



Denuder sampling techniques for the determination of gas-phase carbonyl compounds: A comparison and characterisation of in situ and ex situ derivatisation methods[☆]

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ABSTRACT

Two denuder sampling techniques have been compared for the analysis of gaseous carbonyl compounds. One type of denuder was coated with XAD-4 resin and the other type of denuder was coated with XAD-4 and 2,4-dinitrophenylhydrazine (DNPH) to derivatise gaseous carbonyl compounds to their hydrazone forms simultaneously. A detailed protocol for the denuder coating procedure is described. The collection efficiency under dry (RH <3%) and humid conditions (RH 50%) as well as filter positive artefacts were evaluated. The XAD-4/DNPH coated denuders showed significantly less break-through potential and hence collection than the XAD-4-only coated denuders. The performance of the XAD-4/DNPH denuder was better under humid conditions with no detected break-through for hydroxyacetone, methacrolein, methylglyoxal, campholenic aldehyde and nopinone. Calibration experiments were performed in a simulation chamber and carbonyl-hydrazone concentrations determined in the extracts of both the denuder types were related to the mixing ratios of gaseous carbonyl compounds in the chamber to overcome losses and errors associating with the denuder sampling, extraction and sample preparation. The application of on-tube conversion for the XAD-4/DNPH denuders resulted in higher R^2 values than the XAD-4 denuder, ranging up to 0.991 for nopinone. The XAD-4-only coated denuders showed acceptable calibration curves only for lower vapour pressure carbonyl compounds though larger relative standard deviations (RSD) were observed. Carbonyl compounds that were formed during the oxidation of nopinone were collected using the XAD-4/DNPH denuders. The results showed that the denuder sampling device was able to provide reproducible nopinone mixing ratios that remained in the chamber after about 1 h of the oxidation. One isomer of oxo-nopinones was tentatively identified from off-line HPLC/(–)ESI-TOFMS analysis. Based on the TOFMS response of the nopinone-DNPH derivative, the oxo-nopinone molar yield of $0.7 \pm 0.1\%$ ($n=3$) was determined from the reaction of nopinone with OH radicals. Depending on target analytes, accuracy and sensitivity requirements, the present method can be employed for the determination of gaseous carbonyl compounds that are formed during the oxidation of monoterpenes.

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1. Introduction

Substantial amounts of volatile organic compounds (VOCs) are released into the atmosphere from various natural and anthropogenic sources such as vehicle exhaust, solvent utilisation, combustion processes and biogenic processes. VOCs react with atmospheric oxidants such as OH, NO₃ radicals and O₃, leading to the formation of functionalised oxidation products and sec-

ondary aerosols. Carbonyl compounds, which are produced in the VOC oxidation, are highly reactive and can undergo photolysis or react further with atmospheric oxidants. These oxidation pathways lead to further radical production that influences the oxidation capacity of the atmosphere. Due to their roles in atmospheric chemistry and their potential impacts on human health a number of studies have been performed in the past years to characterise carbonyl compounds that are formed in the atmospheric VOC oxidation e.g. [1–10]. Due to their broad range of physical and chemical properties, several sampling and analytical techniques have been developed for the determination and quantification of carbonyl compounds in the atmospheric gas-phase (see the reviews [11–13] and references therein). The advantages of in situ spectroscopic methods are their compound specificity and high time resolution. A number of techniques have been reported

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for formaldehyde measurements including tunable diode laser spectroscopy (TDLAS) [14,15], differential optical absorption spectroscopy (DOAS) [16,17], Fourier transform infrared spectroscopy (FT-IR) [18] and remote spectroscopic methods using satellite based sensors [19–21]. Other specific techniques for formaldehyde are laser induced fluorescence [22], fluorimetric methods based on the Hantzsch reaction [23,24] and an enzymatic method [25]. Intercomparison measurements can be found e.g. in [26,27]. Furthermore, such on-line techniques utilising specific ionisation techniques prior to mass spectrometric (MS) detection have also been applied for carbonyl compound measurements. Those techniques are atmospheric pressure chemical ionisation MS (APCI-MS) [28], selected ion flow tube MS (SIFT-MS) [29,30], chemical ionisation MS (CIMS) [31] and proton transfer reaction MS (PTR-MS) [32,33]. On-line MS techniques require no complicated sample preparation procedures but difficulties need to be accounted for the ionisation efficiency of unknown compounds or isobaric isomers which cannot be separated (i.e. ketones and aldehydes) in these instruments, hence hindering the molecular characterisation of unknown compounds. Off-line methods utilise different gas collection techniques, followed by a pre-concentration, a derivation step when necessary, and chromatographic separation and detection which can provide further structural information of unknown compounds. The most common analytical methods involve GC and HPLC techniques, and derivatisation methods allow us to improve detection of highly polar, reactive and volatile carbonyl species. Among the various derivatisation reagents available for carbonyl compounds (see review by Vogel et al. [34]), hydrazine based substances such as 2,4-dinitrophenylhydrazine (DNPH) are most commonly used. DNPH forms stable hydrazones with many carbonyl compounds under acidic conditions that have high UV absorption and can be easily separated by liquid chromatography. Another commonly used derivatisation reagent is the *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) that forms volatile oxime derivatives which can be separated and analysed by GC-MS.

Carbonyl compounds often partition into different phases and their simultaneous determinations in multiple phases offer a chance to obtain more information about their distribution and fate in the environment. In the atmosphere, they can contribute to particle formation and aerosol growth through the formation of oligomers, organosulfates and hemiacetals/acetals (see review by Hallquist et al. [35] and references therein). A number of mechanisms involving carbonyl compounds have been postulated for particle-phase accretion reactions (see [36,37]) including the Mannich reaction [38]. A denuder/filter combination is able to measure and discriminate between gas- and particle-phases and is widely used to avoid positive artefacts on particle samples [39]. Denuders have been used for the sampling of polycyclic aromatic compounds [40–42], carbonyl compounds [43–47], diisocyanates [48,49], gaseous mercury [50,51], reactive iodine species [52] and other inorganic and organic compounds (see also [53,54] and references therein). Typically denuders are coated with a medium suitable for retaining the target compounds. XAD-4, a styrene-divinylbenzene polymer which has high surface area and good adsorptive properties, is widely used as a coating medium. Since off-line derivatisation procedures are time-consuming and labour intensive, *in situ* derivatisation techniques for carbonyl compounds have also been developed for denuder tubes. These techniques utilise denuders coated with DNPH [55–57], PFBHA [58,59] or other reagents [60–64] without an adsorbent as well as the combination of XAD-4 and a derivatisation reagent [65–67]. The combined use of a trapping medium and a derivatisation reagent resulted in an improved collection efficiency [65]. Although denuder sampling techniques are widely used, the denuder-coating procedure, sampling parameters, analyte extraction methods and

