General Aspects

Passive sampling

Contents

1 Passive sampling

1.1 The fundamental principles of passive sampling

1.1.1 The use of diffusion for passive sampling

Passive sampling makes use of the laws of diffusion. There are various sampling systems for passive sampling.

Such systems are made up of a sampling phase (e. g. activated carbon) mounted a short distance behind an opening of known cross-section which is in contact with the ambient air. The molecules are transported from the opening to the collection phase by diffusion. To minimise the effect of air currents, either the whole diffusion layer can be made of porous material or the opening of the diffusion sampler can be covered with a porous membrane. In the latter case the substance is transported in a first step by permeation, followed by diffusion [1]. With very small diffusion cross-sections and very long diffusion paths, such layers or membranes are not necessary.

Figure 1 shows diagrams of diffusion samplers:
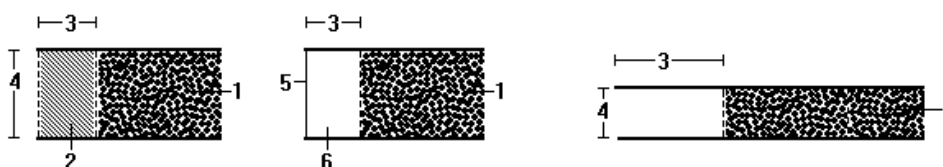
Fig. 1. Diagrams of diffusion samplers. 1 sampling phase, 2 covering (porous material), 3 diffusion path, 4 diffusion cross-section, 5 porous membrane, 6 air volume (diffusion chamber).

Diffusion samplers used to determine the concentration of a substance directly in accordance with the standard DIN EN 838, so-called reaction samplers, are called type A [2]. Characteristic of reaction samplers is that the substance to be collected produces a specific chemical reaction with a reagent on the surface of a collection phase; it makes sense that this reaction should result in a colour change. The concentration of the substance to be collected is determined either by estimating the intensity of the colour, which is approximately proportional to the amount of substance reacted, or by using a scale for the length of the coloured zone.

On the other hand, diffusion samplers used for indirect determination of the concentration with sampling by diffusion and adsorption and subsequent analysis in a separate step are called type B samplers.

1.1.2 The laws of diffusion

Diffusion is the molecular transport of a substance and is observed in gaseous, liquid and solid media. The forces behind this substance transport are differences in concentration, partial pressure and temperature. Characteristic of diffusion processes is that transport of the substance takes place without any apparent flow, i.e. without movement of the whole medium.

In general, diffusion is understood to be the process whereby molecules migrate within a system as a result of differences in potential [3].

During passive sampling the only force behind the transport of the substance is the difference in the concentration of the substance in the ambient air and that on the surface of the collection phase. To calculate the amount of substance which has diffused within a certain period of time, geometric parameters, such as the length of the diffusion path over which the concentration differs, and the cross-section through which a certain amount of substance diffuses within a defined period of time, must be taken into account. The diffusion process can be described mathematically by Fick's first law of diffusion [4]:

$$\frac{\Delta n}{\Delta t} = -D \cdot q \cdot \frac{\Delta c}{\Delta x} \tag{1}$$

where:

n	is the number of moles of the substance transported
$\Delta n/\Delta t$	is the rate of diffusion in mole/s
c	is the substance concentration in mole/cm^3
x	is the diffusion path in cm
$\Delta c/\Delta x$	is the difference in concentration in mole/cm^4
q	is the diffusion cross-section in cm^2
t	is the time in s
D	is the diffusion coefficient in cm^2/s

Assuming that, as everything is adsorbed, the concentration of the substance directly above the collection phase is zero and that the concentration of the substance in the vicinity of the sampler corresponds with that in the ambient air, formula (1) can be simplified [1]:

$$n = -D \cdot q \cdot \frac{c}{x} \cdot t \tag{2}$$

The diffusion coefficient is a substance-specific proportionality factor with the dimensions cm^2/s, which is dependent on pressure and temperature and other parameters. Its value can be read from tables or determined experimentally. The following equation can be used to correct for pressure and temperature [5]:

$$D_{\mathrm{T}} = D_{298} \cdot \left(\frac{T}{298}\right)^{1.5} \frac{101.3}{p} \tag{3}$$

where:
D_T is the corrected diffusion coefficient at T and p in cm^2/s
D_{298} is the diffusion coefficient at 298 K and 101.3 kPa in cm^2/s
T is the actual temperature in K
p is the actual air pressure in kPa

The distance moved by the substance per unit time and concentration in the ambient air can be defined as the adsorption or diffusion rate. It can be calculated from Fick's first law of diffusion (Equation 2):

$$\frac{n}{(c \cdot t)} = D \cdot \frac{q}{x} \tag{4}$$

Correspondingly the rate of adsorption U can be calculated from

$$U = \frac{m}{(c \cdot t)} \tag{5}$$

where:
m is the weight of substance adsorbed in mg.

For comparison of passive with active sampling, the rate of adsorption is also commonly given in mL/s or mL/min, i.e. it is expressed as the weight of the substance present in the given volume per unit time. It must be remembered, however, that the volume flowrate is fictive. In reality, transport of the substance takes place without any airflow. Furthermore, Equation (4) shows that the rate of adsorption is dependent solely on the geometry of the diffusion sampler and, of course, on the substance-specific diffusion coefficient. A larger diffusion cross-section and a shorter diffusion path therefore yields a higher rate of adsorption, while a reversal in the relationship between these dimensions results in less of the substance being transported per unit time and concentration.

