Thermal Desorption Technical Support

Note 10: Use of Diffusive Samplers with Thermal Desorption - Capillary GC Analysis for Monitoring Volatile Organic Compounds (VOCs) in Ambient Air

Keywords

passive, urban regulations, badge, atmospheric concentration, VOCs, Fick's Law, uptake rate

Abstract

Diffusive (passive) samplers of all kinds fulfil many of the logistical requirements of an ideal ambient air monitor. They are low cost, easy to distribute/use, suitable for a wide range of common volatile organic air pollutants, reliable, applicable to long-term sampling and do not require power. Several different kinds of diffusive sampler have been developed for VOCs. These were predominantly designed for occupational hygiene work and most require solvent extraction prior to GC analysis. The analyte dilution necessary with solvent extraction has been found to limit sensitivity and to preclude general application to ambient air assessment.

A tube-form, sorbent-based diffusive monitor, specifically designed to minimise the air speed limitations of conventional badge-type diffusive samplers and to be compatible with analysis by thermal desorption-GC, was first reported in 1979. In common with other diffusive samplers for VOCs, this device was initially developed for use as a personal monitor for occupational hygiene measurements. However, several recent reports have demonstrated that it can also be applied to the measurement of low concentration VOCs in indoor and outdoor ambient air.

This paper reviews the reported experiences of indoor and outdoor air monitoring using a tube-form diffusive monitor. Specific attention is paid to general sampling/analytical procedures, concentration/detection limits, applicable analyte ranges, minimising artefacts, quality assurance and method limitations. Practical recommendations regarding sampling and analytical parameters are also presented.

Introduction

Diffusive (passive) samplers, based on reversible sorption, fulfil many of the logistical requirements of an ideal ambient air monitor. They are relatively low cost, easy to distribute/use, suitable for a wide range of common volatile organic air pollutants, do not require power and can be used for long-term, time-averaged monitoring (1-4 weeks[1,2,3,4,5]) The extended sampling times facilitate compliance with urban regulations which quote limit levels in terms of annual time weighted average. It also benefits monitoring in remote rural locations.

The diffusive sampling mechanism is well understood[6,7,8] and has been used for monitoring ppm-level industrial solvents and hydrocarbons in workplace environments9 for many years. Many different types of sorbent-based diffusive sampler are commercially available for VOCs. These include badge designs, which predominantly require solvent desorption prior to GC analysis, and tube designs – most of which may be thermally desorbed.

Why a Tube-form, Thermally-Desorbed Diffusive Sampler?

Minimum and maximum air speed/face velocity limitations

Air speed/face velocity restrictions are an inherent feature of all diffusive samplers. In short, if the velocity of air at the sampling surface of a monitor is not sufficient to replenish compounds as they are adsorbed, the atmospheric concentration in the immediate vicinity of the sampling surface will become depleted thus giving an erroneously low reading. Conversely, too fast an air flow at the sampling surface can cause turbulence within the diffusive air gap and disturb the diffusion gradient unless protected by a draught shield.

As discussed by Cao and Hewitt (1991)[10], the larger the diameter and shallower the diffusion gap of a monitor the worse the face velocity restrictions become. Typical 2 cm diameter, flat, badge-type samplers, for example, may not be suitable for outdoor environments where air speeds are subject to wide and unpredictable variation. Minimum air speed restrictions typically also preclude their use as static (as opposed to personal) monitors in indoor environments. Tube-form samplers overcome these limitations by using a relatively long and narrow air gap - see below.

Solvent extraction versus thermal desorption (TD)

Most badge-form diffusive samplers are restricted to solvent desorption, which also renders them less suitable for ambient air monitoring - Solvent desorption/extraction methods involve an inherent dilution step and are approximately three orders of magnitude less sensitive than equivalent thermal desorption procedures. From a practical perspective solvent extraction procedures are also manual/labour intensive, susceptible to artefacts from impure solvents and subject to masking of peaks of interest by the solvent itself. In addition, desorption efficiencies are typically 75-80% at best (versus >95% for TD 11) and can be as low as 20-30% when monitoring polar analytes or used in high humidity atmospheres[12,13]. Variability in solvent desorption efficiency can result in analytical errors which are absent in thermal desorption methods.

Reusable tube-form diffusive sampler

A tube-form, sorbent-based diffusive monitor was specifically designed by Brown, Charlton and Saunders in 1979 to overcome the air speed limitations of conventional badge monitors and to be compatible with analysis by TD-GC. The tube is 3.5-inch long by 1/4-inch OD stainless steel with an internal diameter of 5.0 mm. In this case, the diffusion barrier is an air gap 15 mm deep by 0.193 cm^2 surface area[14]. The air gap is defined by two stainless steel, 100-mesh gauzes - one in the sampling cap defining the sampling surface of the monitor and the other located in a groove on the inside of the tube. The gauze inside the tube both supports the sorbent bed and defines the sorbent sampling surface. Some commercial diffusive sampling caps alternatively or additionally include a semi-permeable membrane as the diffusion barrier to reduce water ingress. The depth and narrowness of the air gap plus the gauze barrier at the sampling surface, prevent turbulence and distortion of the diffusion gradient even at extreme air speeds. The air gap dimensions also allow the monitor to be used with air speeds as low as 3-5 $cm.sec^{-1}$ - ideal for static indoor air work. Vapour uptake rates are low with this sampler configuration - typically equivalent to around 0.5 ml/min pump flow. However, slow sampling rates facilitate long term ambient air monitoring and thermal extraction/desorption more than compensates for any sensitivity limitation.

