

Application of a denuder-filter sampling technique for the determination of carbonyl compounds from the ozonolysis of β -pinene

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Introduction

Biogenic volatile organic compounds (BVOCs) such as isoprene, monoterpenes and sesquiterpenes are considered to be major secondary organic aerosol (SOA) precursors due to their high contributions to non-methane hydrocarbons burden in the atmosphere. Multifunctional oxidation products with lower vapour pressure are formed during their atmospheric degradation. In particular, carbonyl compounds that are formed in the early stage of the VOC oxidation can contribute to the formation of atmospheric aerosol. The knowledge of the gas/particle partitioning of these products is essential towards a better understanding of specific oxidation processes and products which lead to SOA formation.

The denuder-filter sampling technique is commonly used for the simultaneous determination of gas- and particle-phase carbonyl compounds. Denuders are often used to avoid positive artifacts on filter sampling and are usually coated with a retaining medium such as XAD-4. The collection efficiency can be improved by application of a derivatisation reagent on the denuder surface. 2,4-Dinitrophenylhydrazine (DNPH) or *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) are often used as derivatisation reagents. In addition, the combined application of XAD-4 and PFBHA was shown to improve the collection efficiency compared to XAD-4 coated denuders (Temime *et al.*, 2007).

In this study results are shown from the β -pinene ozonolysis in the presence of CO performed in an aerosol chamber. The gas- and particle-phase products were sampled using a denuder/filter setup. The combination of XAD-4 and DNPH on the denuder surface was applied to enable in-situ derivatisation of carbonyl compounds.

Experimental

Table 1: Experimental conditions for the performed β -pinene ozonolysis in the presence of CO as an OH scavenger.

Chamber experiment

Initial HC	50 ppb
Consumed HC	14 ppb
O ₃	60 ppb
CO	110 ppm
RH	50 ± 0.9%
T	20 ± 0.2°C
Reaction Time	6 h
Sampling Volume	0.6 m ³
Sampling Time	1 h
Seed particles	(NH ₄) ₂ SO ₄ /H ₂ SO ₄ (pH = 2)