further sample preparation procedures have not been evaluated in detail. It is very important to evaluate all these steps to achieve a satisfactory denuder performance and a reliable analysis. The aim of this study was to set up an optimal denuder protocol from the coating procedure to the analysis of different carbonyl compounds. In addition, a comparison study of XAD-4 coated and XAD-4/DNPH coated denuders was performed in which the performance of *ex situ* derivatisation from single resin coated denuders and *in situ* derivatisation of carbonyl compounds on the denuder surface was compared. The combination of XAD-4 and DNPH on the denuder has also been applied to the oxidation of nopinone to determine carbonyl products.

2. Experimental

2.1. Chemicals and materials

The derivatisation reagent 2,4-dinitrophenylhydrazine (DNPH) was purchased from Fluka ($\geq 99\%$ assay, delivered in 50% water, St. Louis, MO, USA). It was recrystallised twice in HPLC grade acetonitrile prior to use. The following carbonyl compounds were obtained from Sigma-Aldrich (St. Louis, MO, USA): acetone (99.5%), acetaldehyde (99%), glyoxal (40 wt.% in H₂O), methylglyoxal (40% in H₂O), methyl vinyl ketone (99%), methacrolein (95%) and (1R)-(+)-nopinone (98%). Benzaldehyde ($\geq 99\%$) was obtained from Fluka, hydroxyacetone (95%) was obtained from ABCR GmbH & Co. KG (Karlsruhe, Germany) and formaldehyde (36.5%) was purchased from Riedel-de Haën (St. Louis, MO, USA). They were used without further purification. Campholenic aldehyde and pinonaldehyde were synthetically prepared. Campholenic aldehyde was synthesised from α -pinene oxide as described by Castro et al. [68]. Pinonaldehyde was prepared following the procedure described by Glasius et al. [69]. LC-MS grade methanol and acetonitrile were used in this study and were purchased from Sigma-Aldrich. Phosphoric acid (85 wt.% in water) was obtained from Riedel-de Haën.

Supelco carbonyl-DNPH mix 1, a commercially available hydrazone standard solution, was purchased from Sigma-Aldrich and was used for the quantification of methacrolein, formaldehyde, acetone and acetaldehyde. Hydrazone crystals were prepared for benzaldehyde, hydroxyacetone, methyl vinyl ketone, glyoxal, methylglyoxal, campholenic aldehyde, nopinone and pinonaldehyde. Benzaldehyde-DNPH, campholenic aldehyde-DNPH, nopinone-DNPH and pinonaldehyde-DNPH were purified by recrystallisation from ethanol and pure stock solutions in acetonitrile were prepared. All other synthesised carbonyl-DNPHs were purified using a solid phase extraction method (OASIS HLB 30 mg adsorbent, Waters Milford, MA, USA). The concentration of individual stock solution containing synthesised carbonyl-DNPH was determined using high performance liquid chromatography (HPLC, Agilent 1100 series, Santa Clara, CA, USA) coupled to a Corona charged aerosol detector (Corona CAD, ESA, Chelmsford, MA, USA) that provides similar detector responses regardless of chemical structures of the analytes. The synthesised benzaldehyde-DNPH was chosen as a calibrant because it showed no trace of impurity in the chromatograms (Fig. 1S, Supporting Information). In addition, the mass spectrometric response of the synthesised benzaldehyde-DNPH was compared to that of the benzaldehyde-DNPH in the Supelco carbonyl-DNPH mix 1. The difference in the intensity was about 13% ($n=3$) between commercial and synthesised benzaldehyde-DNPHs, confirming the concentration of the benzaldehyde-DNPH (Fig. 2S, Supporting Information). A quadratic regression coefficient obtained for the benzaldehyde-DNPH calibration curve using HPLC-Corona CAD was 0.992 (6 points, 0.19–14.9 mg L⁻¹). Cyclohexanone-2,4-DNPH (Sigma-Aldrich) was

used as an internal standard for the quantification of all target analytes.

2.2. Annular denuders

In this study 5-channel annular denuders with 400 mm in length and 1 mm annular spacing (URG-2000-30B5, URG Corporation, Chapel Hill, NC, USA) were used.

Denuder coating procedure

The following coating protocol is developed based on a denuder coating procedure described by Eaton et al. [70]:

(1) XAD-4 resin needs to be washed prior to use. This removes salts which are added to prevent bacterial growth. 80 g of XAD-4 resin (Sigma-Aldrich) was washed four times with 100 mL ultrapure water and subsequently with 50 mL LC-MS grade methanol. After drying for 12 h in a fume cupboard at room temperature the fine free flowing dry XAD-4 resin was further ground using a planetary ball mill (Planetary Mill pulverisette 5 with 4 bowl fasteners, Fritsch GmbH, Idar-Oberstein, Germany) for 6 h at 300 rpm.

(2) First the denuder tube was rinsed with 25 mL methanol, dried by passing a gentle flow of nitrogen, washed with 25 mL of n-hexane (HPLC Chromasolv, >97%, Sigma-Aldrich) and dried again by a gentle flow of nitrogen. 0.65 g of the ground XAD-4 resin was mixed with 100 mL of n-hexane in a beaker and covered with aluminium foil. The solution was sonicated for minimum 30 min to prepare an homogeneous slurry.

Critical step: It is important to keep the slurry homogenous during the denuder coating. This prevents non-uniform coating on the denuder surface.

