Characterisation of atmospheric semi-volatile organic compounds

Patricia B.C. Forbes[1]*, Erwin W. Karg[2], Genna-Leigh Geldenhuys[1,3], Sifiso A. Nsibande[1], Ralf Zimmermann[2,4] and Egmont R. Rohwer[1]
[1] Laboratory for Separation Science, Department of Chemistry, University of Pretoria, Lynnwood Road, Pretoria, 0002, South Africa, patricia.forbes@up.ac.za
[2] Cooperation Group "Analysis of Complex Molecular Systems", Joint Mass Spectrometry Centre, Helmholtz Zentrum München, D-85758 Neuherberg, Germany
[3] Mineral Processing Laboratory, Impala Platinum Limited, 123 Bethlehem Drive, Rustenberg, 0299
[4] University of Rostock, Division of Analytical and Technical Chemistry, D-18059 Rostock, Germany

Atmospheric semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), are ubiquitous environmental pollutants, which may be present in the gaseous phase and adsorbed onto the surface of aerosol particles. A novel portable miniature denuder consisting of two multi-channel silicone rubber traps separated by a quartz fibre filter has been developed for such applications. It allows for the concentration of SVOCs in each phase to be determined, which is important for human health risk assessments. The overall particle transmission efficiency through the denuder was found to be 92 ± 4% for particles between 16 and 320 nm. SVOCs in the traps (gas phase) or on the filter (particle phase) are analysed by GC-MS, or by GCxGC-MS for enhanced separation capability. This enhances detection limits and allows for lower sampling flow rates and shorter sampling times. These denuders have been applied in studies involving the monitoring of emissions from domestic fires, vehicles and underground mine diesel engines.

Keywords: denuder, particulate matter; aerosol; semi-volatile organic compounds; polycyclic aromatic hydrocarbons; silicone; GCxGC-MS; air quality; human health.

1. Introduction

Atmospheric semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), are emitted from widespread anthropogenic sources such as domestic fires and internal combustion engines. This is of concern due to the potential human health effects of a number of these compounds, especially in light of the recent declaration of diesel exhaust emissions as a human carcinogen (IARC, 2012).

In the atmosphere, SVOCs partition between the vapour phase and particulate phase, where they are adsorbed onto the surface of aerosols. This partitioning depends on the vapour pressure of the particular SVOC as well as the total suspended particulate loading and may be described in terms of a partition coefficient, K_{vp} (Krieger and Hites, 1994).

It is important to be able to quantify the relative contributions of each of these phases of the analyte, as they may have different environmental impacts. Deposition and uptake of inhaled toxic species in the human respiratory system depends on phase distribution (Temime-Roussel, 2004a). Environmental cycling, such as atmospheric transport and transformations, are also phase dependent (Bidleman, 1988).

Sampling of each of these phases is complex, as it must be ensured that blowoff of particle adsorbed analyte does not occur (which would underestimate the particle phase concentration and overestimate the gas phase). Similarly, adsorption of gas phase analyte onto the particles collected during sampling must be prevented (this would underestimate gas phase concentrations and overestimate particle phase loading).

This paper describes a novel, miniature and portable denuder device which has been shown to be effective in sampling and pre-concentrating atmospheric SVOCs in both the gas and particle phases.

2. Methodology

2.1 The denuder device

The denuder consists of two multi-channel silicone rubber traps in series, which are separated by a 6 mm diameter quartz fibre filter held in place by a Teflon connector. Each trap contains 22 parallel polydimethylsiloxane (PDMS) tubes (55 mm long, 0.3 mm i.d. and 0.64 mm o.d.) which are housed in a 178 mm long glass tube (Fig. 1).

The gas phase SVOCs are sorbed into the PDMS in the first (primary) trap (Ortner, 1996), whilst particle phase analytes pass through the trap and are collected on the downstream filter. The transmission efficiency was evaluated theoretically and was found to be promising, therefore particle transmission tests were performed to confirm these results, as discussed in Section 2.2. Blowoff of SVOCs from the filter should be minimal due to the low pressure drop across the sampling system, the short sampling time (10 min) and the constant ambient sampling temperature. However, any gas phase analytes which breakthrough the primary trap are collected on the downstream secondary PDMS trap.

2.2 Laboratory particle transmission tests

A multi-channel silicone rubber trap and a bypass line were connected in parallel by means of electrically conducting tubing with valve connections to allow for switching of aerosol flow between them (Forbes, 2012). The flow rate in each line was maintained at 500 mL.min^{-1}, which is the same flow rate as used in the denuder field applications.

