PERSONAL MONITORING | Passive☆

M Harper, National Institute for Occupational Safety & Health, Morgantown, WV, USA

Disclaimer: The opinions expressed in this work are those of the author and do not necessarily represent the policies of the US National Institute for Occupational Safety and Health. Mention of any commercial product does not constitute an endorsement from the Federal Government, and does not imply that other products are unsuitable for any particular use. Mention of products of the American Conference of Governmental Industrial Hygienists also does not imply endorsement by the Federal Government.

Basic Theory

Acute or chronic exposure to the thousands of minor components that can be present in the air we breathe may cause adverse health effects. Such exposure may occur in the workplace, home, or outdoor environment. Monitoring of these components is required to ensure compliance with recommended or regulated air quality standards. The preferred monitoring method would give a continuous and accurate measurement of instantaneous changes in the concentration of each harmful species present, in a manner that would model human exposure. The compromise most often applied in practice is to extract the components from a large volume (to provide sensitivity) of breathing zone air together with subsequent laboratory analysis (to provide selectivity).

In the 'active' method of extracting the gas and vapor components of air, a known volume is passed through an apparatus containing liquids in which the components can dissolve, porous solids on which the components can be adsorbed, or liquids or solids containing chemicals with which the components can react. The total volume of air passed is metered by the pump, and both pump and extraction apparatus are placed appropriately about the person to obtain a representative sample. The pumps have been criticized as bulky, heavy, and noisy, and therefore an encumbrance to the wearer, and also as expensive.

An alternative method known as 'passive' or diffusive sampling, which does not require a pump or air mover, has gained popularity in recent years. Diffusive samplers operate by allowing the gas and vapor molecules to make their own way to the collection medium by diffusion along a carefully controlled path. The rate of movement, which is a function of the diffusion coefficient of the gas or vapor in air and the path geometry (Figure 1), can be derived from Fick's first law of diffusion: $W = -DA\frac{\mathrm{d}c}{\mathrm{d}x}$ where W is the rate of mass transfer (ng s^{-1}), D is the diffusion coefficient ($\mathrm{cm}^2\ \mathrm{s}^{-1}$), A is the cross-sectional area of the diffusion path (cm^2), and $\mathrm{d}c/\mathrm{d}x$ is the rate of change in concentration over the diffusion path ($\mathrm{ng\ cm}^{-3}\ \mathrm{cm}^{-1}$). If the diffusion path is considered to be the length L (cm) of the air gap in the sampler, and the concentration at the sorbent is considered to be negligible (the so-called 'zero-sink' condition), then the mass M (ng) adsorbed by the sampler from an atmosphere of concentration C ($\mathrm{ng\ cm}^{-3}$) in time t (s) is given by $\mathrm{M} = D\frac{A}{L}Ct$. The uptake rate of the sampler is given by the expression $D(A/L)$, which has units ($\mathrm{cm}^3\ \mathrm{s}^{-1}$) dimensionally equivalent to a volume flow rate. The geometry of the sampler is known from measurement, but very few diffusion coefficients have been measured. They can be calculated, assuming certain rules for calculating molecular size, but these need to be correlated with experimental determinations of uptake rates from atmospheres of known concentration. This gives a correction factor that depends on the chemical makeup of the molecule, and which can then be used to adjust the calculated values of other, similar molecules.

Fick's second law of diffusion can be used to derive an expression for the time required to set up steady-state conditions within the sampler once the diffusion path is exposed to an ambient vapor concentration, which can also be applied to the behavior of molecules within the diffusion path after the sampler is closed. The time taken for a molecule to traverse the diffusion path is given by L^2/D, which for benzene is 11 s when the diffusion path is 1 cm. When diffusive samplers, especially those where the diffusion path is long, are used to sample for short periods of time, these time-related effects can be significant sources of error. Sampling transient and rapidly fluctuating peaks of concentration provides another source of time-related errors. In this case, however, the

---

☆*Change History:* May 2013. M Harper made changes in sections 'Types of sampler and 'Validation of the Sampling Method, and 'Active Vs. Passive Sampling' added a new reference in 'Further Reading' section, and added new Figure 2,3,4,5,6.

