

Introduction

- Denuders are commonly used to avoid positive artefacts on filter sampling.
- The inner walls of denuders are typically coated with a retaining medium such as XAD-4.
- Gaseous compounds are trapped by the sorption medium due to their high diffusion coefficients and particulate products pass through the tube.
- An additional option is to derivatise the gaseous compounds directly on the denuder surface to improve the collection efficiency, especially for polar compounds such as carbonyl compounds.
- Commonly used derivatisation reagents include 2,4-dinitrophenylhydrazine (DNPH) (Possanzini and Di Palo, 1999) or the combination of XAD-4 and *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (Temime *et al.*, 2007) to enhance the collection of carbonyl compounds.
- Semi-volatile carbonyl compounds are produced during the atmospheric oxidation of different biogenic and anthropogenic volatile organic compounds and can partition between the gas- and particle-phases.
- For understanding their contribution to atmospheric aerosol formation and specific oxidation processes, the simultaneous determination of gas and particle-phase compounds is important.
- In the present study the performance of two sets of denuder/filter sampling systems was evaluated using carbonyl compounds originating from the monoterpene oxidation (campholenic aldehyde, nopinone and pinonaldehyde).
- In addition, the yields of pinonaldehyde and nopinone in the gas- and particle phases were determined from the photooxidation of α -pinene and β -pinene using an optimised denuder/filter sampling system.

Experimental

Denuder evaluation

- To evaluate the optimal denuder operation parameters, selected carbonyl compounds were injected into the 19 m³ IFT chamber (Figure 1) at known concentrations (see Table 1).
- Two sets of parameters were varied:
I: Flow rate: 5 l/min, 10 l/min and 30 l/min
II: Relative humidity: 0 %, 50 % and 60 %

Table 1: Concentrations of the carbonyl mixture used in this study.

Compound	Campholenic-aldehyde	Nopinone	Pinonaldehyde
Concentration [ppb]	23	27	2.4

- The gas-phase samples were collected using 40 cm long five channel denuders.
- The break-through for the denuders was determined using denuders connected in series (see Figure 2a and 3a).
- The absorption on the filter material was determined from a PTFE filter placed after the denuder (see Figure 2b and 3b).