(3) The slurry was left for 15 s to settle larger particles after the sonication. The denuder tube was filled with 70 mL slurry (approximately 80% of the denuder volume), capped and carefully inverted 20 times. Afterwards the slurry was decanted back into the beaker and sonicated further to homogenise the slurry. A gentle stream of nitrogen was passed through the denuder to dry the surface, followed by a vacuum drying for at least 1 min using a small membrane pump. Each coating and drying cycle was repeated 7 times. The denuder tube was washed with 25 mL n-hexane to remove loose XAD-4 particles after the final coating and the N₂ and vacuum drying cycle was repeated twice.

Critical step: Vacuum drying provides a higher packing density for the absorbent material and reduces surface roughness that results in a better denuder performance (see Fig. 5S, Supporting Information).

(4) The threads at both the denuder ends were dipped vertically and sonicated in a clean n-hexane solution for 15 s without wetting the coated surface. Afterwards the denuder ends were dried under a nitrogen stream followed by vacuum drying and the ends were wrapped with Parafilm (Pechiney Plastic Packaging Inc, Chicago, IL, USA). The coating was renewed after five experiments.

(5a) A set of XAD-4 coated denuders were used for the ex situ derivatisation of trapped carbonyl compounds. Prior to the usage, the denuders were cleaned with 50 mL methanol followed by N₂ and vacuum drying.

(5b) Another set of XAD-4 coated denuders were further coated with DNPH for on-tube conversion of carbonyl compounds on the denuder surface. The DNPH coating solution was made of 10 mM DNPH and 90 mM H₃PO₄ in 50 mL acetonitrile. The solution was freshly applied before each experiment. The denuders were first rinsed with 50 mL acetonitrile and dried by a gentle stream of nitrogen. Afterwards 10 mL of the DNPH coating solution was filled into the denuder tube and the inner surface was wetted by inverting the denuder carefully 20 times. Afterwards the denuder was dried by a gentle stream of nitrogen followed by vacuum drying.

Table 1

Mixing ratios injected into chamber for the calibration experiments.

Compound	Mixing ratios (ppb)
Formaldehyde	11–171
Acetone	17–136
Acetaldehyde	5–87
Hydroxyacetone	5–43
Methyl vinyl ketone	2–38
Methacrolein	2–36
Glyoxal	3–54
Methylglyoxal	1–20
Benzaldehyde	8–60
Campholenic aldehyde	2–36
Nopinone	3–43
Pinonaldehyde	0.02–0.13

Table 2

Signals and characteristics for the PTR-MS monitoring.

	<i>m/z</i> used for PTR-MS monitoring
Formaldehyde	31
Acetone	59 ^a
Acetaldehyde	45
Hydroxyacetone	75
Methyl vinyl ketone	71 ^b
Methacrolein	71 ^b
Glyoxal	59 ^a
Methylglyoxal	73
Benzaldehyde	107
Campholenic aldehyde	152
Nopinone	139
Pinonaldehyde	151

^a Sum of acetone and glyoxal.

^b Sum of methyl vinyl ketone and methacrolein.

The DNPH coated denuder was used immediately for the chamber experiment.

2.3. Chamber experiments

A 19 m³ PTFE indoor Teflon chamber (S/V = 2 m⁻¹) was used for this study. Before each experiment the chamber was flushed with dry purified air at 200 L min⁻¹ for a minimum of 16 h. The carbonyl compounds were introduced into the chamber using a syringe with an air stream of 200 L min⁻¹ for 2 min. The ranges of mixing ratios that were used for the calibration experiments are given in Table 1. The calibration experiments were performed at 50% RH. A proton-transfer mass spectrometer (PTR-MS, IONICON, Innsbruck, Austria) was used to measure mixing ratios and possible wall losses of the injected compounds. Detailed description of the instrument can be found elsewhere, e.g. [71,72] and references therein. The injected compounds were measured at their protonated mass [M+1]⁺ except for pinonaldehyde, which dehydrated and protonated form (*m/z* 151) yielded the highest detection intensity [30,32]. Further details of the PTR-MS measurements are summarised in Table 2. The gas-phase compounds were sampled using both denuder types operated in parallel when the PTR-MS signals reached a plateau (typically 10–15 min after the injection). The samples were collected at 10 L min⁻¹ for 1 h (0.6 m³). For selected experiments a second XAD-4/DNPH denuder was connected in series to the end of the first denuder to determine the breakthrough for each denuder type (Fig. 4S A, Supporting Information). In addition, a PTFE filter (borosilicate glass fiber filter coated with fluorocarbon, diameter 47 mm, PALLFLEX Fiberfilm T60A20, PALL, NY, USA) was used for these experiments to determine the amount of carbonyl compounds on the filter material (Fig. 4S B, Supporting Information). The filter samples were stored in a freezer at –28 °C until analysis.

2.4. Application of the denuder sampling technique to nopinone oxidation studies

A series of nopinone oxidation experiments were performed in the aerosol chamber. All oxidation studies were carried out at 50% RH and at 21 ± 1 °C. The hydroxyl radicals (OH) were produced from the photolysis of methyl nitrite in the presence of NO. Methyl nitrite was introduced first into the chamber followed by NO and nopinone. Average initial mixing ratios were: 40 ppb methyl nitrite, 70 ppb NO and 50 ppb nopinone. The reaction was initiated by turning black lamps (Philips TL-D 36W BLB Hg) on. The mixing ratios of nitrogen oxides were monitored by a NO_x analyser (Thermo Environmental Instruments Inc., Model 42). The oxidation studies were carried out for approximately 1 h and after turning the black lights off, the sampling was immediately started using the optimised sampling method on XAD-4/DNPH coated denuders at a flow rate of 10 L min⁻¹ for 1 h. The denuder was extracted directly after the experiments and further treated as described in the section below.

Wall losses were determined separately by injecting 50 ppb nopinone into the chamber under the same conditions to the oxidation experiments. The nopinone mixing ratio was measured at m/z 139 [M+1]⁺ using the PTR-MS instrument and a wall loss rate of 2 ppb h⁻¹ was determined. Before each experiment chamber blanks were taken.

