TDTS 8

Principles of diffusive monitoring

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 programmes.

Key applications include:

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

Diffusive monitors must be capable of maintaining the following conditions during sampling:

- ambient concentration of the analyte at the surface of the monitor
- zero concentration of the analyte at the surface of the sorbent
- a linear concentration gradient between the two.

When these conditions apply, Fick's First Law of Diffusion applies, and analytes will migrate to the surface of the sorbent at a rate that is dependent on:

- the distance between the sorbent surface and the monitor surface
- the cross-sectional area of the sampler
- the time of exposure
- the diffusion coefficient of the analyte through air
- the ambient concentration of the components

This is expressed by the following formula:

$$U_{ideal} = 60\,D_1 A/Z$$

where:

U_{ideal} = ideal uptake rate (mL min^{-1})

D_1 = diffusion coefficient through air of the vapour under study (cm^2 s^{-1})

A = cross-sectional area of the sampling tube (cm^2)

Z = air gap path length (cm)

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 never effectively be established. Badges were also unsuitable for analysis by TD–GC.

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 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 positioned 14.3 mm from the sampling end of the tube. This typically gives a diffusive path length (air gap) of ~1.5 cm.

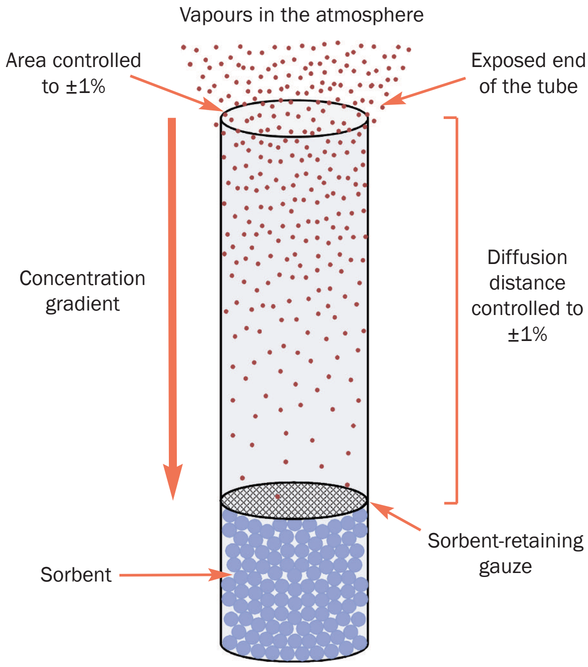

Figure 1: Axial diffusive sampling onto sorbent tubes.

Using this diffusive tube, the atmospheric concentration of a compound (*C*, in ppm) is determined using the following equation:

$$C = W/U_{ideal}T$$

where:

W = weight of sample on tube (ng)

U_{ideal} = ideal uptake rate (ng ppm^{-1} min^{-1})

T = sampling time (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.

However, as the actual uptake rates of many analytes on a range of sorbents have now been published, little, if any, experimental work is required on the part of a user. Application Note TDTS 1 presents a current listing of uptake rates.

If an uptake rate is not available for a given analyte, there are three options:

1. Calculate an ideal value from Fick's equation and diffusion coefficients published in the literature.
2. Determine the uptake rate experimentally using one of the following internationally recognised protocols:
   - Protocol for assessing the performance of a diffusive sampler; UK Health & Safety Executive, Methods for the Determination of Hazardous Substances No. 27.
   - CEN Pr EN 838: Workplace atmospheres – requirements and test methods for diffusive samplers for the determination of gases and vapours, CEN/TC 137/N55 (1991)
   - Protocol for the evaluation of passive monitors; E.T. Kennedy *et al.*, US National Institute for Occupational Safety and Health (NIOSH). Published in 'Diffusive sampling: An alternative approach to workplace air monitoring', CEC Publication No. 10555EN (1986)
   - American National Standard for Air Sampling Devices – Diffusive Type for Gases and Vapours in Working Environments, ANSI/ISEA 104-1998
   - Standard Practice for Evaluating the Performance of Diffusive Samplers, ASTM D6246-98.

   These protocols recommend a series of laboratory and field experiments to determine and validate effective uptake rates, which can be time-consuming.
3. Predict the uptake rate by using a combination of simple short experiments and a computer software programme. See Application Note TDTS 2 for further information.

Axial diffusive sampling in practice

Axial diffusive samplers consist of the industry-standard (89 mm × ¼″ o.d.) stainless steel sorbent tube, pre-packed with the sorbent of choice, a ¼″ brass SwageLok-type storage cap (fitted with a PTFE ferrule) for the non-sampling end of the tube, and a diffusion cap fitted to the sampling end of the tube (Figure 2).