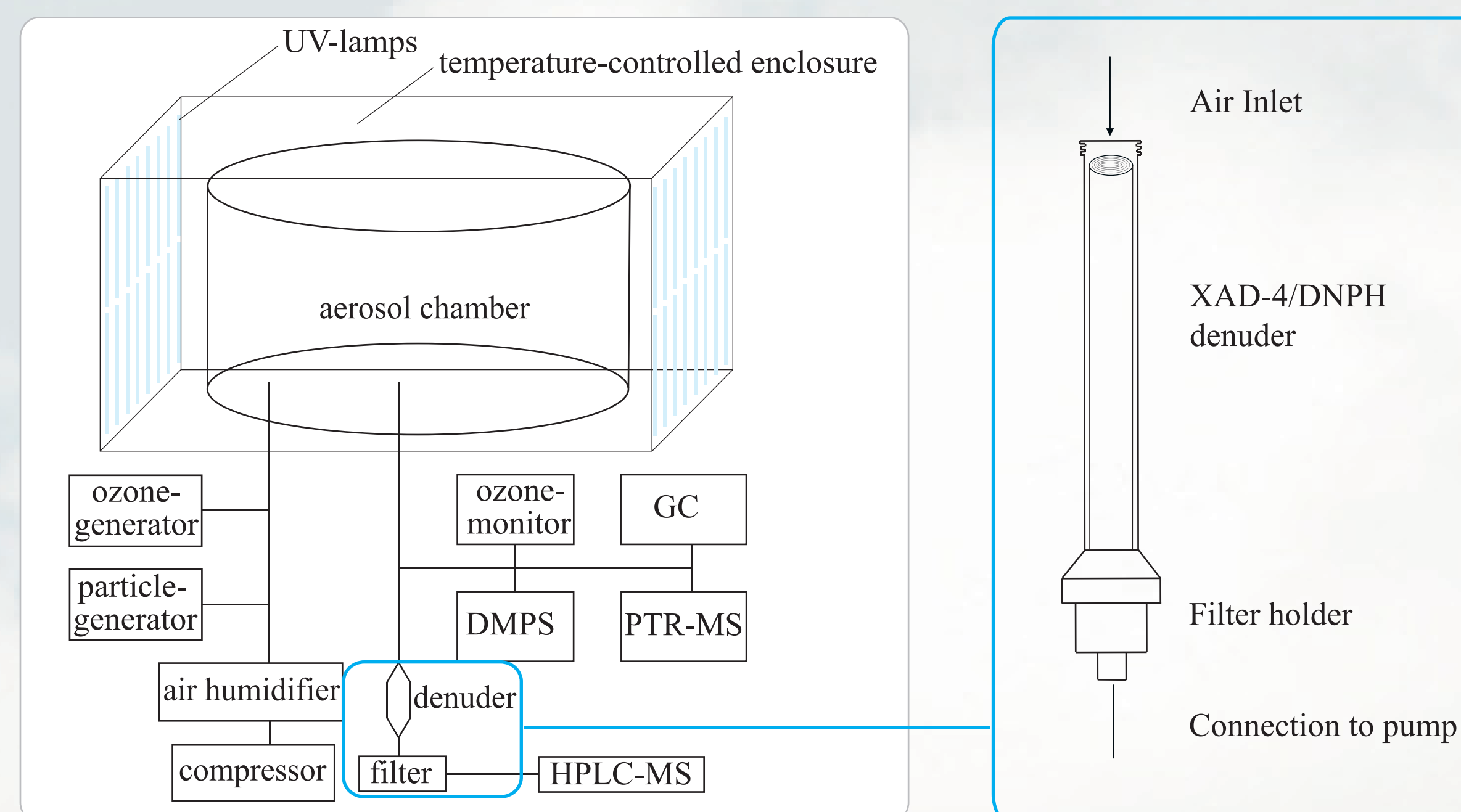