Ammonium sulphate aerosol particles were generated by a jet nebulizer (Trijet, Model 3460, TSI, USA). The particle size distribution had a modal diameter of ~50 nm and there were >10^{5} particles.cm^{-3}. Particle size analysis was performed by a scanning mobility particle sizer (SMPS, Model 3081, TSI, USA) and a condensation particle counter (CPC, Model 3775, TSI, USA) was used to determine particle number concentrations (Fig. 2).

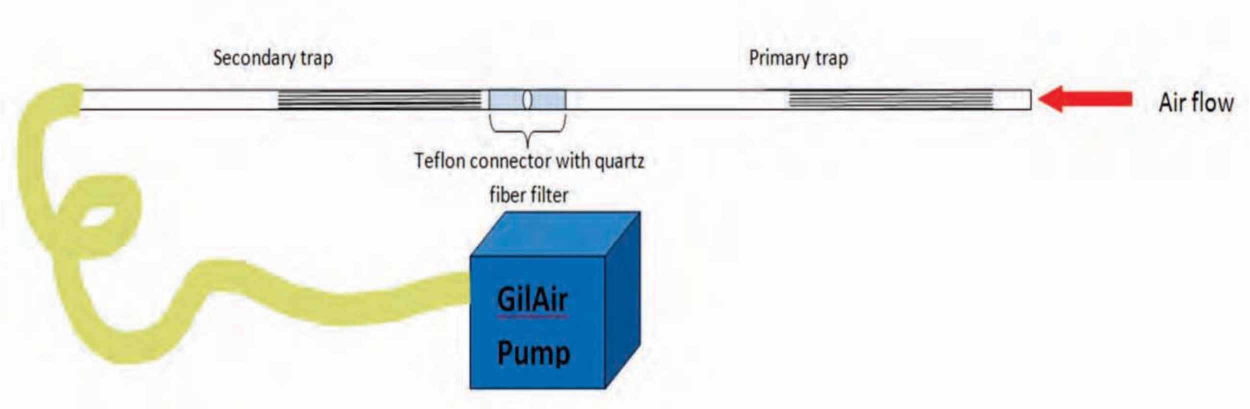

Figure 1 Multi-channel silicone rubber trap based denuder device.

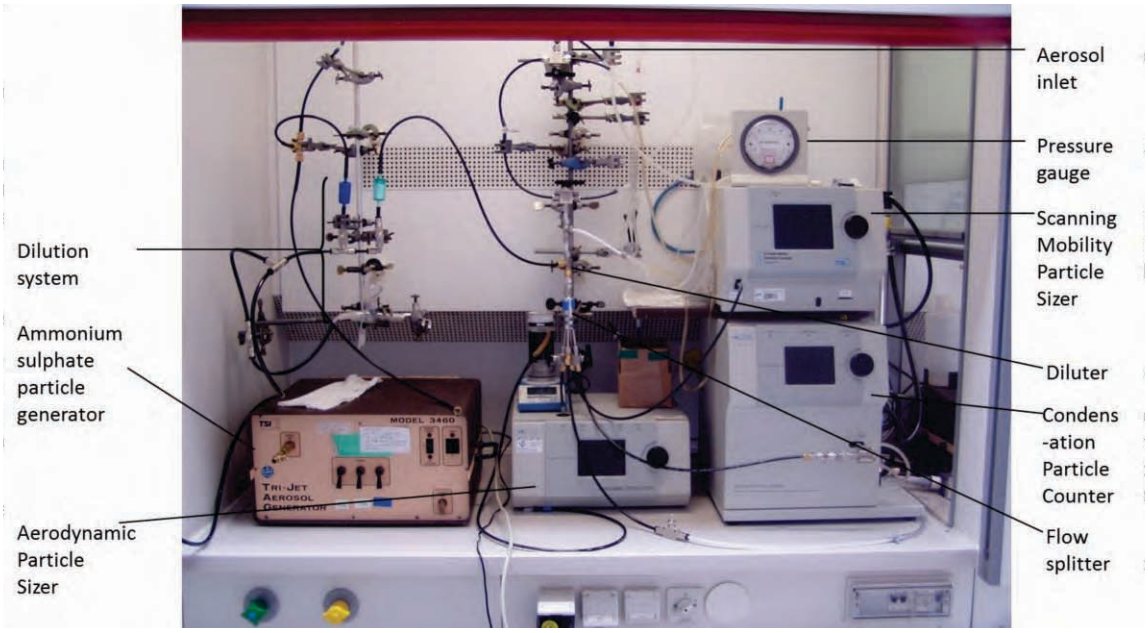

Figure 2 Experimental setup used for the determination of the denuder particle transmission efficiency.