Note that the need for a precisely defined air gap for diffusive sampling usually precludes using glass or quartz wool to support the sorbent bed inside the tube. Note also that glass tubes of the same, 1/4-inch O.D., as the stainless steel monitors described, have thicker walls and hence smaller (~4 mm) I.D.s and sorbent sampling surface areas. Diffusive uptake rate constants (see below) determined for the stainless steel monitors can thus not be applied/transferred to glass tubes.

The stainless steel monitor designed in 1979[6] has been used extensively for occupational hygiene monitoring over the last decade[7,9,15-25] and has been validated for multiple workplace air applications according to relevant protocols[11,26-29]. Several recent reports have demonstrated that it is also possible to successfully apply these monitors to the measurement of VOCs in ambient indoor and outdoor air[1-5,30-46]. The most obvious procedural difference is that sampling/exposure times are significantly longer (2 days to 6 weeks) than the 4 to 8 hour exposure times typically used for industrial hygiene.

Even with the extended sampling times however, the sensitivity required for ambient air measurements - where individual VOCs are typically at sub to low-part per billion concentrations ($ng\text{-}mg.m^{-3}$) - presents a severe challenge to the analyst. Sorbent selection, tube conditioning/storage/transport procedures, sampling/analytical details and calibration techniques are among the factors critical to method success.

Applicable Analyte Range

Workplace air monitoring methods specifying diffusive sampling tubes with TD-GC(/MS) analysis - for example UK MDHS 8025 - reference a broad range of applicable VOCs together with relevant sorbent and associated (typically 8 hour) uptake rate data. Applicable compounds include: n-alkanes from pentane, aromatics from benzene to trimethylbenzene and naphthalene, 1,3-butadiene, styrene, halogenated solvents, halothane and related anaesthetics, perfluorinated tracer gases, freons, esters, epichlorohydrin, glycol ethers, furfural, ketones, isopropanol, organic nitriles, CS_2, N_2O, ethylene oxide and 1,4-dioxane. This range of analytes parallels that monitored using sorbent tubes in industrial and ambient air *via* pumped sampling and TD-GC analysis[47-50].

Generally speaking, to be compatible with sorbent tube sampling (pumped or diffusive), a compound must be thermally stable, present in the atmosphere in the vapour phase, be less volatile than ethane and readily compatible with analysis by gas chromatography. (Note that thermal desorption is essentially an extension of simple, packed column gas chromatography.) If a compound meets these basic criteria and is, additionally, sufficiently stable to withstand 2-day to 4-week sampling times (and the associated increased exposure to atmospheric agents such as O_3, NO_2, H_2O, *etc*.), it should be feasible to measure it in ambient air using an extended sampling version of workplace diffusive monitoring procedures. The diffusive uptake rate (U) required for long-term ambient monitoring may differ from that applied to the same monitor-analyte combination during 8-hour industrial hygiene tests - see below.

Those VOCs reported in the literature as successfully monitored in ambient outdoor or indoor air using a diffusive tube - TD-GC procedure are listed in Table 1. Associated data, including literature references, sorbent used, uptake rate, sampling time, GC detector type and method detection limits, are tabulated.

It is interesting to note that no VOCs outside the volatility range C_5 - C_{12} hydrocarbons and few polar compounds are listed. The analyte set does, however, closely reflect the most widely reported range of indoor air pollutants, regardless of measurement technique[46,51]. The list also includes the critical volatile aromatics - benzene, toluene, ethyl benzene and xylenes (BTEX) - featured in recent ambient air regulatory developments on either side of the Atlantic[52,53].

Sorbent Selection and Diffusive Uptake Rates

If the sorbent-analyte interaction is sufficiently strong to be effectively irreversible under ambient conditions, 'back-diffusion' of analytes from the sorbent surface will be negligible and the vapour phase analyte concentration at the sampling surface will be zero. Under this 'perfect sink' assumption, a steady state situation exists, and a straightforward mathematical solution can be derived for Fick's first law of diffusion:

$$\mathbf{M = AD/L \times T \times C} \qquad \text{(Equation 1)}$$

Where:

M is the mass of analyte adsorbed

T is exposure time

C is atmospheric concentration,

D is the diffusion coefficient

A and L are the area and length of the diffusive air gap respectively.