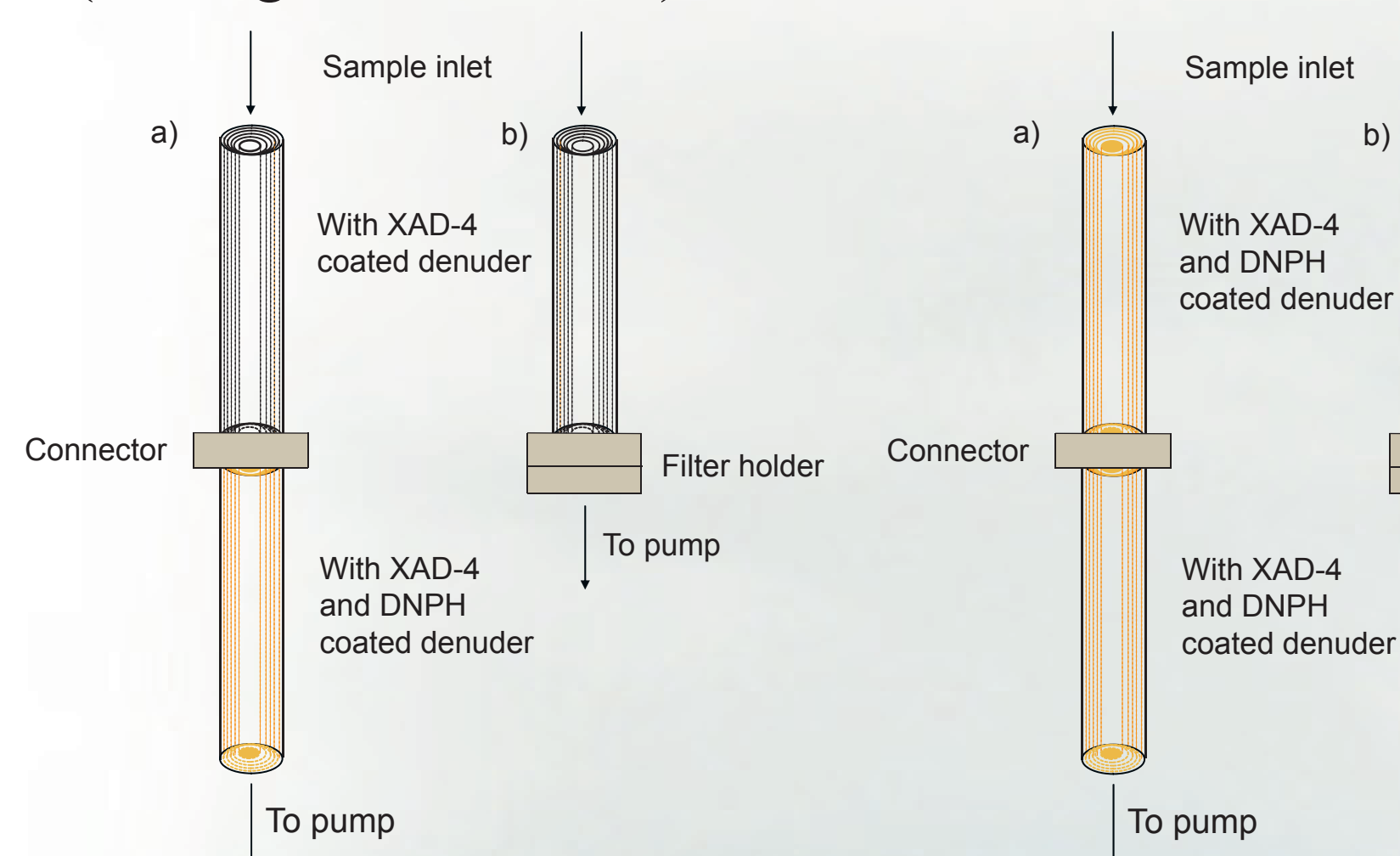


Fig. 2 (left) and Figure 3 (right): A schematic diagram of the denuder/filter sampling system used in this study.

left: XAD-4 and right: XAD-4/DNPH coated denuders.

Chamber experiments

- α -pinene and β -pinene were photooxidised in the presence of NO_x. For the experimental conditions see Table 2.
- Gas- and particle-phase products were collected under optimal denuder/filter sampling conditions determined in this study. (RH 50 %; sampling flow rate 10 l/min).
- Two sets of denuders (XAD-4 and XAD-4/DNPH coated denuders) were used to compare their performance.
- An additional XAD-4/DNPH denuder was connected after the filter holder to determine a positive artefact on a filter.
- Quantification of the first generation oxidation products (nopinone and pinonaldehyde) in gas- and particle-phases was performed using the authentic standards which were derivatised under the same conditions as the samples.

Table 2: Experimental conditions for the photooxidation.

	α -pinene	β -pinene
Initial HC concentration [ppb]	50	50
Consumed HC Concentration [ppb]	20	32
OH source	MeONO/NO/UV-light	MeONO/NO/UV-light
RH [%]	48 ± 1	50 ± 1
T [°C]	22 ± 0.3	21 ± 0.3
Reaction time [h]	0.6	0.8
Sampling time [h]	3	3
Sampling volume [m ³]	1.8	1.8
Seed particles	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	(NH ₄) ₂ SO ₄ /H ₂ SO ₄

