Application and validation of a pocket diffusive sampler for determination of VOCs in air using TD–GC–MS

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Introduction

Diffusive – or passive – sampling has been widely adopted as a sampling technique for determination of volatile organic compounds (VOCs) in air. It offers a convenient, low-cost and unobtrusive solution for a range of applications, including industrial hygiene and indoor air monitoring, and is well suited to large-scale environmental monitoring campaigns. Whilst axial and planar (badge) samplers remain the most widely adopted passive sampling approaches, radial samplers with their increased sampling rate can offer advantages for short-term monitoring or longer-term sampling at trace levels.

Principles of diffusive sampling

Diffusive samplers work on the basis of Fick's first law of diffusion, whereby analytes will migrate to the surface of a sorbent at a rate that is proportional to the concentration of the analyte in the atmosphere (C), as illustrated in Figure 1.

Fick's law relies on the following conditions being met:

- Ambient analyte concentration at the sampling surface.
- Zero concentration of the analyte at the surface of the sorbent.
- A linear concentration gradient between the two.

The proportionality constant is known as the uptake rate (U) – or sampling rate – and once this is known, it enables airborne concentrations to be calculated from the mass of analyte collected on the sorbent.

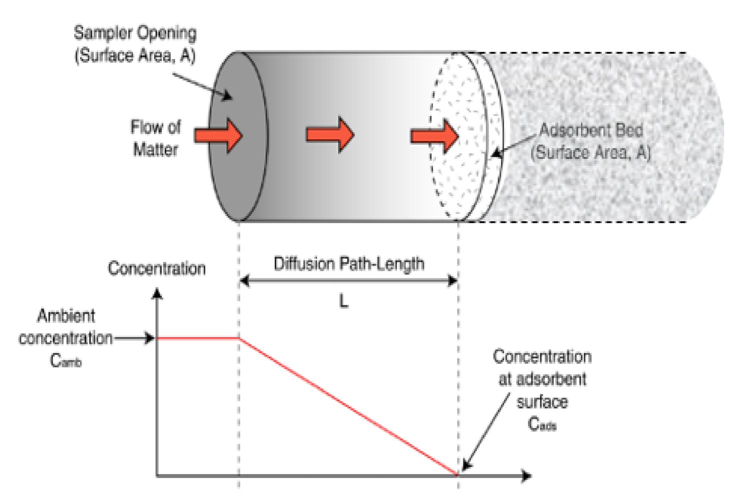

Figure 1: The principle of diffusive (passive) sampling.

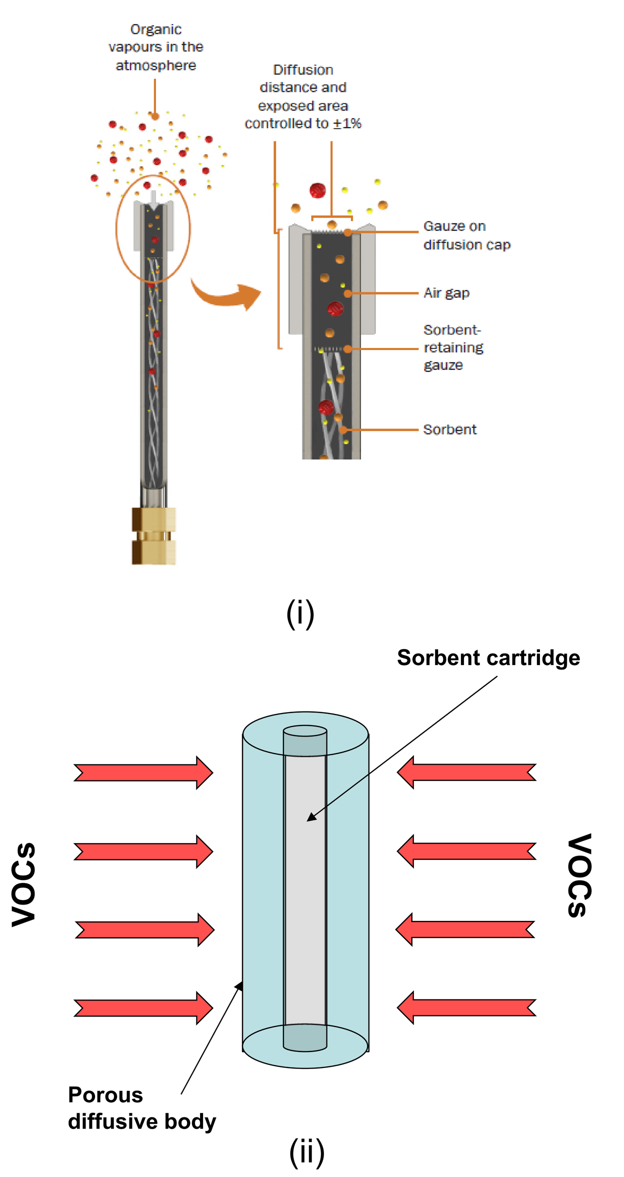

Figure 2: Schematic showing diffusion process for (i) axial and (ii) radial diffusive samplers.