1.1.3 The effect of environmental conditions on passive sampling

1.1.3.1 The effect of fluctuations in concentration

If a diffusion sampler is exposed to a constant concentration of a substance, after a brief equilibration period, a linear concentration gradient is established in the diffusion zone of the sampler and determines the rate of adsorption. The time t_{equil} needed for equilibration of the linear concentration gradient may be calculated from the following equation:

$$t_{equil} = 1.5 \cdot X^2 D \tag{6}$$

If the concentration fluctuates, the rate of adsorption should adjust as quickly as possible to these changes. The time needed is referred to as the response time. If the concen-

tration gradient is linear, the response time can also be defined as the average period t_r spent by the individual molecules in the diffusion zone before adsorption [6].

$$
t_r = \frac{\left(\dfrac{c \cdot q}{2x}\right)}{\left(\dfrac{D \cdot q \cdot c}{x}\right)} = \frac{x^2}{2D} \tag{7}
$$

It may be readily seen from Equation (7) that samplers with short diffusion paths, which according to Equation (4) also have a high rate of adsorption, have a very short response time and are therefore well-suited for use with fluctuating concentrations. Generally the response times of diffusion samplers are in the range from 0.5 seconds to several seconds [7].

1.1.3.2 The effect of temperature and air pressure

Temperature and air pressure influence the diffusion coefficient and sampling rate and therefore also the amount adsorbed. According to Equation (3), this influence is small and in practice can be ignored. The theoretical increase in the adsorption rate is 0.2 %/K [8].
For reaction samplers (type A), the manufacturers generally prescribe a temperature range from about 0 °C to 40 °C.

1.1.3.3 The effect of humidity

With diffusion samplers (type B), whose sampling phase is able to adsorb water, interference from humidity must be expected.
A general statement cannot be made, as substance-specific properties and also the geometry of the sampler and the type and capacity of the sampling phase play a role.
For example, Ikeda *et al.* [9] investigated the behaviour of activated carbon as sampling phase for *n*-hexane, ethyl acetate and toluene at relative humidities between 40 % and 93 %. Relative humidity above 40 % was found to have considerable influence on the sampling of *n*-hexane but not on that of ethyl acetate or toluene. Many authors regard the threshold for the influence of water vapour to be around 50 % relative humidity [10]. *Blome* und *Hennig* [11] report for various types of sampler an influence of relative humidity on the rate of adsorption of toluene, 1-butyl acetate, 2-butanone and dichloromethane in the range from 10–75 %. It was found that samplers with a high weight of an adsorbent such as activated carbon, and therefore a high adsorbing capacity, are advantageous.
With reaction samplers the analytical principle is such that the substance to be sampled is not expected to be displaced. However, the effect of humidity on such samplers depends on the specificity of the reagent. The manufacturer's instructions should be observed; these usually state a maximum water content of about 15 mg/litre (which corresponds to 65 % relative humidity at 25 °C).

To conclude, the effect of water vapour or humidity must be investigated and known for each analysis to be carried out.

1.1.3.4 The effect of air currents

Air currents can make the diffusion rate different from that in still air. Fick's first law of diffusion is only valid for constant conditions, i.e. the concentration of the substance in the environment of the sampler must be constant. This ideal situation is not always found in practice. Convection currents, laminar currents and still layers of air in the area of the sampler can cause interference, so that quantification of the amount of substance adsorbed using Fick's law of diffusion can lead to incorrect results.

If a diffusion sampler is exposed in still air, the concentration of the substances being sampled is reduced in the immediate vicinity of the sampler as a result of diffusion to the surface of the adsorbent. This concentration gradient causes the substance to be transported from the environment into the zone with the lower concentration. However, this process is slower than transport of the substance to the surface of the sampler, so that in the immediate vicinity of the diffusion sampler the concentration of the substance is lower than in the environment. This fact leads to less substance being adsorbed than is predicted by Fick's first law of diffusion.

Investigation of the relationship between transport of the substance and the velocity of the air currents yielded the curves shown in Figure 2 [10].

This undesirable effect can be avoided if constant and sufficient transport of the substance to the surface of the sampler is guaranteed by an appropriate air current. The diffusion sampler must, however, be constructed in such a way that convection currents cannot enter the sampler, as this leads to uncontrolled movement of the substance [12]. There is a linear relationship between transport of the substance and the velocity of the air currents (Fig. 2, curve b). To achieve behaviour of the sampler which is as ideal as possible, the sampling phase is often protected by porous layers

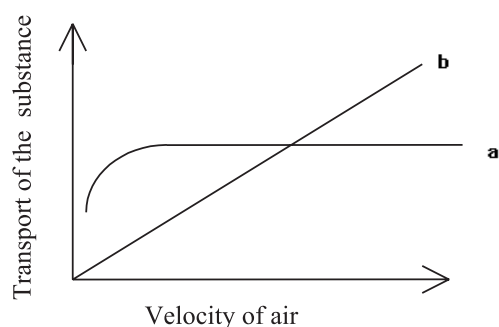
Fig. 2. Diagram of the effect of convection currents on transport of a substance for two types of samplers.
a = Curve for samplers protected against the entry of convection currents.
b = Curve for samplers which convection currents can enter.

or covers, for example by wire mesh, thin and porous synthetic membranes and thick permeable membranes. All of these measures serve to impede diffusion as little as possible while presenting convection currents with as large a resistance as possible, so that transport of the substance to the sampling phase occurs exclusively by diffusion and not by convection.

