration system

The geometry of the diffusion tube used in our calibration system is shown in Fig. 1a. The diffusion device was made by a glass tube (6 mm O.D., 4–8 cm in length) connected to a 4-ml glass vial through a polyethylene screw cap. Glass tubes were characterized by internal diameters ranging from 0.7 to 1.0 mm. Silicon o-rings coated with a thin Teflon layer were used to ensure a tight connection between the glass tube and the vial. They were obtained by modifying septa commonly used in GC. Shorter lengths and wider inner diameters of the glass tubes were selected for less volatile compounds (such as

nonanal), whereas combinations characterized by longer lengths and smaller diameters were used for the most volatile ones (hexanal, heptanal).

Fig. 1b shows a schematic diagram of the gasphase calibration apparatus developed for semi-volatile carbonyls. The general design was similar to that described by Larsen et al. [31]. Four diffusion tubes, each one containing a single n-alkanal from hexanal to nonanal, were placed at the bottom of the diffusion chamber, which was able to accommodate up to 12 tubes held in vertical position. The chamber was immersed into a water-bath kept at $25.0\pm0.1°C$. It was maintained at a slight overpressure (3 kPa) by means of a micromanometer connected to the gas cylinder. Fine regulations of the inlet pressure and the gas flow-rate were obtained by using a needle valve placed downstream of the micromanometer.

The calibration system was realized in such a way that carbonyl vapours were always in contact with glass or Teflon surfaces. Pure nitrogen was continuously passed through the chamber at a constant flow-rate (100 ml/min). Different mixing ratios of alkanals were obtained by diluting the exit of the diffusion chamber with flow-rates of clean air ranging from 1 to 10 l/min. An air generator (Claind, Lenno, Italy) provided diluting air free from hydrocarbons. Both flows of nitrogen and diluting air were accurately conveyed into the system by using mass flow controllers (Aalberg, Monsey, NY, USA). They were characterized by an accuracy and precision better than 1% of the full-scale value. Before reaching the mixing chamber, the diluting air was humidified at values of relative humidity ranging between 50 and 55% by using an electronic system supplied by Humicon (DAS, Palombara Sabina, Italy). The humidifier was composed by a thermostatic bath in which water evaporation was controlled by a microprocessor receiving the signal from a water vapour sensor placed in proximity of the diffusion tubes. The calibration system was designed in such a way that other gases, such as ozone, could be added to the system.

2.3. Collection and analysis of semi-carbonyls from the dynamic calibration system

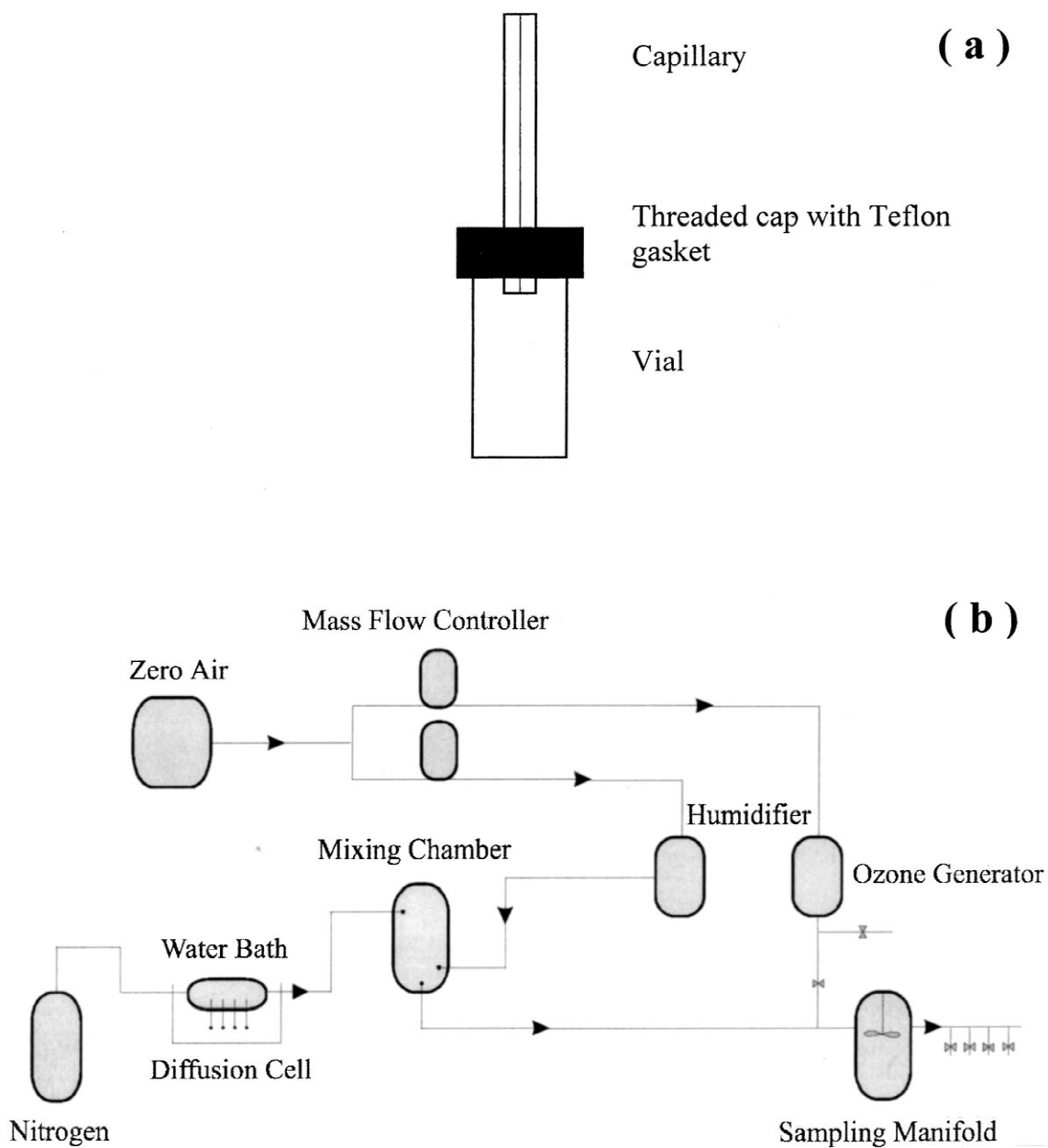The mixing chamber was connected to a sampling