Compound	Sorbent	Uptake rate	Sampling	GC detector	Lowest air concentration
1-Pentene	Carbotrap [33]	1.76 ng.ppm^{-1}.min^{-1} **I**	15 h [33]	RGD [33]	0.06 ppb (33)
Isoprene	Carbotrap [33,45]	1.5 - 1.79 ng.ppm^{-1}.min^{-1} **I**	15 h [33]	RGD [33]	0.03 ppb (33)
	C106 [45]	1.71 - 1.8 ng.ppm^{-1}.min^{-1} **X**	-	FID [45]	-
1-Hexene	Tenax GR [33] & Carbotrap [33]	1.87 ng.ppm^{-1}.min^{-1} **I**	15 h [33]	RGD [33]	0.04 ppb (33)
Benzene	Tenax TA [1,2,4,44,45]	0.2 ml.min^{-1} [2] **X**	29 d [2]	FID [1,2,4]	60 ng.m^{-3} (1)
		1.3 ng.ppm^{-1}.min^{-1} **V**	8 h [4]	-	160 ng.m^{-3} (4)
	Tenax GR [3,45]	1.81 ng.ppm^{-1}.min^{-1} **X**	5 h [3]	-	-
	Chrom. 106 [5,31,32,34,35]	1.6 ng.ppm^{-1}.min^{-1} [31] **X**	30 d [31]	FID [31,32,34]	0.5 ppb (31)
		3.0 mg.m^{-3}.week^{-1} [34] **X**	14 d [32,34,35]	-	-
		1.45 ng.ppm^{-1}.min^{-1} [5] **V**	7-28 d [5]	FID [35,44]	-
	Carbograph [5,35]	2 ng.ppm^{-1}.min^{-1} [5] **V**	7-28 d [5]	-	-
	Carbotrap [45]	2.02 ng.ppm^{-1}.min^{-1} [45] **X**	-	-	-
Toluene	Tenax TA [1,2,4,44,45]	1.67 ng.ppm^{-1}.min^{-1} [4] **V**	8 h [4]	FID [1,2,3,4]	30 ng.m^{-3} (1)
		0.32 ml.min^{-1} [2] **X**	29 d [2]	-	180 ng.m^{-3} (4)
	Carbotrap [45]	2.11 ng.ppm^{-1}.min^{-1} [45] **X**	-	-	-
	Tenax GR [3,45]	2.12 ng.ppm^{-1}.min^{-1} [3,45] **X**	5 h [3]	-	-
	Chrom. 106 [5,31,32,34,35]	1.9 ng.ppm^{-1}.min^{-1} [31] **X**	30 d [31]	FID [31,32,34]	2.5 ppb (31)
		4.8 mg.m^{-3}.week^{-1} [34] **X**	14 d [32,34,35]	-	-
		1.9 ng.ppm^{-1}.min^{-1} [5] **V**	14 d [5]	FID [35,44]	-
	Carbograph [5,35]	2.11 ng.ppm^{-1}.min^{-1} [5] **V**	14 d [5]	-	-
Xylenes	Tenax TA [1,2,4,44,45]	0.5 ml.min^{-1} [1,44] **E**	1-7 m [1,44]	FID [1,2,3,4]	10 ng.m^{-3} (1)
		0.45 ml.min^{-1} [2] **X**	29 days [2]	-	~100 ng.m^{-3} (4)
	Carbotrap [45]	2.37 ng.ppm^{-1}.min^{-1} [45] **X**	-	-	-
	Tenax GR [3,45]	2.34 ng.ppm^{-1}.min^{-1} [45] **X**	-	-	-
	Chrom. 106 [5,31,32,34,35]	2.1 ng.ppm^{-1}.min^{-1} [45] **X**	30 days [31]	FID [31,32,34]	1.3 ppb (31)
		5.5 mg.m^{-3}.week^{-1} [34] **X**	14 d [32,34]	-	-
		2.08 ng.ppm^{-1}.min^{-1} [5] **V**	14-28 d [5]	FID [35,44]	-
	Carbograph [5,35]	2.19 ng.ppm^{-1}.min^{-1} [5] **V**	14-28 d [5]	-	-
Ethyl benzene	Tenax GR [3]	2.43 ng.ppm^{-1}.min^{-1} [3] **X**	5 h [3]	FID [3,4,31]	20 ng.m^{-3} (4)
	Tenax TA [4]	2 ng.ppm^{-1}.min^{-1} [4] **V**	8 h [4]	-	-
	Chrom. 106 [31]	2.26 ng.ppm^{-1}.min^{-1} [31] **X**	30 d [31]	-	-
1,2,4-Trimethyl benzene	Tenax TA [1,2,44]	0.5 ml.min^{-1} [1] **E**	3-6 w [1]	FID [1,2,38]	10 ng.m^{-3} (1)
		0.54 ml.min^{-1} [2,44] **X**	1-7 m [2,44]	-	-
n-Octane	Tenax TA [4]	2 ng.ppm^{-1}.min^{-1} [4] **V**	8 h [4]	FID [4]	120 ng.m^{-3} (4)
n-Nonane	Tenax TA [4]	2.12 ng.ppm^{-1}.min^{-1} [4] **V**	8 h [4]	FID [4]	100 ng.m^{-3} (4)
Decane	Tenax TA [4]	0.5 ml.min^{-1} [1] **E**	3-6 w [1]	FID [1,2,44]	20 ng.m^{-3} (1)
		0.51 ml.min^{-1} [2,44] **X**	1-7 m [2,44]	-	-
Undecane	Tenax TA [1,2,44]	0.5 ml.min^{-1} [1] **E**	3-6 w [1]	FID [1,2,44]	10 ng.m^{-3} (1)
		0.53 ml.min^{-1} [2,44] **X**	1-7 m [2,44]	-	-
Benzyl alcohol	Tenax TA [1]	0.5 ml.min^{-1} [1] **E**	3-6 w [1]	FID [1]	50 ng.m^{-3} (1)
Naphthalene	Tenax TA [1]	0.5 ml.min^{-1} [1] **E**	3-6 w [1]	FID [1]	20 ng.m^{-3} (1)
2-Methyl naphthalene	Tenax TA [1]	0.5 ml.min^{-1} [1] **E**	3-6 w [1]	FID [1]	10 ng.m^{-3} (1)
2-Ethyl hexanol	Tenax TA [43]	**-**	-	ITD [43]	-

Key to uptake rate letters:

"E" indicates estimated/calculated uptake rate

"V" indicates uptake rate validated via lab and

"I" indicates ideal uptake rate

"X" indicates uptake rate validated via lab and field tests

Table 1: Summary of reported data using sorbent-tube-type diffusive monitors and thermal desorption for ambient air analysis

In such cases a constant 'ideal' uptake rate (UID) will apply and can be calculated simply from diffusion coefficients[54-56] and diffusion gap dimensions (AD/L). In other words, provided the concentration of the analyte immediately above the sorbent surface remains at zero, the ideal rate of analyte uptake can be calculated from physical constants and is independent of the sorbent in the sampler.