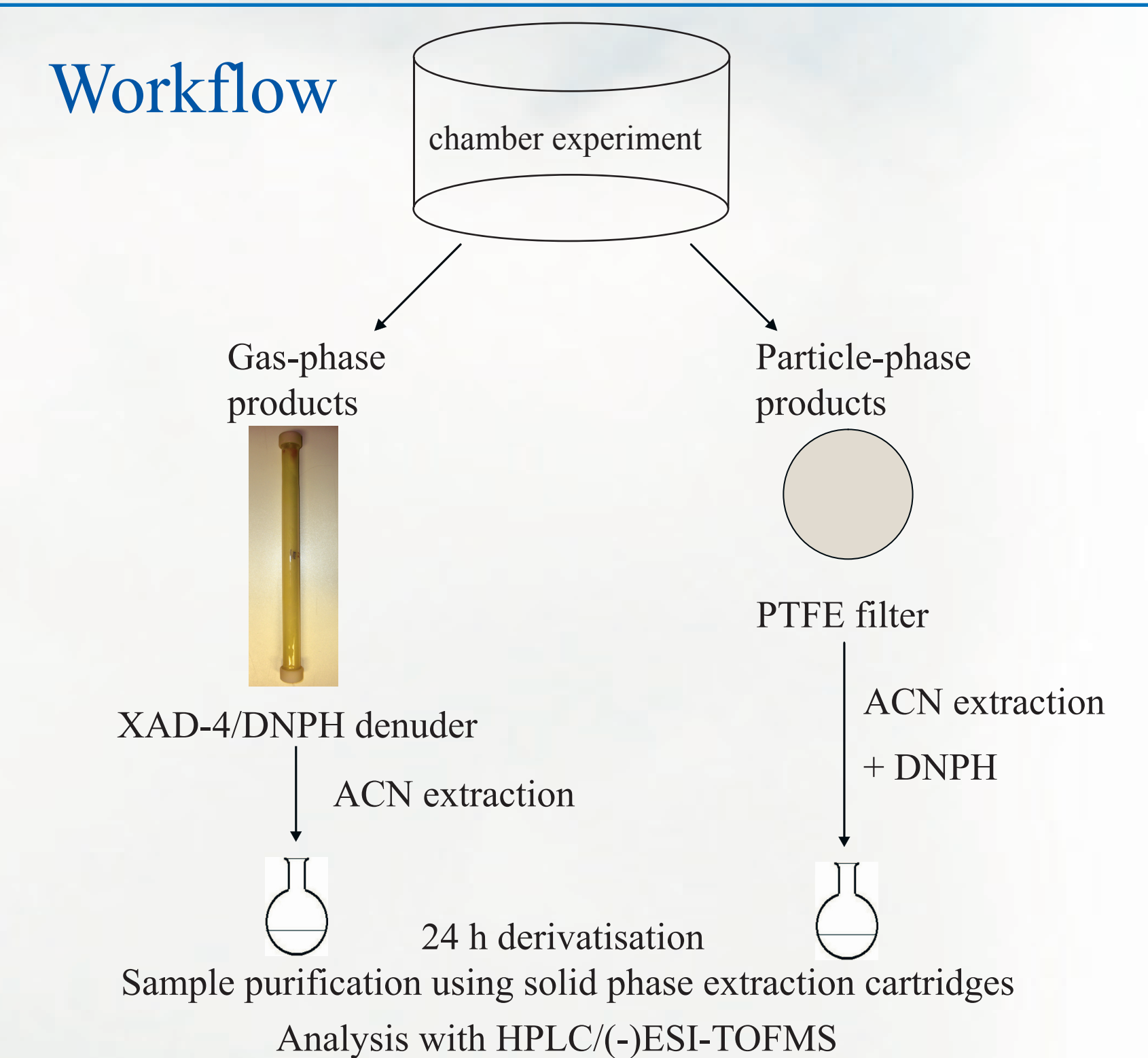