Another way of avoiding transport of the substance by convection lies in the geometry of the sampler, i. e. in the ratio of length to cross-section of the openings. Transport of the substance by diffusion is influenced on the one hand by the resistance to diffusion presented by the porous cover, and on the other also by the resistance to diffusion within the sampler and the sampling phase. Decisive is always the greater value. If the diffusion chamber is relatively short with a large cross-section, the resistance to diffusion inside the sampler is negligible, i. e. the resistance to diffusion of the cover is decisive for transport of the substance. If the diffusion chamber behind the cover is longer with a small cross-section, the resistance within the sampler is accordingly increased and thus becomes the decisive factor.

The least influence of convection currents and the least deviation of the experimentally determined concentrations from the theoretical value was observed by Pozoli and Cottica [10] when the two sources of resistance to diffusion were approximately equal. For the construction of a diffusion sampler, the anti-convective resistance of the porous cover must therefore be taken into consideration when calculating the length and the cross-section of the diffusion chamber.

When diffusion samplers are used in practice, a minimum velocity of air currents is required to ensure a constant adsorption rate, as shown in Figure 2, curve a. This is shown also in the results of Blome and Hennig [11]. For most of the types of samplers available commercially, the minimum velocity of the air currents is in the range from about 0.1 to 0.2 m/s. The position of the sampler relative to the direction of the air currents is not seen to have an effect at low wind speeds. The manufacturer's instructions on this point should be observed.

1.1.3.5 The effect of the duration of exposure and the concentration of the substance

The duration of exposure and the concentration of the substance have a great influence on the constancy of the rate of adsorption. The rate of adsorption can only remain constant for as long as the difference between the concentration of the substance in the environment and that on the surface of the adsorbent in the sampler is unchanged. When the concentration of the substance in the environment is constant, this concentration gradient is dependent only on the amount of substance already adsorbed and on the capacity of the sampling phase (see Section 1.1.2). If the sampling phase is exposed until its capacity is exhausted, the rate of adsorption decreases, or desorption and back diffusion of the collected substance into the workplace atmosphere takes place. Also very high concentrations, which initially cause a high rate of adsorption, lead to rapid exhaustion of the capacity of the sampling phase and then to a corresponding decrease in the rate of adsorption. Both factors – exposure duration and substance concentration – are therefore responsible for the constancy of the rate of adsorption and thus for a

reliable result. It therefore makes sense to establish the relationship between the product of exposure time t and concentration of the substance c and the rate of adsorption. The optimum is a product $t \cdot c$ which is as high as possible at a constant rate of adsorption. This can be achieved by using a large amount of adsorbent with a sampler whose geometry ensures a low rate of adsorption. Such samplers have the disadvantage, however, that they react only very slowly to fluctuations in concentration (see Section 1.1.3.1).

1.1.3.6 The effect of substance-specific properties

In adsorption samplers, not only the substance-specific diffusion coefficient but also the behaviour of the substance towards the sampling phase is very important for the results of the analysis.

Substance-specific properties, such as e.g. molecule size, polarity and boiling point determine the adsorbed weight of substance per weight of adsorbent. If several substances are present simultaneously, competition can occur during adsorption. As a result of the substance-specific properties mentioned above, some substances are adsorbed to a greater degree than others, i.e. substances which are very strongly bound (high adsorption enthalpy), can displace others, so that desorption is observed.

The behaviour of the diffusion sampler towards mixtures must therefore be tested experimentally. In the case of reaction samplers (type A), the specificity of the reagent or the levels of interfering reactions is the limiting factor.

1.2 The construction of diffusion samplers

Passive samplers are available in various models, which, depending on the sampling to be carried out, can have advantages or even disadvantages. These specific properties must be taken into consideration when planning sampling and when using the various types of passive samplers. Adsorption samplers and reaction samplers must be distinguished. Adsorption samplers are merely systems for collecting samples, which must subsequently be analysed in the laboratory. Reaction samplers are available both as sampling systems and as analytical systems with which the results can be directly evaluated at the site of sampling, e.g. by a change in the colour of an indicator. The diagram below shows the types of passive sampler available.

1.2.1 Adsorption samplers

Adsorption samplers are made up of a sampling phase (e.g. activated carbon) mounted a short distance behind an opening with a known cross-section which is in contact with the ambient air. The molecules are transported from the opening to the collection phase by controlled diffusion.

At present the following types of adsorption sampler are available commercially:
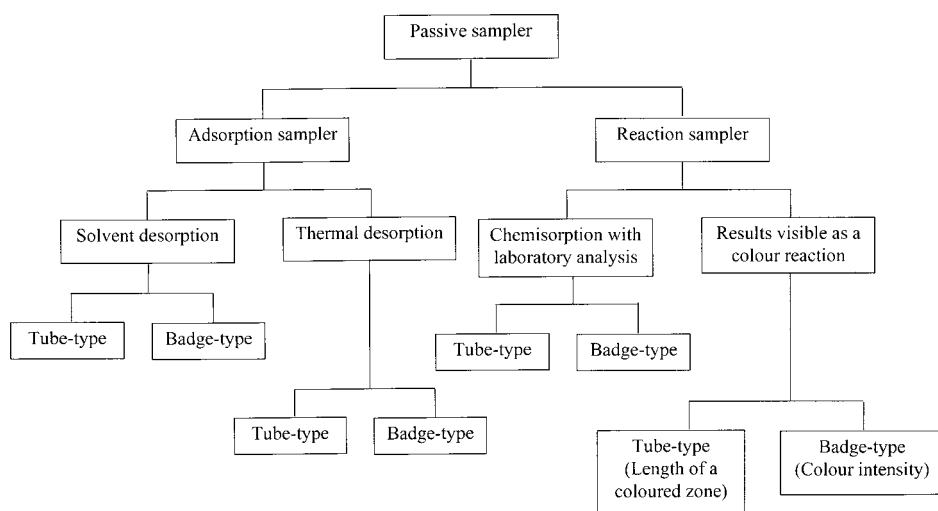
Fig. 3. Types of passive samplers classified according to DIN EN 838 [2].