Uptake rates are commonly quoted in units of nanograms adsorbed per part per million in the atmosphere per minute of exposure ($ng.ppm^{-1}.min^{-1}$).

"Ideal" diffusion requires a strong sorbate - sorbent interaction. Retention volume (RV) is one common and well understood measure of sorbent strength[47,57]. It is typically expressed in litres of vapour retained per gram of sorbent (Note: A straightforward chromatographic method for determining sorbent tube retention volumes is described in reference 49.) In general terms, for sorbent tube-type monitors, ideal diffusive uptake rates will be applicable whenever the retention volume for a particular analyte exceeds 10,000 $L.g^{-1}$ [14,47]. It is possible to select sorbents with such a high retention volume for most compounds less volatile than benzene. Detailed retention volume information for a wide range of common compounds on several sorbents is presented in reference 47.

For more volatile analytes, or in situations where it is undesirable to use a strong sorbent (see note below), analytes will begin to back diffuse from the sorbent over time causing an increase in vapour phase analyte concentration at the sampling surface. This consequently reduces the diffusion gradient and the rate of analyte adsorption/uptake.

Note: Although it would seem sensible, in the interests of ideal diffusion conditions, to invariably select the strongest sorbent available for the analytes of interest, there are practical limitations - The most obvious of these is the need to thermally desorb/extract the compounds back from the tubes again during analysis without thermally degrading the analytes or sorbent bed. Other issues, such as sorbent hydrophobicity, may also be important practical considerations.

When back diffusion occurs, an actual or effective uptake rate (UEFF) will apply. Work from a laboratory intercomparison carried out in Mol, Belgium in 1991/2[14] shows that, in cases of moderate back diffusion, there is an empirical relationship between the actual (or effective) diffusive uptake rate and the analyte retention volume (Equation 2) for exposure periods of a few hours[58].

$$\mathbf{U_{EFF}/U_{IDEAL} = 0.154\ log_{10}RV + 0.4} \qquad \text{(Equation 2)}$$

In other words, for sorbent - sorbate (analyte) interactions described by retention volumes between 100 and 10,000 $L.g^{-1}$, the effective diffusive uptake rate U_{EFF} for a sorbent tube-type monitor over 8 hours will be less than the ideal but can be reliably calculated from the retention volume. As back diffusion typically increases over time and is sorbent dependent for a given analyte, applicable exposure time and specific sorbent details should be quoted with every U_{EFF}. For the monitor discussed in this paper, stable long-term U_{EFF}s are quoted for up to 4 weeks and typically fall between 1.4 and 2.5 $ng.ppm^{-1}.min^{-1}$. If a U_{EFF} is determined to be much below 1.3 $ng.ppm^{-1}.min^{-1}$ for a given sampling scenario, this can be indicative of significant back-diffusion and is a warning that uptake may vary significantly with time.

In any event, the relationship between analyte retention volumes and effective diffusive uptake rates on sorbent tubes, does mean that sorbent selection guidance given for pumped tube sampling (Table 2) can generally be applied to diffusive sampling also.

Note that even under extreme conditions of back-diffusion (*e.g.* pentane on Tenax), research work into uptake rate prediction carried out at Shell in the Netherlands and continued at Stockholm University[56,59,60] has demonstrated that, for typical workplace (8 hour) studies, quantitative atmospheric concentration data can be iteratively derived post analysis using the mass of analyte retained and the relevant Freundlich isotherm. However, the software algorithms derived from this research may not be valid for long-term, 1 to 4 week, sampling periods[36].