Fig. 1: Instrumentation of the Ift aerosol chamber.

Workflow



Results and Discussion

PTR-MS

Scan mode

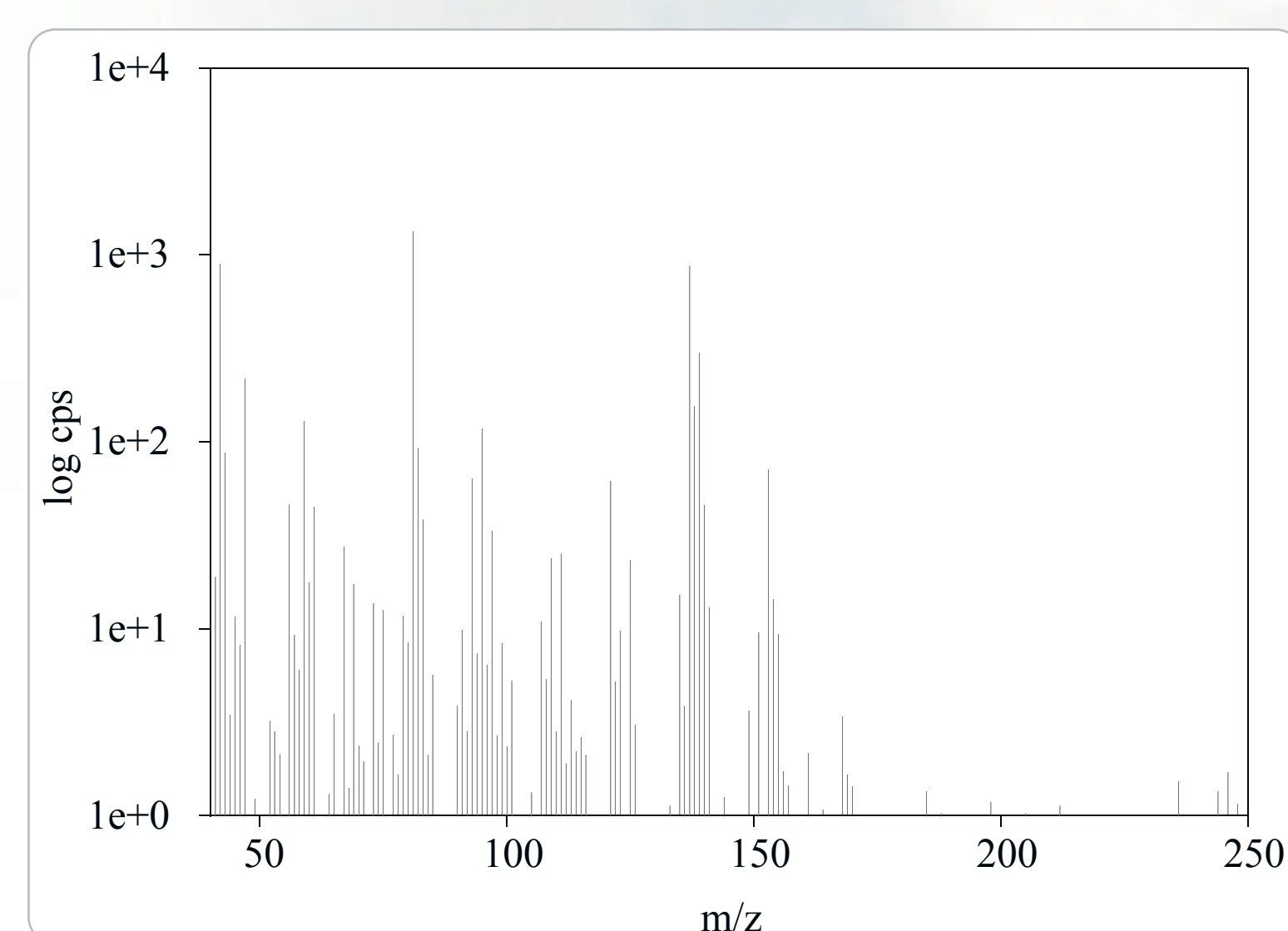


Fig. 2: Detected compounds and fragments after 6h of reaction derived from PTR-MS.