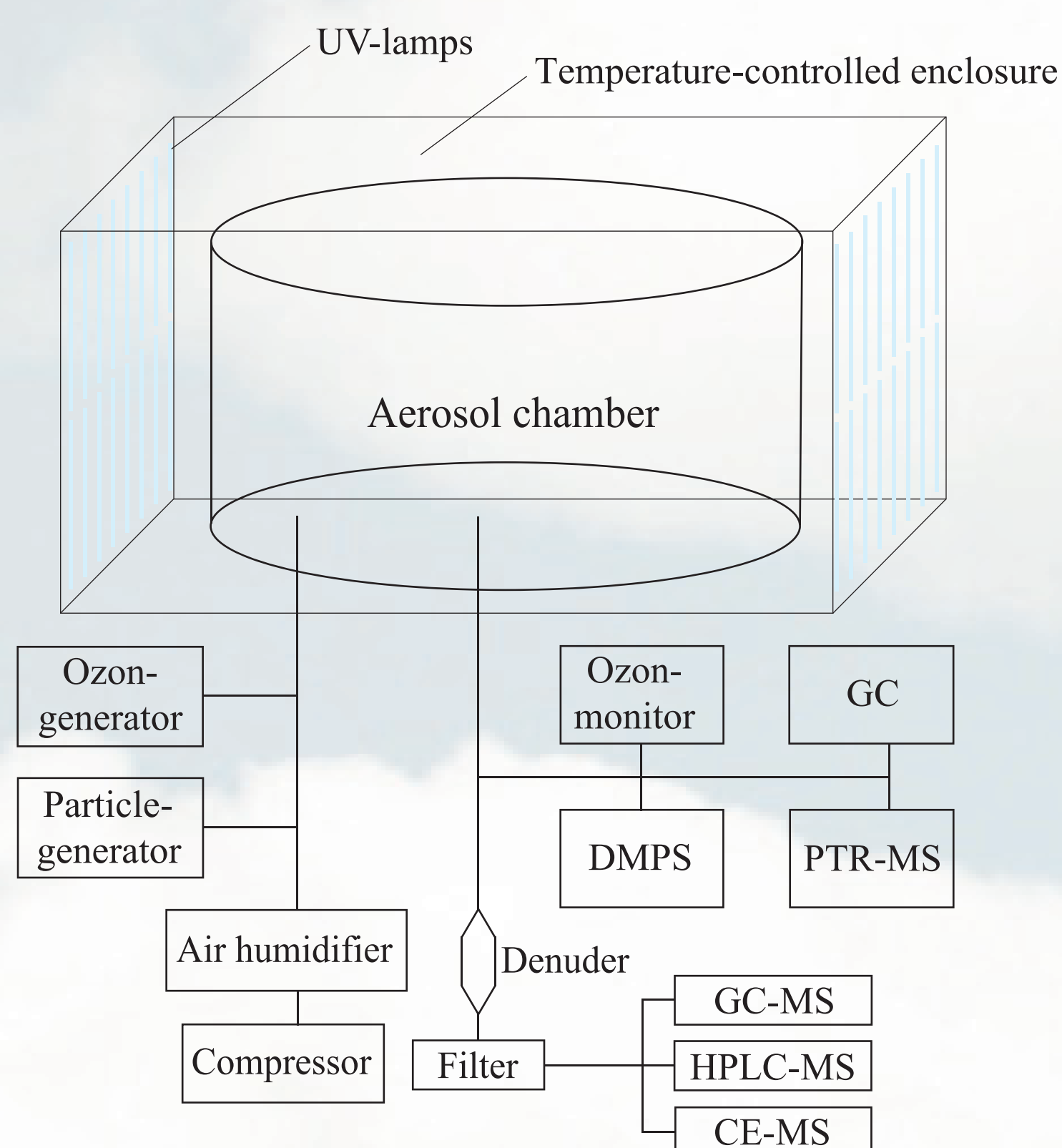


Fig. 1: Diagram of the gas- and aerosol-phase instrumentation of the IFT aerosol chamber.

- After the sampling, the XAD-4/DNPH denuders were directly extracted with acetonitrile, whereas the XAD-4 denuders were extracted with methanol and derivatised off-line.
- The extracts were purified using solid phase extraction cartridges (SPE) and were analysed with HPLC/ESI-TOFMS.

Results and Discussion

Denuder evaluation

- Figure 4 shows recoveries for both the XAD-4 and XAD-4/DNPH denuders at RH 0 %.
- Good recoveries were found for all compounds except for the XAD-4/DNPH denuder used at 30 l/min sampling flow rate.
- Hence, 10 l/min was chosen as the optimal flow rate.
- The off-line derivatisation method (XAD-4 denuders) shows consistent recoveries regardless of flow rates.

Residence time in denuder [s]	5 [l/min]		10 [l/min]		30 [l/min]		
	DNPH	XAD-4	DNPH	XAD-4	DNPH	XAD-4	
Break-through to 2nd DNPH denuder [%]	2.0	0.4	0.3	0.4	3.5	1.7	
Amount detected in filter [ng/m ³]	Campholenic-aldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	
	Nopinone	n.d.	4.5	n.d.	n.d.	14.9	22.0
	Pinonaldehyde	n.q.	n.q.	n.q.	n.q.	0.1	3.0

Fig. 4: Denuder performance at different flow rates including break-through and possible artefact formation on filter. In this plot the mean values of two experiments are shown. The bars represent the range of the recovered amount.

- The break-through is in the same range for both XAD-4 and XAD-4/DNPH denuders (see Figure 4 and the Table therein).
- Based on the break-through values, there is a little difference between XAD-4 and XAD-4/DNPH denuders for the trapping efficiencies.
- The reason for the different recoveries may originate from the derivatisation methods (online vs. off-line).
- As shown in Figure 5 the relative humidity also plays an important role due to available H₃O⁺ that acts as a catalyst for the derivatisation reaction.
- Higher recoveries and less variability were obtained at higher RH.

Application of denuders to chamber studies

- The yields determined using the XAD-4/DNPH denuder agree well with values reported in the literature (see Table 3).
- Both pinonaldehyde and nopinone were below quantification or detection limits in the particle-phase.
- Due to low HC concentrations used in this study, carbonyl compounds most likely stayed in the gas-phase and did not partition into the particle-phase.

