Diffusive monitoring – A cost-effective and quantitative approach to environmental monitoring

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Introduction

Diffusive monitoring is widely used in all air monitoring scenarios, *i.e.* occupational hygiene plus indoor air and ambient air monitoring. By eliminating the requirement for a sampling pump, diffusive monitoring provides a simple and cost-effective method of collecting the large number of samples required in many air monitoring programs.

Key applications include:

- personal exposure monitoring
- large-scale environmental studies
- indoor air monitoring.

Various types of diffusive sampler are available, and the decision on the type of sampler depends on the monitoring scenario.

Figure 1: Personnel and fence-line monitoring, both popular applications for diffusive monitoring.

Radial diffusive samplers

Radial 'Radiello®-type' diffusive samplers are ideal for short-term diffusive sampling (30 minutes to 6 hours). Typical sampling scenarios include monitoring the effects of industrial processes, changes in traffic volumes or weather patterns.

In radial diffusive samplers, the diffusion path is *parallel* to the radius of the tube. They have a cylindrical diffusive surface area of 23.6 cm^2 (over 100× greater than tube-type samplers). This, combined with the short diffusive path, means that they have an effective sampling rate typically 100 times that of normal axial tubes.

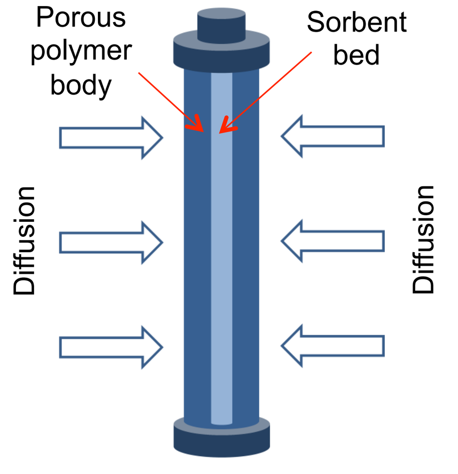

Figure 2: Schematic of a Radiello® radial diffusive sampler.

Tube-type axial diffusive samplers

Early diffusive samplers were badge-type designs, with large cross-sectional areas and short path lengths. However, they suffered from severe restrictions because of air speed effects at the surface of the badge – the stable conditions required for diffusion according to Fick's Law could not be established. Badges were also unsuitable for analysis by thermal desorption–gas chromatography.

In 1979 Working Group 5 of the UK Health & Safety Executive specified a 3½″ × ¼″ o.d. tube-type diffusive monitor, compatible with thermal desorption, that has since become accepted as the 'industry standard'. The first publication detailing the design was published in 1981.[1]

The tube has a cross-sectional area of 0.191 cm^2 and a sorbent-retaining gauze 14.3 mm from the sampling end. This typically gives a diffusive path length (air gap) of ~1.5 cm.

Figure 3: An industry-standard axial diffusive sampler for analysis by thermal desorption.

Using this diffusive tube the atmospheric concentration of a compound is determined using the following equation:

$$\text{Concentration (ppm)} = \frac{\text{Weight of sample on tube (ng)}}{U_{ideal} \times \text{Sampling time (min)}}$$

where U_{ideal} = ideal uptake rate (ng/ppm/min)

The actual uptake rate, which applies to a particular analyte being sorbed onto a particular sorbent under a set of monitoring conditions, may differ significantly from the ideal uptake rate, and will depend on the strength of the analyte–sorbent interaction.

