

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. The gaseous compounds are trapped by the sorption medium and particulate compounds can 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 for this purpose 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).

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. The advantage of a denuder-filter sampling technique is these simultaneous collection of gaseous and particulate compounds at the same time.

In the present study the performance of two sets of denuder types was evaluated using carbonyl compounds (benzaldehyde, campholenic aldehyde and nopinone).

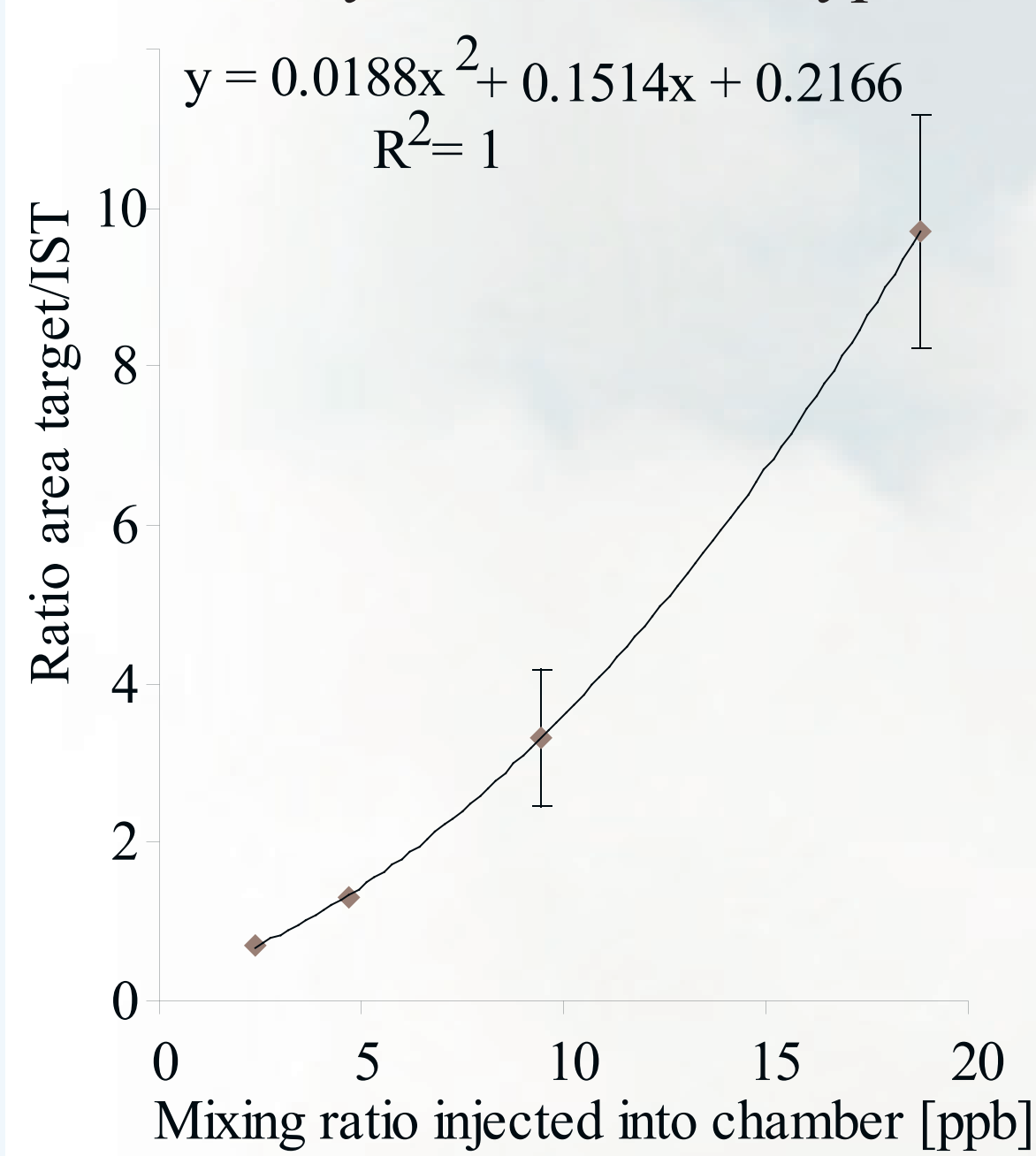
The denuder type A, which was singly coated with XAD-4, was used for the ex-situ analysis of carbonyl compounds with the derivatisation reagent DNPH. The denuder type B, which was coated with XAD-4 and DNPH, was used for the in-situ derivatisation of carbonyl compounds on the denuder surface (see Figure 1).

In this study results are shown from calibration studies on denuders using a chamber. Absolute recoveries from each denuder type were also determined by comparison to authentic hydrazone standards which were synthesised and recrystallised from ethanol.

