Passive sampling and its pivotal role in 'greener' sampling of VOCs in various industrial settings

Hannah Calder[1], Nicola Watson[2], Caroline Widdowson[1]

[1] Markes International Ltd, 1000B Central Park, Western Avenue, Bridgend, CF31 3RT, UK. [2] Markes International, Inc., 2355 Gold Meadow Way, Gold River, Sacramento, CA 95670, USA.

Introduction

Passive (or diffusive) sampling has been widely adopted as a sampling technique to analyze volatile organic compounds (VOCs) in air. It is a convenient, low-cost and unobtrusive approach for a range of applications, including industrial hygiene and indoor air monitoring, and is well-suited to large-scale environmental monitoring campaigns.

Passive sampling originally involved solvent extraction from a charcoal sorbent. However, thermal desorption is a more environmentally friendly approach, and for this reason is now widely adopted.

The principle of passive sampling

Passive 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.

If these criteria are not met, the sampler would have an inconsistent sampling rate, and generate spurious results.

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

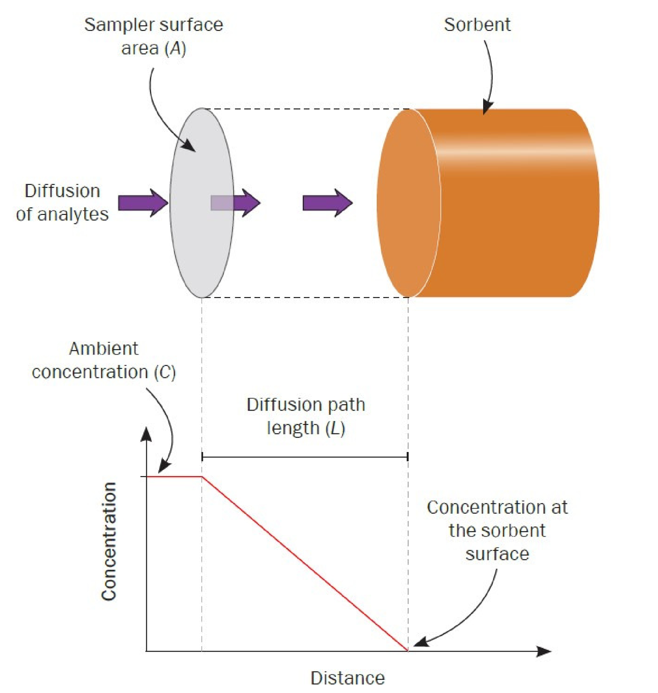

Figure 1: The principle of passive sampling.

Sampler types

Passive sampling devices are available in a range of geometries, depending on the type of sample, the sampling duration, and the concentrations of the (known or expected) target compounds. Samplers to collect VOCs in air are divided into two categories:

Axial passive samplers rely on diffusion of analytes onto a single surface of sorbent at one end of a sampling tube (Figure 2A). For consistency of uptake rates, the majority of international standard methods for passive sampling are standardized on a specific tube dimension (3.5 inch × ¼ inch) for TD analysis.

Radial passive samplers use a different geometry. They comprise a cylindrical sorbent cartridge that is housed within an outer casing, which enables air to diffuse through it (Figure 2B). This 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).