http://dx.doi.org/10.1016/B978-0-12-409547-2.00399-1

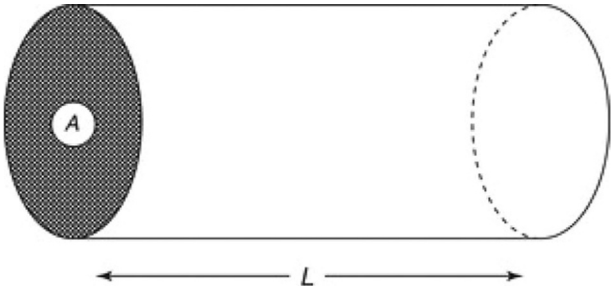

Figure 1 The geometry of the diffusion path.

finite bounds on the height and width of real peaks are a finite bound on the maximum error. These types of errors have been carefully considered and discussed in the literature. Experimental validations often provide evidence of a higher uptake rate during short (<15 min) exposure periods.

The diffusion coefficient is affected by temperature and pressure, but so too is the concentration. The mass collected by the sampler is therefore proportional to the square root of the absolute temperature and independent of pressure. The temperature effect should be less than 0.2%$°C^{-1}$, and is normally ignored, since the variation from the measured uptake rate should be less than 5% from room temperature to 0 °C and from room temperature to 40 °C.

Results from diffusive sampling are often provided in terms of parts per million by volume ppm under the sampling site conditions of temperature and pressure. When the limit values to which these concentrations will be compared are stated in the same terms, then the statements in the preceding paragraph hold true. However, the origin of many limit values used around the world are the TLV®s of the American Conference of Governmental Industrial Hygienists (ACGIH). These values are stated in units of mass per unit volume (e.g., mg m^{-3}), while TLVs for gases and vapors are also stated in units of ppm at NTP (or 25 °C, 1 atm, in the USA). In order to compare a result to these values, the diffusion coefficient is corrected for the difference between NTP and the sampling site pressure and temperature, but the concentration is not. This procedure is to be used, for example, for comparing results to the US Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs). The potential effect of this calculation is significant and could be as much as 20%, given extremes of temperatures or altitude.

The diffusion pathlength is affected by ambient air movement. Strong air currents around the face of the sampler may cause turbulent effects within the diffusion gap, effectively reducing the diffusion path, while weak air currents may not be sufficient to replenish molecules that have migrated to the sampler, effectively extending the diffusion path beyond the sampler face. The diffusion pathlength is also affected if the concentration at the sorbent face is not zero; therefore, the two principal factors that need to be considered in the application of a diffusive sampler are the geometry of the sampler and the type of sorbent. These two factors have the greatest influence on sampler performance.

Types of Sampler

'Tubes' versus 'Badges'

The diffusion path to the sorbent can take many forms. The simplest version is an open tube. This was the construction used for sampling nitrogen dioxide in the original investigations into diffusive sampling by Palmes, and it is still in use today (Figure 2). An open tube may be affected by air currents disturbing the still air conditions required in the diffusion path, so that tubes without a windscreen must be long with respect to their diameter, with a ratio in excess of 3:1. Unfortunately, a long diffusion path results in a lower uptake rate (typically ~0.3–3.0 ml min^{-1}) and much increased response time, reducing the application for short-term exposure determinations. However, the low uptake rate also reduces the possibility of starvation at the open face, so that the tube design can be used in areas of reduced air movement; and the low uptake rate also decreases the possibility of sorbent saturation, so that much longer sampling periods, of the order of weeks or months, can be used.

One major advantage of a tube design is the potential for gas-flushing organic vapors from open-ended tubes in a thermal desorption system directly into an analytical device, usually a gas chromatograph with flame-ionization detector or mass spectrometer. An example is shown in Figure 3. The convenience of this procedure is undeniable, although few quantitative methods are available. The analysis is limited in earlier thermal desorption systems to a single shot, but more recent systems allow re-collection of split samples for later analysis.