Selected ion mode

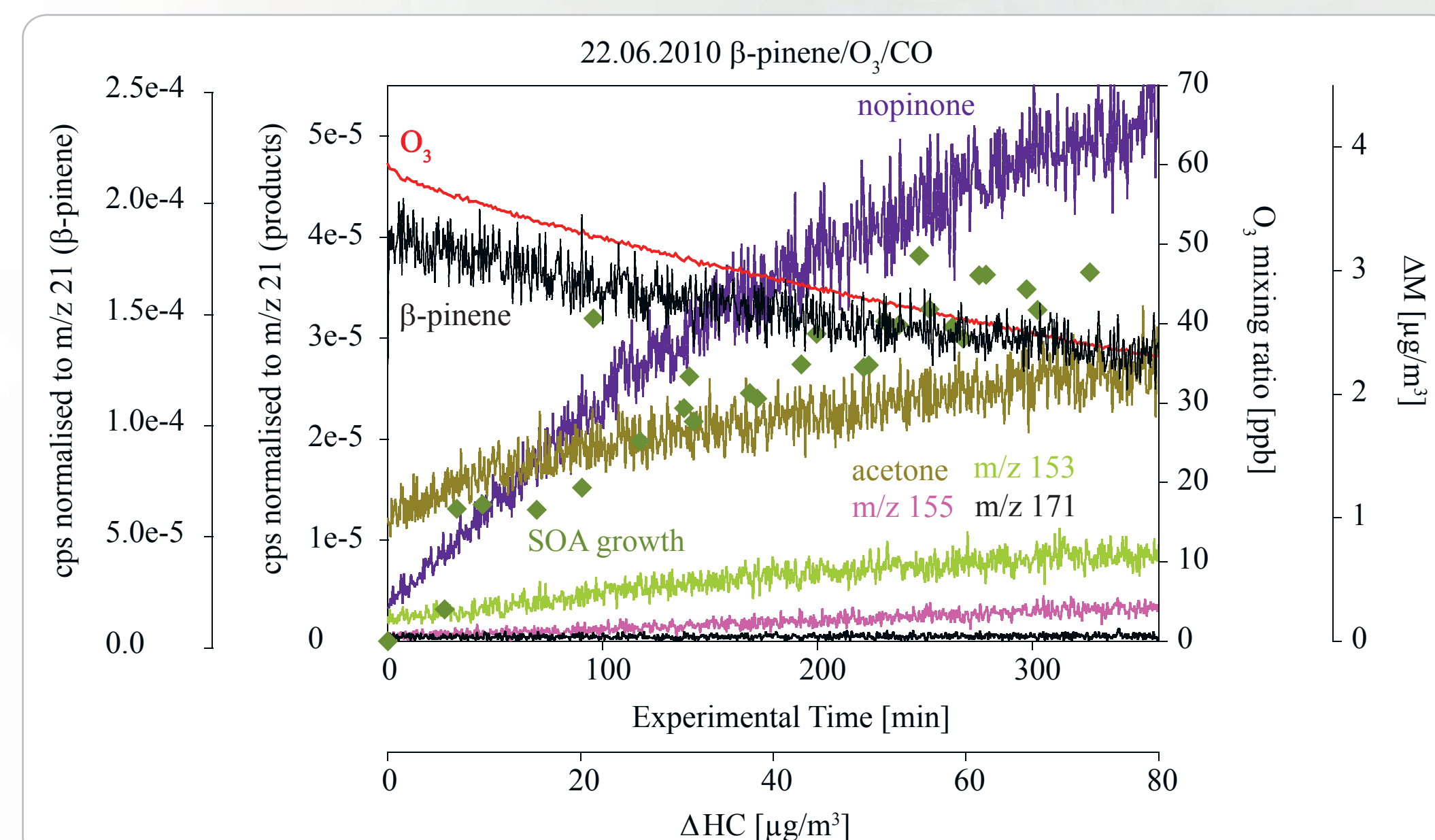


Fig. 3: Time series of gas-phase compounds and SOA growth for a β -pinene ozonolysis.

Table 2: Summary of detected compounds by PTR-MS and comparison to literature.

This study m/z	Suggestion	Lee <i>et al.</i> , 2006 m/z	Suggestion
42	C ₈ H ₁₄ fragment	31	formaldehyde
43	unidentified		
47	HCOOH	45	acetaldehyde
59	acetone	47	HCOOH
61	CH ₃ COOH	59	acetone
81	monoterpene fragment, isotope	61	CH ₃ COOH
82	monoterpene fragment, isotope	81	monoterpene fragment, isotope
83	unidentified	82	monoterpene fragment, isotope
93	C ₈ H ₁₄ fragment		
95	C ₈ H ₁₄ fragment		
97	nopinone fragment	97	nopinone fragment
107	unidentified	103	nopinone fragment
109	unidentified	107	unidentified oxidation product
111	unidentified	109	unidentified oxidation product
		111	unidentified oxidation product
		113	unidentified oxidation product
		119	unidentified oxidation product
121	nopinone fragment	121, 122	nopinone fragment
125	unidentified	123	unidentified oxidation product
		125	unidentified oxidation product
		129	unidentified oxidation product
137	monoterpene isotope	137	monoterpene isotope
138	monoterpene	138	monoterpene
139	nopinone	139	nopinone
140	nopinone fragment	140	nopinone fragment
141	nopinone fragment	141	nopinone fragment
153	β -pinene oxide, oxo-nopinone, myrtanol, myrtol	153	unidentified oxidation product
154	unidentified	155	unidentified oxidation product
155	OH-nopinone, dioxirane	169	unidentified oxidation product
		171	unidentified oxidation product
		185	unidentified oxidation product

- A slight increase in an unknown compound with m/z 171 was observed.
- The SOA growth curve derived from PTR-MS and DMPS data showed similar form to Ng *et al.*, 2006.