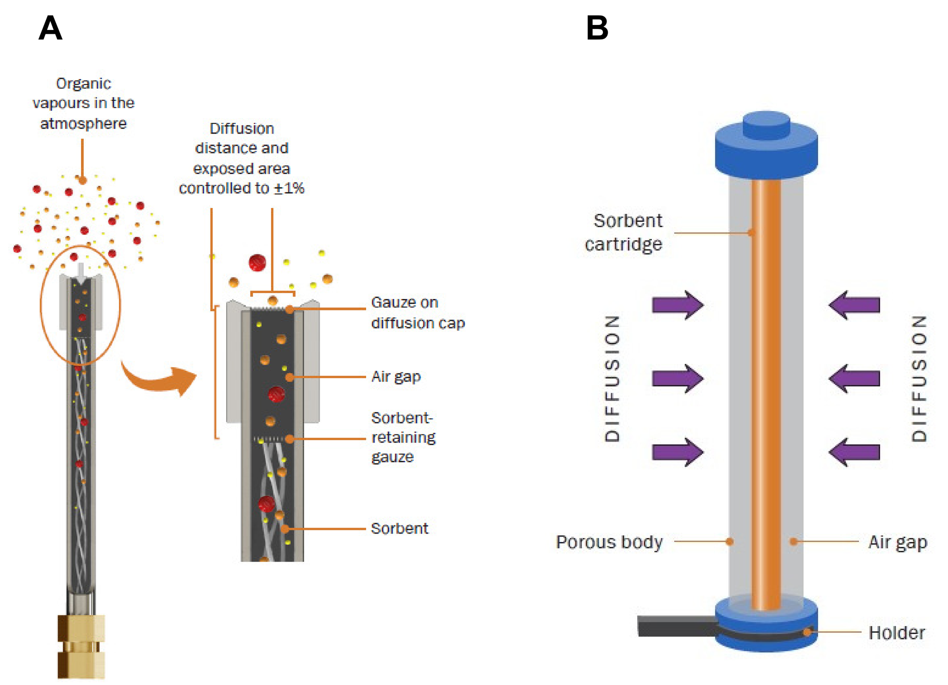

Figure 2: The diffusion process for passive samplers: (**A**) axial and (**B**) radial.

Where can passive sampling be used?

Passive samplers are commonly used for:

- Occupational health monitoring
- Industrial perimeter monitoring
- Pollution mapping in urban areas
- *In situ* soil contaminant mapping (looking for contaminated areas when doing land remediation)
- Vapor intrusion investigations
- Indoor air quality assessments.

For further information on which sampler to choose, please see standard methods ISO 16017:2, EN 838, EN 14412, EN 13528 and MDHS 80.

Passive sampling with thermal desorption *versus* solvent extraction

Solvent extraction (SE) was the first method used to extract compounds from passive sampling devices. However, due to the hazardous nature of the solvents employed (some are more hazardous than the compounds being extracted), a safer technique was sought.

Thermal desorption (TD) does not require a solvent, making it safer to use. Also, it is more environmentally friendly because disposal of waste solvent is avoided. As well as being a 'greener' approach, TD has other advantages:

Better sensitivity

With TD, the entire mass collected over the sampling period can be injected into the GC. This removes the 'dilution' effect of using solvents, whereby only a small portion of the sample is injected (*e.g.* 1 µL from a 1–2 mL extract). This limits the sensitivity to ~0.1–1 ppm, and is a disadvantage in cases such as identifying trace levels of benzene. Benzene has no safe exposure limit, and concentrations of 0.05 ppb are known to cause leukaemia in one person per million.

Better chromatography and reliable results

Without solvent, there is no solvent interference in the analysis, and consumables last longer. In addition, the typical desorption efficiency for TD is >95%, compared to ~20–80% for SE. Figure 3 shows a typical TD analysis for industrial hygiene monitoring. Volatile compounds, such as pentane, can be monitored accurately, whereas they could have been missed using SE.