 Table 3: Yields of the major carbonyl compounds from α -pinene/OH (left) and β -pinene/OH (right) oxidation determined in this study.

Compound	Molar Yield	References	Compound	Molar Yield	References
Gas-phase			Gas-phase		
XAD-4/DNPH denuder	0.26	This study	XAD-4/DNPH denuder	0.19	This study
XAD-4 denuder	0.14	This study	XAD-4 denuder	0.23	This study
On-line PTR-MS	0.34 ± 0.09	Wisthaler <i>et al.</i> (2001)	On-line FT-IR	0.25 ± 0.05	Larsen <i>et al.</i> (2001)
TENAX TA, GC-FID	0.28 ± 0.05	Aschmann <i>et al.</i> (2002a)	On-line PTR-MS	0.25 ± 0.03	Wisthaler <i>et al.</i> (2001)
Particle-phase			Particle-phase		
PTFE filter connected after XAD-4 denuder	n.q.		PTFE filter connected after XAD-4 denuder	n.d.	This study
Detected amount in XAD-4/DNPH denuder connected after filter	0.003				

References

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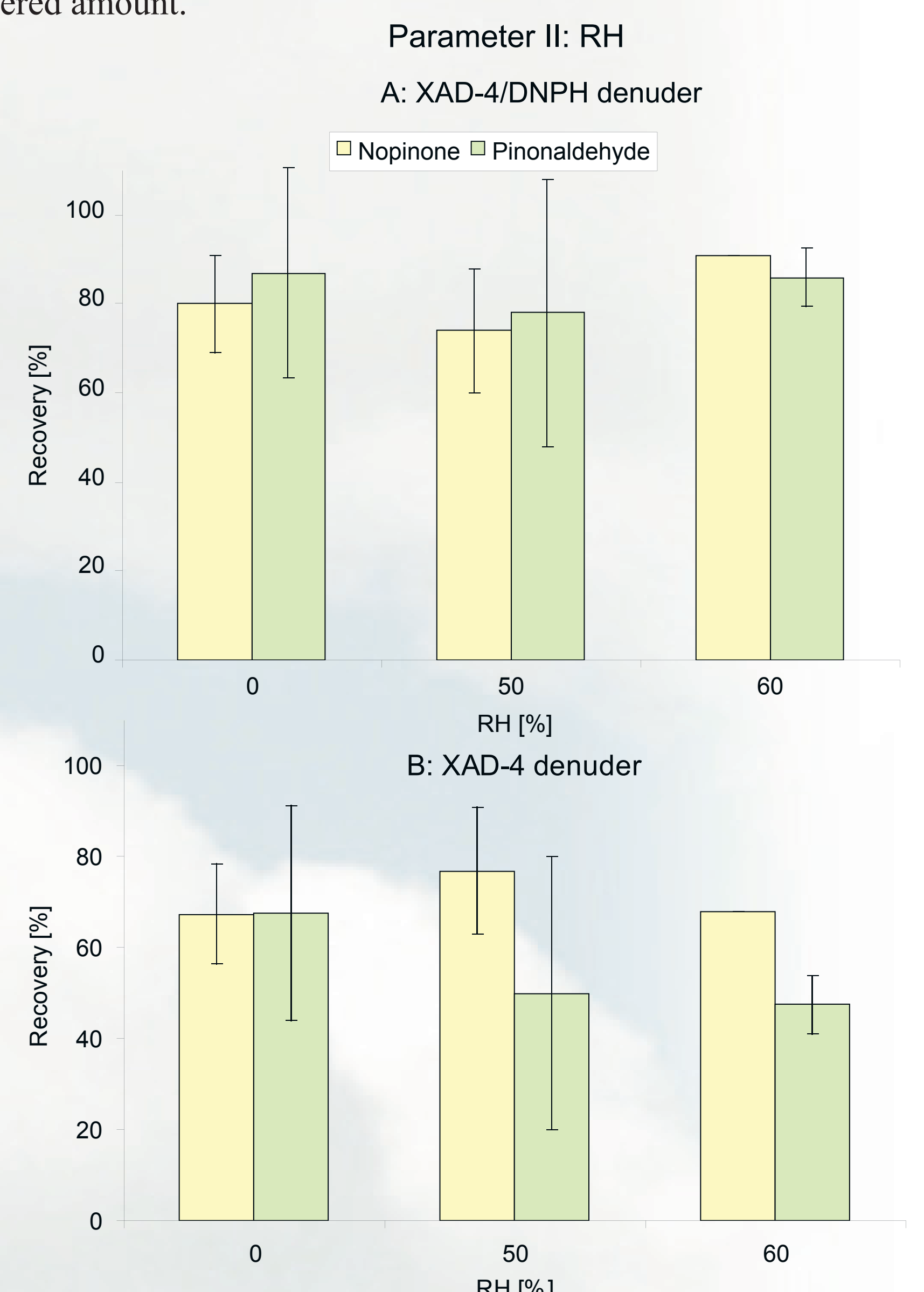
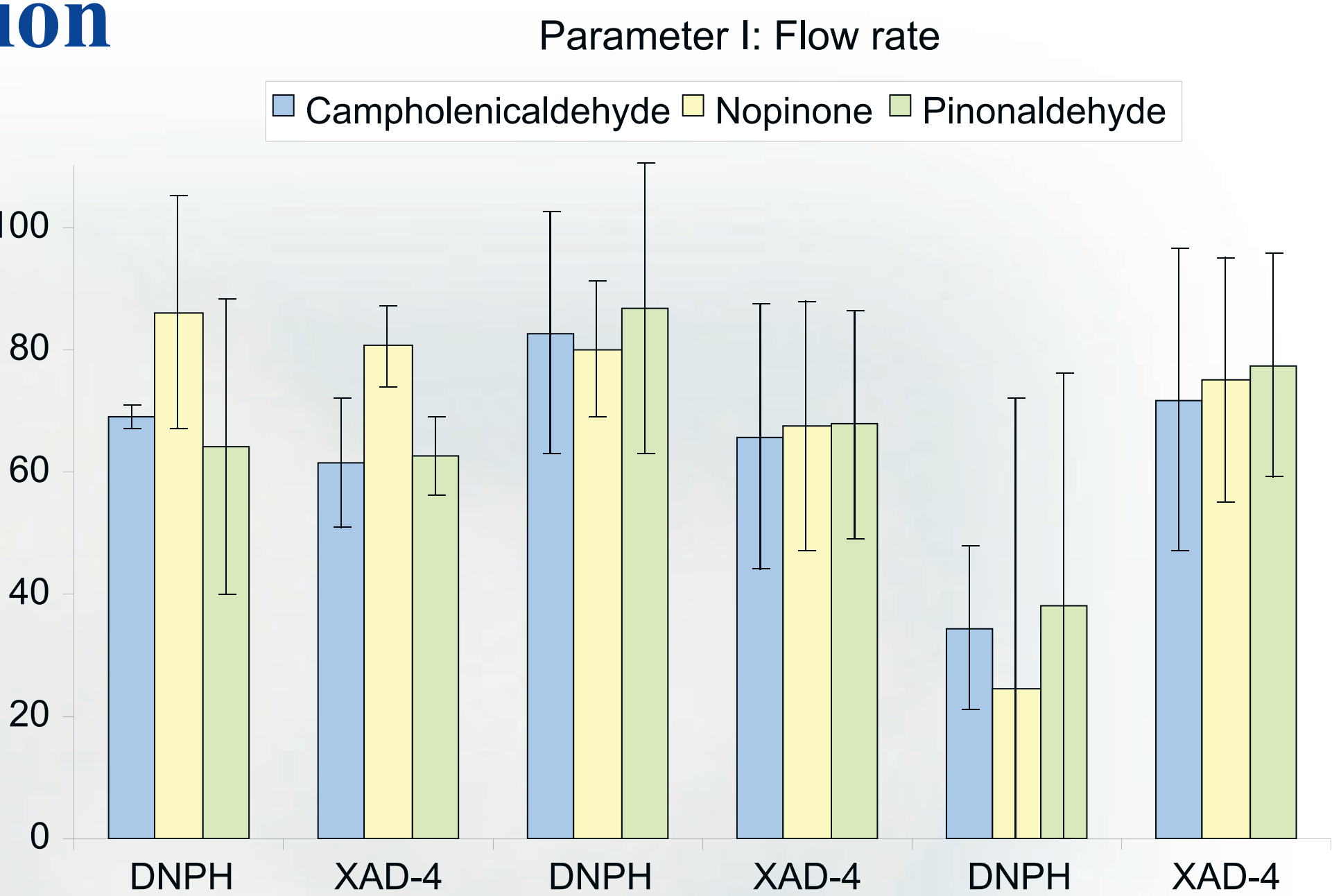


Fig. 5: Denuder performance at different RH. This plot also shows the mean values of two experiments with bars representing the maximum and minimum.

Summary

- The online derivatisation method using XAD-4/DNPH denuders improves the collection efficiency under certain conditions.
- To obtain reliable and quantitative results, standards need to be derivatised under the same conditions (RH, flow rate) as samples to include the different derivatisation efficiency and possible losses during the sample preparation procedure.