A second form of construction is to use a number of shorter, narrower tubes, which at the extreme can be reduced to a thin, porous membrane. The short diffusion path results in a faster response time, and also combines with the larger overall sorbent surface area to give much higher uptake rates. This situation is better for short-term sampling, but may lead to the possibility of overloading at high exposure doses. The higher uptake rate of these samplers (typically 6–60 ml min^{-1}) requires more air movement, normally at least 10–20 cm s^{-1}, around the open face in order to prevent starvation. With personal monitoring, natural movements of the body are assumed to give rise to sufficient air movement, but problems can still arise where workers are in sedentary occupations or where their movements are severely restricted. While badge-type samplers are not prone to effects from

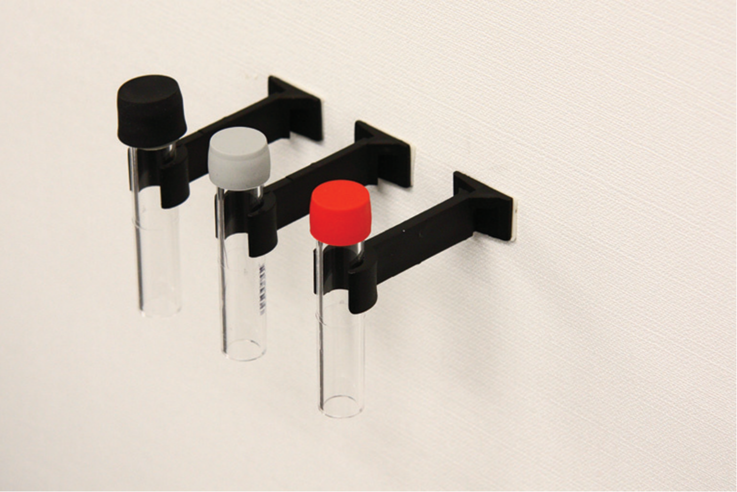

Figure 2 “Palmes-tube”diffusive sampler for nitrogen dioxide. Reproduced with permission from Gradko, Ltd.

Figure 3 Stainless steel diffusive tube for thermal desorption analysis. Reproduced with permission from Markes International, Ltd.

air movement parallel to the face, since each individual diffusion element normally has a length-to-diameter ratio of at least 3:1, perpendicular air movement has been shown to be able to cause a ‘scooping’ effect if there is communication between the bases of the tubes. A windscreen made from a porous membrane, sited above or below the diffusion path, will prevent this. Examples of these ‘badge-type’ samplers are shown in Figure 4(a)–4(f). A more recent development in high-uptake rate sampling is the ‘radial’ diffusive sampler shown in Figure 5. Gases and vapors diffuse onto a cylinder of sorbent, protected from air movements by a surrounding diffusion element. The diffusion element can be exchanged to modify the uptake rate and the sorbent can be optimized to the chemical of interest. Since diffusion occurs onto the whole body of the tube of sorbent rather than just at one end uptake rates are higher than for the same chemicals on tube-type samplers.

The Choice of Sorbent

The best choice of sorbent is one that will react with the component of interest to produce a nonvolatile, easily analyzable derivative. Indeed, if the derivative is colored, the analysis can be of extremely low cost and can be performed onsite. This was a very exciting possibility that was investigated at an early stage in the development of diffusive samplers, and a number of samplers have been produced commercially. Many use water-soluble reagents in aqueous solution as the sorbent, held in place by hydrophobic or high-water-content polymer membranes. These membranes can act as the control over mass transfer, or they can be used together with a diffusive air gap. Analysis requires an inexpensive spectrophotometer. Reagents coated onto an inert substrate can also be used and can be analyzed by reflectance spectrophotometry, although cheap and accurate field instrumentation has only recently become available.

There are a number of drawbacks to this technique, such that it is generally employed for certain specific gases and vapors. The reagents and products must be stable, and the analysis must be sensitive and free from interference. Finally, the method must satisfy stringent precision and accuracy requirements for use in hygiene investigations where compliance with government regulated exposure guidelines must be demonstrated; otherwise, the technique still has value in screening tests. Greater precision and accuracy are normally attainable with a laboratory analytical technique, such as liquid chromatography (LC), ion chromatography, or polarography. The gases and vapors most frequently applicable to this method are inorganic compounds; for example, chlorine, ammonia, sulfur dioxide, and hydrofluoric acid. Formaldehyde is the compound most frequently determined by this method.

The use of colorimetric detector tubes in a diffusive mode is an extension of this type of method. In this case, reaction with a substrate contained in a tube produces a color change, the extent of which is related to the applied dose. In addition to the drawbacks of colorimetric analysis mentioned above, there is a further inaccuracy involved in reading the extent of the color change, which is complicated by being nonlinear with respect to exposure dose (concentration multiplied by time). An example of this type of sampler is shown in Figure 6. Semi-quantitative colorimetric devices are also available (Figure 7(a) and 7(b)).