- Tube-type (e. g. glass) with 2 openings over the cross-sections and diffusion barrier for sampling, enrichment of volatile organic compounds on activated carbon, liquid desorption, and analytical determination [13].
- Tube-type (e. g. glass, metal) with one opening over a cross-section for sampling, enrichment of volatile organic compounds on an organic polymer (e. g. Tenax), thermal desorption, and analytical determination [14].
- Tube-type (e. g. glass) with one opening over a cross-section for sampling, enrichment of nitrous oxide (laughing gas) on a molecular sieve, thermal desorption, and analytical determination [15].
- Badge-type (e. g. plastic) with a large inlet (membrane as diffusion barrier) for sampling, enrichment of volatile organic compounds on activated carbon, liquid desorption, and analytical determination [13].
- Badge-type (e. g. metal) with a large inlet (membrane as diffusion barrier) for sampling, enrichment of volatile organic compounds on an organic polymer (e. g. Tenax), thermal desorption, and analytical determination.

Whereas commercially available passive samplers for liquid desorption are ready to use and do not need any pretreatment, passive samplers for thermal desorption must usually be conditioned by heating in the laboratory before sampling.
The main features of the various types of adsorption sampler are summarised below.

1.2.1.1 Tube-type adsorption samplers (liquid desorption)

- Sampling rate lower than that of badge-type samplers; therefore lower sensitivity (generally this is not of importance for sampling at the workplace)
- A minimum wind speed of 1 to 2 cm/s is necessary

– Adsorption capacity is high relative to the sampling rate; therefore the constancy of the sampling rate is usually guaranteed even with high substance concentrations and long sampling periods
– The response time is 1 to 2 seconds (therefore even short changes in concentration are recognised)
– The sampler can only be used once
– Liquid desorption (analysis can be repeated several times)

1.2.1.2 Badge-type adsorption samplers (liquid desorption)

– Sampling rate higher than that of tube-type samplers; therefore greater sensitivity
– A minimum wind speed of 10 to 20 cm/s is necessary
– Adsorption capacity is low relative to the sampling rate; therefore the constancy of the sampling rate is not always guaranteed with high substance concentrations and long sampling periods
– The response time is 5 to 10 seconds (concentration peaks which last for a shorter period are not recognised)
– The sampler can only be used once
– Liquid desorption (analysis can be repeated several times)

1.2.1.3 Tube-type adsorption samplers (thermal desorption)

– Sampling rate lower than that of tube-type samplers with liquid desorption; high sensitivity as the whole sample is analysed at once (no dilution effect due to liquid desorption agents)
– A wind speed of <1 cm/s is sufficient
– Constancy of the sampling rate depends on the adsorbent
– Various adsorbents may be used, e. g. Tenax, Porapak, Chromosorb
– The adsorption capacity depends on the adsorbent. The constancy of the sampling rate must therefore be tested for various substance concentrations and sampling periods
– The response time is a few seconds (therefore even short changes in concentration are recognised)
– The sampler can be re-used after analysis
– Thermal desorption allows only one analysis per sample

1.2.1.4 Badge-type adsorption samplers (thermal desorption)

– Sampling rate higher than that of tube-type samplers; corresponds to that of badge-type samplers for liquid desorption
– High sensitivity as the whole sample is analysed at once (no dilution effect due to liquid desorption agents)

– A minimum wind speed of 10 to 20 cm/s is necessary
– Short sampling periods are possible. It must be remembered that the sampling rate is
  not linear; even with longer sampling periods and in particular with high substance
  concentrations the constancy of the sampling rate must be checked
– The response time is 5 to 10 seconds (concentration peaks which last for a shorter
  period are not recognised)
– The sampler can be re-used after analysis
– Thermal desorption allows only one analysis per sample

1.2.2 Reaction samplers

Unlike adsorption samplers, with which the substance to be determined is enriched on
the sampling phase only as a result of physical adsorption and remains unchanged, re-
action samplers enrich and immobilise the sample by chemical transformation of the
substance. The enrichment phase containing the chemical reagents can be made of
granulate (e.g. silica gel), strips of paper, wire mesh or solutions. With reaction sam-
plers which display the results directly, the reaction product causes a change in the col-
our of an indicator, whose colour intensity (for badge-type samplers) or length of the
coloured zone (for tube-type samplers) is evaluated after sampling. In addition to reac-
tion samplers with a chemical colour reaction, samplers are available which work on an
enzymatic basis. Reaction samplers which do not display the result directly must be
analysed in the laboratory after sampling, like the adsorption samplers.
At present, the following types of reaction sampler are available commercially:

– Reaction samplers with an inlet for sampling, filled with absorption liquid; in gen-
  eral analysis in the laboratory is necessary.
– Tube-type samplers with an inlet over the cross-section for sampling, chemisorption
  on impregnated wire mesh; desorption; reaction; in general analysis in the laboratory
  is necessary [16].
– Badge-type samplers which display the results directly; evaluation of the colour in-
  tensity.
– Tube-type samplers which display the results directly, made of a glass tube with an
  opening for sampling, filled with granulated indicator material or impregnated strips
  of paper; evaluation of the length of the coloured zone.
– Reaction samplers on an enzymatic basis, evaluation of the colour intensity.

