

Development of a method for the detection of carbonyl compounds in monoterpene oxidation



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Introduction

- The atmospheric oxidation of monoterpenes produces a number of multifunctional compounds.
- Important intermediates during the first oxidation step are carbonyl compounds that are semi-volatile.
- Due to their properties the carbonyl compounds can partition between the gas- and particle-phases.
- The knowledge on both gaseous and particulate products is important for better understanding of the oxidation processes and the formation of secondary organic aerosol (SOA).
- Carbonyl compounds can be further oxidised to form lower volatile compounds, contributing to SOA.
- Commonly used methods for the analysis of carbonyl compounds involve derivatisation steps prior to UV or mass spectrometric (MS) detection.
- 2,4-Dinitrophenylhydrazine (DNPH) has been used to derivatise aldehyde- and keto-groups to form the hydrazone.
- The HPLC/ESI-MS offers several advantages over UV detection, such as higher sensitivity and the determination of the exact chemical formula for the identification of unknown carbonyl compounds.

- In this study, commonly available carbonyl compounds originating from monoterpenes are used. These are campholenic aldehyde, endolim, nopinone and pinonaldehyde.
- These standards were derivatised with DNPH, purified and analysed with an HPLC/ESI-TOFMS.
- Figure 1 shows the structures of DNPH derivatised compounds used in this study.

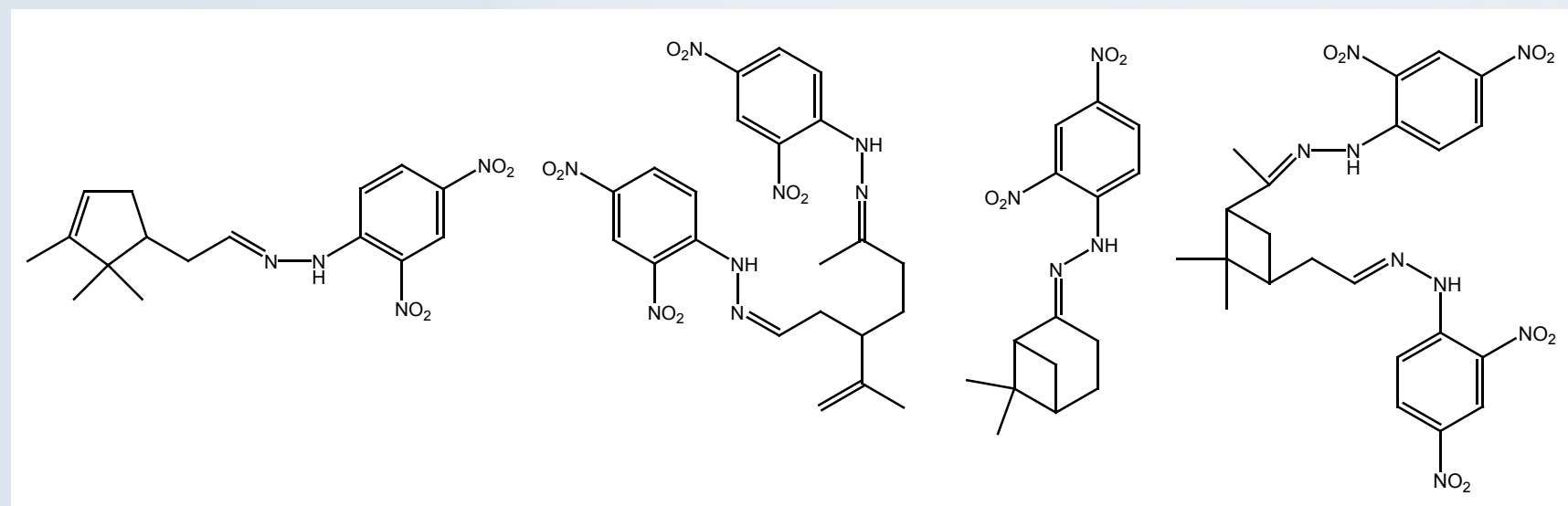


Fig. 1: Derivatised authentic standards: campholenic aldehyde-2,4-DNPH; endolim-di-2,4-DNPH, nopinone-2,4-DNPH and pinonaldehyde-di-2,4-DNPH

- Furthermore, an in-situ derivatisation method for the detection of carbonyl compounds in the gas-phase was developed to sample products from chamber experiments.
- The method utilises the combination of the sorbent XAD-4 and DNPH on denuders.

