Sampling and Analysis of Gases and Vapours

Contents

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1 Introduction

Employees during their work at many workplaces are exposed to gases and vapours. Herein, an overview is given on how these exposures can be categorized and measured analytically, describing in particular strategic and technical sampling, as well as the possibilities of analysis. We further emphasize active sampling procedures, for which workplace air is drawn onto a collection medium using especially designed sampling pumps. Passive sampling procedures, i. e. collection through diffusion, are discussed in Volume 6 ("Passive sampling") of this publication [1]. However, the descriptions in sections 5 ("Transport and storage of samples") and 6 ("Analytical determination of gases and vapours"), can also generally be considered valid for both the active and passive sampling. Furthermore, direct-reading devices are discussed, which in the meanwhile are applied for the analysis of numerous gases and, with some restrictions, of solvent vapours [2].
In the following, only substances are discussed that occur in gaseous form in the atmosphere of workplaces. Besides of substances permanently existing in gaseous form (e. g., CO, NO and NH_3), vapours are described that are released from liquids (e. g., toluene and ethyl acetate) due to vapour pressure. While gases during work activities mainly derive from various systems or upon combustion processes, vapours are released mostly during working with solvents. Herein, these kinds of vapours are referred to as "solvent vapours". Vapours can further be released from aerosol droplets (in particulate form) after liquids have been stirred or sprayed so that splashes were caused. Such aerosols are not the

subject of this chapter, as for their sampling, special systems are applied that must fulfil the necessary requirements for both the gas phase and the particulate phase. A description of how, e. g., lacquer aerosols [3, 4], or metal-working fluid aerosols and vapours [5], can be determined is given in the literature.
Table 1 shows examples of work activities and workplaces where workers‘ are exposed to gases and vapours. During analytical practice, the question often arises as to which sampling system should be used in order to cover all relevant gases and vapours. If inorganic gases and organic (solvent)-vapours occur simultaneously, then it is normally necessary for a correct analysis to apply several sampling systems. In some cases, gases or vapours existing in workplace air can serve as indicator components to correctly evaluate the total exposure. A detailed description of the required criteria in this regard is given in Section 4.

Table 1. Examples of workplaces and activities, as well as gases and vapours, which can occur at workplaces occupational settings.

Workplace or activities	Gases and vapours	Remarks
Car repair shops	CO, CO_2, NO_2, fuel vapours, etc.	CO feasible as indicator component for determining the total exposure [5, 6]
Printing plants	Organic solvent vapours from printing colors and purifying agents (e. g., 2-propanol in offset printing)	
Surgeries/anaesthetic recovery	N_2O, anaesthetic gases	N_2O suitable as indicator component for determining total exposure [7]
Painting works	Solvent vapours from colors, lacquers, and dilutors	
Chemical industry	Inorganic and organic gases and vapours	

2 Measurement principles

To estimate the exposure of hazardous substances, in principal the workplace air is drawn through an adequate collection medium using a pump. The complete measurement procedure comprises the following steps:

1. Sampling
2. Transport and storage
3. Analytical determination
4. Assessment

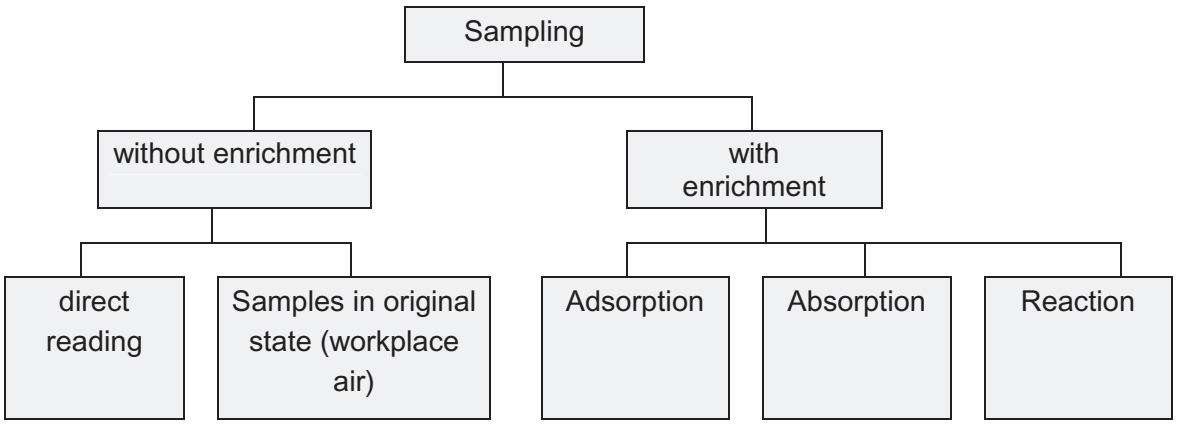

Fig. 1. Measurement principles of gases and vapours during collection at workplaces.

As can be seen from Figure 1, the gases and vapours that occur in workplace air can be separated and enriched in the collection medium. In addition, workplace air can also be analysed in its original state. In both cases, the analysis can be performed directly on location or in the laboratory. To date, enrichment procedures for workplace measurements are prevalent.
During enrichment by adsorption or absorption the analyte is collected in its original state. In addition, respective reactions of the analysed substances can be used also for derivatisation and enrichment.
In the case the workplace air sample is collected without enrichment and analysed afterwards in the laboratory, then normally the same analytical methods may be used as for the treatment of samples collected by enrichment techniques.

3 Sampling

In the following, sampling systems required for active sampling are described.

3.1 Sampling with enrichment

For sampling with enrichment, the substances to be determined are either adsorbed onto a solid collection phase, or absorbed in a solution. The samples afterwards need to be prepared so that they can be subsequently analysed.

3.1.1 Sampling pumps

During sampling at workplaces, it is necessary to distinguish between personal and stationary sampling. For an assessment of the exposure at the workplace, personal air samplers are normally preferred. Therefore, only sampling pumps that are used in this way

are discussed in the following. However, normally it is also possible to apply these pumps for stationary sampling.
In active personal sampling, pumps according to EN 1232 [8] are needed, which are small and light-weight, work quietly, and are easily and safely fixable to the worker. A detailed overview on the requirements of sampling pumps is given in "Sampling and determining aerosols and their chemical components" [9]. If sampling is performed in areas endangered by explosion, only pumps that are designed to resist such an incident are allowed to be used.
As sampling necessitates the exact determination of the total air volume, pumps capable of keeping the flow electronically constant are currently used. The air sample volume is calculated according to equation (1).

$$V = \dot{v} \times t \tag{1}$$

where:
V is the air sample volume in L
$\dot{v}$ is the flow rate of the sampling pump in L/min
t is the sampling duration in min

It should be noted for the sampling of gases and vapours that the threshold limit values quoted in mg/m^3 are related to the air volume at the temperature of 20 °C and air pressure of 1013 hPa (1013 mbar). If sampling is carried out under different physical conditions, and if a comparison of threshold values with alternative units is needed, a conversion of the measurement values regarding air pressure and temperature is necessary. In contrast, threshold values of gases and vapours given in units of mL/m^3 (or ppm) are independent from temperature and air pressure [10].
The following equation (2) applies for the conversion to standard conditions (20 °C, 1013 hPa):

$$\rho_0 = \rho \times \frac{273 + t_a}{293} \times \frac{1013}{p_a} \tag{2}$$

where:
ρ is the mass concentration of a component in mg/m^3
ρ_0 is the mass concentration (in mg/m^3) related to 20 °C and 1013 hPa
t_a is the temperature during sampling in °C
p_a is the atmospheric pressure of the ambient air during sampling in hPa

The required flow must be regulated before the sampling and checked afterwards, for which the entire sampling system, consisting of the pump, the collection medium and the sample holder (sampling head), must be used. Both flows should not deviate from each other by more than $\pm 5\%$ [8].
In Appendices 10.1 and 10.2, an overview is given on sampling pumps and devices frequently used for the adjustment and validation of the air sample volume and flow.

3.1.2 Adsorption tubes

For sampling using adsorption tubes, a sample holder to affix the tube is needed, as well as a pump together with a hose to connect the sample holder to the pump. The sample holder has the purpose of protecting the adsorption tube, which is normally made of glass, and to affix the sampling device to the worker. Detailed information on the currently used adsorption agents, as well as tips for their correct choice is given in "Adsorbents for the adsorption of organic compounds" [11]. Table 2 provides examples of frequently used adsorbents.

Table 2. Examples of commonly used adsorbents.

Kind of desorption	Adsorbents
Solvent desorption	Activated carbon, silica gel, XAD-2, XAD-4
Thermal desorption	Tenax (TA, GR), Chromosorb, Porapak

3.1.3 Impingers and washing bottles

Impingers and washing bottles use suitable liquids in order to enrich the substances occurring in workplace air. For personal air sampling, the washing bottle should be unbreakable to protect the worker and to keep the sample safe from running out. An example for this is given by the Absorber B 70, which is also feasible for collecting aerosols according to the definition of inhalable dust [12].

3.1.4 Reaction samplers

A sampling that utilizes chemical reactions is applied if the investigated substance fulfils the following requirements:

- The substance (e. g., diisocyanates) is reactive and, on the collection phase, can be converted into a more stable form in the presence of a reagent
- The enrichment or desorption of the substance is enhanced (e. g., aldehydes, ammonia, hydrazine, amines)
- The substance can be detected more sensitively (e. g., epoxides)
- The analysis of the substance of interest is hindered due to other present components (e. g., diisocyanates)

The sampling occurs using either a washing bottle, in which the reagent is dissolved in an appropriate liquid, or with sample media (filters or adsorbents) that have been pretreated with a reagent. The reaction between the investigated substance and the reagent takes place *in situ* during sampling.
Examples for this kind of sampling are the collection of aldehydes using enrichment systems impregnated with dinitrophenylhydrazine, of diisocyanates collected on filters

impregnated with 2-methoxyphenyl-piperazine, or of hydrogen peroxide in solutions containing titanium.

3.1.5 Denuders

A denuder is an active sampling system which is based on the diffusion principle. At laminar flow conditions, the separation of gaseous substances relies on the diffusion of gas molecules in a direction transverse to the flow. If the flow in the tube is adjusted to obtain laminar flow conditions, gaseous air components can have contact with the tube's wall already after a short distance. The gaseous and vaporous substances are separated and enriched through adequate coating of the wall, which becomes a mean of sample collection [13]. Thereby, the enrichment occurs due to absorption or reaction mechanisms.
For better handling, annular denuders have been developed that consist of several concentrically positioned glass tubes [14]. Denuders usually are only applicable for stationary sampling.

3.2 Sampling without enrichment

Sampling without enrichment distinguishes between the analytical methods used to obtain the result. The method can either deliver the result instantly on location (e. g., via direct reading), or by analysis in the laboratory after sample collection in a suitable vessel.

3.2.1 Gas storage vessels and gas sample bags

For air sampling at which the enrichment of substances is neither possible, nor necessary, gas storage vessels (e. g., gas mouse) or gas sample bags (e. g. Tedlar™-bags) can be used. Gas storage bags are available in different sizes. Sampling thereby requires that the bags are connected to a pump and that the air sample is drawn with a flow rate of 1 – 3 L/min. It is suggested that the air volume for flushing the bag is at least fourfold higher than that of the gas storage bag or vessel.
This type of sampling is also used for the determination of organic gases that occur permanently in the air of workplaces (e. g. propane, propene). It further enables the measurement of short-term exposures for many substances (sampling duration of few minutes). After sampling, either an aliquot is taken in laboratory and analysed afterwards, or a volume portion is separated from the gas storage bag and enriched on adequate adsorption materials prior to analysis.

3.2.2 Test tubes

For the determination of hazardous substances in workplace air using test tubes, a reaction of a substance (or a substance class) with the filling of the tube is utilized. This effect, which leads to a change in color, can be used for verifying the occurrence of the substance of interest and/or for determining its concentration. The sampling procedure basically is performed drawing a defined volume through the test tube using a pump (e. g. piston stroke pump). The length of colored layer is proportional to the concentration of the substance (or substance class) under investigation.
The advantage of using test tubes is that the measured concentration is obtained quickly and directly after sampling. In practice, the use of test tubes has been proven valuable in particular for determining the following substances in workplace air: carbon monoxide, carbon dioxide, hydrogen sulfide, ozone, nitrogen dioxide, ammonia, chlorine, phosphine, hydrogen cyanide, and sulfur dioxide [15]. However, there are also disadvantages to recognize, such as the following:

- Normally, the selectivity is restricted,
- Restrictions in determining shift average values,
- Possible cross-reactions with accompanying substances,
- Problems in reading the colored edge, which is a measure for the concentration of the analyte.

3.2.3 Direct-reading instruments

Direct-reading instruments are capable of working either selectively for a specific substance (e. g., carbon monoxide), or non-selectively for a mixture of substances (e. g., solvent vapours). It is important to consider that different tasks are involved when working with such devices.
For example, devices capable of warning and signalling without displaying the concentration of the substance can give optical and/or acoustic signals once the default or threshold limit value at the workplace is reached. These simple direct-reading instruments are relatively inexpensive and easy to handle. However, an exposure assessment using shift average values and/or short-term exposure values cannot be achieved.
The second group of direct-reading instruments possesses, besides the warning function, the possibility of storing the time-dependent concentration for exposure assessment. This enables to examine the shift average and short-term exposure values. Furthermore, short-term exposure peaks can be concretely assigned to certain work activities.
The following section gives a brief description of some important direct-reading instruments.

3.2.3.1 Flame ionization detector (FID)

The flame ionization detector (FID) can be used for determining the sum of inflammable gases and vapours occurring in workplace air. The air is drawn with an internal

pump and fed afterwards to the FID. The ions and electrons formed during combustion in an electric field generate a current, of which the level is proportional to the concentration of all inflammable gases and vapours.
Due to its dimensions, the FID is not suitable for personal air sampling. The advantage of the FID lies in the high time resolution, allowing for recording the course of concentration over time and to observe exposure peaks. However, due to the restricted selectivity, a specific measurement of substances in mixtures is not possible so that a direct comparison with threshold limit values cannot be made. The range of measurement with FID extends from the lower mL/m^3-level (ppm) up to percentage level.

3.2.3.2 Photoionization detector (PID)

In principle, the air is drawn by an internal pump into the photoionization detector and passes a discharging tube (usually a UV-lamp). Ionization of the substance to be determined occurs when its ionization potential is lower than the energy of the irradiating beam. Depending on the given conditions, the PID delivers a sum signal of all ionisable substances. The selectivity of the detector can be varied within limits according to the lamp that is chosen.
As PIDs are usually compact and portable devices with battery operation, they can be used for personal air sampling. The high time resolution of the instrument is also an advantage and, thus, it offers the possibility of recording courses of spatial and time-dependent concentrations, and to determine exposure peaks. Classes of substances that can be detected are: aromatic hydrocarbons, chlorinated hydrocarbons, amines, oxygen-containing substances, and inorganic compounds such as ammonia or hydrogen sulfide. However, as the selectivity for mixtures is restricted, a substance-specific measurement for direct comparison with threshold limit values is not possible. The PID is preferably used for measurements of concentrations at higher $\mu L/m^3$- (ppb) and/or mL/m^3 (ppm) levels.