The main features of the various types of reaction sampler are summarised below.

1.2.2.1 Badge-type reaction samplers (laboratory analysis)

Transport of the substance from the ambient atmosphere to the enrichment phase (ab-
sorption solution) takes place e.g. via a membrane. After sampling, reagents, which
may be integrated in the sampler, are added. The colour intensity is evaluated spectro-
metrically. The possibility of interfering components (cross-reaction) must be taken
into consideration.

1.2.2.2 Tube-type reaction samplers (laboratory evaluation)

Transport of the substance from the ambient atmosphere to the enrichment phase, which is made of e.g. impregnated wire mesh, takes place via a diffusion path within a tube. After sampling, the wire meshes are eluted and reagent solutions are added. Evaluation is carried out spectrometrically. The possibility of interfering components (cross-reactions) must be taken into consideration. The tube and wire mesh can be used repeatedly. Reaction samplers of this type are used e.g. for monitoring the NO_2 concentration in the outdoor ambient air [17].

1.2.2.3 Badge-type reaction samplers (evaluation of the colour intensity)

Reaction samplers of this type yield a comparatively high sampling rate as they have a large diffusion cross-section and a short diffusion path to the reaction phase. This leads to great sensitivity. Chemical transformation to produce a coloured reaction product takes place in the reaction phase. Evaluation is carried out visually e.g. by comparison with a colour standard. With high substance concentrations the reagent is completely used up within a short period. Evaluation of the colour intensity is then no longer possible. The possibility of interfering components (cross-reactions) must be taken into consideration.

1.2.2.4 Tube-type reaction samplers (with a scale for the length of the coloured zone)

The sampling rate is a function of the coloured zone formed in the tube. To start with, the sampling rate is comparatively high as the diffusion path to the carrier material with unused reagent tends towards zero. As the length of the coloured zone increases, the diffusion path becomes longer, which results in a reduction in the sampling rate. Evaluation is carried out visually using the length of the coloured zone formed and a scale printed on the tube. The calibration curves take the form of a parabola [18]. The possibility of interfering components (cross-reactions) must be taken into consideration.

1.2.2.5 Reaction samplers on an enzymatic basis (evaluation of the colour intensity)

Reaction samplers on an enzymatic basis are similar to badge-type samplers with regard to the sampling rate and evaluation. Instead of a chemical reaction, such systems are based on biochemical reactions which lead to a colour change in the reaction phase. Reaction samplers on an enzymatic basis are characterized by high sensitivity and selectivity. Reaction samplers of this type are used e.g. for estimating formaldehyde concentrations [19].

1.3 Demands made of diffusion samplers

Workplace air is monitored to check that threshold limit values are observed. Both the mean values for the shift and short-term exposure peaks must be determined. The procedure for carrying out workplace monitoring described in TRGS 402 [20] makes certain demands on the monitoring procedure which must also be fulfilled when using diffusion samplers.

To make it easier for the user to decide about the use of a diffusion sampler, the requirements and test procedures for diffusion samplers under prescribed laboratory conditions are laid down in the standard DIN EN 838 [2]. It is the responsibility of the manufacturer of the diffusion sampler to carry out this suitability test. The performance characteristics tested must include the inaccuracy associated with the analysis as stipulated in DIN EN 482 [21].

1.3.1 Standard requirements according to DIN EN 838

The requirements laid down in DIN EN 838 [2] for diffusion samplers apply both for samplers used for direct determination of the concentration (type A, e.g. diffusion tube with colour zone display), and also for all types of sampler used for indirect determination of the concentration with sampling and analysis in separate steps (type B). The latter are sub-divided into types B1 (adsorption on a solid phase and desorption using a solvent with subsequent analysis of the desorbed substance), B2 (adsorption on a solid phase and desorption by heating, with subsequent analysis of the desorbed substance) and B3 (absorption in a liquid with subsequent analysis of the solution). Standard requirements are summarized in Table 1.

Table 1. Standard requirements.

Parameters	Requirements	Comments
Desorption efficiency	Type B1: ≥ 0.75 with a coefficient of variation of ≤ 0.1 Type B2: ≥ 0.95 with a coefficient of variation of ≤ 0.1	applies for each use of the sampler
Shelf-life of the loaded samplers	Type B: the mean recovery after storage should not differ from that before storage by more than 10%	shelf-life of 2 weeks at room temperature or according to the manufacturer's instructions
Rate of adsorption	Type B: if it can be calculated according to equation (5), the nominal value must be within ± 25 % of the theoretical value	
Labelling the sample	a suitable surface must be available for the user to label the sample	

Table 1. (continued)

Parameters	Requirements	Comments
Temperature range	5 °C to 40 °C, but at least from 10 °C to 30 °C	the requirements for analytical error must be fulfilled in this range (correction factors only permissible outside the range 10 °C to 30 °C)
Relative humidity	20 % to 80 %	the requirements for analytical error must be fulfilled in this range (without the use of correction factors)
Blank value	less than a third of the calculated rate at which the sampler adsorbs the substance during an exposure period of 30 minutes and at an exposure concentration of 0.1 of the threshold limit value	determined using 6 unspiked samplers
Sampler integrity	the additional concentration of the substance to be analysed determined above the blank value must be less than a third of the calculated rate at which the sampler adsorbs the substance during an exposure period of 30 minutes and at an exposure concentration of 0.1 of the threshold limit value	determined using closed samplers of type B, which were exposed for 4 hours to an atmosphere of the substance to be determined at twice the threshold limit value
Wind speed and position of the sampler	wind speed varies between 0.01 m/s and 4.0 m/s; positioning parallel to or at right angles to the air current	samplers only for personal air sampling worn by the individual: must be tested at 0.1 m/s to 1.5 m/s for indoor workplaces and at 0.1 m/s to 4.0 m/s for indoor workplaces and outdoor workplaces
Shelf-life (closed unloaded samplers)	Type A: at the end of the storage period the results should not differ from the original results by more than 10 %	the shelf-life of the samplers in the original packaging must correspond with the manufacturer's declaration
Mechanical durability	test with prescribed test apparatus	
Inaccuracy associated with the analysis	must lie within the requirements of DIN EN 482 for all types	

