Chapter 7

Conclusions

Two approaches for concentrating analytes in PDMS were investigated in this study, namely, 1) the on-line concentration and *in-situ* derivatization of volatile polar analytes from air followed by resonance-enhanced multiphoton ionization time-of-flight mass spectrometric (REMPI-TOFMS) detection, and 2) the concentration of phenolic lipophilic analytes from water requiring derivatization prior to analysis by GC/MS. The study has demonstrated that the PDMS MCT is versatile and has the ability to concentrate volatile aldehydes and amines at the low ppb level from the gas phase, and alkylphenols at the low ppt level from the aqueous phase.

In this study we set out to (1) reduce the complexity and cost of the sampling system involved (2) reduce the experimental uncertainties/errors (3) lower the limit of detection.

7.1. On-line analysis of volatile aldehydes and amines from air using PDMS traps

This study is a novel investigation of on-line *in-situ* derivatization of volatile aldehydes and amines in silicone rubber traps in order to pre-concentrate and render them visible to a REMPI-TOFMS. Formaldehyde was detected for the first time in an on-line study by single photon ionization time-of-flight mass spectrometry (SPI-TOFMS).

Unlike most other pre-concentration devices used to determine aldehydes and amines, the silicone rubber trap is inert, rugged, simple and inexpensive.

In the study, recovery of the derivatives was achieved by thermal desorption which (1) reduced the time required for on-line analysis (2) removed the need for expensive, toxic solvents and (3) rendered the silicone trap immediately reusable. No thermal degradation products from the silicone rubber trap were detected with this technique. No deterioration in the performance of the traps was observed.

Permeation tubes were successfully prepared and calibrated to provide reliable aldehyde and amine gas standards in the ppm range. The thermal depolymerization of paraformaldehyde yielded a stable formaldehyde gas standard.

Phenylhydrazine and benzaldehyde were selected as the most suitable derivatizing reagents for the on-line study. Simultaneous introduction of the analyte and headspace vapour of the derivatization reagents into the silicone rubber was successfully achieved. This reduced sample preparation time and allowed for the rapid introduction of reagent and analyte into the system.

SPME was used to determine reaction efficiencies for the analytes, in a PDMS matrix, with the selected reagents. The results were satisfactory, especially considering that the reactions occurred at room temperature without the assistance of a catalyst. Formaldehyde yielded a low reaction/concentration efficiency of 41% with phenylhydrazine in PDMS, while acetaldehyde, acrolein and crotonal displayed improved values of 92%, 61% and 74% respectively. Both propylamine and butylamine yielded 28% reaction/concentration efficiency with benzaldehyde in the PDMS matrix.

The analytes were successfully converted in the on-line *in-situ* derivatization set-up. The derivatives were detected by the REMPI-TOFMS and identities confirmed by GC/MS. Analytes that were previously undetectable by REMPI-TOFMS could now be detected. Using this concept other compounds should now also be amenable to REMPI-TOFMS analysis.

Testing two different types of PDMS concentrators proved that larger PDMS volumes provide increased analyte capacity. Larger quantities of derivatives were concentrated on the combined OTT-PDMS MCT than on the open tubular PDMS trap alone. However, thermal desorption from the thermal modulator array, used to desorb the OTT, provided shorter desorption times than the enrichment desorption unit used to desorb the PDMS MCT.

Both PDMS concentration devices provided detection limits that were significantly lower than the permissible exposure limits (PELs) for the volatile aldehydes and amines investigated, set by the Occupational Safety and Health Administration (OSHA).

7.1.1.Further work

Further testing using a stable formaldehyde gas standard is recommended. Obtaining external calibration curves using permeation gas standards would then allow for quantification of real samples. Testing the method on-line in industrial factories or the office workplace would be required to emphasise the concentration ability of PDMS and the selectivity of the detection technique.

7.2. Determining endocrine disruptors from water by concentration and derivatization in PDMS traps

Trifluoroacetate derivatives of bisphenol-A, the alkylphenols: *tert*-octylphenol, 4-*n*-nonylphenol, and the estrogens: estrone, estriol and 17β-estradiol were successfully formed in the PDMS MCT and detected by GC-(EI) MS. However, 17α-ethinylestradiol, the crucial estrogen urgently requiring detection, could not be converted. In addition, to reach the mandatory ultra trace detection levels needed for estrogens, it would be better to convert them into their pentafluorobenzoyl derivatives and analyse these by GC- (NCI) MS. Although methods used to derivatize the estrogens with PFBCl alone were not successful, dual derivatization using PFBCl and TFAA showed promising results. Further investigation of these reactions is recommended.