Figure 2: Axial diffusive sampler fitted with brass storage cap, penclip, and diffusion cap.

Axial diffusive sampling is generally valid for the measurement of airborne vapors of volatile organic compounds (VOCs) in a concentration range of approximately 2 µg m^{-3} to 10 mg m^{-3}, for individual VOCs for an exposure time of 8 h. For an exposure time of four weeks the concentration range is 0.3–300 µg m^{-3} for individual organic compounds. Axial diffusive sampling is also suitable for the measurement of the airborne concentrations of individual components of VOC mixtures, provided that the total loading of the mixture does not exceed the capacity of the tube.

A suitable sorbent must be selected for the compound or mixture to be sampled (see Application Note TDTS 1). If more than one sorbent is required (due to the different volatilities of the compounds in question), two or more samplers, packed with different sorbents, should be exposed simultaneously in parallel.

Immediately before sampling, the storage cap should be removed from the sampling end of the sample tube and replaced with a diffusion cap. It is important to ensure that the diffusion cap is properly seated and that the storage cap at the other end of the tube is left in place.

When used for personal sampling/occupational hygiene, the tube should be mounted in the person's breathing zone, for example on the lapel of a jacket. When used for fixed location sampling, a suitable sampling site should be chosen. In either case, the diffusion tube should be mounted vertically with the sampling end at the bottom. The diffusion end cap should have unrestricted access to the sampled atmosphere, *i.e.* it should not be obscured by the wearer's clothing or other objects.

The typical exposure time for the VOCs covered by this method is 8 h for workplace monitoring and 1–4 weeks for ambient and indoor air monitoring. Sampling over shorter periods is possible, down to 30 min for workplace monitoring and one day for ambient and indoor air monitoring, but the working concentration range will be affected accordingly. For example, for a 4 h sampling period, the working range is approximately 0.004–20 mg m^{-3}.

Although much of the early work done with axial tube-type diffusive samplers focused on occupational hygiene monitoring (and hence 8 h exposure of the tubes to atmospheric concentrations of several ppm), it has since been shown that diffusive monitoring is suitable for sampling over much longer periods of time (up to six weeks) and for much lower atmospheric concentrations (sub-ppb)[2], providing the correct sorbent is used.

However, when atmospheric concentrations are very low (<1 ppb) and when a result is required within a few hours, tube-type axial diffusive sampling does not provide a sufficient mass of analyte on the tube. In these instances radial diffusive samplers provide a novel solution.

Radial diffusive samplers

Tube-type axial diffusive samplers have a typical sampling rate equivalent to 0.5 to 1 mL min^{-1}, and are highly suitable for short-term diffusive sampling of low atmospheric concentrations (as discussed above).

Although much environmental monitoring takes place over a 2–4 week period, there are many occasions where a much shorter sampling period (30 min to 6 h) would be preferable – perhaps to monitor the effects of industrial processes, changes in traffic volumes or short-term climate effects. In these instances use of tube-type diffusive samplers is hampered by their slow uptake rate, and they are unsuitable for monitoring concentrations less than 10 ppb.

In radial diffusive samplers (Figure 3), the orientation of 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 times greater than tube-type samplers). Due to the high adsorbent surface area combined with the short diffusive path, they have an effective sampling rate typically 100 times that of normal axial tubes.

However, due to the much higher sampling rate, care must be taken not to saturate the sorbent with the components of interest.

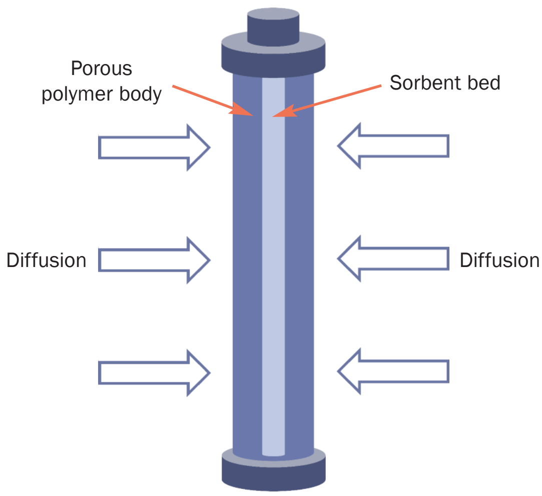

Figure 3: Radial diffusive sampling.