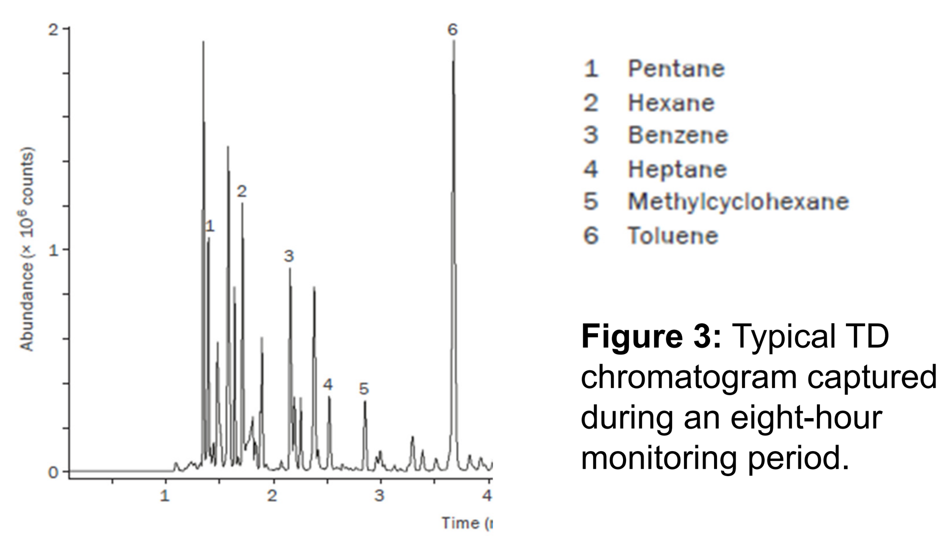

Figure 3: Typical TD chromatogram captured during an eight-hour monitoring period.

TD fully automates the sample introduction process and is cost-effective

With a TD system, such as the one in Figure 4, laboratory productivity is increased because the process is fully automated, so there are no manual steps to extract compounds of interest. Also, running costs are lower, as gases and power are the only utilities required. Unlike SE samplers, TD-compatible samplers are re-usable, lowering consumable costs.

Figure 4: Markes' TD100-xr™ system.

Applications of passive sampling in industrial monitoring

The ease-of-use, comparatively low cost and unobtrusive nature of passive sampling make it well-suited to a range of industrial monitoring applications. Axial and planar (badge) samplers remain the most widely adopted passive sampling approaches, with many sampling rates having been published, particularly for 8-hour workplace monitoring and fenceline emission testing. Building on this, radial samplers with their increased sampling rate relative to axial diffusive samplers, extend the applicability of passive sampling to short-term monitoring or longer-term sampling at trace levels, such as the effects of industrial emissions, changes in traffic volumes, or short-term weather events.

When used for personal exposure monitoring, the sampler should be mounted in the person's breathing zone, for example on the lapel of a jacket (Figure 5), but care should be taken to ensure that it is not obscured by clothing.

When used for fixed-location sampling, the sampler can be placed on a flat surface, or hung in position using a dedicated holder. If sampling outdoors, it is usual to protect the sampler from the elements using a shelter constructed from non-emitting materials (Figure 6).

Figure 5: Markes International's radial diffusive sampler and holder, for personal exposure monitoring.

Figure 6: Markes International's axial tubes deployed within a shelter for ambient monitoring.

Practical considerations in passive sampling workflow

1. Choose your axial or radial sampler. Barcodes and RFID technology can be used to track the sampler through its lifetime and during sampling campaigns.
2. Samplers can be cleaned in off-line apparatus or on the TD system, which can be set to automatically run blanks to confirm their cleanliness.
3. Samplers can be deployed for workplace exposure monitoring, long-term monitoring of industrial emissions, and ambient environmental monitoring.
4. Sample information and the sampler ID can be logged automatically using the barcodes.
5. Samplers are placed in the TD instrument for automated analysis of up to 199 samples. The thermal desorption process enables the samplers to be re-used multiple times.

Conclusions

- Various types of sorbent-based passive samplers, with different geometries, have been designed since the introduction and validation of sorbent-based samplers.
- For successful results, passive samplers must have a constant sampling rate and zero sink.
- TD has many advantages over SE, such as:
    - Increased sensitivity
    - No solvent waste (environmentally friendly)
    - Automated, quantitative re-analysis.
- Passive sampling devices are easy to deploy in the field by untrained operators, making them accessible for many monitoring needs, not just IH monitoring.