Axial diffusive samplers rely on diffusion of analytes onto a single surface of sorbent at one end of a sampling tube, as in Figure 2(i). For consistency of uptake rates, the majority of international standard methods for diffusive sampling are standardised on a specific tube dimension (3.5 inch x ¼ inch) for thermal desorption (TD) analysis.

The geometry for diffusion onto radial samplers, however, is different. They comprise a cylindrical sorbent cartridge that is housed in an outer casing, which enables air to diffuse through it, as in Figure 2(ii).

This approach means that the entire curved cylindrical surface of the sorbent cartridge is exposed to the atmosphere, resulting in a larger surface area of adsorption, thus increasing the rate of diffusion onto the sorbent (*i.e.* sampling rate).

The cartridge and casing are normally fixed in place using a holder or adaptor during sampling. Subsequently, empty 'carrier' TD tubes are used for transporting/storing the sorbent cartridges (before and after sampling) and for TD analysis.

Design considerations for a novel diffusive sampler

A novel diffusive sampler – the pocket diffusive (POD) sampler – has been developed with the aim of improving existing commercially available designs. The dimensions and geometry of the sampler incorporate several enhanced design features, including:

- Porous diffusive body fits snugly over an adsorbent cartridge (Figure 3). No air gaps plus a short porous diffusion path minimise the effect of air speed variation and improve reproducibility of results.
- Compact sampler requires a reduced level of sorbents, aiding detection of VOC/SVOCs at lower levels due to reduced sorbent artefacts.
- Push-on cover prevents migration and ingress of sample during transport. Removing and replacing the cover acts as a convenient start/stop mechanism for sampling.
- Sampler's design ensures that analytes that are diffusing through the body at the end of the sampling period continue to transfer onto the cartridge. This provides improved data reliability, especially when using short sampling times.

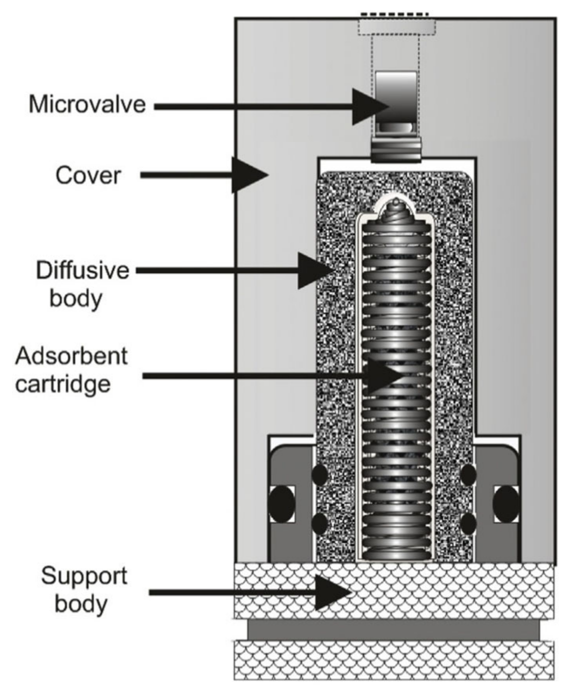

Figure 3: Cross-sectional view of a POD sampler.

Figure 4: Component parts of a POD sampler.

Straightforward sampling workflow

1. Deploy the POD sampler in the desired location. Record the time and temperature.
2. Remove the cover to begin sampling.
3. Replace the cover after the sampling period. Record the sample time and temperature.
4. Transfer the adsorbent cartridge to a carrier tube with negligible manual handling of the cartridge (the POD is compatible with industry-standard tubes and 4-mm i.d. glass tubes).
5. Analyse by TD–GC–MS. POD samplers can be reused multiple times.

Validation of sampling rates

The POD sampler is initially validated under laboratory and field conditions for the measurement of a range of VOCs.[1] Experimentally determined sampling rates for a range of commonly monitored VOCs are shown in Table 1.

Good reproducibility has been determined, with average coefficients of variation being ~3%. In field studies, within the range of tested wind velocities (0.1 to 5 m/s) and temperatures (-30 to 40°C), the overall uncertainty estimated for the sampling of benzene, for instance, was ~9%. This is compliant with the data quality objectives of the EU air quality directive 2008/50/EC.