Fig. 1. Schematic diagrams of the diffusion tubes (a) and of the dynamic system (b) used for generating constant mixtures of semi-volatile alkanals in air.

manifold from which aliquots of the effluent could have been simultaneously sampled on different enriching devices. Electronic samplers (Sequair 92, DAS, Palombara Sabina, Italy) were used to aspirate the effluent from the calibration system through the

different traps used. They were able to maintain a constancy better than 1% in the whole range of flow-rates used (1 l/min for DNPH cartridges and 0.2 l/min for carbon traps). The sampling duration used in our experiments ranged from 10 to 60 min.

After sample collection, DNPH cartridges were extracted with 3 ml of acetonitrile and the eluate analyzed by HPLC [32]. The HPLC unit consisted of a Jasco 880 PU isocratic pump, a Rheodyne 1294 injecting valve with a 20-µl loop, a 150×4-mm Hypersil ODS 5 µm reversed-phase column, a photometric detector (Jasco 875 UV) set at 360 nm and a Jasco-Borwin data acquisition/chromatogram processing system. The mobile phase was acetonitrile–water (80:20, v/v). HPLC calibration was performed by direct injection of dilute solutions prepared from the standard stock solutions of DNPH derivatives of C_6–C_9 aldehydes.

Carbonyls collected on carbon traps were analyzed by GC–MS [33]. The sample was injected into the capillary column by thermal desorption. A Chrompack (Middelburg, The Netherlands) purge and trap injector was adapted for this purpose by eliminating the purging and drying units. Traps were desorbed under a flow of helium (20 ml/min) by rising the temperature from 25 to 250°C in 5 min. Desorbed compounds were cryofocused on an empty fused-silica liner kept at −180°C. They were injected into a capillary column (0.32 mm I.D.) coated with a film of DB-1 (0.25 µm) by heating the liner from −180 to 200°C in less than 30 s. The column used was supplied by J&W (Folsom, CA, USA). It was maintained at 0°C for 3 min after the injection, then programmed to 50°C at 3°C/min and, finally, to 220°C at 5°C/min. A Hewlett-Packard (Palo Alto, CA, USA) gas chromatograph (model 5890) connected to a quadrupole mass spectrometer (model 5970B), supplied by the same company, was used for analysis. The MS system was operated in the scan mode by recording the total ion current produced by all ions from m/z 20 to 300. The quantification of semi-volatile carbonyls was performed by

measuring the area of the peak produced by plotting the current generated by the ion with $m/z=44$. Linearity curves were generated after controlling that the intensity of this ion was fully consistent with that of the major fragments (at least three) produced by the decomposition of the molecular ion.

3. Results and discussion

Since diffusion tubes can be used as primary standards only if their weight losses are sufficiently high to be accurately measured over a reasonable time interval (1–3 months), the first step was to theoretically estimate the diffusion rates of semi-volatile carbonyls from our tubes. This was done by using the diffusion equation of a vapour through a capillary tube, which states that:

$$r_t = DMPS \ln[P/(P-p)] (RTL)^{-1} \qquad (1)$$

where r_t, D and M are the diffusion rate (g/s), the coefficient of molecular diffusion (cm^2/s) and the molecular mass (g/mol) of the compound investigated, respectively. S and L are the cross-sectional area (cm^2) and the length (cm) of the capillary, respectively. P is the total pressure in the diffusion cell (kPa), p is the partial pressure (kPa) of the diffusing vapour at the absolute temperature T (K) and R is the gas constant ([ml kPa]/[mol K]).