The gravity sampling procedure for the analysis of water using the PDMS MCT was very simple. Water was allowed to run through the trap at a flow rate determined by the restrictor at the exit end of the trap. During this process the analytes partitioned into the trap. Thereafter the water was purged from the trap and derivatizing reagent was added to the trap using a syringe. The trap was capped and the reaction was allowed to occur at room temperature. The PDMS MCT was then thermally desorbed and analysed by GC- (EI) MS.

At room temperature and without the presence of a catalyst, the reaction of the alkylphenols with trifluoroacetic acid anhydride in the PDMS matrix was 100% complete after 5 minutes. Bisphenol-A reacted to less than 50% completion during this period, however, the amount of derivative formed remained constant.

Complete transfer of the formed derivatives off the PDMS MCT was achieved through optimization of thermal desorption and injection conditions.

Determination of the extraction efficiencies of the alkylphenols and bisphenol-A revealed a problem with the PDMS MCTs. Poor batch-to-batch repeatability in extraction efficiency indicated that the PDMS matrix is not homogenous. For two different PDMS batches: t*ert*-octylphenol displayed extraction efficiencies of 70% and 79%, nonylphenol 84% and 43% and bisphenol-A 10% and 26% respectively. A t-test confirmed that the mean results obtained between batches for each analyte were significantly different.

Our study has revealed that although the PDMS MCT has potential as a pre-concentration device for aqueous samples using *in-situ* derivatization it has several limitations. Persistent carry-over problems inside the desorption unit restricted the limits of detection for the alkylphenols and bisphenol-A. In addition poor reproducibility between PDMS batches decreased the reliability of the extraction technique. The silicone proved inert and reusable only when all the water had been removed. Removal of water from the PDMS MCT was a time-consuming step.

7.2.1.Recommendations

Placing an excess of sample, reagent or analyte on the MCT for thermal desorption should be avoided as it leads to contamination of the desorption unit. Regardless of the presence of a permanent purge flow in the desorption unit, carry over does occur, causing memory effects and compromising detection limits.

Only derivatization reagents that produce neutral by-products should be used directly in the PDMS matrix. Examples would be diazomethane reagents, which release harmless nitrogen gas and phenylhydrazine or benzaldehyde that form water as a by-product. In all other cases, derivatization should be performed in the sample matrix, followed by extraction into the PDMS. The extraction step should also selectively exclude the absorption of excess reagent.

Unless working with 100 % pure PDMS, it cannot be assumed the PDMS matrix is inert and hydrophobic. It was observed in this study that the trifluoroacetic acid by-product forms hydronium ions (H_3O^+) in the presence of water retained by the fumed silica (SiO_2) filler in the PDMS. The hydronium ions catalysed the degradation of the PDMS matrix.

7.2.2. Further work

The possibility of manufacturing a pure PDMS matrix for further studies needs to be explored, particularly for extraction of analytes from aqueous matrices.

The extraction efficiencies for the analytes were not repeatable. The reason for this will need to be investigated further. The entire process for repeat extraction-derivatization-thermal desorption is lengthy. In addition, the EI MS source becomes contaminated with PDMS degradation product deposits and large quantities of liquid nitrogen are consumed in the process. A more cost-effective and efficient manner to investigate the analyte partitioning into the PDMS would be to use a syringe pump and UV detector setup as applied by Ortner [63].

Extraction efficiency tests should also be conducted on new and used traps as it is suspected that *damage to the traps caused by H_3O^+ ions may contribute to differences in partitioning between new and old traps*. The setup as applied by Ortner [63], can also be used to determine the optimum sampling flow rate for the analytes through the MCT. A sampling flow rate of 50 µl/min was used in our study. This selection was based on results obtained by Ortner [63] where benzene in water yielded 11 plates on a 32 MCT at a flow rate of 75 µl/min.

Since it remains desirable to use the MCT for on-site concentration followed by derivatization, the use of derivatization reagents, yielding neutral by products, such as the fluoroacylimidazoles instead of the acyl acid anhydrides should be investigated. The reaction may not proceed to completion as rapidly as for the acid anhydrides, but the by-product is the relatively inert imidazole. Thus the need to remove every last bit of water vapour may be reduced and sample preparation further simplified.

From the theory discussed in chapter 2, it appears that the PDMS MCT has potential as a concentrating device, due to its open tubular nature and very large analyte capacity. Provided the above limitations are resolved the trap could be tested in the field.

It would also be interesting to examine the extraction and derivatization of ultra trace-level analytes, for example the estrogens, using electron-capturing derivatives analysed by GC-NCI-MS, GC-ECD and even GCxGC-ECD or GCxGC-TOFMS to obtain improved detection levels and simplicity in sample preparation.