Experimental

Analytical Procedures

Derivatisation Procedure

- The derivatisation is based on the method described in the literature [1].
- The DNPH solution was prepared by adding 1 ml phosphoric acid to 0.26 g DNPH and then adding dropwise 2 ml water followed by 7 ml methanol.
- 1 ml of a 0.1 M solution of each carbonyl compound in methanol was added to 1 ml of the freshly prepared 0.1 M DNPH solution.
- After 24 hours the derivatisation was assumed to be completed.

Clean-up Procedure

- The solutions containing the derivatised carbonyl compounds were purified with solid phase extraction cartridges (SPE).
- The following cartridges with the same dimension (1 ml) were tested:
 - Oasis HLB cartridges (10 mg adsorbent; Waters, Milford, MA, USA).
 - Strata X cartridges (30 mg adsorbent; Phenomenex, Torrance, CA, USA).
- The procedure for the SPE is summarised in Table 1.
- The carbonyl derivatives were detected using an HPLC/ESI-TOFMS.
- The acetonitrile solution of the hydrazones was evaporated to dryness with a gentle steam of nitrogen, and reconstituted in acetonitrile/water (50/50) (v/v).
- The solution was diluted by a factor of hundred.
- The conditions for the analytical procedure are given in Table 2.

Table 1: SPE method

Conditioning	5 ml methanol
Equilibration	5 ml deionised water (MilliQ water)
	5 ml water/hydrochloric acid mixture (90/10) (v/v)
Sample load	1 ml in methanol
Wash	5 ml deionised water
Elution	6 ml acetonitrile

Table 2: HPLC/ESI-TOFMS conditions

Column	Phenomenex Gemini C6 Phenyl (3.5 µm, 150 x 2mm)
Eluent	0.2 % acetic acid in water (A) and 0.2 % acetic acid in acetonitrile (B) (program: 70 % A to 10 % in 15 min)
Temperature	30 °C
Flow rate	0.5 ml/min
Injected sample volume	2.5 µl
Mass calibration	0.2 % acetic acid / 5 mM NaOH in 50/50 (v/v) in water/iso-propanol at the beginning and end of each analysis
MS detection mode	negative

- Two hydrazone standard mixtures were prepared because of the isobaric isomere formation of endolim and pinonaldehyde.
- Mixture 1:** campholenic aldehyde-2,4-DNPH, endolim-di-2,4-DNPH and the internal standard (ISTD) valeraldehyde-2,4-DNPH.
- Mixture 2:** nopinone-2,4-DNPH, pinonaldehyde-di-2,4-DNPH and the ISTD.

Chamber studies

- The aerosol chamber at the IFT is made of Teflon with a cylindrical geometry.
- The volume is 19 m³ with a surface/volume ratio of 2.1 m⁻¹.
- A two step coating of the denuders was performed to sample gas-phase carbonyl-compounds.

- First the denuders were coated with finely ground XAD-4 resin using a standard coating procedure [2].
- The preparation of the DNPH coating was adapted from Possanzini and Palo (1999).



Fig. 2: Denuder coated with XAD-4 and DNPH

- The temperature and relative humidity in chamber was kept constant (T=21 °C, RH~50 %) and the amount of injected campholenic aldehyde was varied.

- After 10 minutes mixing time, the compound was sampled by the denuder/PTFE filter technique.
- The denuder was extracted with acetonitrile and after dilution of the leachate, the product was analysed by HPLC/ESI-TOFMS.

Table 3: Concentration of campholenic aldehyde in chamber

injected concentration [ppbv]
10
40
80
160

Results and Discussion

- Figure 3 shows the extracted ion chromatograms (EICs) of the two standard mixtures.
- Detected mass to charge ratios (m/z), retention times (RT), correlation coefficients for calibration curves (R², quadratic, 5 points), limits of detection (LOD) and relative standard deviations for the peak areas (RSD%) are summarised in Table 4.
- As can be seen from Figure 3 and Table 4, the developed derivatisation procedure and the HPLC/ESI-TOFMS method are sensitive and stable. The reproducibility of the method is satisfactory for the analysis of carbonyl compounds from monoterpene oxidation.