The theoretical estimate of the diffusion rates provided useful indications to assess if the volatility of compounds investigated was sufficiently high to make the gravimetric method reliable and not time-consuming. The results obtained by applying Eq. (1) to C_6–C_9 n-alkanals are reported in Table 1. Diffusion coefficients of individual components were

Table 1
Values of the diffusion rates (r_t) of n-alkanals from C_6 to C_9 calculated by using the diffusion equation of a vapour though a capillary tube[a]

n-Alkanal	p (kPa)	D (cm^2/s)	S/L (cm)	r_t (ng/min)
n-Hexanal	0.854± 0.027	0.068±0.004	(4.8±0.1) 10^{-4}	68±4
n-Heptanal	0.362±0.016	0.063±0.003	(8.4±0.2) 10^{-4}	52±4
n-Octanal	0.155±0.010	0.058±0.003	(19.6±0.4)10^{-4}	50±4
n-Nonanal	0.063±0.006	0.054±0.003	(19.6±0.4)10^{-4}	26±3

[a] Data of r_t, of the partial pressure of the diffusing vapour (p) and of the coefficient of molecular diffusion (D) were calculated at $T=298$ K for a total pressure in the diffusion cell (P) of 105 kPa. S/L is the ratio between cross-sectional area and capillary length.

estimated with the Gilliland approximation [34], whereas the values of their vapour pressures were calculated by using the Antoine algorithms [35].

From the data reported in this Table, weight losses of 2.9, 2.3, 2.1 and 1.1 mg/month were estimated for *n*-hexanal, *n*-heptanal, *n*-octanal and *n*-nonanal, respectively. Although ideal for generating concentrations at ppbv levels with flow-rates larger than those usually required for the sampling with DNPH-

coated silica cartridges (ca. 1 l/min), these weight losses were rather small and their determination by the gravimetric method would have required several months before an accurate measure of the diffusion rates could have been accomplished by a regression analysis of experimental data. Although preliminary determinations showed that diffusion rates were in the range predicted by Eq. (1), serious problems were encountered in achieving the constancy of the
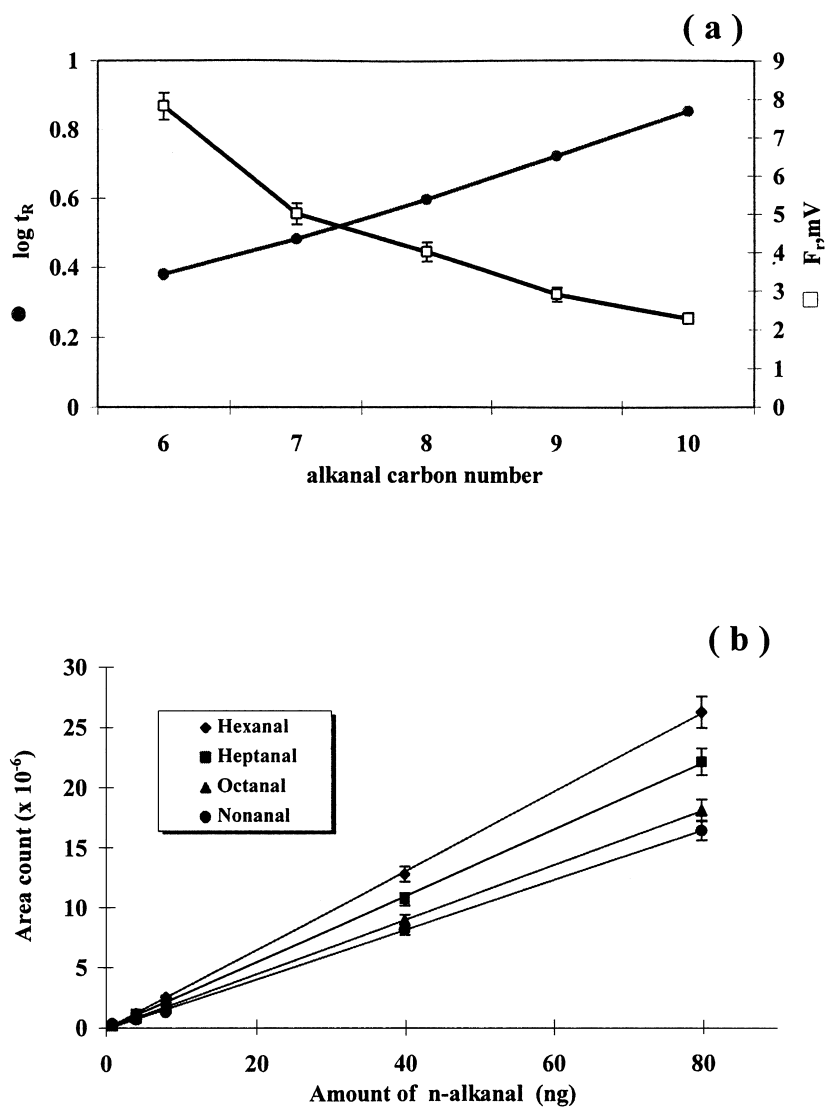