Figure 4 Badge-type diffusive sorbent badges for volatile organic compounds (a-e), aldehydes (f) and mercury (g). (a) Reproduced with permission for 3 M (© 2013 3 M Company. All rights reserved.), (b) and (c) Reproduced with permission from Assay Technology, Inc., (d-f) Reproduced with permission from SKC, Inc.

(Continued)

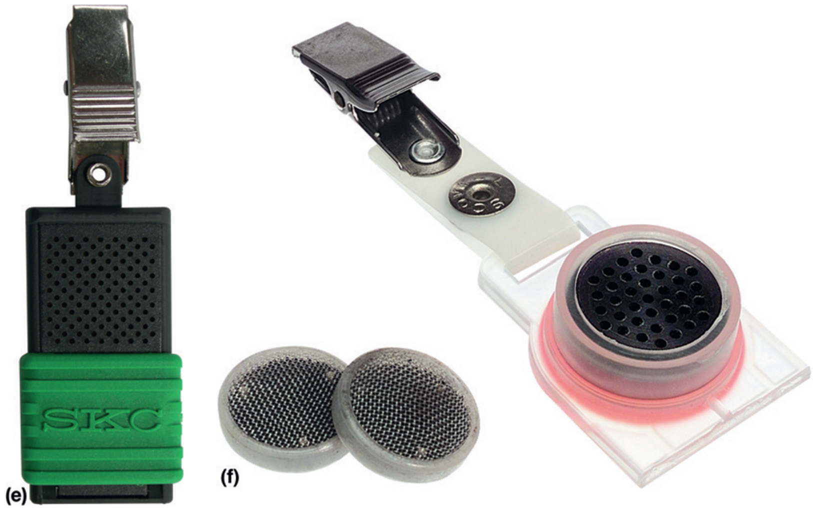

Figure 4 (Continued)

Figure 5 Radiello(TM) radial diffusive sampler.

The preferred technique for sampling organic vapors is collection on a porous sorbent by the van der Waals forces of adsorption (particularly the London dispersion force), with later desorption and instrumental analysis. The rate of adsorption at the sorbent surface is extremely fast and is not normally considered a rate-controlling step, and the adsorption equilibrium is normally shifted far enough in the direction of the adsorbed phase that the concentration at the sorbent surface can be regarded as insignificant. All molecules that arrive at the surface are therefore adsorbed. The adsorbed vapors are extracted from the sorbent by means of a solvent or heat, and analysis is normally carried out by gas chromatography (GC), or less often by LC.

Sorbents differ in their affinity for different vapors, and sometimes this will cause a particular sorbent–vapor combination to deviate from the ideal behavior described above. Weak sorbent–sorbate interactions can cause the concentration of the

Figure 6 Colorimetric diffusion tube sampler. Reproduced with permission from Draeger Safety, Inc.

Figure 7 Semi-quantitative colorimetric badges. Reproduced with permission from Morphix technologies, Inc.

(Continued)

vapor to be significantly greater than zero at the sorbent surface, and to increase with increasing exposure dose. This will result in saturation where the sorbent is a thin layer, as in badge-type samplers, or a progressive increase in the diffusion path through the sorbent where it is disposed in a thick bed as in many tube-type samplers. Both effects produce the same result, a progressive reduction in the sampling rate with time, leading to an underestimation of the applied concentration. In addition, if the concentration at the open face of the sampler is reduced to zero, adsorbed sample can re-equilibrate with the vapor phase and diffuse back out of the sampler. This is known as reverse diffusion, and it too results in an underestimate of the true exposure dose.

In general, the sorbents used in the tube-type samplers for thermal desorption tend to be porous aromatic polymers, or graphitized carbon blacks that adsorb little water to interfere with the GC analysis, and where the van der Waals forces of adsorption are not so strong as to require excessive temperatures for desorption. Because of these weak interactions, saturation

Figure 7 (Continued)

and reverse diffusion must be expected and guarded against in the method evaluation. Carbon and zeolite molecular sieves have been used to adsorb the most volatile molecules, but water adsorption makes analysis by thermal desorption more complex.