HPLC/MS from denuder (gas-phase)

- Further analysis of denuder extracts for product identification (see Figure 4)

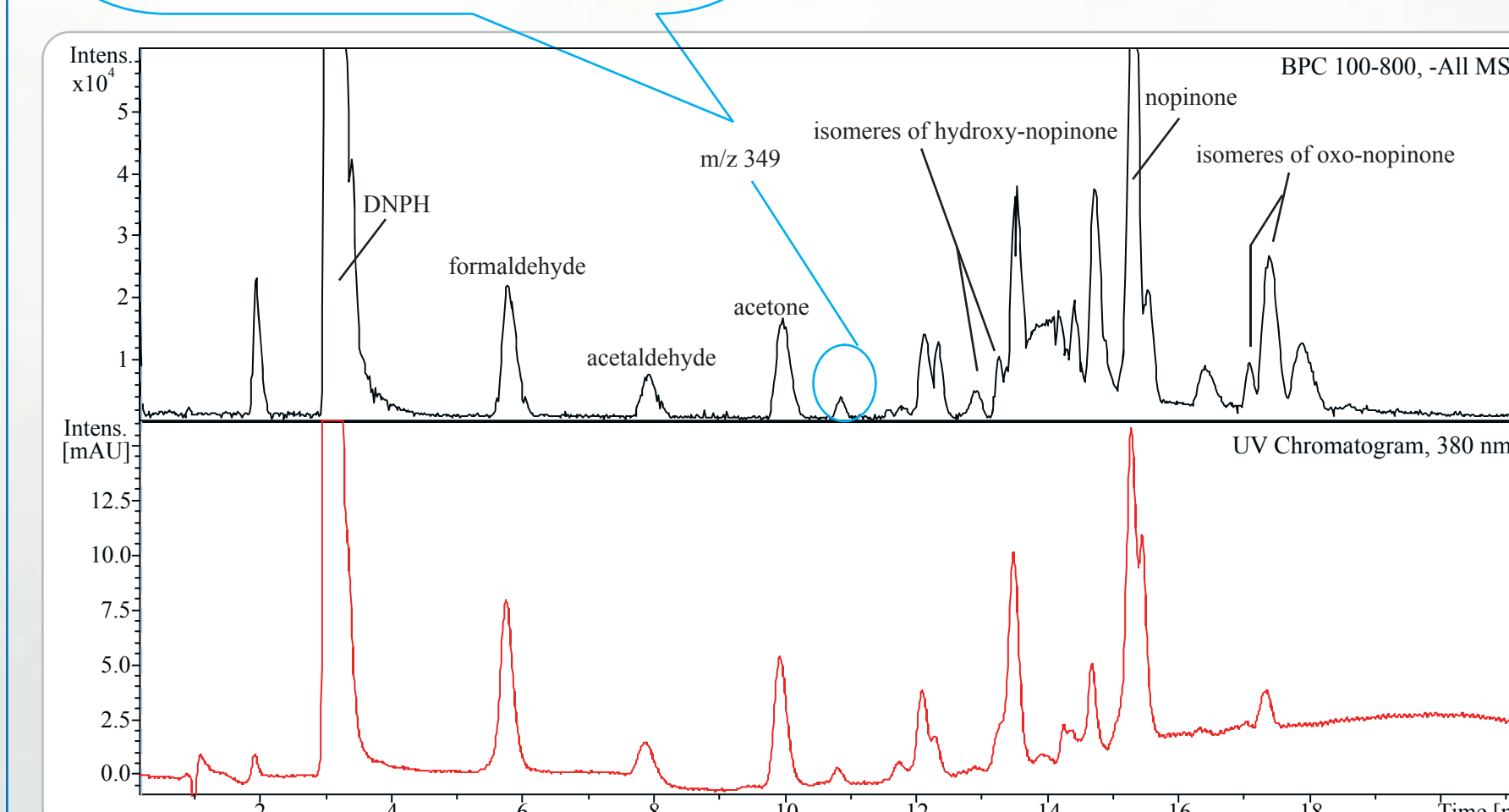
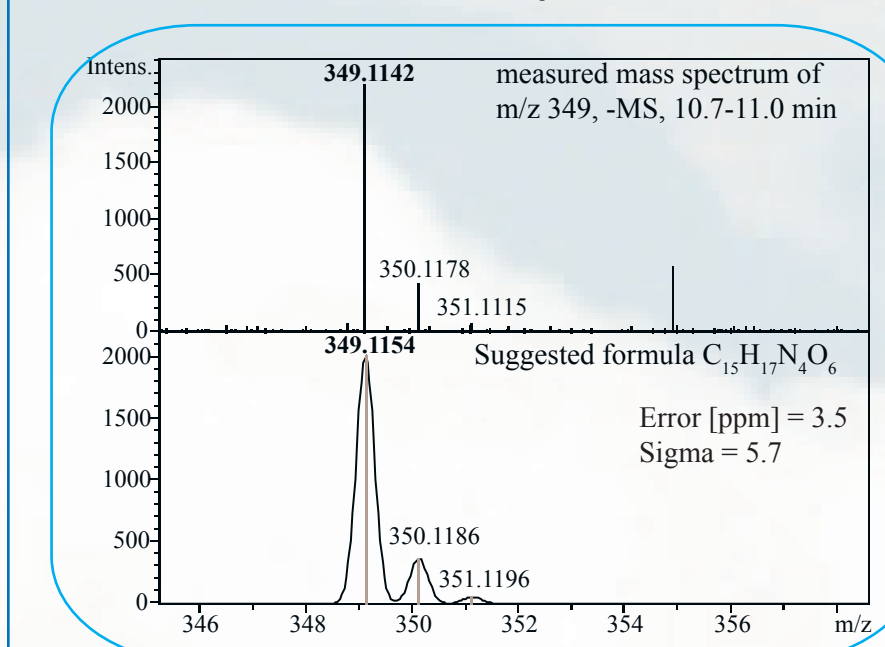