Fig. 2. (a) Retention times and response factors measured by HPLC-UV using standard solutions of 1 ng/ml of DNPH-derivatives of *n*-alkanals from C_6 to C_{10}. (b) Calibration curve of *n*-alkanals in GC–MS obtained with liquid standard solutions injected into traps filled with carbon materials.

emission source. It was found that changes of temperature, pressure and relative humidity to which the tubes were subjected during the transfer from the diffusion chamber to the weighting system were strongly affecting the diffusion rates. The most frequent problem encountered was the formation of liquid droplets inside the capillary tube that were dramatically affecting the diffusion process. We found that the equilibration time necessary to reach the same steady state reached before the weighting process was much longer than 15 days, probably due to the high viscosity and surface tension of compounds investigated and their low vapour pressure. In these conditions, accurate determinations of the weight losses could have only been accomplished by making gravimetric determinations every 2 months. We estimated that at least 1 year was necessary to derive the diffusion rates of semi-volatile alkanals with this approach if disturbances arising from the weighting procedures were minimized. Since the achievement of this goal was not easy, it was decided that the best way to reach and to maintain the stationarity of the diffusion process was to keep the tubes inside the thermostatic chamber all the time and to determine the weight losses by indirect methods requiring the collection of carbonyls on trapping materials followed by chemical analysis. Graphitic carbons and DNPH-coated silica particles were selected as suitable sorbents for the efficient collection of semi-volatile carbonyls in air mixtures. In the former case the analysis of semi-volatile carbonyls was accomplished by GC–MS after thermal desorption. This was possible because compounds are linked to the graphitic surface through dispersion (mainly van der Waals) forces. In the latter case, compounds were quantified by HPLC using specific detectors (UV or MS) after liquid extraction. This approach was needed because DNPH-derivatives are not stable enough to be thermally desorbed.

One desirable feature of both methods was that carbonyls could have also been quantified with liquid standard solutions. It has been shown that spiking the carbon cartridges with few μl of methanol solutions containing test compounds at ppm (w/w) levels does not substantially affect the retention features of the adsorbent and complete recoveries are obtained for compounds with carbon number higher than 5 when methanol is eliminated by passing suitable volumes

of helium, nitrogen or air free from hydrocarbons through the trap [33]. The reaction of carbonyls dissolved in acetonitrile solutions with DNPH is also free from artifacts providing that the reagent is in large excess and a suitable time is allowed to the reaction to take place (15 min) [36]. In both cases, the linearity and sample recovery can be verified by comparing the chromatographic profiles of the original solutions with those obtained by thermal desorption or liquid extraction of the sample. The only problem is represented by the fact that pure hydrazones must be available with DNPH cartridges for controlling the recovery of carbonyls and their response by UV detection.

Fig. 2a shows plots of retention times and response factors of DNPH-derivatives of C_6–C_{10} n-alkanals versus carbonyl carbon number. Recoveries were measured by spiking 10 DNPH-silica cartridges with 100 μl of an acetonitrile solution containing 1 μg/ml of each aldehyde. They were consistent within $\pm 10\%$ with the amount injected for all the aldehydes tested. Linear regression lines were obtained when the amounts of aldehydes injected into the DNPH-silica cartridges ranged from 50 to 1000 ng/ml. All regression lines showed correlation coefficients higher than 0.99 and slopes with relative standard deviations of less than 5%. In all cases, the experimental curves were characterized by zero intercepts within the experimental errors. The precision of the DNPH method was checked by using a mixture containing 100 ng/ml of hydrazones of C_6–C_{10} aldehydes. Values of the standard deviation ranging from 4 and 7% were measured. Since the blank of unreacted cartridges yielded undetectable

Table 2
Theoretical (r_t), experimental (r_{HPLC} and $r_{GC–MS}$) and averaged (r_{av}) diffusion rates of n-alkanals from C_6 to C_9 obtained from the calibration system shown in Fig. 1b[a]

n-Alkanal	r_t	r_{HPLC}	$r_{GC–MS}$	r_{av}
n-Hexanal	68 ± 4	63 ± 3	70 ± 2	67 ± 3
n-Heptanal	52 ± 4	55 ± 6	49 ± 7	52 ± 6
n-Octanal	50 ± 4	51 ± 4	46 ± 5	49 ± 4
n-Nonanal	26 ± 3	23 ± 4	28 ± 2	25 ± 3

[a] Experimental data were obtained by averaging eight determinations carried out with both HPLC-UV and HRGC–MS. Determinations were performed over 1 month. $T = 298$ K, $P = 105$ kPa, R.H. 55%.

contents of C_6–C_{10} *n*-alkanals, detection limits variable from 20 to 80 ng as a function of the carbon number of the aldehydes collected were established for a single cartridge.