Sample tube sorbent	Approximate analyte volatility range	Maximum temperature (°C)	Specific surface area ($m^2.g^{-1}$)	Example analytes
Carbotrap C™ Carbopack C™	n-C_8 to n-C_{20}	>400	12	Alkyl benzenes and aliphatics ranging in volatility from n-C_8 to n-C_{16}. Do not use for monoterpenes.
Tenax™ TA	Bp 100 - 400°C n-C_7 to n-C_{26}	350	35	Aromatics except benzene. Apolar compounds (bp >100°C) and less volatile polar compounds (bp >150°C). Suitable for monoterpenes.
Tenax™ GR	Bp 100 - 450°C n-C7 to n-C30	350	35	Alkyl benzenes, vapor phase PAHs & PCBs and as above for Tenax TA. Do not use for monoterpenes.
Carbotrap™ Carbopack B™	(n-C_4) n-C_5 to n-C_{14}	>400	100	Wide range of VOCs including ketones, alcohols, and aldehydes (bp>75°C) and all apolar compounds within the volatility range specified. Perfluorocarbon tracer gases. Do not use for monoterpenes.
Chromosorb™ 102	Bp 50 - 200°C	250	350	Suits a wide range of VOCs including oxygenated compounds and haloforms less volatile than methylene chloride. Do not use for monoterpenes.
Chromosorb™ 106	Bp 50 - 200°C	250	750	Suits a wide range of VOCs including hydrocarbons from n-C_5 to n-C_{12}. Also good for volatile oxygenated compounds. Do not use for monoterpenes.
Porapak Q	Bp 50 - 200°C n-C_5 to n-C_{12}	250	550	Suits a wide range of VOCs including oxygenated compounds. Do not use for monoterpenes.
Porapak N	Bp 50 - 150°C n-C_5 to n-C_8	180	300	Specifically selected for volatile nitriles: acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, *etc*.
Spherocarb*	-30 - 150°C n-C_3 to n-C_8	>400	1200	Good for very volatile compounds such as VCM, ethylene oxide, CS_2 and CH_2Cl_2. Also good for volatile polars *e.g.* MeOH, EtOH and acetone.
Carbosieve SIII™*/Carboxen 1000™*	-60 - 80°C	400	800	Good for ultra volatile compounds such as C_3 & C_4 hydrocarbons, volatile haloforms and freons
Molecular Sieve	-60 - 80°C	350	-	Used specifically for 1,3-butadiene and nitrous oxide. *Significantly hydrophilic. Do not use in high humidity atmospheres unless silicone membrane caps can be fitted for diffusive monitoring purposes.*
Charcoal* [**Do Not Use** unless no other sorbent available]	-80 to 50°C	>400	>1000	Rarely used for thermal desorption because metal content may catalyze analyte degradation. Use with care for ultra volatile (C_2), C_3, C_4 hydrocarbons.

* Exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (>90%) relative humidity

Table 1: Sorbent selection guidelines

Protocols for the validation and determination of Uptake rates

There are now several internationally recognised validation protocols for diffusive monitors[11,26-29,61]. Though the first five of these were designed specifically for workplace air monitoring applications most require only minor modification to be applicable to ambient outdoor and indoor air. Reference 61 is a provisional CEN standard specifically targeted at ambient air monitoring. This document is currently in draft form. Final approval is expected in 1999.

Most protocols involve both laboratory and field tests and investigate sampler and overall sampling/analysis performance (precision and bias) under the varying influence of parameters such as temperature, humidity, analyte concentration, atmospheric interferences, exposure time, *etc*. The ideal diffusive monitor is one that has a constant rate of uptake for the analyte concerned under the extremes of sampling times and atmospheric conditions likely to be encountered in field work. Note that most validated uptake rates, are quoted at 20 deg. C. Uptake rates vary slightly with temperature - decreasing ~0.2%.°C^{-1} rise in temperature[47] provided the sorbent – sorbate interaction is relatively strong (retention volume >100 $L.g^{-1}$). Atmospheric pressure is an insignificant variable. Note also that the impact of straightforward competition for adsorption sites between target analytes and other compounds present in the atmosphere is not likely to be significant for typical trace-level ambient air applications – with the exception of water (see below.) However, the potential for chemical interaction with one or more of the active inorganic gas species present in air - ozone, NO_2, *etc*. - may affect data quality for some labile species during long term ambient exposure periods.

Database of uptake rates

An advantage of diffusive sampling is that, provided sampler dimensions are maintained and provided sorbents of consistent (batch-to-batch) quality and behaviour are used, uptake rates are transferable from sampler to sampler without recalibration. This is an advantage versus pumped sampling where flow is normally required to be calibrated both at the beginning and end of sampling on each individual sample train[62]. It also means that a database of uptake rates can be created for specific monitors. Generation and refinement of such a database will, almost by definition, be a continuous process. However, the quality and quantity of data currently available on the most 'popular' air pollutants - BTEX- are already good[5].

Note that diffusion gap dimensions must be carefully controlled and kept constant for a database of uptake rates to be useful. Note also that the need for sorbent consistency, referred to above, rules out most conventional charcoal packings for diffusive monitoring. (Conventional charcoal is also not recommended for thermal desorption-GC analysis as the presence of trace metals can catalyse compound degradation at high temperatures.) If the sorbent strength of a charcoal is required, an ultra-pure carbon of consistent composition and particle size such as Spherocarb™, should be selected.

Multiple sorbents

As the position of the sorbent surface, relative to the sampling face of the monitor, is a critical dimension, it is uncommon for multiple sorbent beds (ie sorbent beds arranged in series of increasing sorbent strength from the sampling end) to be used in a single diffusive tube. This said, re-usable diffusive monitoring tubes are generally sufficiently cost-effective and unobtrusive (even in personal monitoring studies) to facilitate parallel sampling onto multiple tubes, each containing a different sorbent. This allows a wide volatility range of analytes to be monitored simultaneously.

Sorbent selection for minimal artefact formation and water retention

In summary, there are two basic issues that determine sorbent selection for diffusive monitoring:

1. Which sorbent(s) will quantitatively retain the target analyte(s) without significant back diffusion for the sampling time required?

2. Can those analyte(s) then be readily and quantitatively desorbed/recovered from that sorbent during analysis?

A secondary, but important practical consideration is the availability of existing, well validated uptake rate data.

It is not uncommon for more than one sorbent to be considered suitable for a given application by these simple criteria. In this situation, additional factors such as resistance to artefact formation and hydrophobicity should be taken into consideration.