2.3 Field applications

Domestic fires (wood and charcoal fuel mix) were lit in traditional braziers using either the traditional or the basa njengo Magogo (upside down) methods of lighting a fire. Air samples were taken at the fire using our denuder device coupled to a portable Gilair sampling pump operating at 500 mL.min^{-1} for 10 min. The traditional fire was sampled 40 min after ignition, whilst the basa njengo Magogo fire was sampled directly after ignition.

Similarly, air samples were taken at the exhaust of an idling diesel passenger vehicle under cold start conditions. Here 2 traps in series as well as an empty glass tube followed by a filter and a secondary PDMS trap were used to sample both in parallel to a full denuder setup.

In a third study, air samples were taken onto denuders in underground platinum mines.

2.4 Analytical methodology

Comprehensive two-dimensional gas chromatography with time of flight mass spectrometric detection (GCxGC-TOFMS, LECO Pegasus 4D) was employed in the analysis of thermally desorbed (TD) (Gerstel TDS 3) filter samples (particle associated SVOC emissions) and silicone rubber traps (gas phase SVOC emissions). Helium was used at a desorption flow rate of 50 mL.min^{-1} and analytes were cryogenically focussed at -40 °C. The primary column was a 30 m RTx 5SilMS (250 μm id; 0.25 μm film thickness) and the secondary column was a 0.790 m RTx 200 (180 μm id; 0.2 μm film thickness). The modulation period was 4 s.

3. Results and discussion

The particle transmission efficiency was determined from the ratio of the denuder and bypass particle concentrations, and was found to be 92 ± 4% and the particles ranged from 16 to 320 nm. The transmission efficiency was found to be constant during the sampling period. The median diameter of the particles transmitted by the denuder was 64 nm and 59 nm for the bypass.

The particle size distributions of transmitted particles was very similar for the denuder and bypass line for particle sizes >100 nm. However, the transmission efficiency of the denuder decreased for particles <80 nm, with transmission efficiencies of <60% for particles <20 nm. It is likely that electrostatic and diffusional effects contributed to loss of these very small particles inside the denuder.

TD-GCxGC-MS analysis of the gas phase domestic fire samples yielded chemical fingerprints of the semi-volatile organic compounds present based on relative peak areas and MS library matching (Fig. 3). Differences between the two compound classification profiles are evident, and the traditional fire appeared to have poorer combustion conditions (higher unsaturated hydrocarbon levels) even 40 min after ignition, by which time combustion conditions should have been favourable. Higher levels of PAHs and PAH derivatives were found in the case of the traditional fire.