The HRGC–MS method was also calibrated with alkanal standard solutions containing amounts of C_6–C_9 *n*-alkanals ranging from 1 to 80 ng. The solvent was evaporated with a flow-rate of 100 ml/min of helium before thermal desorption. A total volume of 1 l was sufficient for solvent evaporation. Calibration curves obtained with liquid standards are shown in Fig. 2b. They were linear for the four carbonyls investigated. The deviation from the regression line was less than 3% and correlation coefficients higher than 0.999. A reproducibility close to 5% was determined for the method using
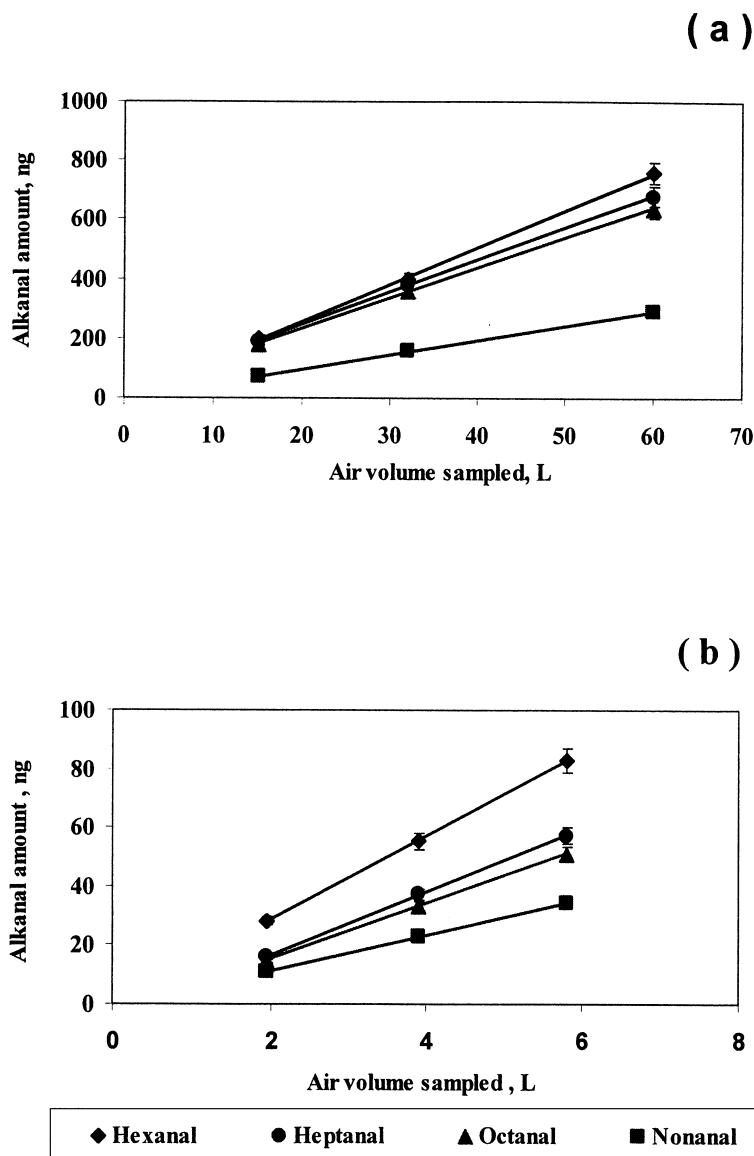

Fig. 3. Amounts of *n*-alkanals detected by HPLC-UV (a) and GC–MS (b) when increasing volumes of the air mixtures generated by the system shown in Fig. 1b were passed through DNPH-coated and carbon cartridge, respectively.

carbon adsorption in combination with thermal desorption and HRGC–MS. It was measured with repeated injections (at least three) of solutions containing alkanals in the range of 1–10 ng.

Amounts used for controlling the linearity of methods used were selected by taking into account the maximum volume that could have been safely sampled on carbon and DNPH-coated samples in order to achieve a reliable quantification of semicarbonyls in air at levels ranging between 0.1 and 20 $\mu g/m^3$.