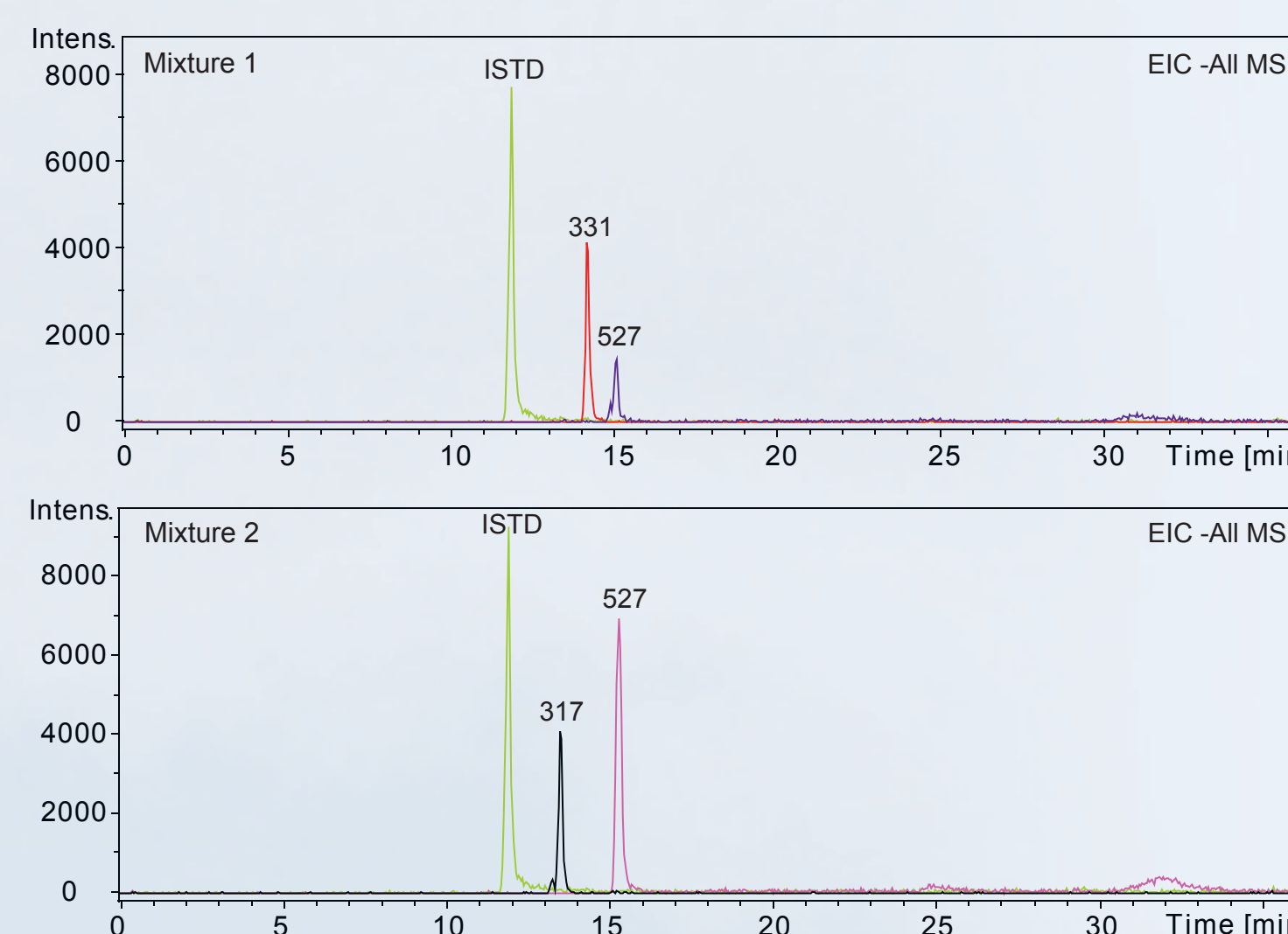


Fig. 3: Extracted ion chromatograms (EICs) of the HPLC-MS analysis of the hydrazone standard mixtures.

Table 4: Summary of quantification parameters

Hydrazone standard	MW [g/mol]	Detected m/z	RT [min]	R ²	LOD [µg/ml]	RSD [%]
Campholenic aldehyde-2,4-DNPH	332.3	331	14.2	0.998	0.024	15.2
Endolim-di-2,4-DNPH	528.5	527	15.1	0.999	0.097	10.3
Nopinone-2,4-DNPH	318.3	317	13.5	0.998	0.072	10.4
Pinonaldehyde-di-2,4-DNPH	528.5	527	15.1	0.999	0.005	8.3

- The recoveries for the two reversed phase SPE cartridges, StrataX and Oasis HLB, are shown in Figure 4.
- StrataX showed higher recoveries, ranging from 75 % for pinonaldehyde to 133 % for endolim.
- The lower recoveries from the Oasis HLB cartridges might be due to the lower absorbent content.
- Overall, both cartridges showed reasonable results, but further characterisation is necessary.
- Figure 5 shows the result of the application for the on-tube derivatisation of gas-phase carbonyl compounds from chamber studies.
- A good correlation was obtained for the injected amount and the recovered concentration.