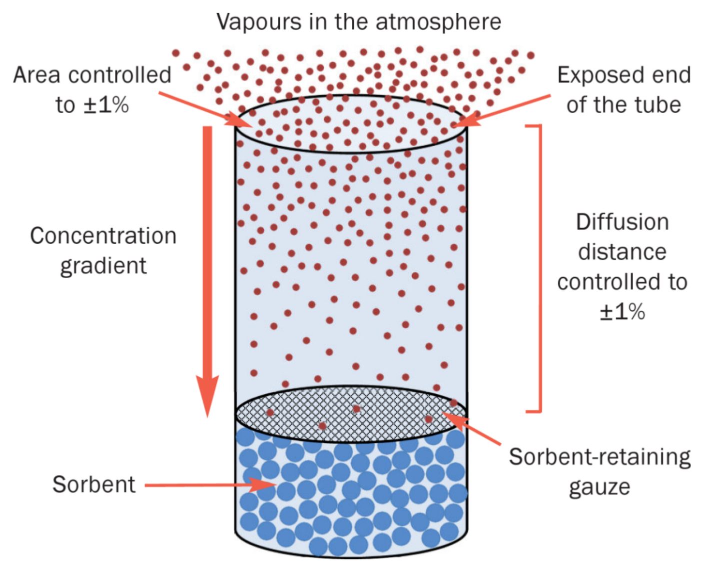

Figure 4: Schematic showing axial diffusive sampling on sorbent tubes.

1. R.H. Brown *et al.*, The development of an improved diffusive sampler, *American Industrial Hygiene Association Journal*, 1981, 42: 865–869.

Diffusive sampling in practice

Is your industrial site a good neighbor? Unobtrusive diffusive (passive) samplers may be placed around a factory fence-line for extended time periods (*e.g.* 3–14 days) to monitor key 'criteria' pollutants (*e.g.* benzene and 1,3-butadiene) (Figure 5).

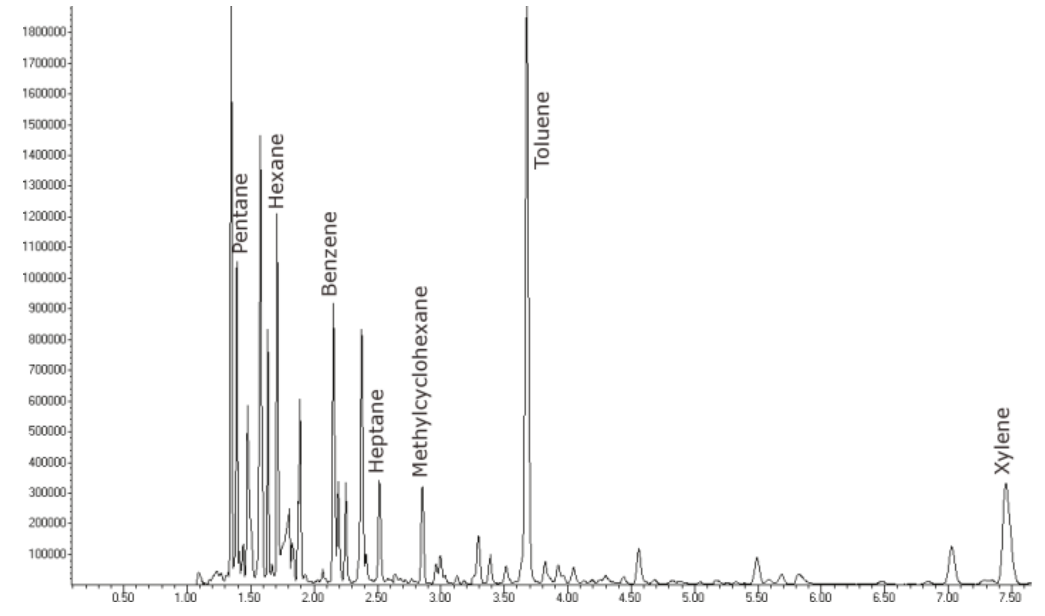

Figure 5: Two-week diffusive sampling around a refinery perimeter. VOCs detected include benzene, toluene and xylene.

Fence-line monitoring data, together with ancillary results taken upwind/downwind of the plant and in local population centers, may simply be used to demonstrate that a particular industrial site is not contributing significantly to ambient hydrocarbon concentrations. Perimeter measurements can also be used in combination with wind speed and direction data to determine emission levels and distribution of emitted hydrocarbons.