Once calibrated with liquid standards, methods were used for measuring the diffusion rates of semivolatile alkanals from our calibration system. Repeated collection of samples was performed from the generation system by selecting the best flow-rates and volumes for each system. Eight independent determinations were performed with each trapping system. They were carried out twice a week for a time period of 1 month. Data obtained are reported in Table 2 together with the values of the diffusion rates of *n*-hexanal, *n*-heptanal, *n*-octanal and *n*-nonanal that were calculated by using Eq. (1). They show that the agreement between the two experimental methods used was between 10 and 15% with

relative standard deviations lower than 10%. A good agreement was also found with the theoretical values. Since there were no reasons to believe that one approach was more accurate than the others were, the average values of the diffusion rates provided by the three methods (r_{av}) were assumed to be the true values generated by our apparatus.

The ability of the dynamic system to act as a suitable source of semi-volatile carbonyls in air was tested by carrying out additional experiments 3 months after the diffusion rates were measured. They were aimed at confirming the constancy of the generation source and at establishing the linear response of methods based on carbon and DNPH-coated cartridges under conditions simulating those occurring in moderately polluted atmospheres. The results of these experiments are displayed in Fig. 3a,b, where the amounts of carbonyls detected in carbon and DNPH-coated cartridges are plotted against increasing volumes of the standard mixture that were passed through them. In these experiments, sampling flow-rates and volumes collected were those prescribed for achieving the most efficient retention of carbonyls from air samples. To directly compare data obtained, different aliquots of the same

Table 3

Experimental conditions used in the parallel sampling of *n*-alkanals from the dynamic calibration system shown in Fig. 1b and concentrations determined by GC–MS and HPLC-UV[a]

Sampling run	Sampling method	Volume sampled (l)	Flow rate of sampling (ml/min)	Sampling time (min)
1	Carbon traps	2±0.01	200±2	10±0.03
2	Carbon traps	4±0.02	200±2	20±0.03
3	Carbon traps	6±0.03	200±2	30±0.03
1	DNPH-coated silica	15±0.03	1000±10	15±0.03
2	DNPH-coated silica	32±0.06	1000±10	32±0.03
3	DNPH-coated silica	60±0.12	1000±10	60±0.03
n-Alkanal	Method	Correlation coefficient	Slope of the regression line (ng/l)	Expected concentration (ng/l)
n-Hexanal	GC–MS	0.999	14.2	13.4±0.6
n-Hexanal	HPLC-UV	0.999	12.8	
n-Heptanal	GC–MS	0.996	10.5	10.4±1.2
n-Heptanal	HPLC-UV	0.998	10.9	
n-Octanal	GC–MS	0.999	9.8	9.8±0.8
n-Octanal	HPLC-UV	0.996	10.2	
n-Nonanal	GC–MS	0.997	5.9	5.0±0.6
n-Nonanal	HPLC-UV	0.995	4.9	

[a] The values of *T*, *P* and R.H. were the same as those reported in Table 2.

effluent were passed through carbon and DNPH-coated cartridges. To reduce uncertainty, parallel sampling was performed. The experimental conditions used in the linearity study are listed in Table 3, whereas examples of the GC–MS and HPLC-UV profiles obtained are shown in Fig. 4a,b. Table 3 also reports the correlation coefficients and the slopes of the linear plots reported in Fig. 3a,b and a com-

parison between the amounts expected to be generated by the gaseous system operated at a constant flow-rate of air of 5 l/min and those actually measured by the two methods used.

