



# A New Protocol for Sampling and Analysis of Semi-volatile Organic Compounds and Application to Simulation Chamber Studies of Aromatic Photo-oxidation



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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 makes use of the fact that gases diffuse orders of magnitude faster than particles. The denuder tube removes the gas-phase organics by diffusion to a sorbent on the walls (Figure 1).

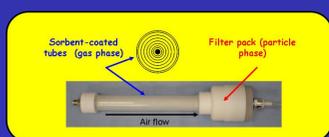


Figure 1: A five-channel annular denuder with filter-pack

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.

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, it reduces the polarity of the carbonyl compounds and enables 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 2).

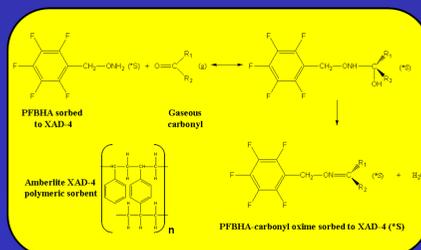


Figure 2: On-sorbent (XAD-4) PFBHA derivatization of carbonyl functions (\*S: sorbed)

A 6 m<sup>3</sup> atmospheric simulation chamber was used to evaluate the gas-phase trapping efficiency of the denuder. A range of carbonyl compounds were introduced into the chamber through a gently heated impinger system resulting in a concentration of (0.3-0.7) ppm (Figure 3).

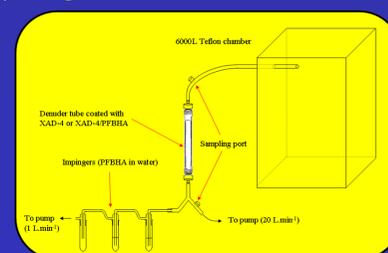


Figure 3: Apparatus for denuder trapping efficiency experiments

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 the PFBHA on the XAD-4 dramatically improved the trapping efficiency of 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. Figure 4 compares the trapping efficiency of hydroxyacetone, glyoxal, methylglyoxal and benzaldehyde with XAD-4 and with XAD-4 + PFBHA.

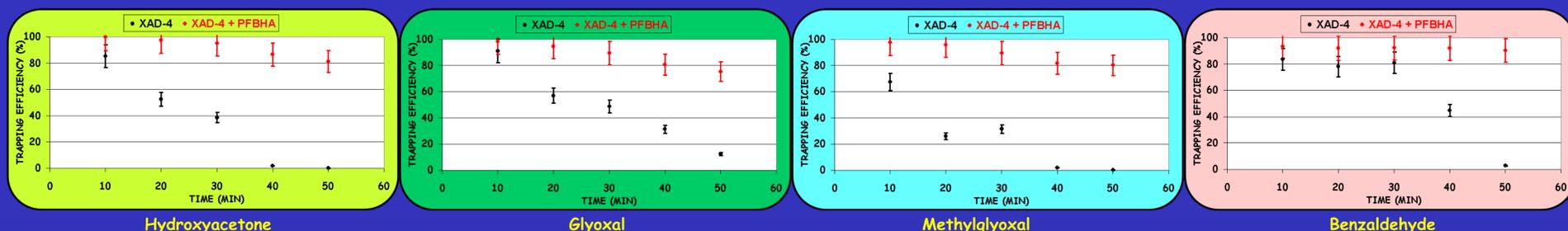


Figure 4. Effect of the PFBHA on the trapping efficiency of selected carbonyls

The results can be explained by the different mechanisms involved in the trapping process. When using just XAD-4, only weak intermolecular interactions (Van der Waals) between the analytes and the sorbent are involved. Consequently polar compounds such as carbonyls are expected to have low binding affinity for the non polar XAD-4 sorbent and thus not to be efficiently trapped. When using XAD-4 combined with PFBHA the trapping efficiency for carbonyl compounds is greatly increased as the analytes react readily with the PFBHA sorbed at the surface.

The resulting oximes have a much lower polarity than the parent carbonyl compounds and therefore exhibit a much higher binding affinity for the XAD-4 resin. Evidence for the rapid reaction of the carbonyl compounds with sorbed PFBHA is shown in Figure 5, where chromatograms of a denuder extract analysed 5 minutes and 24 hours after the sampling run are presented. The results show that there is no significant difference in the signal intensity indicating that fast and complete on-sorbent derivatization occurred during the sampling run (10 mins) and that no further derivatization took place in the extracted solution.

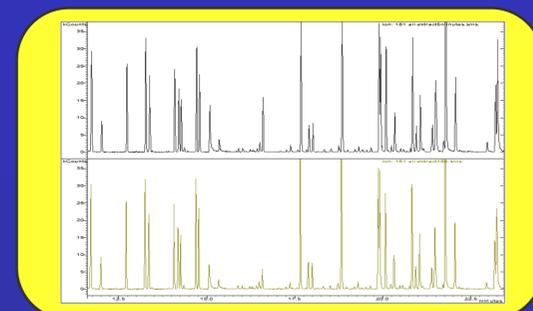


Figure 5. Extract of a PFBHA/XAD-4 coated annular denuder 5 minutes & 24 hours after the sampling run

## Application to a chamber study

The sampling system was used together with a scanning mobility particle sizer (model 3081 long DMA with model 3010 CPC) in a preliminary study of the gas-particle partitioning of selected products of toluene photooxidation. The study was carried out in a 4.7 m<sup>3</sup> simulation chamber (Figure 6) equipped with *in situ* FTIR spectroscopy.

	Initial conditions	Final conditions
Toluene (ppm)	0.91	0.42
Particle (µg m <sup>-3</sup> )	0.00128	2.9 x 10 <sup>3</sup>

Figure 6. The large volume Simulation chamber

A denuder sample was collected for 20 minutes at the end of the experiment. The filter pack and the denuder tube were extracted separately and analysed by GC-MS (Figure 7).

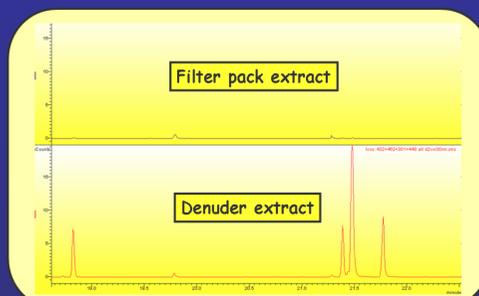


Figure 7. Chromatogram of the extracts of the denuder and filter

The 3 carbonyl oxidation products, benzaldehyde, glyoxal and methylglyoxal, were found to be predominantly (>99.5% by mass) in the gas-phase. Work on identifying species in the particle phase is in progress.

## Conclusions & future work

- > The annular denuder method coupled with the use of PFBHA and GC-MS analysis is suitable for investigating the gas-particle partitioning of carbonyl compounds in photooxidation systems
- > This sampling technique may eliminate uncertainties due to sampling artefacts in simulation chamber experiments of SOA formation (e.g. glyoxal in particle phase)
- > Adapt this method for field measurements (longer sampling time)
- > Apply to simulation chamber studies of the gas-particle partitioning of reaction products in the photooxidation of aromatic compounds and investigate the effect of particle acidity and humidity