The diffusion samplers corresponding to this standard are grouped in classes 1 A and 1 B. Samplers in class 1 A have been tested according to the standardising part of this standard or in some cases by the standardising multi-factor plans contained in this standard. Samplers in class 1 B, which only applies for samplers of type B, are tested using a substance from a homologous series, for which previously both lower and higher members have been tested and found to correspond to class 1 A. For class 1 B at least the desorption efficiency and the diffusive adsorption rate must be determined.

1.3.2 Demands made of diffusion samplers regarding the inaccuracy associated with the analysis

In the European standard DIN EN 482 [21] general requirements for analytical procedures for workplace monitoring have been formulated, and must also be fulfilled by diffusion samplers. It must be remembered that the requirements apply to the whole analytical procedure, i.e. for sampling with the diffusion sampler, and the usual preparation of the sampling phase and analytical determination.

Table 2. Requirements of analytical procedures which use diffusion samplers, defined according to the task [21].

Task	Relative inaccuracy associated with the analysis	Minimum range	Duration of averaging
Determination of the mean concentration	≤ 50 %	0.1 to 0.5 times the threshold limit value	≤ reference time for the threshold limit value
Sampling near the source of an emission	≤ 50 %	0.5 to 10 times the threshold limit value	depends on the source
Comparison with the threshold limit value	≤ 50 %	0.1 to 0.5 times the threshold limit value	≤ reference time for the threshold limit value
	≤ 30 %	0.5 to 2 times the threshold limit value	
Control samples	≤ 50 %	0.1 to 0.5 times the threshold limit value	≤ reference time for the threshold limit value
	≤ 30 %	0.5 to 2 times the threshold limit value	

The other requirement of DIN EN 482, that of obtaining an overview of the temporal and/or spatial exposure situation via the concentration distribution, can often not be met with diffusion samplers for which sampling periods of a maximum of 5 or 15 minutes for averaging are prescribed. In such cases, instruments with a direct display (e.g. flame ionisation detector, electro-chemical sensors) or sampling procedures with active sampling should be used.

The relative inaccuracy associated with the analysis can be calculated as follows:

$$\frac{|\bar{x} - x_{\text{ref}}| + 2\,s}{x_{\text{ref}}} \cdot 100 \tag{8}$$

where:
$\bar{x}$ is the mean of the results in mg/m^3 from n repeated analyses
x_{ref} is the true value or the assumed reference value of the concentration in mg/m^3
s is the standard deviation of the analytical results in mg/m^3

The relative inaccuracy associated with the analysis, must, according to the task, be determined at the lower and upper end of the minimum range shown in Table 2 and for at least one intermediate concentration. It is recommended that the third concentration chosen is at the level of the threshold limit value in air. The number of repeated analyses at each of these concentrations must be at least six.
Testing the analytical procedure can, at present, only be carried out under laboratory conditions, as the generation of a test gas atmosphere of known concentration is the prerequisite for the determination of the relative inaccuracy associated with the analysis [5]. The minimum range prescribed can generally be covered by diffusion samplers by varying the sampling period (averaging period). Limitations are most likely at the lower end of the minimum range if it cannot be guaranteed that the minimum amount can be collected within the period set for averaging concentrations for the threshold limit value.
If a diffusion sampler does not fulfil the requirements for the relative inaccuracy associated with the analysis and for the minimum range, it cannot be used for the sampling task in question.
The requirements of this standard for the specificity and selectivity of diffusion samplers can only be applied to samplers of type A. They must yield a clear result for the concentration in the given range. Interfering components must be known. If the colour zone display of the diffusion tube also reacts to substances in the workplace atmosphere other than those to be determined, this sampler may only be used if the signal is increased by the interfering components. The whole value must then be assigned to the substance to be determined. If as a result of interfering components the values obtained are too low, the sampler is not suitable for this task.
Samplers of type B, with which sampling is usually followed by an analytical procedure in the laboratory, are allowed also to detect substances other than those to be determined. The analytical step must, however, allow the separation of these substances and the clear assignment of the signals. These samplers can be used with the restriction that interfering components must not compete with the substance to be determined. This means that the substance to be determined may not be displaced from the sampling phase by interfering components. In addition, the total amount of all the substances in the workplace air must not exceed the capacity of the sampler.

1.3.3 Determination according to TRGS 402

Diffusion samplers can be used for analyses carried out in work areas to determine whether the threshold limit values are being observed and also for control analyses; observance of the shift average value and the peak value must be monitored.

Diffusion samplers which conform to DIN EN 838 [2] are in principle suitable for monitoring the shift average values. An averaging duration of an hour or more should be used. If the averaging duration is shorter, which means an increased number of samples, the sampling rate of the sampler must be checked beforehand.