Although radial diffusive samplers for thermal desorption are a comparatively new development, there are a number of published uptake rates available, and a current listing may be found in Application Note TDTS 42.

Radial diffusive sampling in practice

Radial diffusive samplers consist of a cylindrical diffusive body, an adaptor to screw onto the diffusive body, and a stainless steel cylindrical sorbent cartridge. Also required are an empty stainless steel carrier tube for thermal desorption, and two ¼″ brass caps with PTFE ferrules for sealing the carrier tube.

Radial diffusive sampling is generally valid for the measurement of airborne vapours of VOCs in a concentration range of approximately 0.3–300 µg m^{-3}, for individual organic compounds for exposure times from 1–6 h. The method is also suitable for the measurement of the airborne concentrations of individual components of VOC mixtures, provided that the total loading of the mixture does not exceed the capacity of the cartridge.

Note that the high sampling rate and related risk of back-diffusion associated with radial diffusive samplers typically restricts the volatility range of these samplers to compounds of equal, or lower, volatility than benzene. It also means that they require stronger sorbents than either axial diffusive or pumped sorbent tubes.

If more than one radial diffusive sample cartridge is to be used, they should be exposed simultaneously side-by-side.

New sorbent cartridges should be thoroughly conditioned before use inside stainless steel or inert-coated stainless steel carrier tubes. After being conditioned, the carrier tube containing the cartridge should be sealed with ¼″ brass SwageLok-type storage caps in the same way as standard sorbent tubes.

Once at the sampling location, the radial diffusive sampler should be assembled by undoing the brass caps and placing the non-grooved end of the carrier tube against the open end of the yellow diffusive body. The sorbent cartridge should be tipped inside the diffusive body, using a TubeMate™ tool or similar rod to gently push the cartridge into the carrier tube if necessary. Care must be taken not to touch the sorbent cartridge directly.

Once the cartridge is inside the yellow diffusive body, the blue adaptor plate should be screwed onto the end of the body and the start time noted – this is the start of sampling.

When used for personal sampling, the sampler(s) should be mounted in the person's breathing zone, for example on the lapel of a jacket. When used for fixed location sampling, a suitable sampling site is chosen. In either case, the diffusive sampling body should have unrestricted access to the sampled atmosphere, *i.e.* it should not be obscured by the wearer's clothing or other objects.

Samplers can be placed on a flat surface using the adaptor, or can be hung in position using the ring on the adaptor. If samples are to be taken outdoors, it is usual to protect the samplers from the elements by means of a shelter constructed from non-emitting materials. At its most rudimentary this can be a piece of sheet metal bent over to form an 'umbrella' over the sampler.

At the end of the sampling period, the time must be recorded. The blue adaptor should be unscrewed and the sorbent cartridge tipped back into the carrier tube, which should be capped as usual. Avoid handling the cartridge itself.

The recommended exposure time for VOCs sampled in this way is up to 6 h for ambient and indoor air monitoring. Sampling over shorter periods is possible, down to 30 min for ambient and indoor air monitoring, but the working concentration range will be affected accordingly. Sampling over longer periods is also possible, provided the sorbent is sufficiently strong to prevent back-diffusion.

Once sealed in the carrier tube, the sample is stable until thermally desorption is carried out. Note that when desorbing radial diffusive cartridges it is sometimes necessary to use more stringent conditions than those used for pumped or axial diffusive sampling. This is because the VOCs are dispersed evenly across the entire surface of the cylindrical sorbent cartridge (rather than being a fixed distance from one end of the tube, as in axial diffusive sampling). Therefore longer primary desorption times and faster flow conditions may be required in order to obtain 100% desorption efficiency of the VOCs from the cartridge.

When diffusive sampling is not applicable

Diffusive sampling is not suitable for all monitoring applications, as it has to be carried out using sorbent tubes packed with a single bed of sorbent. If two or more sorbents are needed because of differing analyte volatilities, then two or more 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 (A) is different to that of the 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 is not available and if there is no time to measure or calculate an uptake rate, then diffusive sampling cannot be used.

References

1. R.H. Brown, J. Charlton and K.J. Saunders, The development of an improved diffusive sampler, *American Industrial Hygiene Association Journal*, 1981, 42: 865–869.
2. V.M. Brown, D.R. Crump, D. Gardiner and C.W.F. Yu, Long term diffusive sampling of volatile organic compounds in indoor air, *Environmental Technology*, 1993, 14: 771–777.

Trademarks

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