Sorbent stability

Some sorbents are inherently more stable than others in terms of artefact formation[63-65]. All sorbents effectively have a 'native' minimum level of artefacts which cannot be eliminated or reduced, however stringent the conditioning or careful the handling. For example; it is hard to reduce individual artefacts much below 0.1 ng for Tenax[65], below 0.01 ng for graphitised carbons (*e.g.* GCB1TM and Carbotrap/pack66) and below 5-10 ng for most Porapak/ Chromosorb type porous polymers[65] - see section on system artefacts and method detection limits below.

Sorbent hydrophobicity and semi-permeable diffusion membranes

Different sorbents also have different affinities for water. Most weak to medium strength porous polymers and graphitised carbons are exceptionally hydrophobic. In this case, analyte retention/uptake is not significantly impaired - even in humid atmospheres. Other stronger sorbents such as pure carbons and carbonised molecular sieves are less hydrophobic and need to be protected by a semi-permeable membrane inside the diffusive sampling cap when sampling humid air. Without the membrane, competition between analytes and water for adsorptive sites reduces the breakthrough volume[47]– though there is no evidence for increased back-diffusion, even at high (>70%) humidities.

The presence of a semi-permeable membrane in the sampling cap is known to reduce diffusive uptake rates by reproducible factors of up to 12% 5 over 4 weeks, depending on the analyte-sorbent combination in question. This minimal adverse effect is usually more than outweighed by the benefits of excluding water both from the sampling process and from the subsequent GC(/MS) analysis.

In short, all other things being equal, it is advisable to use the most stable and most hydrophobic sorbent compatible with the compound(s) of interest.

Analyte Masses Retained on Sorbent Tubes During Diffusive Sampling

The mass of analyte retained during diffusive sampling over a given time period will depend on the uptake rate and atmospheric concentration. Information on typical ambient atmospheric VOC concentrations is presented in reference 49. Table 3 presents analyte masses that would be collected over 3 days, 1 week and 4 weeks monitoring periods, using a range of typical uptake rates and from a range of possible indoor/outdoor atmospheric concentrations.

Even the worst case example (3 days at 0.2 ppb with an uptake rate of 1.4 ng.ppm^{-1}.min^{-1}), results in the retention of ~1.2 ng of analyte and should be well within TD-GC system detection limits. Most GC flame

	U_{EFF} = 1.4			**U_{EFF} = 1.7**			**U_{EFF} = 2.0**			**U_{EFF} = 2.2**		
Atmospheric concentration (ppb)	**3 d**	**1 w**	**4 w**	**3 d**	**1 w**	**4 w**	**3 d**	**1 w**	**4 w**	**3 d**	**1 w**	**4 w**
500	3024	7056	28224	3672	8568	34272	4320	10080	40320	4752	11088	44352
100	605	1411	5645	734	1713	6854	864	2016	8064	950	2218	8870
20	121	282	1129	147	343	1371	173	403	1613	190	444	1774
5	30	71	282	37	86	343	43	101	403	48	111	444
1	6	14	56	7.3	17	69	8.6	20	81	9.5	22	89
0.2	1.2	2.8	11	1.5	3.4	14	1.7	4	16	1.9	4.4	18

Table 3: Analyte masses retained (ng) when monitoring typical ambient air concentrations with diffusive tubes

ionisation and full scan mass spectrometer detectors can comfortably detect 0.1 ng. Other selective GC detectors, such as the electron capture (ECD), offer sub-picogram sensitivity for target analytes such as perchlorethylene. In short, the limiting issue with regard to method sensitivity is more likely to be artefact levels than GC detector sensitivity.

System Artefacts and Method Detection Limits

As described above, artefacts are the most probable limiting factor with regard to method sensitivity. The single biggest source of artefacts in the analysis of diffusive sorbent tubes is likely to be the sorbent bed itself. Some sorbents are inherently more prone than others to artefact formation. Minimum individual artefact levels as high as 5 ng are reported for some porous polymers (see above). However, even these sorbents can still be used for air monitoring at low and sub-ppb concentrations if selective or mass spectrometer detectors are used and if adequate, high resolution capillary chromatography is employed.

Tube conditioning and storage

Stringent tube and analytical system conditioning and careful tube capping and storage procedures are essential[49]. System and sorbent tube conditioning must be carried out using more stringent conditions of temperature, gas flow and time than those required for sample analysis, but without exceeding safe temperature limits for the sorbent selected. Most successful reported long-term storage experiments have used cleaned metal Swagelok-type screw caps with combined PTFE or polyimide/graphite ferrules to seal the tubes during storage[63-67]. Sealed, conditioned tubes are best stored and transported inside clean, sealed glass or metal containers. An open container/cartridge of clean charcoal should also be kept inside the tube storage container to minimise vapour phase concentrations of organics. Some workers go to the lengths of wrapping each individual sorbent tube in uncoated aluminium foil for additional protection during trace level rural air studies. The same procedures are recommended for transportation and storage of diffusive tubes after sample collection and before analysis. Some workers advocate refrigeration/freezing of sampled tubes[49], though this practice is not widespread for typical, single sorbent diffusive tubes – see below.