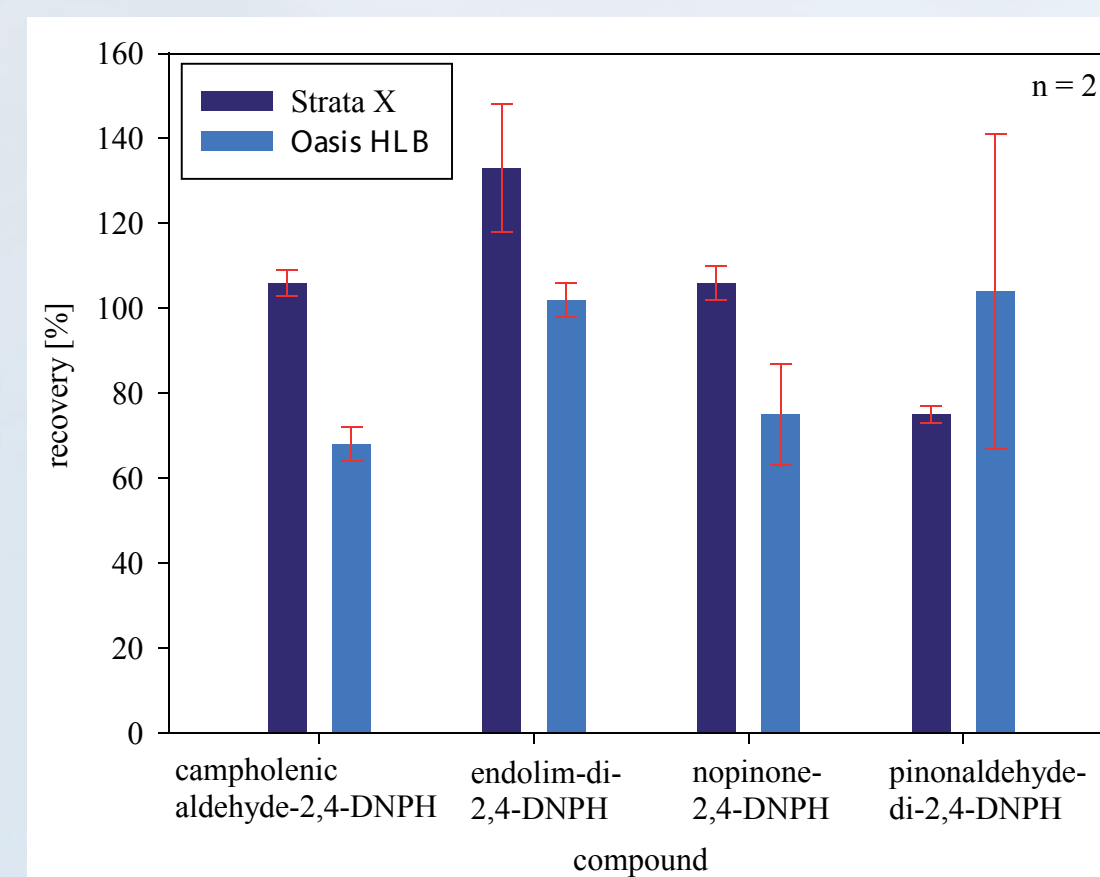


Fig. 4: Recovery of the hydrazone standards on different reversed phase SPE cartridges