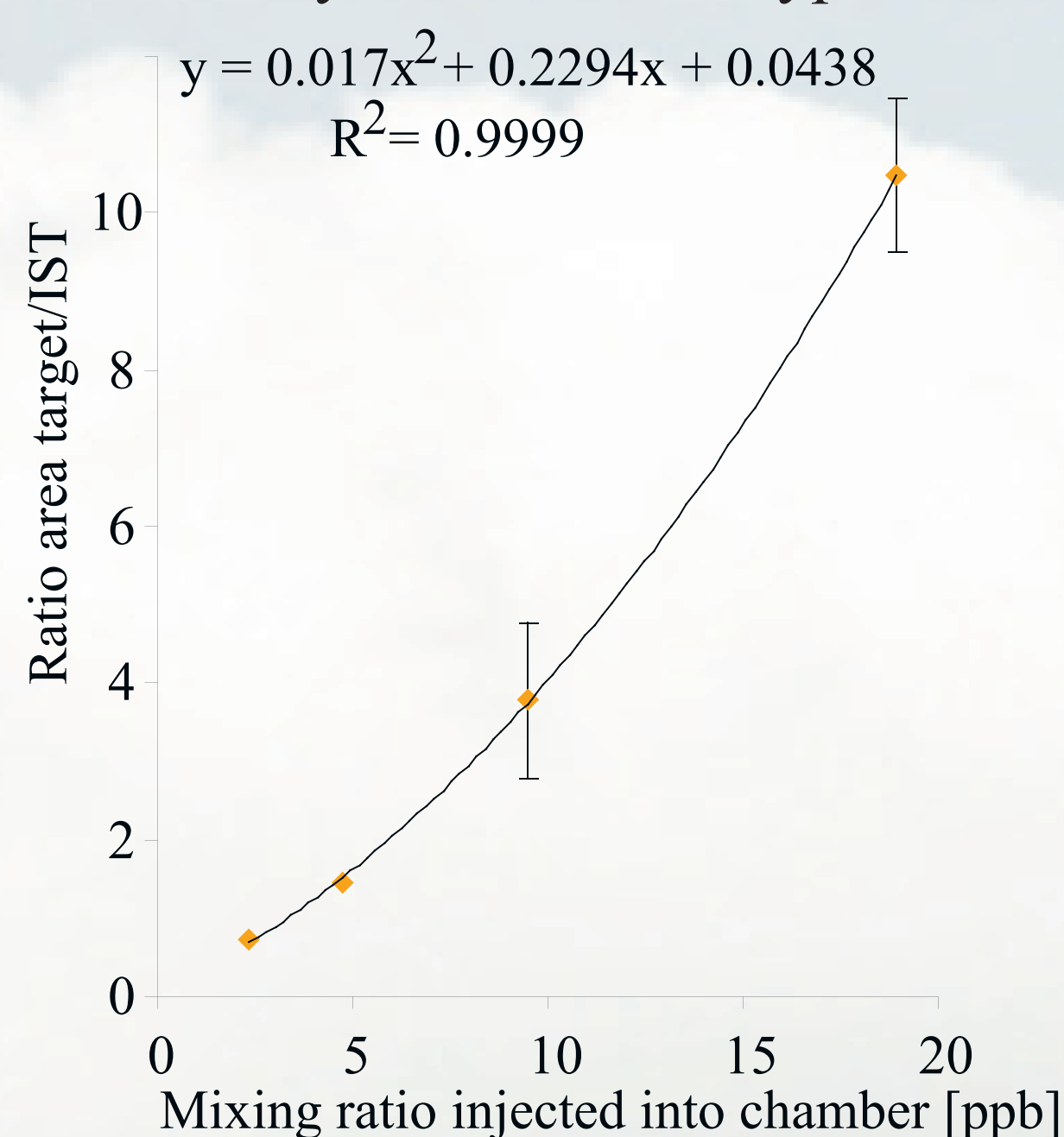
Results and Discussion

Calibration experiments

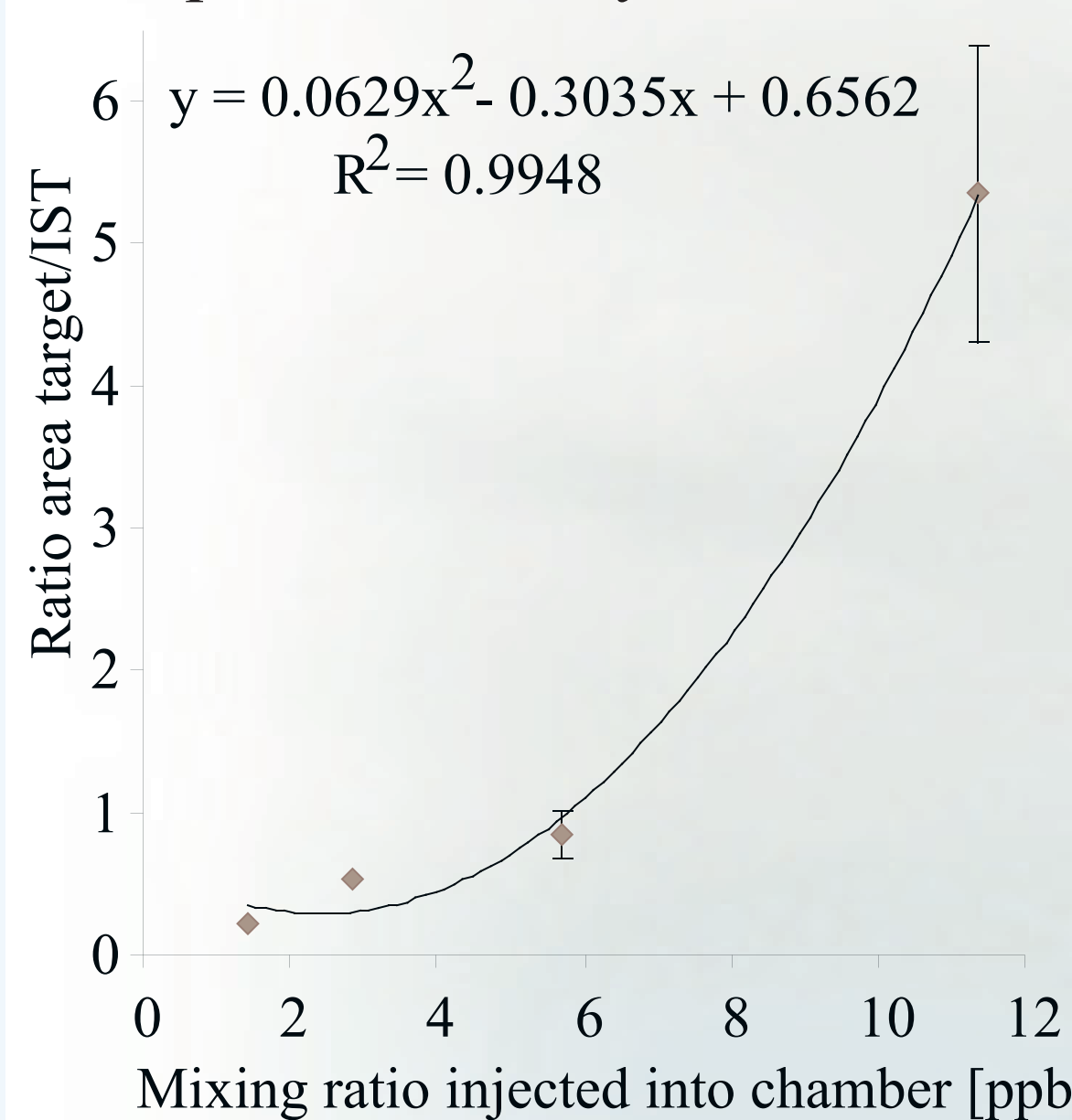
Benzaldehyde on denuder type A:



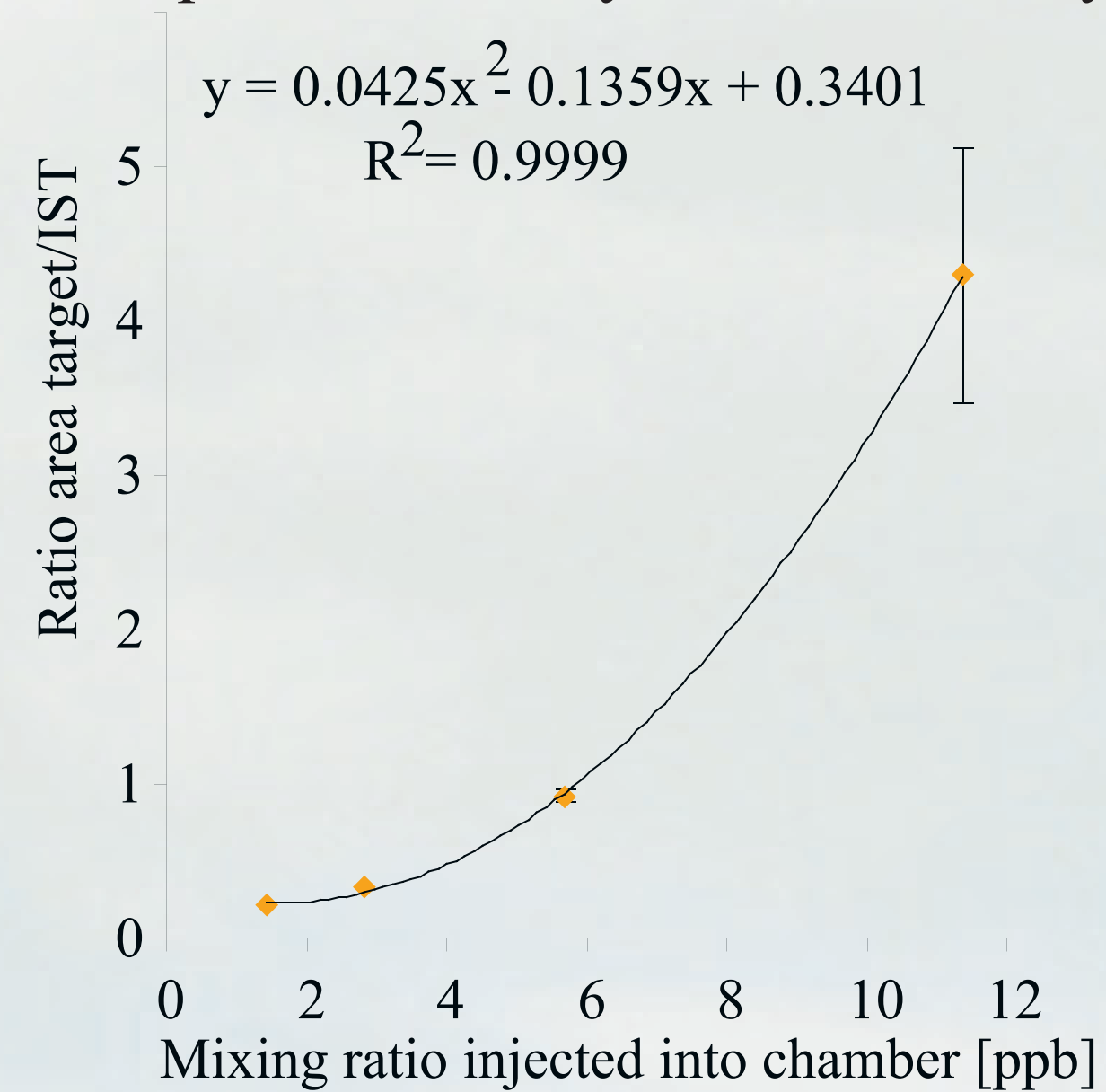
Benzaldehyde on denuder type B:



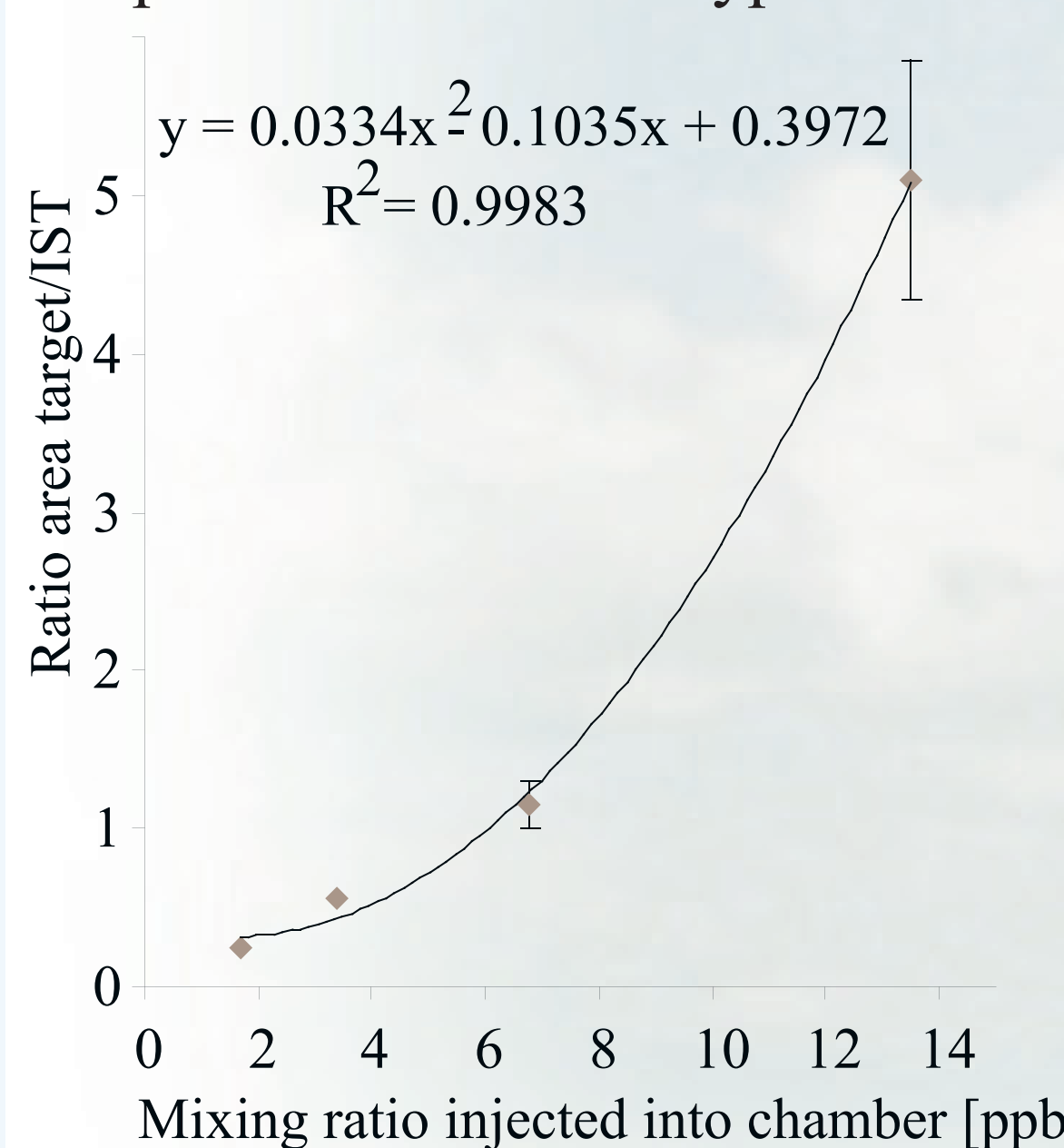
Campholenic aldehyde on denuder type A:



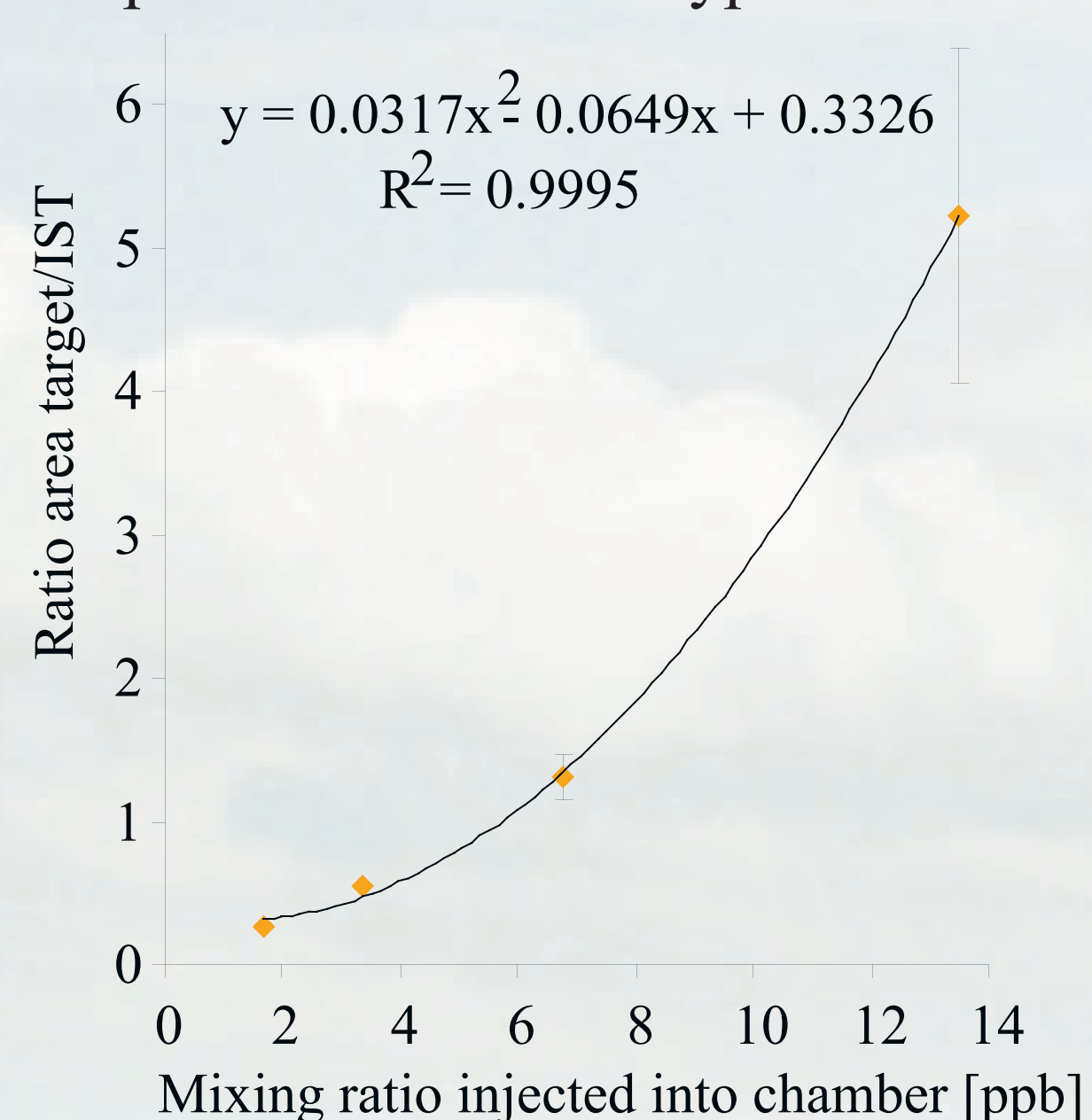
Campholenic aldehyde on denuder type B:



Nopinone on denuder type A:



Nopinone on denuder type B:



Both denuder types showed good R^2 for the calibration experiments. The results show that both sampling types are suitable for trace gas analysis of carbonyl compounds. The ex-situ derivatisation technique (on denuder type A) as well the in-situ derivatisation (on denuder type B) seem to deliver a reliable tool for the quantification of benzaldehyde, campholenic aldehyde and nopinone from the gas-phase.

Experimental

The annular denuders were purchased from the URG Corporation (Chapel Hill, NC, USA) and consist of 5 channels with a length of 40 mm. Both denuder types were manually coated with XAD-4 and were recoated after a denuder usage cycle of five experiments. The additional DNPH coating for the denuder type B was applied just before the experiment.

The selected carbonyl compounds (benzaldehyde, campholenic aldehyde and nopinone) were injected into the 19 m³ IFT chamber (Figure 2) at known concentrations (see Table 1). Each experiment was repeated twice, otherwise indicated.

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

Experiment	Mixing ratio injected into the chamber [ppb] for		
	Benzaldehyde	Campholenic aldehyde	Nopinone
Experiment 1 *	2	1	2
Experiment 2 *	5	3	3
Experiment 3	9	6	7
Experiment 4	19	11	13

* repeated only once

The denuders were extracted directly after the experiments. The trapped carbonyl compounds from denuder type A were extracted with 50 ml methanol and derivatised off-line with DNPH. The denuder type B, which surface contained the derivatisation reagent, was extracted three times with 50 ml acetonitrile. The internal standard (cyclohexanone-DNPH) was added to both denuder extracts, which were left over night to ensure complete derivatisation. After a concentration step using rotary evaporation, the extracts were purified using solid phase extraction cartridges (SPE). Afterwards the extracts were analysed with HPLC/(-)ESI-TOFMS.

Determination of the absolute recoveries from denuders

The extraction efficiency of the target compounds from the denuder itself were determined from spiking tests. Known concentration of the carbonyl compounds (benzaldehyde, campholenic aldehyde and nopinone) were spiked onto the denuder type A, which was dried under a nitrogen stream and extracted afterwards with methanol. The denuder type B was spiked with their respective hydrazones, dried and extracted with acetonitrile. The results from the spiking tests are presented in Table 2.

Table 2: Results from the spiking tests of denuder type A (left) and denuder type B (right) determined in this study. The results show averages of 3 experiments, respectively.

Denuder type A (XAD-4)			Denuder type B (XAD-4/DNPH)		
Compound	Extraction efficiency [%]	Standard deviation [%]	Compound	Extraction efficiency [%]	Standard deviation [%]
Benzaldehyde	71	10	Benzaldehyde	42	17
Campholenic aldehyde	57	16	Campholenic aldehyde	28	5
Nopinone	67	19	Nopinone	78	12

The absolute recoveries for the target compounds and the denuder types are shown in Figure 3. The results show that the combination of trapping and direct derivatisation on the denuder surface improves the collection of carbonyl compounds slightly. Benzaldehyde and nopinone showed an enhancement of their collection by 6% and 4%, respectively. For campholenic aldehyde the recovery for the in-situ derivatisation was half of the off-line derivatisation. Nevertheless, the in-situ derivatisation method showed more constant recoveries than the ex-situ derivatisation technique. Benzaldehyde showed the highest recoveries, due to its higher affinity to the aromatic and hydrophobic XAD-4 resin. A possible explanation for the marginal improvement of an in-situ derivatisation technique might be the competition of trapping and derivatisation. DNPH molecules might occupy XAD-4 pores so that a sufficient trapping may not occur. The derivatisation reaction might be too slow (especially for high molecular weight carbonyl compounds) to compensate this.