Artefacts Generated During Sampling and Analysis

Benzaldehyde, phenol and acetophenone artefacts are reported to be formed via oxidation of the sorbent - Tenax - when sampling high concentration ozone atmospheres (100-500 ppb ozone)[68,69]. This effect is not reported for other common sorbents such as GCB1 and Carbopack/trap. There are no known reports of artefact formation or analyte degradation occurring via interactions of ozone with retained analytes except labile monoterpenes[70,71].

The effect of the process of thermal desorption itself on artefact formation and analyte degradation has been tested[68] for pumped sorbent tube samples by comparing the measurement of atmospheric concentrations of olefinic and alkylbenzenic compounds retained on Carbopack B using

a) solvent extraction - GC and
b) thermal desorption - GC

Diffusively sampled sorbent tubes require identical analytical processes. The experimental data showed that thermal desorption did not contribute to artefact formation or analyte loss. The only known reports of artefact formation/analyte degradation caused by thermal desorption occur

a) when charcoal is used as the sorbent material
b) with particularly labile compounds such as bis-chloromethyl ether and mercaptans in the presence of metal tube surfaces
c) during desorption of terpenes from carbonaceous sorbents[71,72].

Note that for the analysis of less stable VOCs, the inner surface of the tube and the entire sample flow path should be constructed of inert, deactivated or non-metallic materials to minimise degradation of labile components. US EPA Method TO-17 (reference 62 - Pumped sampling of ambient air onto sorbent tubes) specifies maximum sample storage times of 30 days under refrigerated or freezer conditions. Refrigeration and the maximum 30 days storage are recommended for field samples because of the low concentrations and general uncharacterised nature of most real-life atmospheres. However, there is much well validated data demonstrating that single bed sorbent tubes containing ~1 mg levels of VOCs can be stored for months or even years when the analytes are introduced under controlled laboratory conditions[47,73,74].

Practical Considerations

Sampling

Usual guidance regarding the placement of any and all types of ambient air monitor - a minimum distance from major emission sources, sheltered from extreme weather conditions, etc.[62] - should be observed for diffusive samplers. Simple non-outgassing, well ventilated beehive or cone-type shelters will suffice for protection from the weather and tubes should usually be orientated vertically with the sampling end pointing downwards.

Once at a monitoring site, a conditioned tube should be allowed to reach ambient temperature* before replacing the sealing cap with a sampling cap at the sampling end of the monitor. The sealing cap at the non-sampling end of the tube should be left in place. Use of disposable latex gloves is advised during all tube handling operations[67]. It is also recommended to place field blanks (tubes identical to those used for sampling but with both sealing caps left in place throughout the exposure period) at most monitoring locations. At the end of an exposure period, sample tubes must be resealed as per manufacturer's instructions and stored carefully, with the field blanks, for transportation back to the laboratory.

Analysis is recommended as soon as possible.

Analysis

TD-GC(/MS) analytical considerations for ambient air monitoring using diffusively sampled sorbent tubes are the same as those documented for pumped tubes[49,50,62] but with reduced moisture management concerns. One of the advantages of diffusion *versus* pumped air sampling is that humidity can be partly excluded from the monitor during sampling *via* appropriate use of hydrophobic sorbents and/or semi-permeable membranes. This simplifies analytical method development. Two-stage thermal desorption is essential for optimum high resolution capillary GC(/MS) analytical performance[49]. Desorption systems incorporating a small, electrically-cooled secondary trap have been shown to transfer analytes efficiently to the GC analytical column and detector. They also offer practical benefits versus capillary cryofocusing systems in terms of eliminating liquid cryogen consumption and having low risk of ice formation blocking the sample flow path. However, care must be taken to select a system which facilitates complete transfer of target VOCs to the analytical system[75]. Desorbers which require a significant split ratio to prevent band broadening and maintain capillary peak shapes, may compromise analytical sensitivity. The desorber selected should also feature an ambient temperature purge of air and stringent leak test of each system prior to analysis in order to ensure sample/data integrity. Without a thorough air purge prior to desorption sorbent/analyte oxidation and artefact formation would be inevitable.

In general terms, desorption conditions - flow, temperature and time - should be selected to reproducibly achieve >95% recovery of target analytes without risk of thermal degradation of the sorbent or compounds of interest. General guidance on parameter selection and validation procedures for use during TD-GC method development is published in the literature[49,50,62] and is also available from system manufacturers.

* *Note that tubes stored and transported to a monitoring location at freezer or refrigerated temperatures should be allowed to warm up to ambient temperature before monitoring begins to prevent condensation of water inside the sample tube.*

Calibration Techniques

Standard atmospheres

Standard atmospheres are notoriously difficult to generate and sustain reliably at the low concentrations required to simulate ambient air - even for stable compounds such as volatile hydrocarbons. Some information is available in the literature[3,36,76], but it is more practicable for most users to purchase certified, low-level spiked standards from a reputable source. Such certified standard tubes are ideal for internal laboratory quality control and external quality assurance, but are not essential for routine calibration operations - see section on quality assurance.

Standards for routine multi- and single level calibration may be most simply prepared by loading 1-5 mL of gravimetrically prepared liquid solution or 1-5 mL of concentrated gas phase standard onto the sampling end of a blank, conditioned sorbent tube. Analytes should be swept into the sorbent bed using a flow of ultra-pure inert gas[49,50,62]. The mass(es) of analyte(s) introduced onto the standard tube must be representative of those likely to be retained during field monitoring.