2.5. Sample preparation

The denuder samples were directly extracted after the chamber experiments. The XAD-4 coated denuder was filled with 50 mL methanol, capped and inverted carefully 20 times while rotating along its axis. The XAD-4/DNPH coated denuder was extracted three times with 50 mL acetonitrile in the same manner to the XAD-4 coated denuder. The XAD-4 denuder extract was derivatised with a 0.5 mL solution containing 1.5 M H₃PO₄ and 20 mM DNPH. 1 mL of cyclohexanone-DNPH (100 μM) was added to the denuder extracts as an internal standard and both solutions were left overnight to ensure complete derivatisation. After their concentration by rotary evaporation (25 °C at 100 mbar) the extracts were further purified using solid phase extraction cartridges (Waters OASIS HLB, 1 cc barrel size, 30 mg absorbent). The cartridges were flushed first three times with 1 mL acetonitrile before usage, conditioned with 1 mL methanol and ultra-pure water (18.2 MΩ cm resistivity, 4 ppb TOC, Milli-Q Gradient A10 with an UV lamp, Billerica, MA, USA), respectively. The dried denuder extract was reconstituted in 1 mL methanol and loaded on the SPE cartridge. The absorbent in the cartridge trapped the carbonyl-DNPHs and phosphoric acid was washed out twice using 1 mL of a methanol/ultra-pure water solution (5/95, v/v%). The carbonyl-DNPHs were eluted from the cartridge using 6 mL acetonitrile. The SPE elute was dissolved in 10 mL acetonitrile and was kept in the darkness at -28 °C in a freezer until the analysis. 1 mL of this solution was evaporated to dryness using a gentle stream of nitrogen at 10 °C and was brought back to 1 mL acetonitrile/water (50/50, v/v%) for HPLC/(-)ESI-TOFMS analysis.

For the analysis of the filter samples the complete filter was cut into small pieces using a pair of ceramic scissors and immersed in 100 μL acetonitrile solution containing 10 mM DNPH, 1.5 M phosphoric acid. After the addition of 1 mL acetonitrile and the internal standard, the filter was sonicated for 15 min for the simultaneous extraction and derivatisation. The extract was filtered using a PTFE syringe filter (15–17 mm, Phenomenex, Torrance, CA, USA). The remaining filter pieces were rinsed with 500 μL acetonitrile and sonicated again for another 15 min followed by filtration using the same syringe filter. The filter extract was left overnight to ensure complete derivatisation. The same SPE procedure described above was used to wash phosphoric acid. The dried filter extract was

reconstituted in 250 μL acetonitrile/water (50/50, v/v%) and the samples were analysed using HPLC/(-)ESI-TOFMS.

2.6. High performance liquid chromatography hyphenated to electrospray ionisation-time of flight mass spectrometry (HPLC/(-)ESI-TOFMS)

The analysis was performed using an Agilent 1100 HPLC equipped with a vacuum degasser, a quaternary pump, a thermostatic column department, an autosampler and a diode array detector coupled to an electrospray ionisation time of flight mass spectrometer (micrOTOF, Bruker Daltonics, Bremen, Germany). The ESI-TOFMS was operated in the negative ionisation mode. The mass calibration of the instrument was performed with sodium acetate clusters. The Pursuit XRs Ultra 2.8 Diphenyl column (100 mm × 2.0 mm, 2.8 μm, Varian, Paolo Alto, CA, USA) was used for the separation of the hydrazones. The separation was carried out at 30 °C and flow rate of 0.4 mL min⁻¹ using (A) 1% acetic acid in ultra-pure water, (B) acetonitrile and (C) ultra-pure water as eluents. The gradient programme was as follows: held constant for (A) 5%, (B) 30% and (C) 65% for the initial 4 min. Increased to (A) 5% and (B) 95% in 20 min. Increased to (B) 100% and held constant for 5 min. Afterwards the eluent was set to its initial conditions and held for 5 min to re-equilibrate the column. Calibration curves were generated using a quadratic fit for all standard carbonyl-DNPH compounds.

3. Results and discussion

3.1. Method performance for carbonyl compound analysis using HPLC/(-)ESI-TOFMS

The HPLC/(-)ESI-TOFMS method was assessed from the analysis of carbonyl-hydrazone standards (formaldehyde-DNPH, acetone-DNPH, acetaldehyde-DNPH, methyl vinyl ketone-di-DNPH, methacrolein-DNPH, hydroxyacetone-DNPH, glyoxal-di-DNPH, methylglyoxal-di-DNPH, benzaldehyde-DNPH, campholenic aldehyde-DNPH, nopinone-DNPH and pinonaldehyde-di-DNPH). Fig. 3S (Supporting Information) shows typical chromatograms for the carbonyl hydrazone standards. It was noted that methyl vinyl ketone (MVK) forms a di-derivatised form even it contains only one keto group. The formation of a di-DNPH-derivative of MVK was also reported from Duane et al. [73] and can be explained by nucleophilic addition of DNPH to the β carbon of the α,β unsaturated methyl vinyl ketone (Michael addition) [74,75].

Calibration curves for the hydrazones used in this study were obtained by fitting a quadratic curve to a series of the ratios of the standard peak area to the internal standard peak area (10 μM). The mass precision range was set to $m/z \pm 0.5$ and no dynamic range adjustment was applied. Table 3 summarises the merits of analysis including the quantification ranges and the coefficients of determination for the calibration curves. Relative standard deviations (RSD) of the ratio of target area to internal standard area were also determined from the analysis performed on three different analytical days (Table 3). Slightly higher RSD were observed for the dicarbonyl compounds (15 and 16% for glyoxal and methylglyoxal, respectively) though they were still acceptable for quantification. It is noted that both glyoxal and methylglyoxal can form mono- and di-DNPH derivatives and each hydrazone forms cis- and trans-isomers, leading to four possible isomers. An inter-conversion between the isomers is known to occur for carbonyl-DNPH derivatives [76,77] and this might lead to higher uncertainties for the glyoxal and methylglyoxal quantification. The limits of detection for the HPLC/(-)ESI-TOFMS analysis were determined using the standard carbonyl-hydrazones from a series of dilution steps until

Table 3
Quantification range, coefficient of determination (R^2), relative standard deviation of target peak area to internal standard peak area (RSD%) and limit of detection (LOD) for the HPLC/(–)ESI-TOFMS method used in this study.