It should be noted that only limited data are available in the literature, where authentic standards and sampling on denuders were applied to characterise them. Our study demonstrates that a comprehensive characterisation of each target carbonyl compound is required for accurate quantification using denuders. No general prediction can be made for the trapping properties of denuders using in-situ or ex-situ derivatisation techniques.

A reliable quantification can only be achieved when the calibration is performed in the same way as the samples. The results show that spiking tests do not represent a sufficient tool to characterise denuders. When a calibration is performed against a standardised system like a chamber, all possible losses during the sample preparation procedure can be included.

References

- Possanzini, M., and V. Di Palo (1999), *Chromatographia*, 49, 161-165.
Temime, B., et al. (2007), *Environmental Science and Technology*, 41, 6514-6520.

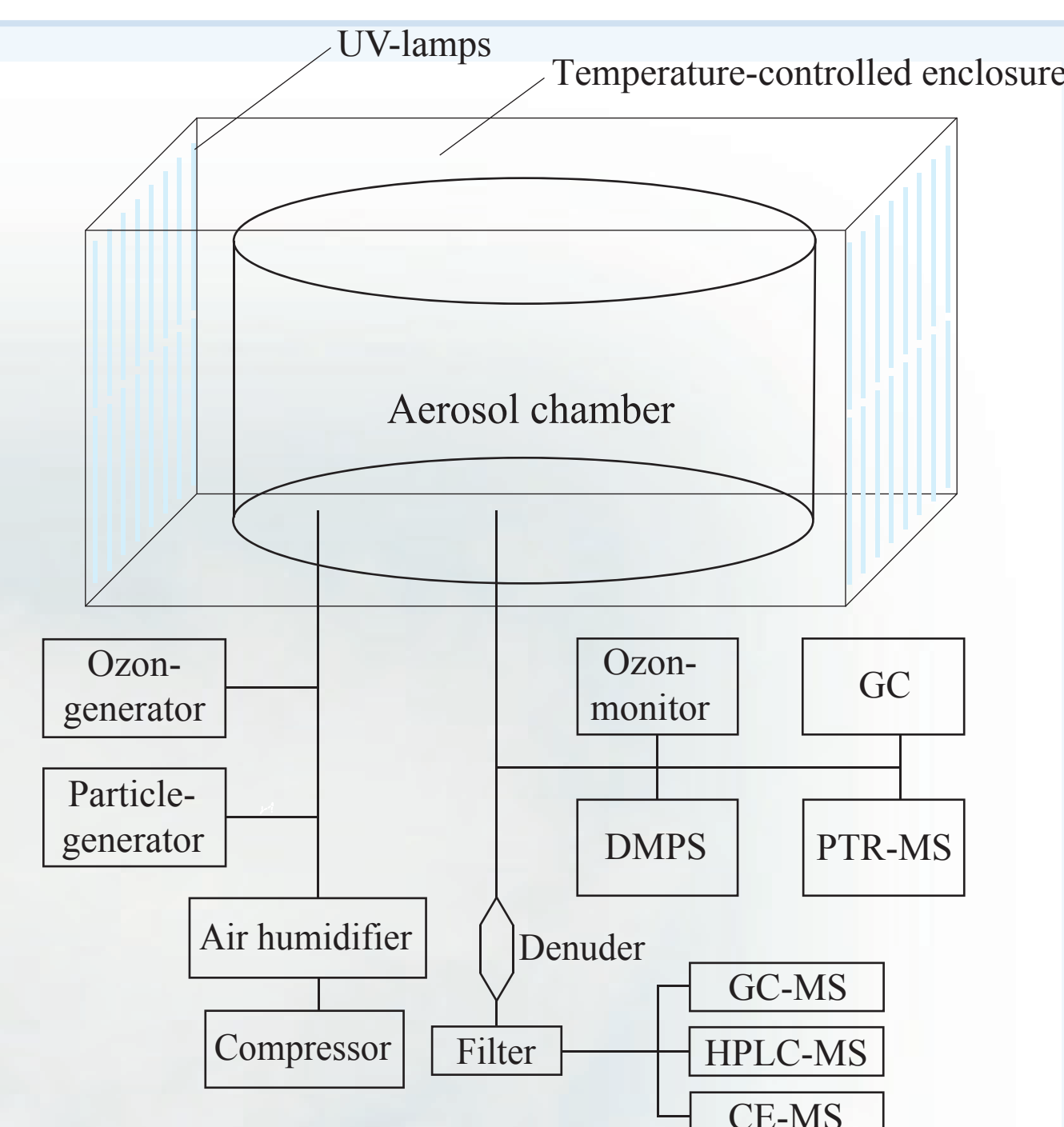


Fig. 2: Diagram of the IFT aerosol chamber.

The experiments were performed at relative humidity of 50% at 21 °C. After a mixing time of 10 minutes the carbonyl compounds were sampled using the denuder types A and B in parallel. The sampling was performed at a flow rate of 10 l/min for one hour (0.6 m³).

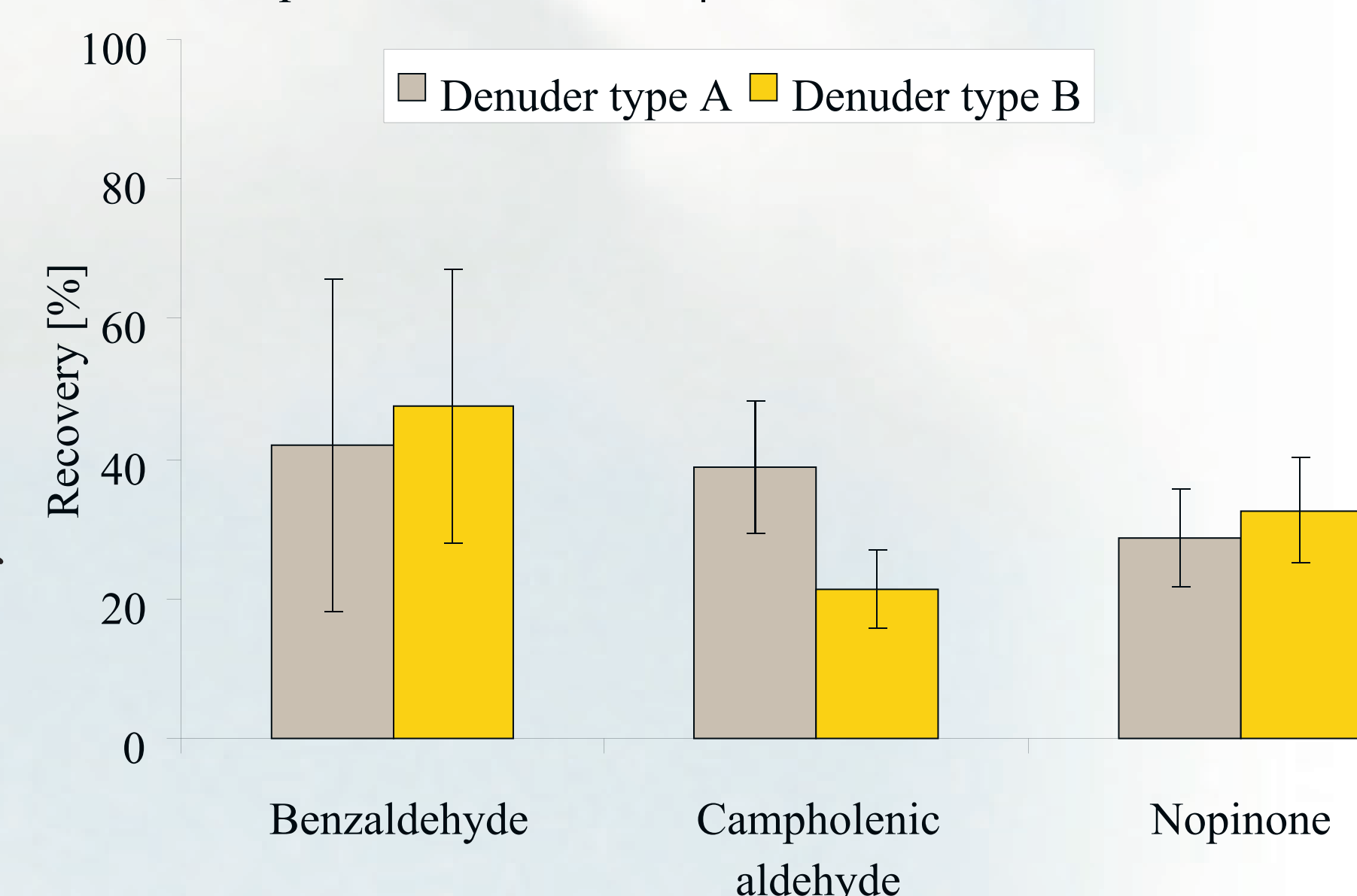


Fig. 3: Absolute recoveries for the carbonyl compounds from each denuder type used in this study. The results show averages of the performed 6 calibration experiments.