The close correlation between volume sampled and amount detected indicated that no substantial losses occurred during the sampling and analysis of semi-volatile carbonyls present in the gaseous stan-
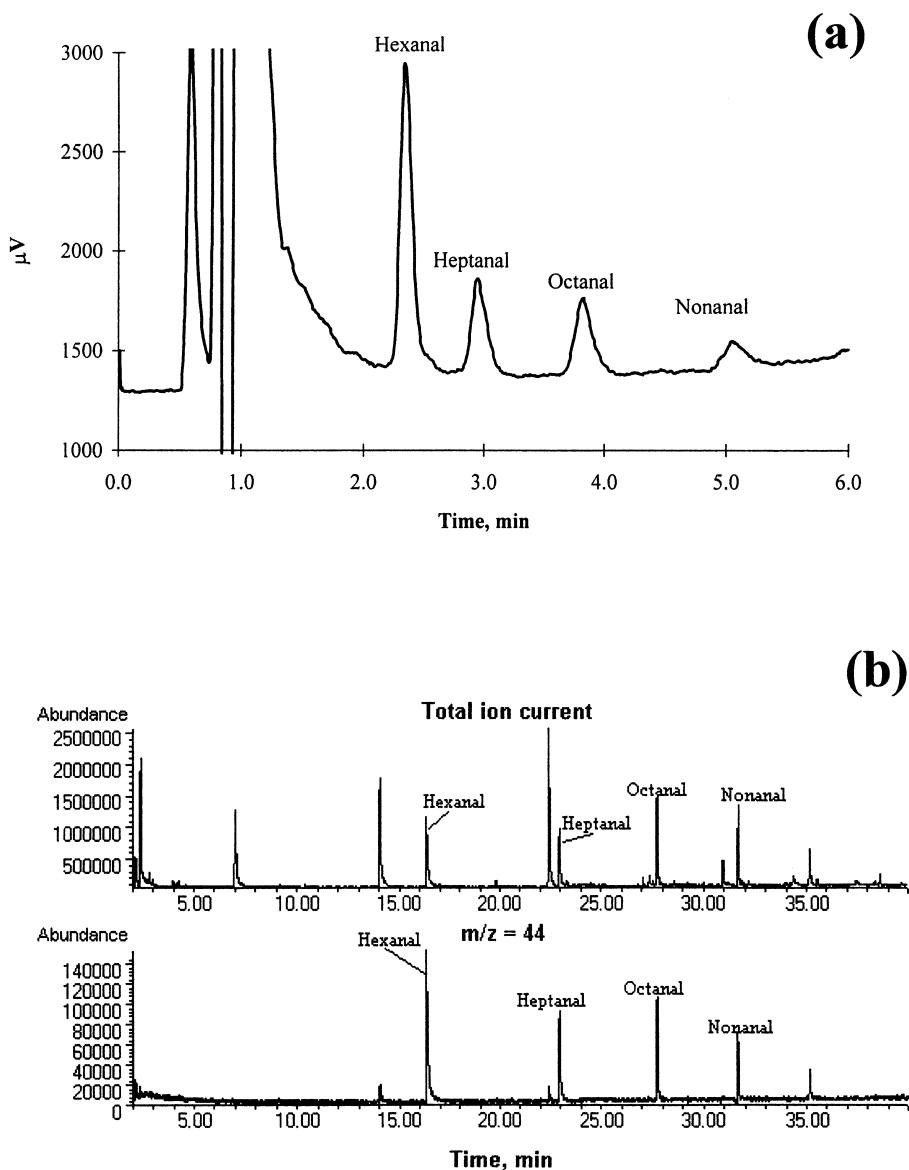