Conversely, the preferred sorbent for the badge-type samplers is activated charcoal, which has a greater capacity for organic vapors. Saturation and reverse diffusion are less likely to occur except with the most volatile compounds, e.g., acetone or methylene chloride. One method of counteracting these effects is by means of two layers of sorbent, the second acting as a backup analogous to the backup section in pumped sorbent sample tubes. Unfortunately, research has shown that reverse diffusion takes place at the same time as migration to the second layer, and sample loss is slowed but not avoided completely. Extra sorbent sections, therefore, are not a completely reliable guarantee of sampling accuracy.

Desorption of these samplers is by means of a solvent, which often can be added directly to the closed sampler. Solvent desorption of active charcoal is not usually as efficient as thermal desorption with porous polymers for a number of reasons. First, desorption efficiency depends on the partition equilibrium of the compound between the solvent and the charcoal. Second, a certain proportion of the sample may be lost irretrievably within bottle-necked pores, by reaction with surface-active sites, or by partition into an aqueous phase resulting from the simultaneous desorption of adsorbed water. This latter can be retrieved by desorption using a more polar solvent mixture. In general, these losses are somewhat balanced by loss of the solvent through adsorption on the charcoal. The resulting recovery can range from 80% to 110% of the applied dose, and this needs to be carefully characterized. Recoveries of polar and reactive compounds tend to fall further at lower loadings. Losses may also occur during storage of the sampler after use, and this too must be carefully characterized. Porous polymers are not immune to sample losses during thermal desorption or storage, although it occurs less often. Perhaps the biggest drawback of solvent desorption is the reduced analytical sensitivity caused by the solvent dilution of the sample. Thermal desorption without focusing also results in sample dilution because the amount of carrier gas required for sample desorption cannot all be passed into a capillary GC column. A splitter valve may be required to dispose off much of the sample.

For most general purposes the choice of tube versus badge revolves practically around the preferred desorption technique, provided the correct sorbent is selected for the tube-type sampler. Tenax® TA is often used, even though it has a small surface area and low capacity for volatile compounds. Porapak N is sometimes employed for polar compounds, but the capacity is also quite low and is compromised by high relative humidities. Chromosorb® 106 is a good all-round medium, with a surface area $\sim$700–800 $m^2\ g^{-1}$ and hydrophobic character, but there is a gradually increasing background caused by slow polymer degradation or trapping of adsorbed material that is released on subsequent uses. This can be a problem in sampling very low concentrations, such as in indoor air-quality surveys.

One important consideration is the possibility of reuse of thermal desorption tubes, since they are cleaned in the desorption step. Charcoal badge-type samplers are of single-use nature but cheaper. Solvent desorption also allows multiple analyses from a single sample to give greater accuracy.

Validation of the Sampling Method

The precision and accuracy of any measurement method must fall within acceptable bounds. Precision is normally denoted by the bias, or deviation of an average measurement from the 'true' measurement as recorded by an unbiased reference method. Accuracy is normally denoted by the spread of results about the mean, and is defined as twice the pooled coefficient of variation of the method. According to the National Institute of Occupational Safety and Health (NIOSH) in the United States, a method is acceptable if 95% of the results fall within 25% of twice the pooled coefficient of variation plus the absolute bias (regardless of sign). In European and international standards the concept of overall uncertainty is currently preferred. A lower level of overall uncertainty for measurements taken at concentrations below regulated limit values is often acceptable and the Committee for European Normalization (CEN) suggests a relaxation to 50% at concentrations below one-half the limit value, or over the full range if the measurements are made for screening purposes only.