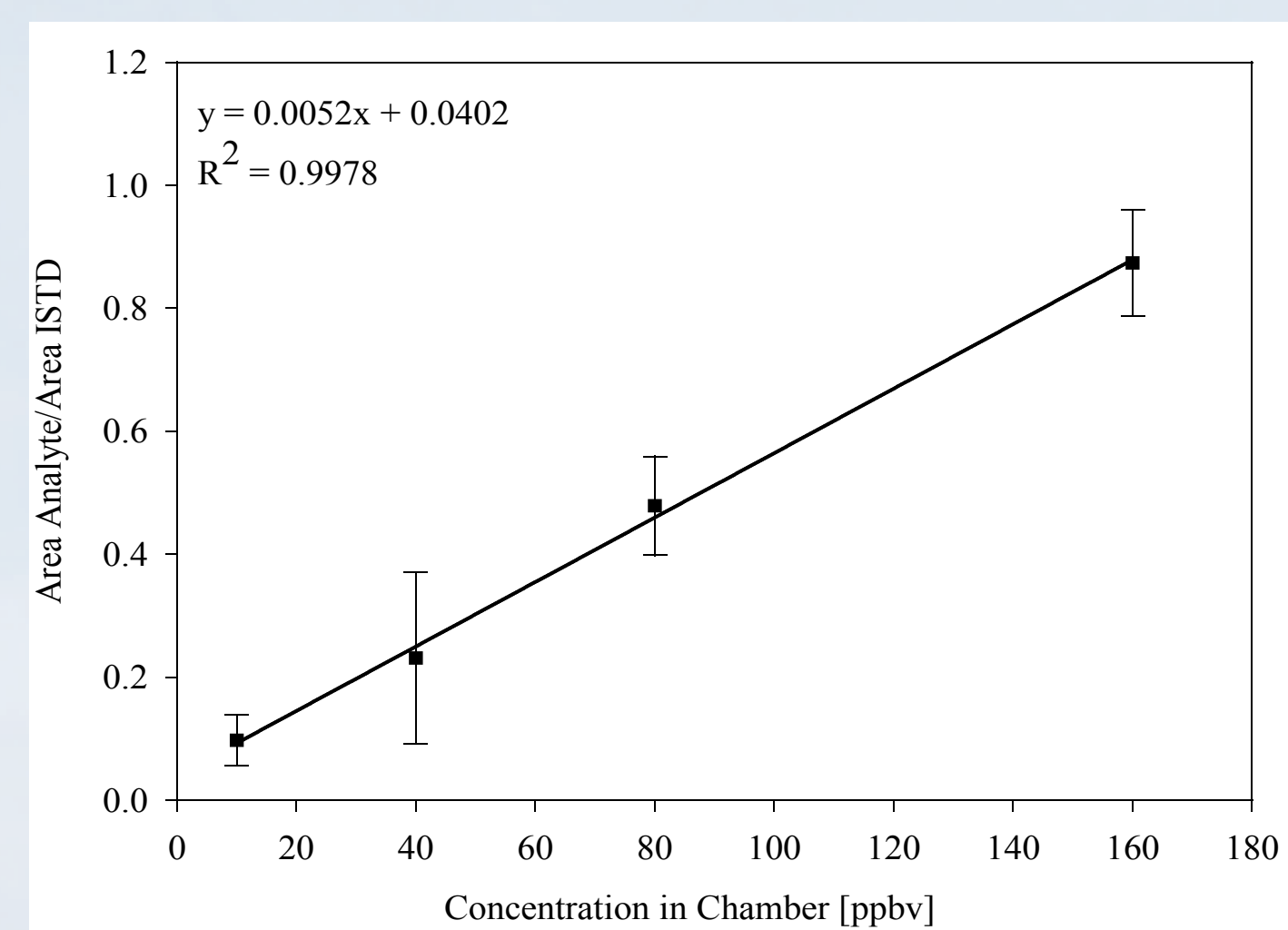


Fig. 5: Graphic presentation of relative response of campholenic aldehyde (area compound/area ISTD) as a function of concentration in chamber

Summary and Outlook

- The developed method has a good potential to improve our knowledge on both gaseous and particulate carbonyl compounds.
- The in-situ derivatisation with DNPH is an ideal tool for the analysis of gas-phase carbonyl compounds in monoterpene oxidation.
- The method can also be applied for the analysis of particle phase carbonyl compounds (off-line analysis).
- The application of the technique for the detection of atmospherically relevant monoterpene oxidation products is planned.

References

- [1] Grosjean, E., and D. Grosjean (1995), Liquid chromatographic analysis of C1-C10 carbonyls, *International Journal of Environmental Analytical Chemistry*, 61, 47-64.
- [2] Gundel, L. A., et al. (1995), Direct Determination of the Phase Distributions of Semivolatile Polycyclic Aromatic-Hydrocarbons Using Annular Denuders, *Atmospheric Environment*, 29, 1719-1733.
- [3] Possanzini, M., and V. Di Palo (1999), Performance of a 2,4-DNPH coated annular denuder/HPLC system for formaldehyde monitoring in air, *Chromatographia*, 49, 161-165.

Acknowledgements

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