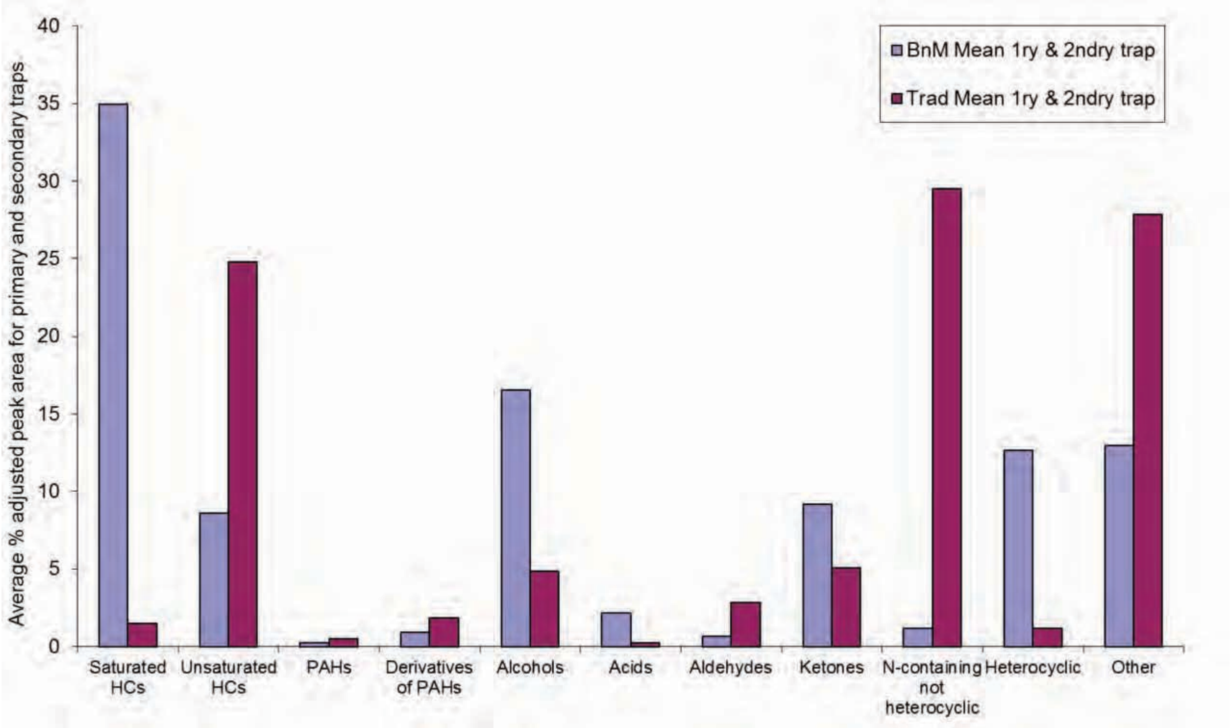

Figure 3 Gas phase semi-volatile organic compound profiles (primary and secondary trap) found for the traditional and the Basa njengo Magogo domestic fire lighting methods.

Analysis of the naphthalene content of the vehicle exhaust samples revealed that no gas phase naphthalene was adsorbing onto the filter or sampled particulate matter, as the same amount of this PAH was found in the primary trap of the trap-trap and in the trap of the tube-filter-trap configurations (Forbes, 2012). Moreover, no breakthrough of naphthalene was evident, in that this compound was not detected in the secondary trap of the denuder sample (the sampling volume was 5 L).

The underground mining samples contained a range of SVOCs, including PAHs, with one of the main sources of these compounds being diesel engine exhaust emissions. The denuder samples were taken in a range of underground environments, and allowed for the chemical fingerprinting of compounds present in both gas and particle phases. The results (which are provided in more detail in a separate paper to this conference) revealed the importance of sampling both phases in order to prevent the underestimation of concentrations and therefore exposures.

There was also a clear difference in SVOC and specifically PAH profiles between the gas and particle phase samples. Heavier PAHs were found associated with the particles, whilst the lighter PAHs, including naphthalene and methylated naphthalene derivatives, dominated the gas phase profiles. In addition, principal component analyses (PCA) confirmed that the denuder was operating effectively, as the gas (trap) and particle (filter) phase samples were clearly separated.

4. Conclusion

From a theoretical perspective, this novel denuder met the requirements to effectively sample gas and particle phase SVOCs concurrently. Particle transmission experiments confirmed that 92 ± 4% of particles ranging from 16 to 320 nm were transmitted by the multi-channel silicone rubber trap. Transmission efficiency through the trap was ~100% for particles >50 nm at a flow rate of 500 $mL.min^{-1}$. It has been reported that >95% of particle bound PAHs are associated with particles in the size range between 0.1 and 8 µm (Temime-Roussel, 2004b), and the denuder transmits particles very efficiently in this size range.

TD-GCxGC-MS analysis allowed for the identification of SVOCs, including PAHs, present in the gas and particle phases, as each component of the denuder (PDMS traps and the filter) is analysed separately.

The denuder has been shown to operate effectively in a range of applications, including domestic fuel combustion and in monitoring emissions from diesel engines, both from passenger vehicles and in underground mines.

The denuder is small and is highly portable, and only requires the use of a small, portable battery operated sampling pump.

5. Acknowledgments

The German-South African Year of Science Programme is acknowledged for funding. LECO South Africa, SASOL and the NRF are thanked for resources provided. The CSIR and Plat Mines are acknowledged for funding and assistance with the mining samples.

6. References

Bidleman T.F., 1988, 'Atmospheric processes', *Environmental Science and Technology*, **22**:361-367.

Forbes P.B.C., Karg E.W., Zimmermann R. & Rohwer E.R. 2012, 'The use of multi-channel silicone rubber traps as denuders for polycyclic aromatic hydrocarbons', *Analytica Chimica Acta*, **730**:71-79.

IARC (International Agency for Research on Cancer), World Health Organisation, 2012, 'Diesel engine exhaust carcinogenic', Press Release no. 213, 12 June 2012.

Krieger M.S., Hites, R.A., 1994, 'Measurement of Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons in Air with a Diffusion Denuder', *Environmental Science and Technology*, **28 (6)**:1129-1133.

Ortner E.K. & Rohwer E.R., 1996, 'Trace analysis of semi-volatile organic air pollutants using thick film silicone rubber traps with capillary gas chromatography', *Journal of High Resolution Chromatography*, **19**:339-344.

Temime-Roussel B., Monod A., Massiani C. & Wortham H., 2004a 'Evaluation of an annular denuder tubes for atmospheric PAH partitioning studies—1: evaluation of the trapping efficiency of gaseous PAHS', *Atmospheric Environment*, **38**:1913-1924.

Temime-Roussel B., Monod A., Massiani C. & Wortham H., 2004b 'Evaluation of an annular denuder for atmospheric PAH partitioning studies—2: evaluation of mass and number particle losses', *Atmospheric Environment*, **38**:1925-1932.