Experimental tests are required to confirm acceptable sampler performance. NIOSH, and the Health and Safety Executive in the United Kingdom, have published diffusive sampler evaluation protocols that cover the effects of exposure, time, concentration, desorption efficiency, storage stability, reverse diffusion, temperature, humidity, presence of interfering compounds, face velocity, and orientation. Many of these factors are varied together in a multifactorial study to determine the possibility of interactions. Precision and accuracy, or overall uncertainty, are determined from the combined results of these experiments. Today, consensus Standards form ASTM, CEN and ISO are also available. All of these protocols require laboratory exposure studies in atmospheres of closely controlled composition. The expense of producing good-quality atmosphere generation rigs together with the time and costs of running the full set of experiments (equivalent to about three technician-months per validated compound) have been a barrier to the widespread adoption of these protocols. A useful suggestion for reducing the number of required experiments is the concept of bilevel validation, which involves performing the full set of validation tests on one member of a homologous series, together with a reduced set of tests on the higher members of the series if the first member passes. This allows the validation of about one series (e.g., aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated aliphatic hydrocarbons, ketones, acrylates, aliphatic alcohols, etc.) per year. In addition to laboratory tests, field trials are recommended or required by the protocols. Two types of field trials are suggested, one being a large set of diffusive samplers and reference methods arranged in a static array, the other consisting of a number of pairs of diffusive samplers and reference methods as static or personal monitors. The results of these tests require cautious analysis to be sure they are effective. For instance, the effects of environmental conditions on the reference methods need to be known and accounted for, and the statistical tests most appropriate to the situation must be applied. It is unfortunate that to date very few samplers have been evaluated according to these protocols, since only through such tests can confidence in the measurements be assured. Table 1 gives a summary of the compounds validated using one particular badge-type sampler containing one or another of two different sorbents, where the validation was undertaken by the manufacturer. Since then, this sampler and others have been evaluated by the Occupational Safety and Health Administration in the USA. Validated methods using these samplers are available on their web-site for a range of organic chemicals including benzene, 2-butanone, butyl acetate (*n*-, *sec*-, *tert*-), hexone, isobutyl acetate, styrene, tetrachloroethylene, toluene, trichloroethylene and xylene (*o*-, *m*-, *p*-), as well as a sampler for nitrous oxide for use in operating theaters. All of the compounds tested according to the full protocol had acceptable overall accuracies. It is normally the case that well-designed diffusive samplers have precision and accuracy characteristics comparable to other accepted methods.

Table 1 Compounds validated using the SKC Inc 575 series badge-type sampler with (A) charcoal and (B) Anasorb® 747 sorbents

(A) Charcoal sorbent		
Aliphatics	*Aromatics*	*Chlorinated*
Pentane[a]	Benzene[a]	Methylene chloride[a]
Hexane	Toluene	*cis*-1,2-Dichloroethylene[a]
Heptane	Ethylbenzene	Trichloroethylene[a]
Octane	*o*-Xylene	Tetrachloroethylene[a]
Nonane	*m*-Xylene	Vinylidene chloride
Cyclohexane	*p*-Xylene	Chloroform
Methylcyclohexane		
	Cumene	Carbon tetrachloride
	t-Butyltoluene	1,2-Dichloroethane
		1,2-Dichloropropane
		1,1,1-Trichloroethane
		1,1,2-Trichloroethane
		1,2,3-Trichloropropane
		1,1,2,2-Tetrachloroethane
(B) Anasorb®747 sorbent		
Ketones	*Acrylates*	
Acetone[a]	Methyl acrylate[a]	
2-Butanone (MEK)	Methyl methacrylate	
Methyl isobutyl ketone	Ethyl acrylate	
Diisobutyl ketone	Butyl acrylate	

[a] Full validation according to NIOSH protocol, all others partially validated according to bi-level validation theory.

Active versus Passive Sampling

As mentioned in the introduction, the chief drawback to the pumped system has been the pump itself, which is normally described as bulky, heavy, noisy, and expensive, and which requires frequent calibration and periodic maintenance and repair. However, manufacturers have addressed these criticisms over the previous decade. Today's models are smaller, lighter, and quieter. In addition, the cost of a pump is spread over a very large number of individual samples, and the major cost per sample is the analysis, which is the same whether the sample is pumped or diffusive. A pump provides the advantage of a series of samples, such as in a backup sorbent layer, to detect breakthrough from the primary collection layer. To ensure the same safety factor in diffusive sampling, two samplers with different uptake rates can be employed, the ratio between the collected samples being the critical factor in proving a good sample. One definite advantage of the diffusive sampler is that it can be left unattended during operation, while the operation of the sampling pumps must be checked regularly during use. In addition, it is not necessary to account for pump error. The most important difference between active and passive sampling is the ability to vary the flow-rate of a pump, while the uptake rate of the diffusive sampler is fixed. Thus the same sorbent tube can be used for very volatile compounds or in high concentrations at a low flow rate, or for less volatile compounds or in low concentrations at a high flow-rate. While diffusive samplers for volatile compounds are generally optimized for a geometry that covers the greatest range of possibilities, there may be situations where there is either insufficient sensitivity or sample overload.