Compound	Detected m/z as DNPH derivatives ($M-1$) ^a	Quantification range (μM)	Coefficients of determination (R^2)	RSD ($n=5$) (%)	LOD ^a (μM)
Formaldehyde	209	8.3–133	0.9999	7.1	0.52
Acetone	237	2.1–34	0.9999	9.2	0.27
Acetaldehyde	223	2.8–45	0.9999	6.5	0.36
Hydroxyacetone	253	0.4–3.5	0.9987	6.9	0.18
Methyl vinyl ketone	447	0.1–1.8	0.9990	13	0.06
Methacrolein	249	1.5–25	0.9998	4.6	0.06
Glyoxal	417	1.6–16	0.9994	15	0.41
Methylglyoxal	431	0.8–15	0.9852	16	0.05
Benzaldehyde	285	1.5–24	0.9998	3.9	0.04
Campholenic aldehyde	331	1.5–24	0.9999	5.3	0.05
Nopinone	317	3.1–50	0.9999	3.4	0.01
Pinonaldehyde	527	1.6–26	0.9989	9.1	0.01

^a Based on the chromatographic peak area of $S/N=3$.

Table 4
Recoveries and RSD% (relative standard deviations) of OASIS HLB cartridge with 30 mg/1 mL absorbent ($n=5$).

Compound	Average recovery (%)	RSD (%)
Formaldehyde	40	8
Acetone	53	13
Acetaldehyde	49	7
Hydroxyacetone	18	4
Methyl vinyl ketone	91	12
Methacrolein	65	10
Glyoxal	91	8
Methylglyoxal	80	29
Benzaldehyde	75	9
Campholenic aldehyde	86	7
Nopinone	90	5
Pinonaldehyde	98	14

the chromatographic peak area showed a signal to noise ratio of 3. Acceptable LODs are achieved ranging from 0.01 μM for pinonaldehyde to 0.52 μM for formaldehyde (2 μL injection). The recovery for the SPE step was determined using the carbonyl-DNPH standards and are summarised in Table 4. Small and functionalised carbonyl compounds showed lower recovery values that might be associated with trapping difficulties of smaller compounds. Overall, the recoveries and RSD values for the SPE procedure indicate acceptable reproducibility for the sample purification.

3.2. Optimisation of denuder sampling

3.2.1. Sampling conditions

The influences of sampling parameters on the performance of the denuders were tested to determine the best operating conditions. The mixing ratios of carbonyl compounds used for this study are summarised in the Supporting Information (Table 1S).

3.2.1.1. Break-through. Break-through values were determined for both XAD-4 and XAD-4/DNPH denuders. The sampling volume was 0.6 m^3 (1 h at 10 L min^{-1}) for all the experiments and a XAD-4/DNPH denuder was used as a second downstream denuder connected in series after the first upstream denuder. The residence time in the denuder tube is approximately 0.5 s for a sampling flow rate of 10 L min^{-1} and the Reynolds number is well below 2000. The denuder break-through was characterised using the break-through potential (%) that was calculated for each compound as follows:

$$\text{Break-through potential [\%]} = \frac{\text{Amount detected in downstream denuder}}{\sum (\text{Amount detected in upstream and downstream denuder})} \times 100$$

A lower break-through potential value means higher performance of the denuder. Table 5 summarises the break-through potential under dry (RH <3%) and humid (RH 50%) conditions. As can be seen from the values, in situ derivatisation on denuders improves the collection except for acetaldehyde that shows no significant difference under all conditions. A similar improvement was reported for the collection by XAD-4/PFBHA coated denuders that showed significantly better collection efficiencies than XAD-4-single coated denuders, especially for longer sampling time [65]. On denuders that were additionally coated with a derivatisation reagent, carbonyl compounds can react directly with surface bonded DNPH that prevents desorption from the denuder surface. It is noted that carbonyl-DNPH-adducts which are formed on XAD-4/DNPH coated denuders might not be well extracted depending on their solubility to the extraction solvent used. For the XAD-4 coated denuder, insufficient adsorption to the resin is suggested to be main reason for high break-through values. Especially, smaller carbonyl compounds are detected only at trace levels from the first XAD-4 denuders and are detected mostly in the second downstream XAD-4/DNPH denuder. It is noted that even if the in situ derivatisation improves the collection efficiency of carbonyl compounds, care must be taken for those compounds that do not derivatise well with DNPH. Glyoxal reacts slowly with DNPH [78] and can also polymerise in any sample apparatus once it is collected from the gas-phase [78]. A relatively small equilibrium constant for the DNPH derivatisation reaction was also reported from hydroxyacetone [79].

As discussed in earlier studies for DNPH coated cartridges, the low break-through value does not necessarily correspond to a complete collection of carbonyl compounds [80–83] on denuders. The derivatisation reaction is reversible and depends on several factors such as relative humidity, temperature, flow rate, sampling duration, substrate moisture content, pH level and the strength of a derivatisation reagent. Inadequate parameters can result in incomplete derivatisation, and cause a low collection efficiency as Herrington et al. [83] described for DNPH impregnated cartridges.

The positive effect of humid air on the sampling of carbonyl compounds were demonstrated in the past for DNPH impregnated cartridges [81] and DNPH-only coated denuders [56]. The collection efficiency of formaldehyde on DNPH-only coated denuders was shown to reach a maximum at 50% RH [55] and a similar effect was observed in this study. This is consistent with the reaction mechanisms of the acid-catalysed derivatisation reaction between DNPH and carbonyl compounds as water is necessary to make protons available for the reaction. Other reasons for the poor performance under dry conditions are the protonation of DNPH and a DNPH salt formation which hinders the derivatisation [81]. The collection of carbonyl compounds on XAD-4 denuders showed a reverse trend,

Table 5
Break-through potential and fraction of carbonyl compounds on filter material for the denuders coated with XAD-4 and XAD-4/DNPH.