Fence-line monitoring of industrial sites can be continuous, but should be carried out at least twice annually – in winter and summer.

Accurate mapping of pollution levels across a major urban centre requires a large number of samplers, which should be dispersed around the area of interest. This allows the generation of maps indicating the degree of pollution around a conurbation, as illustrated in Figure 6.

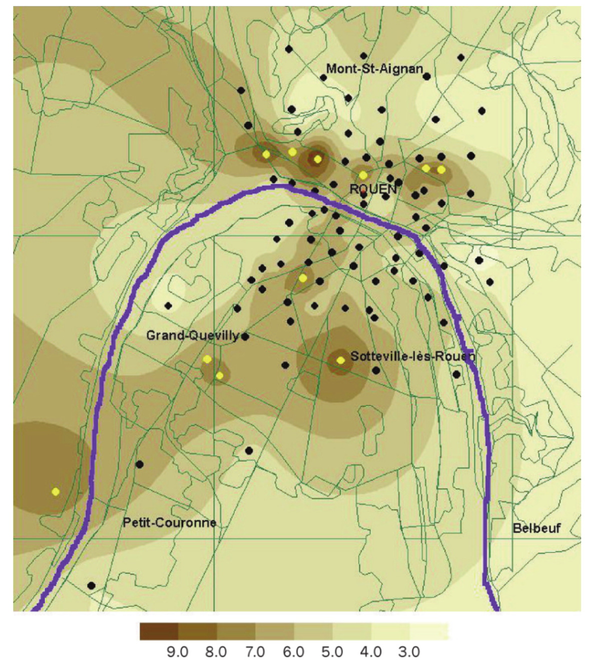

Figure 6: Mapping benzene concentrations around Rouen (France) with low-cost diffusive (passive) samplers.

Diffusive sampling in practice

Diffusive monitoring can not only be used for fence-line monitoring and urban air monitoring, but also to help identify poor health relating to indoor air quality (IAQ) and 'sick building syndrome'. In one case residents were complaining of poor air quality in their home. Diffusive sampling with axial-type sorbent tubes was used to monitor indoor and outdoor air quality and the personal exposure of residents (Figure 7).

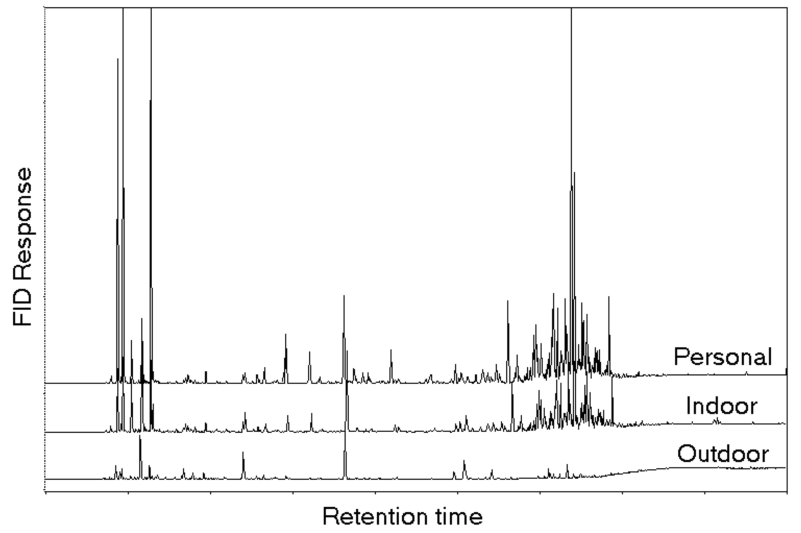

Figure 7: Poor indoor air quality and high personal exposure in this home were linked to a diesel car parked in a garage under the living space.