Table 1: Experimentally determined sampling rates for the VOC POD sampler.[1]

Compound type	Compound	Sampling rate (mL/min)
Alkanes	n-Butane	4.94
	n-Pentane	8.59
	n-Hexane	8.10
	n-Heptane	7.13
	n-Octane	6.29
	n-Decane	3.73
Methyl alkanes	2-Methylpropane	1.28
Alkenes	1-Butene	3.01
	1,3-Butadiene	4.29
	trans-2-Butene	5.97
	cis-2-Butene	4.13
Aromatics	Benzene	8.89
	Toluene	8.10
	Ethylbenzene	6.92
	m- + *p*-Xylene	5.93
	o-Xylene	5.69

Application of radial sampling to environmental monitoring

The faster sampling rate of radial samplers relative to axial diffusive samplers makes them ideally suited to monitoring shorter-term pollution impacts such as the effects of industrial emissions, changes in traffic volumes and short-term weather events. Short-term exposure monitoring for occupational exposure evaluations can also benefit from faster sampling to enable an understanding of the effects of short-term tasks and their exposure potential.

Typical exposure times for sampling of VOCs are:

- Workplace monitoring (up to 6 hours).
- Ambient and indoor air monitoring (up to 30 days).

When used for monitoring personal exposure, the sampler should be mounted in the person's breathing zone, for example on the lapel of a jacket, but care should be taken to ensure that it is not obscured by clothing (Figure 5). When used for fixed-location sampling, monitors can be placed on a flat surface or hung in position using dedicated holders. If sampling outdoors, samplers can be protected from the elements by means of a shelter constructed from non-emitting materials (Figure 6).

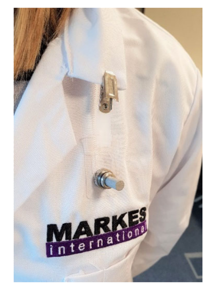

Figure 5: POD sampler with holder for monitoring personal exposure.

Figure 6: POD samplers deployed within a shelter for ambient monitoring.

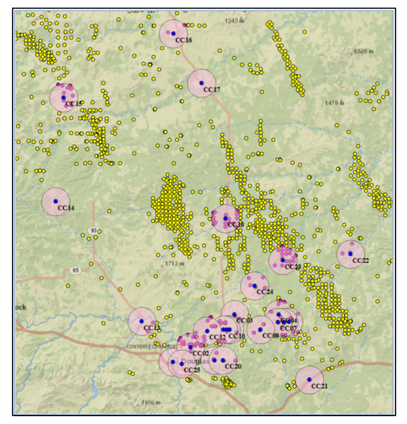

Figure 7: Distribution of samplers in an O&G production region (● = sampler; ◆ = well).

POD samplers have been used for the monitoring of C_4–C_9 hydrocarbons in shale gas in the US, to monitor the impact of oil & gas (O&G) developments on ambient air.

This study demonstrated that POD samplers are effective for measuring air pollutant distributions over wide spatial areas where pollutant concentrations range from background to highly polluted levels.[1]

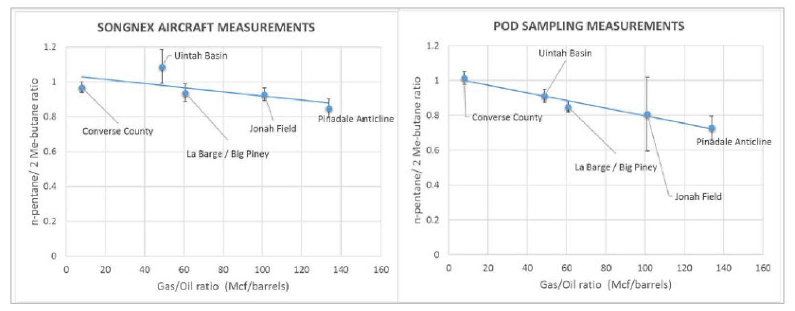

Figure 8: Comparison of data from diffusive and aircraft (Songnex) sampling.

Figure 7 illustrates the wide deployment of diffusive samplers around an area of O&G production. Data collected from these passive samplers were compared to atmospheric data collected by aircraft. A good correlation between the two data sets was shown (Figure 8) when studying the relationship between compound ratios for VOCs linked to O&G production relative to the level of production.

Conclusions

- The POD sampler is a convenient, pump-free approach to sampling VOCs in air and presents a valuable commercial opportunity for environmental sampling.
- The radial diffusive design results in a higher sampling rate than that of conventional axial samplers, facilitating shorter sampling periods or increased detection limits.
- Diffusive samplers may be applied to a range of industrial hygiene and environmental applications. Initial studies demonstrate how POD samplers can be used to provide data on the relative importance of O&G emission sources to ambient air quality.

References

1. P. Pérez Ballesta, R.A. Field, A. Cabrerizo and R. Edie, Unconventional oil and gas development: Evaluation of selected hydrocarbons in the ambient air of three basins in the United States by means of diffusive sampling measurements, EUR 29244 EN, Publications Office of the European Union, Luxembourg, 2018, ISBN 978-92-79-86560-2, doi: 10.2760/818914, JRC108917.

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