Compound		Break-through potential (%)		Fraction detected on filter (%)	
		<3% RH 10 L/min	50% RH 10 L/min	<3% RH 10 L/min	50% RH 10 L/min
Formaldehyde	XAD-4	49	67	0	0.6
	XAD-4/DNPH	44	9.5	0.5	0.2
Acetone	XAD-4	95	96	19	8.7
	XAD-4/DNPH	6.4	2.1	0	0
Acetaldehyde	XAD-4	16	35	0.9	0
	XAD-4/DNPH	24	20	0	0
Hydroxyacetone	XAD-4	19	98	1.9	0
	XAD-4/DNPH	1.4	0	0	0
Methyl vinyl ketone	XAD-4	92	98	1.6	4.9
	XAD-4/DNPH	11	0.9	0	0.1
Methacrolein	XAD-4	100	100	0	0
	XAD-4/DNPH	3.1	0	0	0
Glyoxal	XAD-4	42	91	5.9	36
	XAD-4/DNPH	35	23	1.3	0.9
Methylglyoxal	XAD-4	8.9	100	2.2	12
	XAD-4/DNPH	0	0	7.1	0.6
Benzaldehyde	XAD-4	0	20	0	36
	XAD-4/DNPH	0.2	0.4	0	0
Campholenic aldehyde	XAD-4	0	0	0	0
	XAD-4/DNPH	0	0	0	0
Nopinone	XAD-4	0	0	0	0
	XAD-4/DNPH	0	0	0	0
Pinonaldehyde	XAD-4	0.1	0.3	0.2	0.5
	XAD-4/DNPH	0.4	11	0.3	0.2

i.e. higher break-through potential under humid conditions. This may be explained by a formation of a water layer on top of the XAD-4 resin under humid conditions that hinders the sorption of carbonyl compounds.

3.2.1.2. Positive artefacts on filter. Although no particles were present in these experiments, filters were connected in series to the denuder tube in order to evaluate a positive artefact from the adsorption of gaseous carbonyl compounds. The fraction of carbonyl compounds detected on the filter was calculated as follows:

$$\text{Fraction on filter [\%]} = \frac{\text{Amount detected in filter}}{\sum (\text{Amount detected in denuder and filter})} \times 100$$

When XAD-4/DNPH denuders are used for the sampling of gas-phase carbonyl compounds, positive artefacts on the filters were negligible for all compounds. As described above, the trapping by XAD-4-only coated denuders was not sufficient for some of carbonyl compounds and they were adsorbed on the filter material up to 36%. Especially dicarbonyl compounds showed high adsorption value to the filter material. In an earlier study in which off-line PFBHA derivatisation from a XAD-4 coated denuders was compared to polyurethane foams [43] showed also high adsorption values to filter material for glyoxal and methylglyoxal.

3.2.1.3. Interferences with atmospheric oxidants. Atmospheric oxidants such as OH and NO₃ radicals or ozone can react with the denuder sorbent (XAD-4), DNPH or carbonyl-DNPH derivatives. Both negative and positive sampling artefacts were reported in the literature, mainly for the reactions between DNPH and ozone [80,84,85] or NO₂ [86,87]. The extent of artefact formation depends on the sorbent type, ozone concentration, DNPH loading and the amount of sampled carbonyl compounds [88].

In this study, excess DNPH was applied on the denuder surface so that the DNPH reacts with oxidants rather than the carbonyl-DNPH derivatives. In the present work no evidence for artefact formation inside the denuder tube was found from ozone exposure experiments.

Similar findings were reported from Kallinger and Niessner [56] who studied annular denuders in high NO₂ and ozone environments.

3.3. Relation of gaseous carbonyl compound mixing ratios in a Teflon chamber against measured carbonyl-DNPH concentration in the denuder extract

In order to take into account the losses and errors associated with the denuder sampling, extraction and sample preparation steps, the mixing ratios of the gaseous carbonyl compounds in a Teflon chamber were related to the carbonyl-DNPH concentrations of the denuder extracts determined with HPLC/(–)ESI-TOFMS. It should be noted that total of twelve denuder tubes were used for this study (six XAD-4 and six XAD-4/DNPH coated denuders). Error bars in resulting calibration curves include variations in denuder properties that might result from the XAD-4 or DNPH coating. The denuder sampling parameters used were 10 L min^{–1} and 50% RH for all calibration experiments. Blank values were taken without introduction of carbonyl compounds into the chamber and these values were used as the zero point for the calibration curves. During the calibration experiments, a PTR-MS was used to measure the mixing ratios of carbonyl compounds in the chamber. Their signals were plotted as a function of carbonyl compound mixing ratios in the chamber and good linear responses with small standard deviations were obtained for all the compounds studied, hence variations observed for the denuders originate solely from their performances rather than the standard deviation in the mixing ratios (Fig. 6S, Sup-

Table 6
Calibration range, coefficient of determination (R^2), RSD% and a number of repetitions (n) for XAD-4 coated denuder calibration experiment.

	Mixing ratio range for calibration (ppb)	R^2	RSD (%)	Mixing ratio used for RSD% determination (ppb)	n
Formaldehyde	11–171	–	39	21	3
Acetone	17–136	–	30	34	4
Acetaldehyde	5–87	–	31	11	4
Hydroxyacetone	5–43	0.956	27	5	4
Methyl vinyl ketone	2–38	–	27	5	4
Methacrolein	2–36	–	–	–	N.A.
Glyoxal	3–54	–	16	7	4
Methylglyoxal	1–20	–	–	–	N.A.
Benzaldehyde	8–60	0.942	21	8	4
Campholenic aldehyde	2–36	0.993	40	5	4
Nopinone	3–43	0.993	6	5	4
Pinonaldehyde	0.02–0.13	0.983	11	0.05	4

N.A. = not applicable.

porting Information). As can be seen from Table 6 the RSD values for the XAD-4 denuders were higher than 20% for most of the compounds. Due to large RSD values observed at each calibration point, calibration curves were obtained only for relatively large monoterpene originating compounds. These compounds showed somewhat better RSD values than smaller carbonyl compounds at lower mixing ratios (Fig. 7S, Supporting Information). The XAD-4 denuders appeared to be ineffective for trapping high vapour pressure carbonyl compounds such as formaldehyde, acetone and acetaldehyde and dicarbonyl compounds such as glyoxal and methylglyoxal. This can be also seen in the significantly higher break-through potential for these carbonyl compounds in Table 5. The results illustrate that the XAD-4 coated denuders are not suitable for the sampling of smaller and polar carbonyl compounds.

