

## CHAPTER 8

### CONCLUSION

*In-situ* derivatisation on silicone rubber traps in order to pre-concentrate volatile aldehydes was investigated for the first time. Unlike so many other pre-concentration techniques for determining aldehydes, the silicone rubber trap is inert, rugged, simple and inexpensive. Recovery is by thermal desorption which (1) removes the need for expensive, toxic solvents and (2) renders the silicone trap immediately reusable. Thermal degradation of the silicone rubber resulted in chromatographic peaks, which showed repeatable retention times and peak heights, throughout the study. No deterioration in the performance of the traps was observed.

Diffusion tubes and several types of permeation tubes were successfully prepared and calibrated to provide reliable aldehyde gas standards in the ppm range. A dilution system was successfully constructed in order to obtain concentrations of HCHO in the ppb range. Unfortunately, the sampling set-up for the other aldehydes did not prove leak-tight.

PFBHA was selected as the most suitable derivatising reagent for the study. Sample preparation time was reduced by loading the headspace vapour of the PFBHA directly into the silicone rubber. This was achieved by packing a glass tube with the pure PFBHA reagent. The silicone trap was attached to the one end of the PFBHA tube. From the other end, high purity nitrogen gas was blown through the PFBHA tube towards the silicone trap at a flow rate of 5ml/min. This method however did not load amounts of PFBHA with high repeatability.

The presence of formaldehyde-oxime in the reagent blank, severely restricted our detection level for HCHO. In a 10 minute collection of PFBHA headspace at a flow rate of 5ml/min, 23 ng of HCHO was present. Future work would involve finding a way of trying to clean up the reagent, thereby lowering HCHO detection limits.

We then set out to demonstrate the efficient pre-concentration of the aldehyde gas standards using PFBHA *in-situ* derivatisation on our silicone traps. Two HCHO atmospheres were sampled over time. Comparison of the amount of HCHO trapped and the amount of HCHO released by the gas standard indicated a reaction efficiency of 95% for 0.1ppm HCHO and 75% for 5.98ppm HCHO. HCHO could be detected at the 0.1ppm level. This did not meet the NIOSH Permissible Exposure Limits (PEL) of 0.016ppm. However, the PELs set by the WHO, ACGIH and OSHA could be detected.

A similar test for the other aldehyde gas standards yielded a 4% reaction efficiency, which led us to believe there was a leak in our sampling set-up. Since these aldehydes were not present in the reagent blank, we could determine the minimum detectable concentrations ( $s/n = 3$ ) for acetaldehyde, acrolein and crotonal to be 0.035 ppm, 0.057ppm and 0.064ppm respectively. These concentrations are well below PELs set by the various health organisations. In addition, these detectable levels are for a sampling time of only one minute, as such even lower concentrations will be detectable over longer collection times. These result clearly illustrate that a lower detection limit for HCHO (having close to 100% reaction efficiency) is possible, once the HCHO-oxime impurity is removed from the reagent blank.

Back-up trap sampling of the 0.1 ppm HCHO atmosphere at a flow rate of 10ml/min, indicated no breakthrough of the HCHO-Oxime from the silicone trap after a collection volume of 3 litres.

The contents of the silicone rubber was successfully recovered by thermal desorption with cryogenic focussing. The optimum desorption conditions were determined by desorbing the C12 internal standard (which elutes off the silicone trap after PFBHA and the HCHO-Oxime) from the top of the trap. The optimum desorption temperature was found to be 220°C. No carry-over was detected. In addition, the HCHO-Oxime, PFBHA and C12 peaks displayed consistent retention times.

The aldehyde-oximes were successfully identified using Mass Spectrometry. Based on elution temperatures and retention times the oximes could be identified using the FID. The desorbed analytes were semi-quantitated using the C12 internal standard, which could be related to the FID relative response and the Effective Carbon Numbers (ECN) of the aldehyde-oximes, for which no standards were available. This calculation method gave a very good indication of the trapped aldehyde amounts.

We also demonstrated *in-situ* derivatisation on our silicone rubber traps with real gaseous samples. The results were very promising. Pre-concentration of HCHO from air samples and acetaldehyde from the headspace of beer was achieved. Loading the PFBHA and sampling with the portable pump was quick and easy. No supervision during sampling was required. However, breakthrough and lower reaction efficiencies were observed, differing from our expectations based on our previous studies using the gas standards. The presence of other carbonyls in air also reacting with PFBHA, depleted the reagent thereby decreasing the reaction rate and consequent trapping efficiency. Further work would have to be performed in order to obtain the ideal sampling conditions.

Our study has revealed that the silicone rubber trap is a promising pre-concentration device for *in-situ* derivatisation. The silicone proved inert and reusable. Loading of derivatising reagent requires less time and effort, and the sample collection set-up is cheap, convenient and portable for fieldwork.