Fig. 4: Chromatograms obtained from the analysis of XAD-4/DNPH denuder. TOFMS accurate mass data for the m/z 349 compound is shown above the chromatograms.

Fig. 5: Comparison of extracted ion chromatograms (EIC) between the m/z 349 compound and norpinonic acid-DNPH standard.

Fragmentation study

- MS² spectrum of norpinonic acid-DNPH standard shows an intensive fragment of m/z 249.
- This fragment was also observed from pinonic acid-DNPH by Brombacher *et al.*, 2001 who suggested a butenone-DNPH substructure.

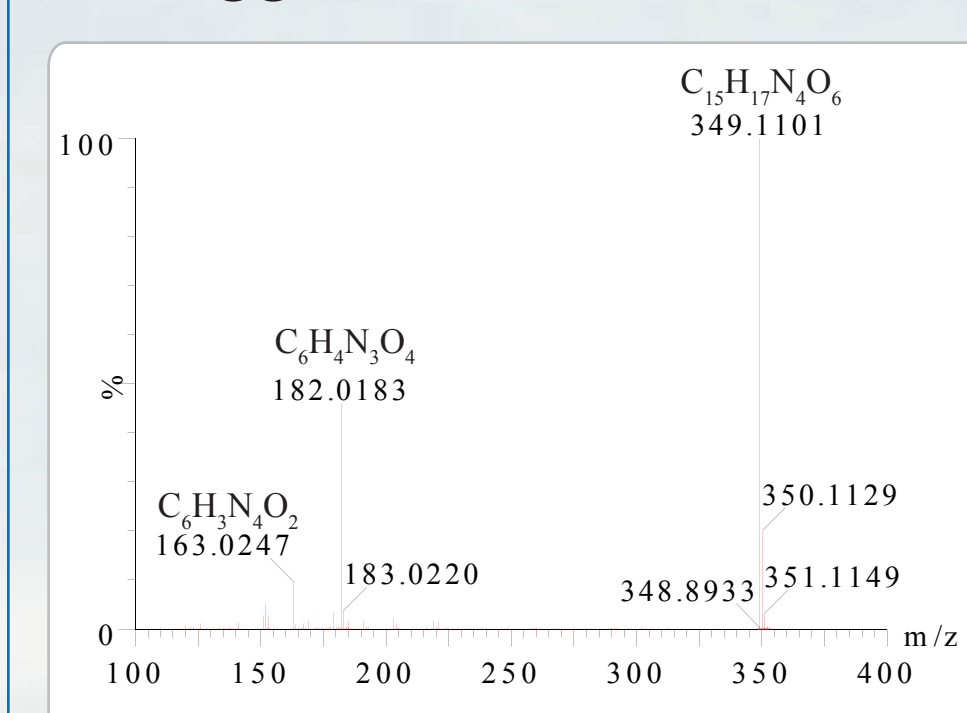


Fig. 6: ESI(-) MS/MS spectrum of norpinonic acid-DNPH standard with proposed fragmentation process.