The XAD-4/DNPH denuders showed much lower RSD values for most of the compounds than the XAD-4 denuder, producing better calibration curves (Fig. 8S, Supporting Information) and thus providing more reproducible measurements. Linear calibration curves were obtained for benzaldehyde, campholenic aldehyde, hydroxyacetone, methacrolein, methyl vinyl ketone, nopinone and pinonaldehyde. A quadratic calibration curve was obtained for acetone. R^2 values ranged from 0.934 for pinonaldehyde to 0.997 for acetone. As can be seen from the calibration curves in Fig. 8S, higher RSD values were observed for higher mixing ratios. For most of the compounds (acetone, acetaldehyde, benzaldehyde, hydroxyacetone, methacrolein, methyl vinyl ketone, campholenic aldehyde and pinonaldehyde) calibration curves were obtained for limited ranges of mixing ratios (Table 7) due to high RSD values obtained for the highest mixing ratio used (Table 1). Nevertheless, the XAD-4/DNPH denuders provide good RSD values and the ranges of quantifiable mixing ratios are sufficiently wide for most of smog chamber applications.

Similar to the XAD-4 coated denuders, no calibration curve could be obtained for formaldehyde, glyoxal and methylglyoxal due to their poor reproducibility and discrepancy between the mixing

ratios in the chamber and determined carbonyl-DNPH concentrations in the extracts. Overall, the notable improvements in lower break-through and RSD values were observed especially for smaller and polar carbonyl compounds when the combination of XAD-4 and DNPH coating was applied on the denuders. Furthermore, XAD-4/DNPH coated denuders were shown to improve the method's LOD values in comparison to XAD-4 coated denuders (Table 8). The denuder extracts from the lowest mixing ratio experiments were used to determine the LOD values. After the extracts were prepared for the analysis, they were diluted stepwise until the analyte peak areas reach three times the baseline noise of the blank samples ($S/N=3$). The LOD values for the XAD-4/DNPH denuder show sufficiently low LOD values that are comparable to reported ambient mixing ratios, indicating that the technique might be suitable for the determination of ambient carbonyl compounds that are tested for this technique. This demonstrates the suitability of XAD-4/DNPH denuders over XAD-4 denuders for the sampling of gaseous carbonyl compounds.

Despite these findings, care must be taken for the LOD values as they are only estimation. The method's LOD values cannot be readily obtained from direct chamber measurements due to large errors associating with vapour loss to an injection and sampling port, and chamber walls in the sub ppb range. A recent study demonstrated also high wall losses especially for those carbonyl compounds with larger carbon numbers [89] and small polar carbonyl compounds such as glyoxal [90].

3.4. Simulation chamber experiments: nopinone oxidation with OH radicals

Nopinone is a first generation product from the atmospheric β -pinene oxidation. The fate of nopinone in the atmosphere was mainly investigated in kinetic studies and rate constants for the reaction with OH [91,92] and NO_3 radicals were determined [91]. Only one study identified oxidation products from the direct reaction of nopinone with OH radicals [91].

Table 7
Calibration range, coefficient of determination (R^2), RSD% and a number of repetitions (n) for XAD-4/DNPH coated denuder calibration experiment.

	Mixing ratio range for calibration (ppb)	R^2	RSD (%)	Mixing ratio used for RSD% determination (ppb)	n
Formaldehyde	11–171	–	28	21	3
Acetone	17–136	0.961	14	34	4
Acetaldehyde	5–87	–	16	11	4
Hydroxyacetone	5–43	0.962	16	5	4
Methyl vinyl ketone	2–38	0.982	9	5	4
Methacrolein	2–36	0.983	18	9	3
Glyoxal	3–54	–	4	7	4
Methylglyoxal	1–20	–	32	3	3
Benzaldehyde	8–60	0.947	7	8	4
Campholenic aldehyde	2–36	0.966	20	5	3
Nopinone	3–43	0.991	7	5	4
Pinonaldehyde	0.02–0.13	0.934	18	0.05	4

Table 8

Limit of detection (LOD) for the XAD-4 and XAD-4/DNPH coated denuders and comparison to reported ambient mixing ratios.

	LOD values determined in this study		Typical atmospheric mixing ratios and their detection methods		
	XAD-4 denuder (ppb)	XAD-4/DNPH denuder (ppb)	Reported values (ppb)	Methods	References
Formaldehyde	0.2	0.2	1.5–13	FTIR White system, DOAS White system, Hantzsch, C18 DNPH cartridges	[26]
Acetone	0.5	0.3	0.9–2.5	Silica DNPH cartridges	[5]
Acetaldehyde	0.2	0.2	0.4–1.5	Silica DNPH cartridges	[5]
Hydroxyacetone	5.4	0.3	0.372	DNPH coil sampler	[79]
Methylvinyl ketone	0.6	0.02	0.245–0.339	PFBHA impinger	[97]
Methacrolein	N.A.	0.1	0.1–3.7 (rural) 0.02–5.7 (urban)	C18 DNPH cartridges	[98]
Glyoxal	0.1	0.02	0.067	PFBHA coated denuder	[59]
Methylglyoxal	0.1	0.1	0.146	PFBHA coated denuder	[59]
Benzaldehyde	0.03	0.01	0.005	C18 DNPH cartridges	[2]
Campholenic aldehyde	0.1	0.04	–	–	–
Nopinone	0.04	0.04	1.59	C18 DNPH cartridges	[2]
Pinonaldehyde	0.9 ^a	0.9 ^a	0.14	CIMS	[31]

N.A. = not applicable.

^a In ppt.

Based on our denuder performance study, nopinone was found to be very suitable for the sampling and analysis by denuders. The combination of XAD-4 and DNPH was shown to minimise positive sampling artefacts associating with the filter sampling and resulted also in significantly lower variability for the quantification from the denuder extracts. The optimised sampling method for the XAD-4/DNPH coated denuders was used to collect and identify carbonyl compounds resulting from nopinone oxidation. The samples were collected after approximately 1 h of reaction. All the nopinone oxidation experiments were conducted under the same conditions. The denuders were extracted and analysed using the identical procedure that was used for the calibration experiments.

This procedure enables us to relate the carbonyl-DNPH concentrations in the denuder extracts to the mixing ratios in the simulation chamber using the obtained calibration curves.

The XAD-4/DNPH coated denuders were able to provide reproducible nopinone mixing ratio of 23 ± 2.5 ppb ($n=3$) after about 1 h of the nopinone oxidation. One isomer of oxo-nopinone was tentatively identified based on the TOFMS suggested chemical formula (see Fig. 1). The derived chemical formula $C_{21}H_{19}N_8O_8^-$ with an error of 0.6 ppm indicates a di-DNPH derivatised molecule. The chemical formula of the original carbonyl compound was obtained after subtraction of the DNPH molecules from the derivatised compound.

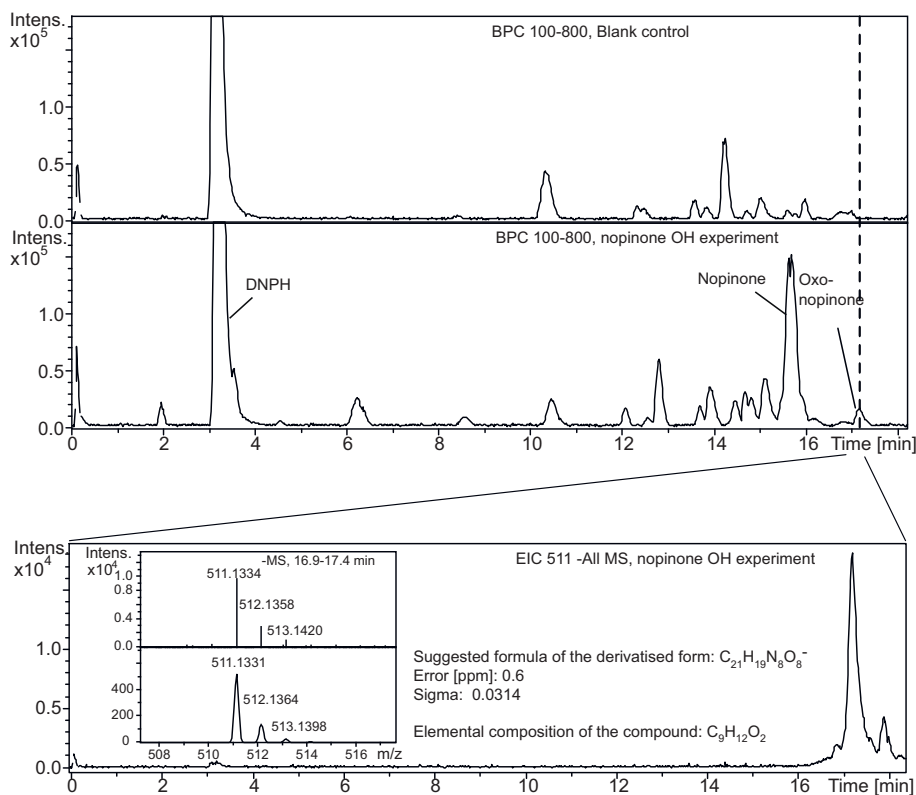


Fig. 1. Base peak chromatograms (BPC) for chamber blank control (top) and XAD-4/DNPH denuder extracts from the nopinone OH reaction (middle). Extracted ion chromatogram (EIC) of the m/z 511 compound (bottom) shows DNPH derivatised oxo-nopinone peaks between 16.5 and 18 min. An insert shows the obtained TOF mass spectrum (top) and the software created isotope pattern as well as a suggested chemical formula for the peak detected between 16.9 and 17.4 min.

The quantification was performed using the calibration curve determined for nopinone and the XAD-4/DNPH denuders as no authentic standard is commercially available. The molar yields of oxo-nopinone were $0.7 \pm 0.1\%$ ($n=3$). The formation of oxo-nopinone was also reported from the ozone [45,93] and OH initiated oxidation of β -pinene [47,94]. Some of these studies [45,47] reported 3-oxo-nopinone as the product but no details were given about the way that the structure was elucidated. One modelling study [95] suggested 3-oxo-nopinone as a likely product for the nopinone/OH reaction though further studies are necessary to confirm the structure of the detected oxo-nopinone isomer. The results show that the XAD-4/DNPH denuders can be quantitatively used for the nopinone/OH reaction; however, target compound specific optimisation and characterisation are necessary for reliable and reproducible collection of gaseous carbonyl compounds using a denuder.

4. Summary

This study demonstrates that the combination of XAD-4 and DNPH as a denuder coating improves the collection of carbonyl compounds in comparison to a single XAD-4 coating. In-situ derivatisation on denuder surface reduces positive artefacts of carbonyl compounds on filters significantly which is in agreement with an earlier study [65] that utilised XAD-4 and PFBHA. The present study also shows that reliable sampling and quantification of carbonyl compounds using a denuder requires careful compound specific sampling parameter optimisation and characterisation. Measurements of carbonyl compounds in dry air were shown to be less effective and reliable for XAD-4/DNPH denuders and alternative sampling methods are recommended such as an impinger for this purpose. Calibration experiments using a simulation chamber and the XAD-4/DNPH denuders showed good coefficients of determination for most of the compounds tested and demonstrated the improvement in linearity and reproducibility in comparison to the XAD-4-only coated denuders. The XAD-4/DNPH denuders were tested in nopinone oxidation studies and shown to be a reliable and effective method for collecting and quantifying carbonyl compounds that originate from the monoterpene oxidation even at low mixing ratios. The analysis of denuder extracts with TOFMS can help elucidating possible structures of unknown carbonyl compounds. It has been demonstrated in the past that MS detection provides better separation of co-eluting compounds, precision and LOD, especially for higher molecular weight carbonyl compounds [96] compared to other detection methods such as UV detection that is commonly used for carbonyl-DNPH analysis. These factors are important especially for the analysis of a complex mixture and trace level carbonyl compounds that are often found in environmental samples. The present XAD-4/DNPH denuder sampling technique provides a useful tool for the determination of gaseous carbonyl compounds and minimising filter sampling artefacts depending on target analytes, accuracy and sensitivity requirements.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jchromb.2011.02.028.

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