Often the cost factor is represented as a contest between diffusive samplers with thermal desorption on the one hand and pumped samplers with solvent desorption on the other. This is not quite an accurate picture, since there are plenty of examples of alternative techniques; that is, diffusive sampling with solvent extraction and pumped sampling with thermal desorption. Both thermal and solvent desorption can be automated and run overnight. The tubes used in pumped sample trains are less expensive than any diffusive sampler, but they are of single-use type, unlike thermal desorption tubes. Overall, the costs are probably not very different, and the differences are minimized further when including other costs of the sampling exercise, such as the costs of taking the sample, the analysis, and the interpretation of the result.

One very important difference between pumped and diffusive sampling occurs when aerosols or dusts containing the compounds of interest are present. Pumps are able to draw these species into an adsorbent tube or impinger, where the compounds of interest will be collected, although not necessarily with 100% efficiency. Diffusive samplers cannot collect anything other than gases or vapors, but if dust or aerosol becomes attached to the face it can outgas volatile components even after the sampler is closed. A heavy loading of dust, grease, or condensation on the sampler face can block the diffusive uptake, and tears or perforations of delicate membranes can also affect the uptake rate. Many problems associated with the use of diffusive samplers have been traced to careless handling and contamination.

Finally, it is important to remember that the sampling rate of a diffusive sampler is different for individual chemicals and it is not possible to provide uptake rates for complex mixtures, and that the sampling rate is fixed, while that of a pump can be adjusted up to 1000 ml min^{-1} or more for additional sensitivity.

Permeation Samplers

Diffusion through materials other than air is possible, and a number of polymer materials have been tried, either alone, or in combination with an air gap. It is important to distinguish these membranes from those that are porous, where the primary control of mass transfer is still diffusion in air. Diffusion through polymers is much slower than through air and is normally referred to as permeation. Permeation samplers have advantages (for instance, organic vapors may permeate through a hydrophobic membrane while interfering water vapor does not) but also have disadvantages, mainly as a result of variations in the thickness or composition of the membranes, and the lower uptake rate. Permeation samplers are not currently commercially available. However, solid-phase micro-extraction (SPME) fibers, which have characteristics of permeation and absorption/adsorption, can be employed as short-term diffusive samplers. For further information on this subject please see Harper 2013.

Further Reading

1. In *Diffusive sampling*: *An alternative approach to workplace air monitoring*, Proceedings of the International Symposium, Luxembourg, 1986; Berlin, A., Brown, R.H., Saunders, K.J.,Eds.; Royal Society of Chemistry (includes the NIOSH validation procotol): London, 1987.
2. Brown, R. H.; Harvey, R. P.; Purnell, C. J.; Saunders, K. J. A diffusive sampler evaluation protocol. *Am. Ind. Hyg. Assoc. J.* **1984**, *45*, 67–75.
3. Guild, L. V.; Myrmel, K. H.; Myers, G.; Dietrich, D. F. Bi-level passive monitor validation – a reliable way of assuring sampling accuracy for a larger number of related chemical hazards. *Appl. Occup. Environ. Hyg.* **1992**, *7*, 310–317.
4. Harper, M.; Purnell, C. J. Diffusive sampling – a review. *Am. Ind. Hyg. Assoc. J.* **1987**, *48*, 214–218.
5. Harper, M. Sorbent trapping of volatile organic compounds from air. *J. Chromatogr. A* **2000**, *885*, 129–151.
6. Harper, M.; Guild, L. V. Experience in the use of the NIOSH diffusive sampler evaluation protocol. *Am. Ind. Hyg. Assoc. J.* **1996**, *57*, 1115–1123.
7. Harper, M. Assessing exposure to workplace chemicals: the role of exposure monitoring. *J. Environ. Monit.* **2004**, *6*, 404–412.
8. Palmes, E. D.; Gunnison, A. F. Personal monitoring device for gaseous contaminants. *Am. Ind. Hyg. Assoc. J.* **1973**, *34*, 78–81.
9. Rose, V. E.; Perkins, J. L. Passive dosimetry – state of the art review. *Am. Ind. Hyg. Assoc. J.* **1982**, *43*, 605–621.
10. Harper, M.; Smith, P. A. Occupational Hygiene: Gas Chromatography. *Chemistry, Molecular Sciences and Engineering.* **2013**, 1–23.