Quality Assurance

Quality assurance of the sampling process

Two standard tests should be used to validate sampling procedures - routine use of blanks and intermittent parallel monitoring with an alternative sampling method such as pumped tubes.

It is always advisable to employ field and laboratory blanks in a monitoring exercise. Blank tubes should be as similar as possible to those used for sampling - same sorbent, packed at the same time, conditioned in the same way, *etc*. Laboratory blanks should not leave the lab., but should be kept sealed and stored under standard conditions. Field blanks should be transported to the monitoring sites with the sample tubes, but left with both sealing caps in place while the monitoring tubes are exposed. It is advisable to analyse blank tubes in the same analytical sequence as the sample tubes. If significant concentrations and/or similar profiles of compounds are found on the blanks as are measured on the sampled tubes, this is a good indication that the sampling procedure has been compromised by inadequate tube sealing or some other contamination mechanism.

Parallel sampling with another monitoring technique is normally not practicable for typical long-term (up to 4 week) diffusive, ambient-air monitoring exercises. Pump rates, for example, cannot be set low enough to avoid breakthrough of most common analytes over such a long time period on a single tube. However, automated sequential pumped tube samplers which do allow continuous long-term sampling with a single pump are commercially available. Automated, online gas chromatographic systems are also available to monitor VOCs on a continuous or semi-continuous basis[77], though these can be expensive. Reports of urban air monitoring campaigns using diffusive tubes in parallel with alternative monitoring technologies do demonstrate reasonable correlation[78].

Quality assurance of the analytical process

As the TD-GC(/MS) analytical process used for diffusive tubes is essentially the same as that used for pumped - the QA tests and associated criteria outlined in methods such as US EPA Method TO-1762 can be applied. Tests typically include:

a) checks on recovery/carryover

b) method stability/precision tests (usually involving at least 6 spiked tube replicates

c) multi- and single level calibration

d) routine checks on sensitivity (may be integrated into a multilevel calibration exercise)

e) regular use of well-validated, commercial standard tubes to determine bias

f) MS tune checks if applicable.

It should be relatively straightforward to select TD-GC flows, split ratios and detector parameters such that method detection limits comfortably allow quantitative measurements from 1 week exposure samples at sub-ppb concentrations.

Participation in a formal audit scheme is also strongly recommended. One such scheme, specifically focused at the trace level VOC, ambient air monitoring community, has recently been introduced as an add-on to the UK Workplace Scheme for Proficiency (WASP).

Extending the Application Range for Diffusive Tubes

Data and information presented in this paper principally relate to monitoring VOCs in ambient outdoor and indoor air. However, other environmental-related applications for diffusive tubes have been developed. These include soil probes - used to screen organic soil contamination around industrial sites, landfill etc. - and ventilation/tracer gas studies.

The diffusive soil probe was first reported by British Petroleum[79] in the UK. Hollow metal probes containing diffusion tubes are simply pushed into the ground in a grid pattern covering the site (primary survey.) Vapours from the soil migrate into the probes and are collected on the diffusive tubes. After ~24 hours exposure the tubes are removed, analysed and areas of high VOC concentration, 'hot spots', identified. Generally these areas are subsequently targeted with tighter/more localised grid patterns of soil probes in a follow-up visit (secondary survey.)

None of the measurements taken are quantitative in the true sense - VOC concentration data are simply compared across all tubes sampled in that survey. However, the approximate location of an underground leak (primary survey) and the precise direction/size of the resultant plume of underground pollution (secondary survey) are easily determined using this two-phase approach. Work with these soil probes may be followed up by one of the more conventional, quantitative soil sampling/analysis procedures, but in many cases it is simply most cost effective to remove or treat the contaminated land without further analysis.

Diffusive sampling for perfluorocarbon tracer gases was first reported by RIVM in the Netherlands in 1992[80], but other centres, such as the UK Building Research Establishment, have also successfully employed the approach for ventilation tests[81]. Perfluorocarbons do offer certain advantages over SF_6 and other more conventional tracers. They comprise a range of similarly behaved, but readily distinguishable compounds - *e.g.* perfluorodimethylcyclobutane and perfluoromethylcyclohexane. Use of two or three of these compounds in a single building survey allows room-to-room air interchanges to be studied. The simplicity and 'passivity' of diffusive samplers can also be of real benefit to studies of indoor air movement.

Conclusion

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 do offer some advantages versus pumped sorbent tubes in terms of simplicity, reduced variability (less to go wrong), cost, extended sampling times and minimal water interference.

Published data are available describing successful field trials of diffusive tubes in both indoor and outdoor air. The samplers have been shown to:

- be suitable for use by untrained personnel,
- offer satisfactory detection limits and
- provide high quality quantitative data relative to parallel monitoring techniques.

Information relating to the diffusive sampling of volatile aromatics - benzene, toluene and xylene - is especially extensive. The cost advantages of diffusion are apparent in some of the large scale, detailed studies of these analytes in major urban agglomerations[32]. Such a study would be impossibly expensive using other methods. Diffusive sampling tubes should play a significant future role in routine urban air monitoring worldwide. They should also facilitate, otherwise impractical, rural monitoring campaigns - such as investigations of environmental crop damage and long-range pollution transport.

Undoubtedly more evaluation work is required; particularly to look in detail at a wider range of common VOC analytes and to validate the technique more extensively versus other proven alternative technologies such as auto-GC. Such programs have been proposed and should support the ongoing development of relevant international standard methods.

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