- The unknown m/z 349 compound showed a different fragmentation pattern, indicating a different structure from norpinonic acid.

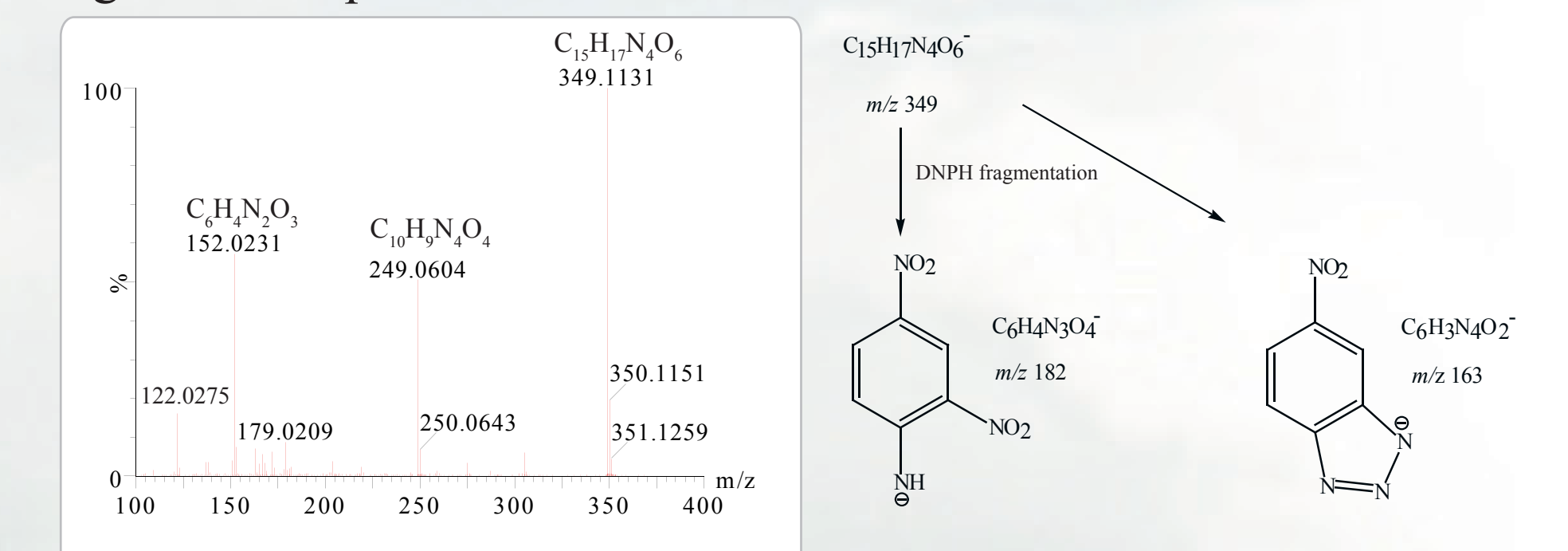


Fig. 7: ESI(-) MS² spectrum of m/z 349 with proposed fragmentation.

Summary and conclusion

The combination of a denuder/filter sampling device is a useful tool to determine gas- and particle-phase products simultaneously. Compared to on-line measurement techniques such as PTR-MS, the denuder sampling and subsequent HPLC/ESI-MS analysis enables us to separate isobaric isomers and provides more detailed information about the structures of oxidation products. DNPH derivatised standard compounds might help to determine substructures of unknown compounds.

References

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HPLC/MS from filter (particle-phase)

Carbonyl group containing products:

