



# A New Protocol for the Measurement of Gas/Particle Partitioning of Atmospheric Oxidation Products

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## Introduction

The investigation of secondary organic aerosol (SOA) content is prevalent today because of its potential effect on health, global climate and visibility interference. The speciation of organics in SOA, however, has not been fully determined. This is partly because of gas/particle partitioning of the SOA-forming compounds and the sampling artefacts associated with common methods, for example filter sampling. The aim of this work was to explore the applicability of a denuder-based gas-particulate phase separation system to a wide range of SOA-forming compounds present in ambient air. The implementation and evaluation of *in situ* derivatization on the walls of the tube using a combination of XAD-4 polymer resin and the derivatizing agent O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) was carried out in an attempt to improve the overall performance of the denuder.

## Experimental

The denuder-based sampling method works on the basis that gases diffuse orders of magnitude faster than particles. The denuder tube strips the gas-phase organics by diffusion to a sorbent on the walls (Figure 1). Particles are collected on a filter placed downstream. Amberlite XAD-4 non-polar polymeric adsorbent is commonly used as the coating, because of its high surface area (725 m<sup>2</sup> g<sup>-1</sup>). However its effectiveness in trapping polar compounds such as atmospheric photooxidation products needs to be investigated.

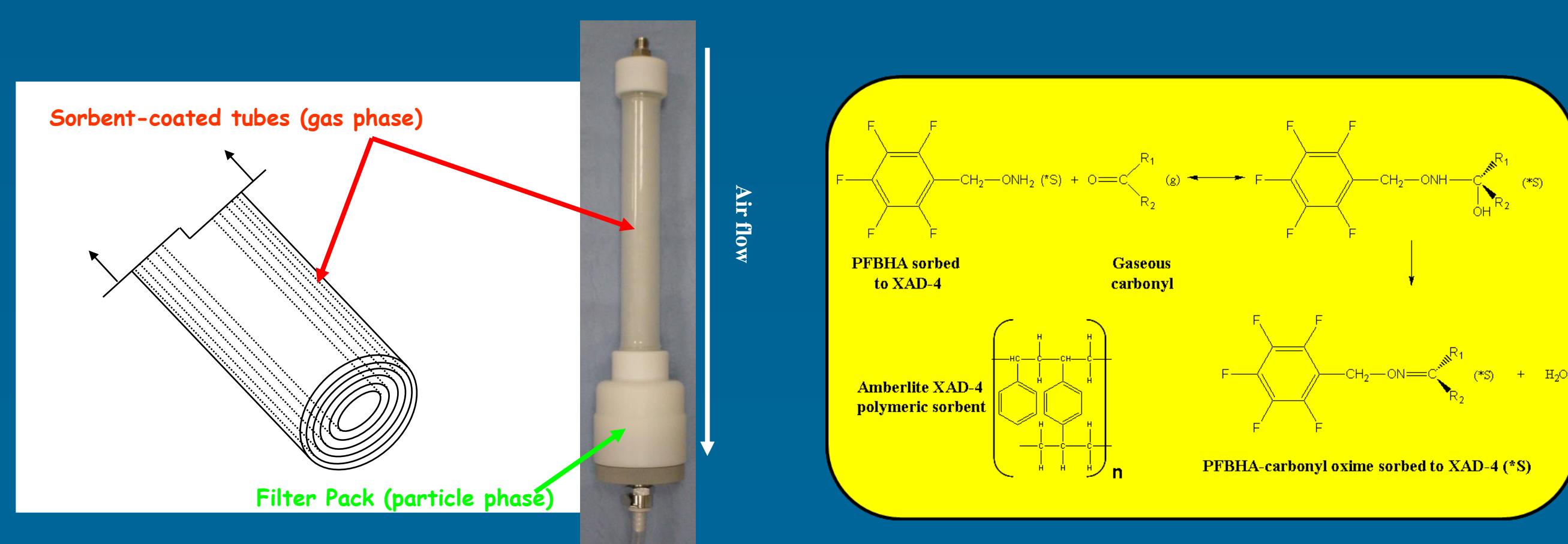


Figure 1: Annular denuder and filter pack

Figure 2: On-sorbent derivatization of carbonyls

PFBHA has been widely used as a derivatizing agent for the detection of carbonyl products in atmospheric photooxidation studies. By conversion of the carbonyl group to an oxime (Figure 2), it reduces the polarity of the carbonyl compounds and improves the use of GC-MS analysis. In order to increase the affinity of the target compounds for XAD-4 and thus optimize the trapping efficiency, PFBHA was added to the non-polar XAD-4 coating prior to sampling.

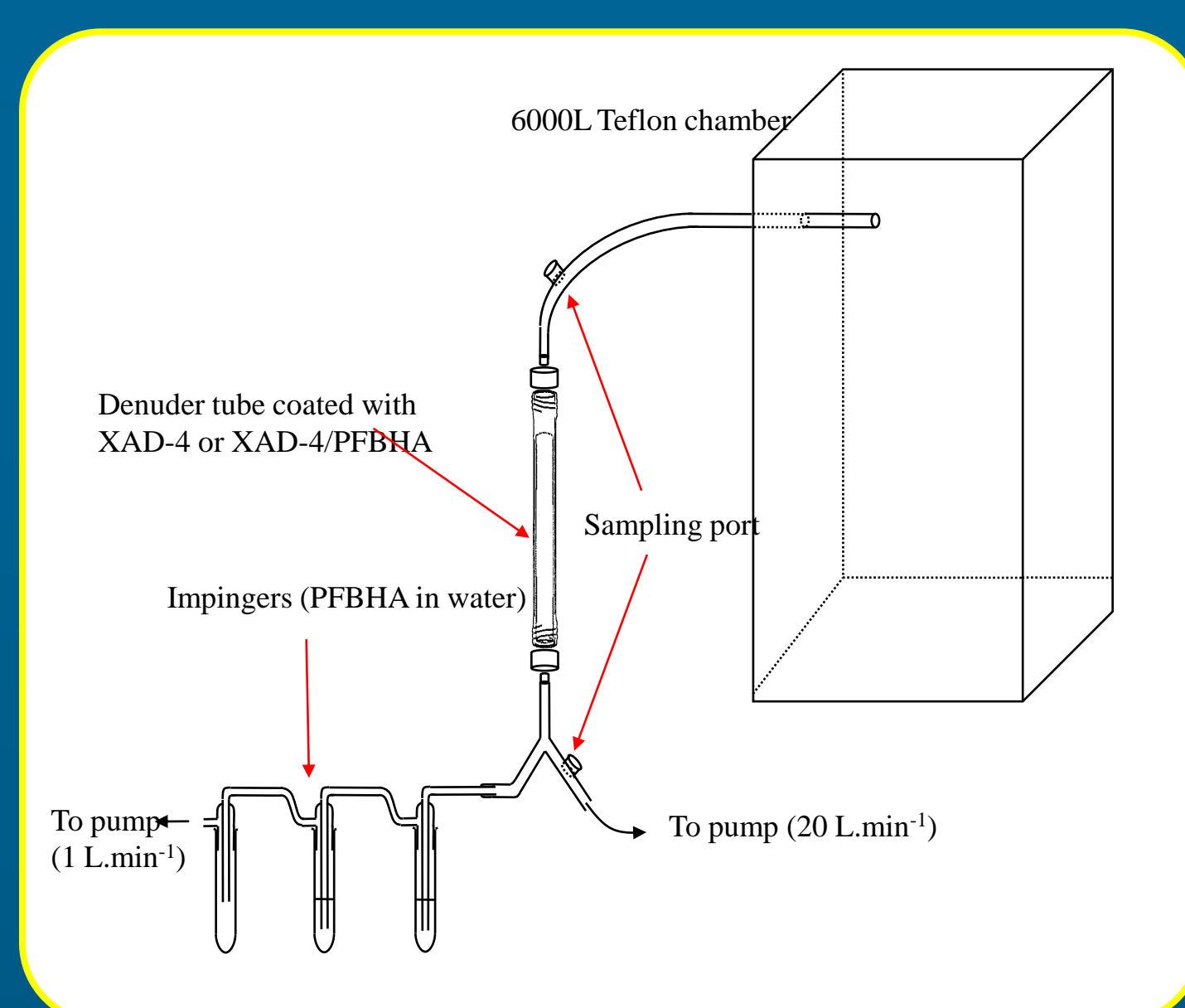


Figure 3: Apparatus for denuder trapping efficiency experiments

A 6000 L atmospheric simulation chamber was used to evaluate the gas-phase trapping efficiency of the denuder (Figure 3). A range of carbonyl compounds were introduced into the chamber through a gently heated impinger system resulting in a concentrations in the range 0.3-0.7 ppm. Samples were taken from the entrance and exit of the tube at regular time intervals and analysed by GC-MS.

## Denuder Trapping Efficiency Tests

The addition of PFBHA to the XAD-4 coating dramatically increased the trapping efficiency of the tube for C<sub>2</sub>-C<sub>5</sub> carbonyls, C<sub>2</sub>-C<sub>6</sub> dicarbonyls and C<sub>7</sub>-C<sub>9</sub> aromatic aldehydes. The following figure compares the trapping efficiency of the tube for a range of carbonyls with XAD-4 and XAD-4/PFBHA coatings.

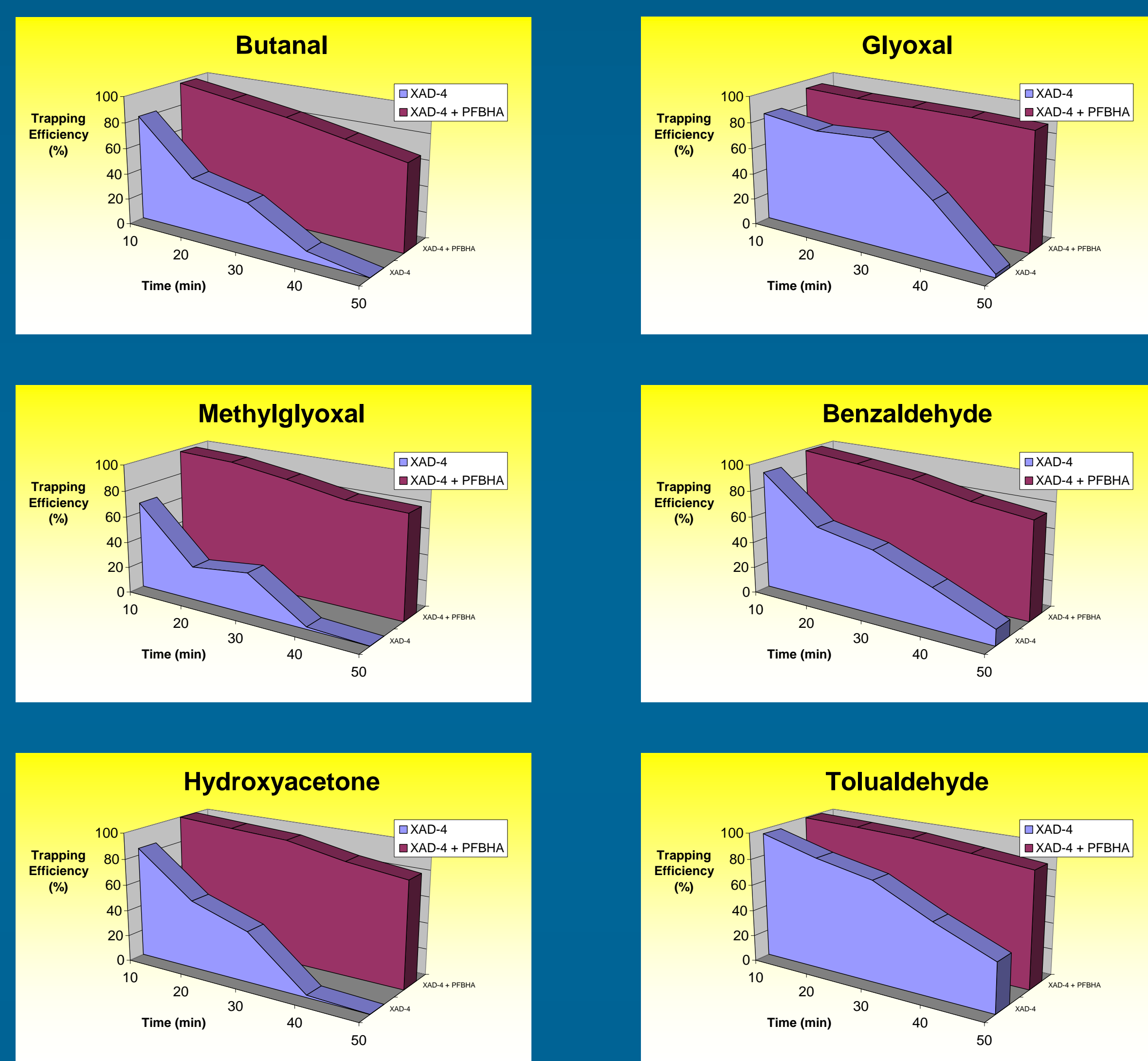


Figure 4: Improvement of trapping efficiency with addition of PFBHA for various carbonyls

The dramatic increase observed may be explained by the mechanisms involved in adsorption at the walls of the tube. With XAD-4 resin the trapping efficiency depends upon weak intermolecular (Van der Waal's) forces between the analyte and sorbent. Therefore, polar compounds exhibit a relatively low binding affinity for the non-polar sorbent and are not trapped effectively.

The addition of PFBHA to the coating creates another pathway for adsorption as carbonyl compounds react readily with the derivatizing agent sorbed at the tube walls. The resulting oximes formed have lower polarity than their parent carbonyls and thus exhibit an improved affinity for the XAD-4 resin.

## Gas/particle partitioning studies

The on-tube derivatization process was applied to photooxidation studies of p-xylene in order to determine the partitioning of selected carbonyl products between the gas and particle phases. Experiments were carried out in a 6000L Teflon chamber coupled with GC-FID for measuring reactant loss and a scanning mobility particle sizer to monitor aerosol growth (Figure 5). The denuder was coupled with a filter pack and sampling proceeded for ten minutes per run. After each run the tube and filter pack were extracted separately and analyzed by GC-MS (Figure 6) to calculate the partitioning coefficients of the products formed.

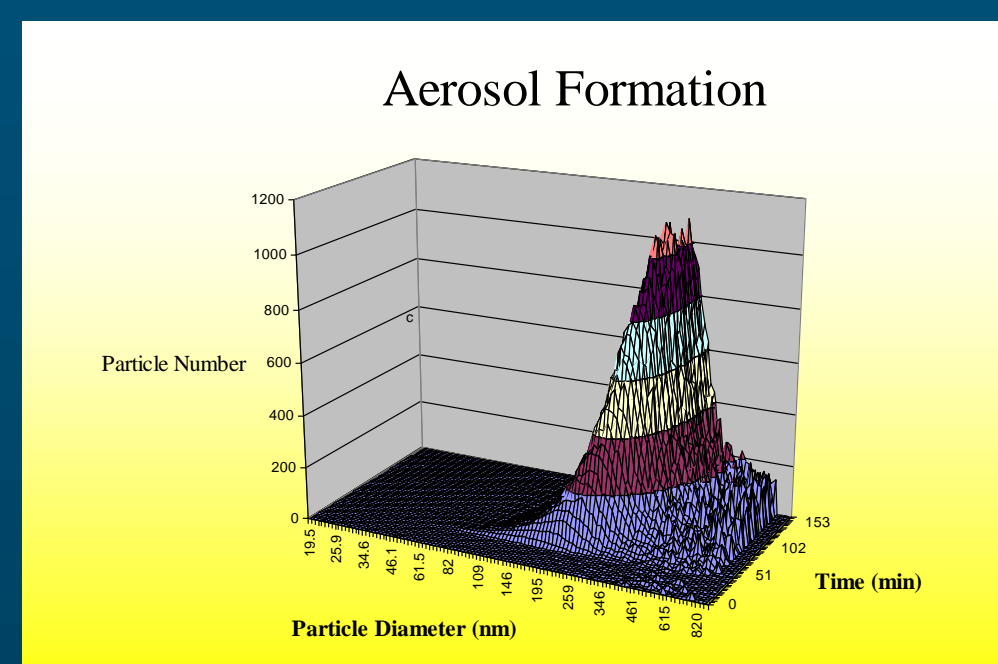


Figure 5: Aerosol growth from p-xylene photo-oxidation

Partitioning values were calculated based on the vapour pressure of each product and compared with those observed experimentally. Glyoxal and methylglyoxal were found to exhibit partitioning to the particle phase orders of magnitude higher than expected (Figure 7) while values obtained for other products such as p-tolualdehyde and 2,5-dimethylbenzoquinone agree well with their theoretical values.

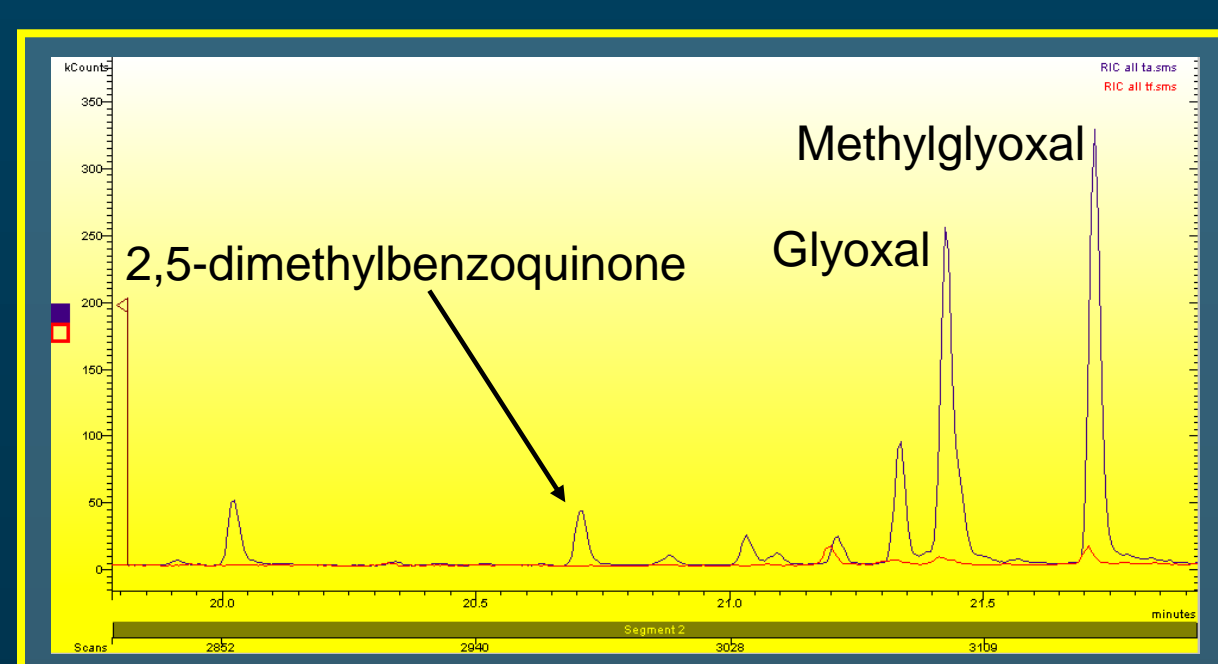


Figure 6: Tube (purple) and filter (red) extracts analyzed by GC/MS

Product	K <sub>p</sub> expected (m <sup>3</sup> /μg)	K <sub>p</sub> observed (m <sup>3</sup> /μg)
2,5-dimethylbenzoquinone	2.8x10 <sup>-6</sup>	6.8x10 <sup>-6</sup>
Glyoxal	4.9x10 <sup>-9</sup>	2.5x10 <sup>-5</sup>
Methylglyoxal	7.5x10 <sup>-9</sup>	4.1x10 <sup>-5</sup>

Figure 7: Theoretical vs experimental partitioning coefficient values

## Conclusions and Further Work

- The coupling of the denuder system with the derivatizing agent PFBHA provides a novel method for the study of gas/particle partitioning of carbonyl photooxidation products
- This method helps to minimize filter sampling artefacts associated with carbonyl measurement in laboratory studies of SOA formation
- Glyoxal and methylglyoxal were found to exhibit partitioning to the particle phase orders of magnitude higher than expected when considering vapour pressure alone
- This phenomenon may possibly be explained by oligomerization of these products within the particles formed

Further work will include

- Altering particle humidity and acidity
- Investigation of the partitioning of photo-oxidation products of other aromatics e.g. trimethylbenzene
- Adapting the method to field studies