Diffusion samplers can only be used with reservations for monitoring short-term exposure peaks. Usually 15-minute average values are determined in this case. If sampling is carried out for less than one hour it must be checked whether the selected diffusion sampler meets the requirements of the analytical procedure with regard to the quantification limit and the concentration range of the substance to be monitored. It must then be decided whether the sampler can be used or not by comparing the data with the threshold limit value to be monitored. The relative inaccuracy associated with the analysis given in DIN EN 482 [21] must be taken into account.

In addition, with shorter sampling times the use of diffusion samplers is restricted by the fact that a procedure for workplace analyses must allow concentrations to be determined at least in the range from one tenth (or at least one fifth) of the threshold limit value to three times of the threshold limit value.

1.4 Analytical use of diffusion samplers

1.4.1 Sample collection

Diffusion samplers are sampling systems, which begin to sample substances as soon as the caps are removed. Before sampling, the sampling strategy is laid down according to TRGS 402. The diffusion sampler is opened at the beginning of sampling. The parameters which are important for the determination of the concentrations in air (date, time, temperature, atmospheric pressure and relative humidity) are noted in a sampling protocol. To determine the shift average value the sampling duration must be recorded to the nearest minute. To monitor the peak values the sampling duration must be recorded to the nearest second.

Sampling is carried out in the breathing zone for personal sampling. When selecting static positions for the sampler, the minimum wind speed given by the manufacturer must be taken into account. The opening of the diffusion sampler must not be obstructed. After sampling, the diffusion sampler is closed with suitable caps. The samples should be analysed immediately. If the samples are stored for a longer period of time until evaluation, they must be sealed with suitable caps. The transport and storage conditions depend on the type of diffusion sampler and the substances to be analysed.

When diffusion samplers are used, even unskilled persons can equip the test persons with the samplers according to the instructions of the analytical laboratory, close the

samplers after sampling and dispatch them according to the transport conditions stipulated by the laboratory.

Calibration, as necessary for personal sampling pumps, is not needed with diffusion samplers.

Systems are used in which the analysis is carried out in external laboratories or a colour reaction is recorded.

1.4.2 Preparation of the samplers

The samplers are prepared in accordance with the analytical procedure to be used. The most usual processes are thermal desorption and the use of liquid desorption agents.

1.4.2.1 Thermal desorption

The preparation of thermal desorption tubes takes place in the thermal desorber, without an extraction step. The diffusion samplers are put into an appropriate thermal desorber and heated; the substances collected are transferred with a carrier gas to a packed cold trap. When desorption is complete, the cold trap is heated very quickly so that the substance reaches the GC column as a concentrated band.

The conditions for the thermal desorber ATD-400 from Perkin Elmer which are recommended for the determination of solvent vapour are given here as an example (Tab. 3).

Table 3. Recommended parameters for thermal desorption from various sampling phases.

Adsorbent	Tenax TA	XAD 4, Chromosorb 106
Desorption temperature	250 °C	170 °C
Desorption time	10 minutes	5 minutes
Temperature of the transfer line	100 °C	100 °C
Cold trap (adsorption)	–30 °C	–30 °C
Cold trap (injection)	300 °C	300 °C
Weight of the adsorbent in the cold trap	20 mg Tenax TA	20 mg Tenax TA
Carrier gas	Helium	Helium
Input split		40 mL/min (input split)
Desorb flow		10 mL/min (desorb flow)
Output split		30 mL/min (output split)

The instrumental conditions have to be chosen according to the configuration of the apparatus if other types of thermal desorbers are used. After setting up the thermal desorber and the gas chromatograph, the calibration standards and the samples are analysed. Thermal desorption in gas cuvettes is also possible. The analytical determination is carried out by FTIR spectrometry [15].

1.4.2.2 Solvent desorption

Solvent desorption is used mainly with diffusion samplers filled with activated carbon. The complete contents of the diffusion sampler are transferred to a glass vessel and covered with a desorption agent. An internal standard is usually added. The adsorbed substances are desorbed by the solvent. The desorption efficiency must be determined using calibration standards. The humidity during sampling is a very important factor. Two procedures are used for the analytical determination.

a) Injection of the solvent

After desorption, the solvent must be separated from the adsorbent layer and transferred to glass bottles. Back diffusion onto the adsorbent is thus prevented. A µl-aliquot is then injected into an analytical system such as e.g. a gas chromatograph or a liquid chromatograph. Carbon disulfide, diethyl ether or mixtures of two or three solvents have proved to be reliable.

b) Headspace analysis

The whole sample – made up of adsorbent and desorption agent – is brought to the right temperature and the headspace above the sample is injected into a gas chromatograph. It is not necessary to separate the adsorbent and desorption agent. The boiling point of the solvent must be sufficiently high. For this procedure, desorption agents such as benzyl alcohol, dimethylacetamide, dimethylformamide and phthalic acid dimethylester are mainly used.

1.4.2.3 Reaction samplers

With reaction samplers, a chemical reaction takes place between the substance to be determined and a chemical in the sampler.
In practice, the reaction samplers used are either Draeger-tubes constructed as diffusion samplers from which the results are read immediately after sampling, or samplers with reagent solutions which must be analysed later in the laboratory. The adsorption agents are either reagent solutions or reactive sampling phases. The samples are usually evaluated photometrically.

1.4.3 Use of the diffusion samplers

Diffusion samplers are selected according to practical considerations.
If the substances are present as mixtures of vapours, chromatographic or spectrometric analytical procedures are used. These procedures always require that enrichment and sample preparation be carried out. Numerous substances can be determined with either solvent desorption or thermal desorption.
Diffusion sampling has proved reliable in these cases.

