Chapter 6

Conclusion

Combustion of fuels, particularly fossil fuels, is a major source of air pollutants in developing countries in addition to industrial emissions. Traffic densities in urban areas are also increasing which mainly involves an aged vehicle fleet without catalytic converters. Poor indoor air quality is often of concern, due to the use of open fires for cooking and heating purposes in the developing world.

Inorganic air pollutants were found to be far more routinely monitored than organic air pollutants in southern Africa, which is of concern due to the potential for release of organic species from the sources present, as well as due to the potential human toxicity of such molecules including polychlorinated dibenzodioxins and polyaromatic hydrocarbons.

The lack of organic atmospheric pollutant monitoring in southern Africa may be due to a number of reasons including socio-political priorities and lack of equipment, funding and skilled human resources. The use of alternative cost-effective analytical methods for air pollutants to the standard comprehensive techniques may therefore provide for more widespread monitoring campaigns in the region. Such alternatives may include the use of passive samplers, the monitoring of indicator compounds, or screening methods.

This study was initiated in order to develop such alternative methods for organic air pollutant monitoring, which are more applicable to developing countries. The techniques were required to be rapid, and have acceptably low limits of detection for the envisaged applications thereof. In addition, sufficient selectivity and minimal sample clean-up and separation processes prior to analysis were needed, and the possibility for interfacing with more comprehensive techniques for further quantitative analysis post screening was preferable.

Multi-channel silicone rubber traps were applied as pre-concentrators of the target organic air pollutants in this study and they provided the advantage of allowing for direct thermal desorption - gas chromatographic analysis of samples, thereby negating the need for solvent extraction and pre-concentration, which can lead to sample loss or contamination. The multi-channel silicone rubber traps, which contained twenty two parallel, 55 mm long 0.3 mm i.d. PDMS tubes housed in a 178 mm long, 6 mm o.d. quartz tube, were inexpensive to manufacture and could be re-used.

It was shown theoretically that these traps can serve as denuders in PAH sampling, where the gas phase analyte is collected on a primary trap, whilst particle associated analyte is collected on a downstream quartz fibre filter. Any gas phase PAHs which break through the primary trap, as well as any analyte which re-volatilises from the particle associated phase, is collected on a secondary trap placed after the filter. The traps can then be analysed directly by LIF and/or TD-GC-MS (which also allows for direct TD analysis of the filters). TD allows for the total transfer of the sampled analytes onto the GC column, which enhances sensitivity as compared to solvent extraction based methods, and thereby facilitates shorter sampling times and lower sampling flow rates. The use of denuders in PAH monitoring is important due to the different potential health and environmental impacts of these analytes in different phases, therefore denudation was tested in various applications of relevance to southern Africa.

Trace organic air pollutant analysis requires reliable gas standards. For the LIF method developed in this study it was also necessary for the analyte to be evenly spread over the 22 PDMS tubes contained in the sample trap. Permeation tubes were found to be suitable for the generation of gas standards of the more volatile trace organic air pollutants such as chlorobenzene and the dichlorobenzenes, with permeation rates in the range of a few to ~40 $ng.min^{-1}$, whilst cost effective, custom made diffusion tubes were found to provide reliable quantities of naphthalene at ~ 2 $ng.s^{-1}$. A portable sampling pump was used to load known amounts of analytes from these tubes onto sample traps.

A gas chromatographic fraction collection method utilizing a GC equipped with a modified FID was optimized for the loading of traps with pre-determined quantities of other trace organic air pollutants which were less volatile than naphthalene, including phenanthrene and pyrene. This collection technique was possible due to the open geometry of the trap, which did not impact on the GC column flow rate. Even though collection efficiencies were not optimal (50 – 60 %), reasonably reproducible recoveries allowed for the correction of analyte losses during loading. Comparison of LIF and GC-MS analyses of the less volatile PAHs was possible with this standard collection method, which would be cost effective for laboratories equipped to analyse the analytes of interest, where GC equipment and solid standards are available. The fraction collection technique offers the additional advantage of loading analytes after capillary chromatographic purification in cases where high purity standards are not readily available, and it may find application in other spectroscopic studies.

The novel LIF method which was developed in this study utilizes the inherent fluorescent properties of PAHs, where a tunable dye laser with a frequency doubling crystal provides excitation radiation of a specific wavelength for the target PAH which has been sampled onto a quartz multi-channel silicone rubber trap. Additional selectivity is provided by the use of a monochromator to detect the fluorescence emission. It was found that a 292 nm excitation wavelength, which was optimal for naphthalene, was also potentially suitable for phenanthrene determinations, but not for pyrene.

The LIF technique was found to be basically non-destructive, with low photodegradation losses over the time interval of a screening analysis, as the photolytic half life of naphthalene was ~35 min. The traps could therefore be subsequently quantitatively analysed by TD-GC-MS without the need for any sample extraction or additional pre-concentration. The LIF method LOD was found to be ~20 ng for a signal to noise ratio of 3:1, and the breakthrough volume (10 %) of the traps was estimated to be in the order of 4 ℓ for naphthalene based on both LIF and TD-GC-MS experiments. This relates to a sampling interval of ~8 min at 500 mℓ.min^{-1}, and as the GC-MS can detect 1 pg with a signal to noise ratio of 400:1 in total ion current (TIC) chromatogram mode, a detection limit of ~0.3 ng.m^{-3} can be calculated for this breakthrough volume.

The variation in incident laser energy proved to be the greatest source of variability in results of LIF repeatability experiments, although the ≤15 % RSD in oscilloscope response was deemed acceptable for a screening method.

The methods developed were successfully tested in a number of applications which are of relevance to southern Africa, as emissions from sugar cane burning, household fires, diesel vehicles and industries were sampled onto the quartz multi-channel silicone rubber traps, which were in the denuder configuration in some cases. The samples were successfully screened by LIF and were subsequently analysed by TD-GC-MS. The LIF method allowed for the differentiation between impacted and non-impacted industrial sampling sites, and the importance of naphthalene as an indicator for atmospheric PAHs was verified in that this PAH was the most abundant in the various applications which were investigated. Our focus on utilizing the LIF method to screen for naphthalene was therefore validated.

The LIF method developed in this study has the potential to serve as a screening tool to avoid the comprehensive analysis of samples which do not contain appreciable levels of PAHs. The experimental procedure is simple and rapid, with acceptably low limits of detection, even with the initial, unoptimized optical arrangement and without extensive time-averaging. LIF also provides selectivity without the need for sample clean-up and separation processes, which may entail the use of organic solvents and cryogenic equipment.

The multi-channel silicone rubber traps allow for the pre-concentration of analytes and in addition they may provide a useful means of simultaneously physically separating mixtures of analytes in air samples in the trap, as a consequence of chromatographic frontal separation processes occurring through the trap during sampling, allowing for the deconvolution of more complex fluorescence spectra.

The LIF method could be further optimised by improving the laser energy stability, as well as by the investigation of possible time resolution techniques, for example. It is possible that the LIF method could be utilized in real-time applications, with continuous air sampling through a multi-channel silicone rubber trap. This could provide an indication of changing PAH levels with good time resolution even at low concentrations, due to the sensitivity of the method.

As equipment cost considerations were important, it is possible that the LIF screening method could find application in a centralized environmental laboratory for the southern African region. Alternatively, a portable atmospheric PAH screening tool based on the principles developed here could be developed. This would facilitate the widespread monitoring of atmospheric PAHs in a cost effective manner.