Fig. 4. HPLC-UV (a) and GC–MS (b) profiles obtained during the parallel sampling of *n*-alkanals from the calibration system shown in Fig. 1b. Data refer to sampling times of 10 and 15 min for GC–MS and HPLC-UV, respectively.
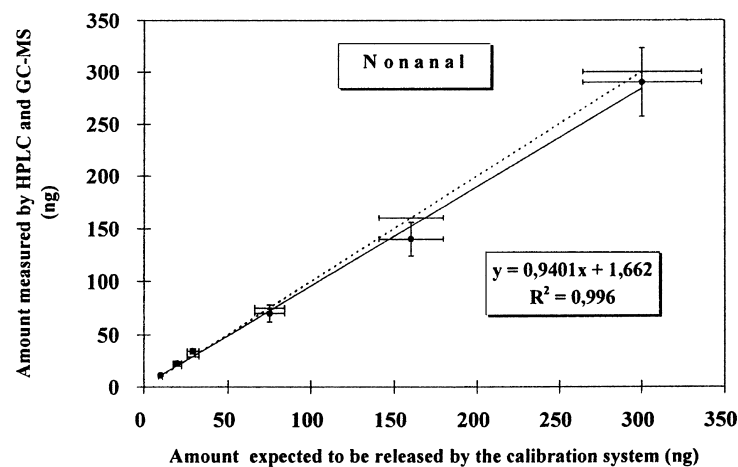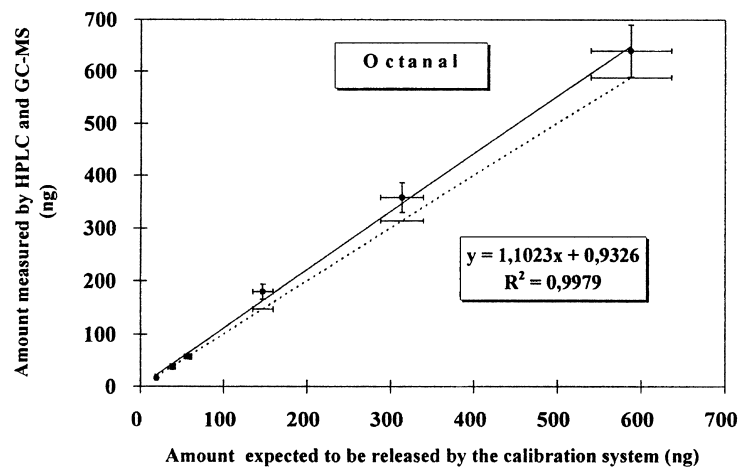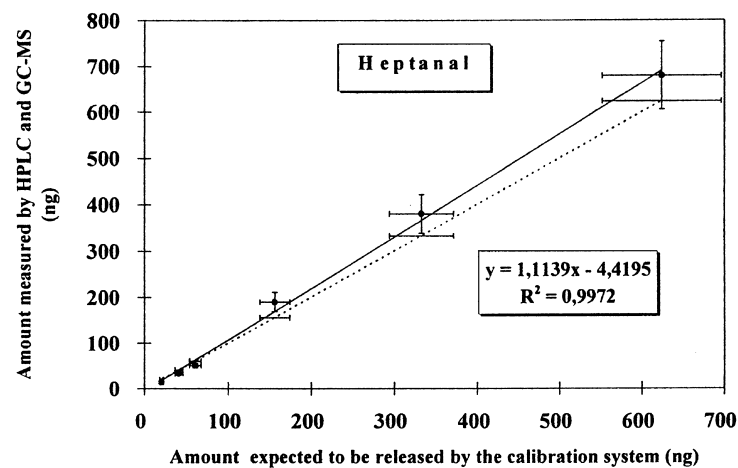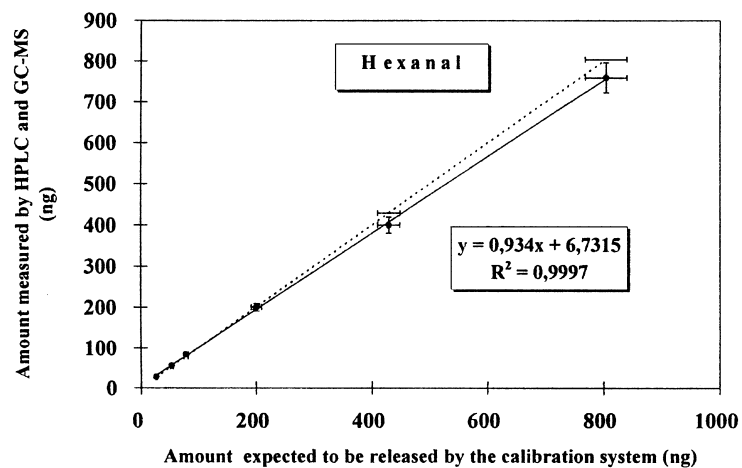
Fig. 5. Differences between the amounts of *n*-alkanals expected to be generated by the gaseous system of Fig. 1b (dotted line) and those actually measured by HPLC-UV and GC–MS (solid lines) calibrated with liquid solutions.

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dard solution. It also suggested that diffusion rates were rather constant during these experiments. The consistency between the concentrations obtained by the regression analysis of linear plots and those expected to be generated by the dynamic system, assuming the average diffusion rates reported in Table 2, fully confirmed the results of previous experiments. By considering the long time lag between the various experiments, the conclusion was reached that the generation system was sufficiently stable to be used for calibration purposes.

Since all considerations made above were based on quantification performed with liquid solutions, it was important to assess the extent to which calibrations performed with the gas phase system were deviating from those obtained by using liquids as primary standard. This information was obtained by plotting the absolute amounts expected to be released by the gaseous system, according to the diffusion rates reported in Table 2, against the amounts that were actually measured by GC–MS and HPLC-UV. Results are displayed in Fig. 5. They were obtained by repeating for three times the protocol described in Table 3. In this case, linear regression analysis was performed on both HPLC-UV (three highest points) and GC–MS (three lowest points) data, as the two methods were calibrated with the same original liquid solution and there was no reason to believe that one method was more accurate than the other in determining semi-volatile carbonyls. This assumption was supported by the fact that random deviations from the regression line were observed with both methods. The cases of heptanal and nonanal well illustrate this point. While GC–MS values underestimate the amount of heptanal relative to the regression line, all HPLC-UV values lies above the line. Exactly the opposite situation is observed with nonanal.

Results shown in Fig. 5 indicate that the amounts expected to be generated by the system were, within the experimental errors, coherent with those measured by HPLC-UV and GC–MS and no substantial errors are introduced in assuming the dotted lines as the actual value released by our generation system.

Based on the results obtained, it can be concluded that the dynamic gas generation system based on diffusion tubes represents a valid alternative to liquid solutions for calibrating instrumentation dedicated to the determination of semi-volatile carbonyls in air. It can be the best choice (if not the only one) for quantifying the effects that interfering gaseous species, such as ozone, have on the collection efficiency and sample recovery of semi-volatile carbonyls from carbon, DNPH-coated silica or other trapping materials where they can be collected. In addition, the influence of physical parameters, such as relative humidity, on the sampling of semi-volatile carbonyls can be adequately investigated and assessed.

Acknowledgements

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