The information presented in this poster principally relates to monitoring VOCs in ambient outdoor and indoor air. However, other environmental monitoring solutions using diffusive tubes have been developed. These include soil probes for screening organic soil contamination around industrial sites, landfill *etc.*, and ventilation/tracer gas studies. Diffusive soil probes (such as Markes' VOC-Mole™) were first reported by BP in the UK. Hollow metal probes containing diffusion tubes are simply pushed into the ground in a grid pattern covering the site. After ~24 hours the tubes are removed, analyzed and areas of high VOC concentration ('hot spots') identified.

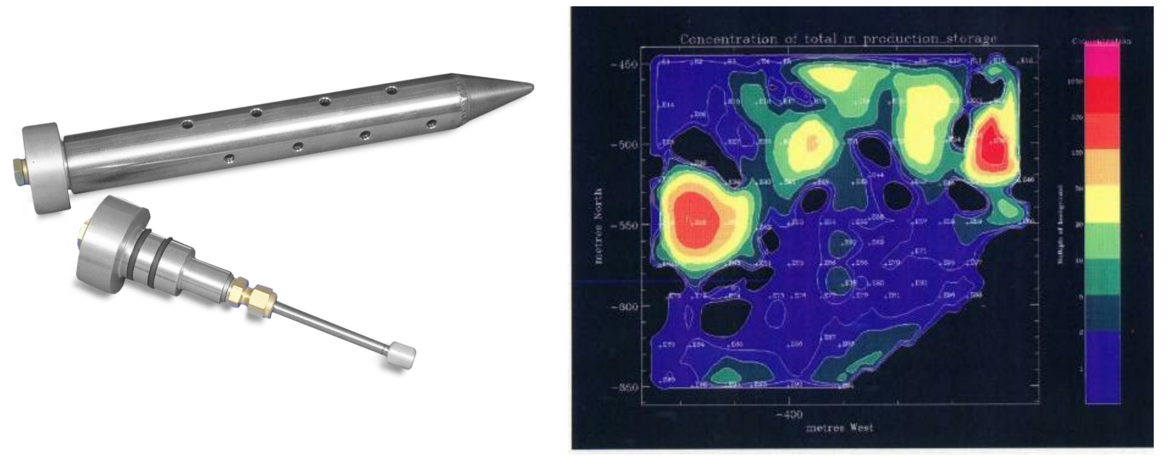

Figure 8: Soil probes such as the VOC-Mole (left) arranged in a grid pattern around an industrial site allow low-cost mapping of contaminated ground.

When diffusive sampling is not suitable

Diffusive sampling is not suitable for all monitoring applications. Diffusive sampling is carried out using sorbent tubes packed with a single bed of sorbent. If several analytes of differing volatilities are to be monitored, requiring two or more different sorbents, then two different diffusive monitors must be used in parallel.

Axial diffusive sampling cannot generally be used with glass or glass-lined tubes, as the cross-sectional area is different from standard stainless steel or Silcosteel® tubes, due to increased wall thickness. The length of the air gap is also hard to define accurately when glass or quartz wool plugs are used to retain the sorbent.

If uptake rate data are not available and if there is no time to measure or calculate an uptake rate, then quantitative diffusive sampling cannot be used.

✓ You know the compound that you are looking for	✗ You are using a multi-bed sorbent tube
✓ There is a validated uptake rate available for that compound	✗ You are sampling a completely unknown atmosphere
✓ The expected concentration of analyte in the atmosphere is such that the desired sampling time (usually between 4–8 hours (occupational) and 1–4 weeks (environmental)) will result in a mass on the tube which is above the limit of detection of the TD–GC(MS) method	✗ You want to sample two (or more) compounds of widely differing volatilities (*e.g.* acetone and toluene)
✓ You are looking for several compounds of the same volatility	✗ There are no uptake rates available for the compounds of interest

Table 1: When should diffusive sampling be used?

Conclusions

Thermally desorbed diffusive tubes have been shown to be viable ambient air samplers. Their sampling mechanism is well understood/validated, and TD–GC(MS) analytical methods developed for pumped sorbent tubes can be applied. They offer several advantages over pumped sorbent tubes in terms of simplicity, reduced variability (less to go wrong), cost, extended sampling times and minimal water interference.

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