Whenever the substances are also present in particulate form, an apparatus suitable for sampling aerosols is required (e. g. SILPP for spray painting [22]). A diffusion sampler is placed behind a glass fibre filter in the sampling current. If the particulate phase cannot be separated from the vapour phase, diffusion samplers cannot be used.

Reaction samplers have proved reliable for inorganic gases and vapours, and for formaldehyde and some halogenated hydrocarbons.

1.5 Summary of areas of use

1.5.1 Analytical procedures for diffusion samplers

Passive sampling is gaining in importance relative to active enrichment procedures. A few tested methods of quantitative evaluation are listed in Tables 4 and 5.

Table 4. DFG methods [23].

Substances to be determined	Source	Sampling phase	Analytical procedure
Halogenated narcosis gases	DFG, No. 1	XAD-4	Thermal desorption/GC
Halogenated narcosis gases	DFG, No. 2	Activated carbon	Liquid desorption/GC
Styrene	DFG, No. 3	Tenax TA	Thermal desorption/GC
Nitrous oxide	DFG, No. 3	Molecular sieve 5Å	Thermal desorption/GC
Nitrous oxide	DFG, No. 2	Molecular sieve 5Å	Thermal desorption/FTIR

Table 5. Other methods of quantitative determination listed in the literature [13].

Substances to be determined	Source	Sampling phase	Analytical procedure
Acrylonitrile	HSE, MDHS 55	Porapak N	Thermal desorption/GC
Benzene	HSE, MDHS 50	Porapak Q	Thermal desorption/GC
1,3-Butadiene	HSE, MDHS 63	Molecular sieve 13X	Thermal desorption/GC
Volatile organic compounds (solvent mixtures)	HSE, MDHS 88	Activated carbon	Liquid desorption/GC
Volatile organic compounds (solvent mixtures)	HSE, MDHS 80	Tenax TA, Chromosorb 106	Thermal desorption/GC
Formaldehyde	HSE, MDHS 78	Silica gel (coated)	Liquid desorption/HPLC
n-Hexane	HSE, MDHS 74	Activated carbon	Liquid desorption/GC
Hydrocarbons	HSE, MDHS 66	Tenax TA, Chromosorb 106, Spherocarb	Thermal desorption/GC
Styrene	HSE, MDHS 43	Tenax TA	Thermal desorption/GC
Styrene	HSE, MDHS 44	Activated carbon	Liquid desorption/GC
Toluene	HSE, MDHS 64	Activated carbon	Liquid desorption/GC
Toluene	HSE, MDHS 69	Activated carbon	Liquid desorption/GC

1.5.2 Suitability of special sampling phases

Various adsorbents can be used for sampling organic substances. The methods described in Tables 4 and 5 are based mainly on these adsorbents.

Table 6 lists the areas of use of various sampling phases for the passive sampling of various substances and groups of substances. The selectivity of some adsorbents is described in [24].

Table 6. Adsorbents for passive sampling.

Adsorbent	Substances
Activated carbon	Solvent *
Carbopack B	Aliphatic and aromatic hydrocarbons
Carbotrap	Perfluorodimethylcyclobutane
Chromosorb 102	Freons, halogenated hydrocarbons
Chromosorb 106 or XAD-4	Aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, alcohols, nitriles, ketones, glycidyl ethers
Graphitised carbon molecular sieves	Halogenated hydrocarbons, alcohols, carbon disulphide, dioxane, ethylene oxide
Porapak N	Nitriles
Porapak Q	Aromatic hydrocarbons, acrylates, glycol ethers
Molecular sieve 13X	1,3-Butadiene
Molecular sieve 5Å	Laughing gas
Tenax GR	Aromatic hydrocarbons, halogenated hydrocarbons, glycol ethers, ketones
Tenax TA	Aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, aldehydes, alcohols, nitriles, glycidyl ethers, terpenes

* 2-Butanone cannot be stored for long after adsorption on activated carbon.

1.5.3 Reaction samplers

Reaction samplers can be used for the direct determination of the substance concentration. Table 7 shows a selection of currently available reaction samplers.

Table 7. A selection of reaction samplers.

Reaction samplers for the determination of	Manufacturer/ supplier*	Reaction samplers for the determination of	Manufacturer/ supplier*
Acetaldehyde	4	Carbon dioxide	2, 4
Acetone	4	Carbon monoxide	2, 4
Formic acid	4	Methyl isobutyl ketone	4
Ammonia	2, 3, 4	Olefins	2
Hydrogen cyanide	2, 4	Perchloroethylene	2, 4
1,3-Butadiene	2, 4	Phosgene	2
2-Butanone	4	Phosphine	2
Chlorine	4	Nitric acid	4
1,2-Dichloroethylene (*trans*)	4	Hydrochloric acid	2, 4
Dimethylamine	4	Sulfur dioxide	2, 4
N,N-Dimethylethylamine	4	Hydrogen sulfide	1, 2, 3, 4
Acetic acid	2, 4	Nitrogen dioxide	2, 3, 4
Acetic anhydride	4	Toluene	2, 4
Ethanol	2, 4	Trichloroethylene	2, 4
Ethene	4	Triethylamine	4
Ethyl acetate	2	Vinyl chloride	4
Formaldehyde	2, 3, 4	Vinylidene chloride	4
Hydrogen fluoride	4	Water vapour	2
Furfural	4	Hydrogen peroxide	4
Hydrazine	4	Xylene	4
Isoprene	4		

* Manufacturer/supplier: 1 Auergesellschaft, Berlin
2 Dräger Sicherheitstechnik GmbH, Lübeck
3 Günter Karl OHG, Gau-Algesheim
4 MTC Messtechnik-Chemie GmbH, Müllheim

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