3.2.3.3 Infrared (IR) spectral photometer

Infrared spectral photometers can be used for the qualitative and quantitative determination of gases and vapours that are infrared active. The air is directed with an internal pump through a measurement chamber which is irradiated by infrared light with wavelengths between 2.5 – 15 µm. The IR-active molecules in the sample are excited to induce oscillations at characteristic IR frequencies, leading to the absorption of light. Additionally, variations of the gas pressure can be measured (photo acoustic IR spectroscopy). Both phenomena can finally be utilized for measurements of airborne gases and vapours.
As the absorption of irradiation is recorded during the measurement, it is a pre-condition for the quantitative evaluation that the absorption bands of substances to be analysed do not interfere with those of other substances contained in the sample. The selectivity of the process can be controlled within limits by the correct choice of the monitoring wavelength. The measurement range reaches the lower mL/m^3 (ppm) levels.
In measurement instruments that utilize the photo acoustic effect, the monochromatic light irradiates through the gas chamber whereupon a changing in the gas pressure can

be measured. The selectivity is equal to the infrared spectral photometer, and the measurement range reaches the lower $\mu L/m^3$ (ppb) levels.
Due to their large size, IR-spectrometers are not feasible for personal air sampling. Both methods, however, have the capability of recording the course of concentration with more or less reasonable selectivity, and can be used to detect short-term exposure peaks. The response time of IR-instruments is higher when compared to FID and PID due to the construction of the system (volume of the chamber).
To date, FTIR spectrometers exist on the market that are particularly feasible for solvent vapours, allowing for the determination of several substances simultaneously. This, however, requires that all substances contained in the workplace air are known prior to the measurement and that there are no interferences to be recognized. The IR response obtained during the measurement is usually composed by single contributions of substances present in the sample. With the help of suitable evaluation algorithms, the response can be used to correctly calculate the concentration of each single substance.

3.2.3.4 Electrochemical gas sensors

Electrochemical sensors can be applied for both the qualitative and quantitative determination of gases and vapours at workplaces. They are normally suitable for personal air sampling. The air, after being drawn with a pump, passes by a gas-permeable membrane, or reaches it due to diffusion. The gases and vapours to be determined diffuse through the membrane into the electrolyte of the sensor, in which a measurement electrode and a counter electrode are located to induce a controlled potential difference. A reference electrode is also integrated to enable accurate potential control. On the measurement electrode, depending on the substance to be determined, either reduction or oxidation occurs, which leads to a current that can be measured with high sensitivity.
Cross sensitivities that may occur with such gas sensors can be ascribed to gases and vapours present in the air, and to changes in the air humidity and temperature. Electrochemical sensors are often applied as warning devices, as it is possible to record time dependent changes in concentrations of hazardous substances in air (e. g., chlorine, carbon monoxide, hydrogen sulfide, formaldehyde, ammonia, hydrogen cyanide, ethylene oxide, or vinyl chloride). The measurement range normally extends between the middle and upper $\mu L/m^3$-(ppb) level.
The lifetime of electrochemical sensors is limited due to expiration of the sensors, on which reactions may take place permanently and irreversibly. The response behaviour of these sensors determined by the system is slower compared to FIDs and PIDs.

3.2.3.5 Other direct-reading instruments

For qualitative and quantitative determinations, other direct-reading instruments can also be used, e. g., ion mobility spectrometers (IMS) or chemiluminescence detectors. Besides electrochemical sensors, different producers use other sensor types based on, e. g., semiconductors. An overview on this is given in the literature [2, 16].

4 Sampling strategy

The basic requirements for the determination and assessment of hazardous substances at workplaces are established in the Technical Rule for Hazardous Substances TRGS 402 [17] and in EN 689 [18]. The aim of measurements is to obtain a representative and capacious assessment of workerś exposure at a defined working area. The area can be defined as a space with known dimensions, or through the activities of employees working during a shift. It has to be defined and described exactly during exposure assessment.
The implementation of the procedure as recommended by TRGS 402 is to ensure an objective assessment of the particular working area by comparing the measured concentrations of hazardous substances in workplace air with the relevant occupational exposure limits. Before sampling can be started, a comprehensive investigation, taking the chosen measuring strategy into account, is necessary in order to select a suitable measuring procedure (i.e., sampling procedure and corresponding analytical method).
A simplification of the occupational exposure assessment at certain working areas is possible by using an indicator component. A substance can function as an indicator component, if it has the capacity to describe representatively the exposure due to all other substances occurring at the workplace. Examples of indicator components, which should be stable and easily measured, are carbon monoxide in car repair shops and nitrous oxide in surgery areas.
To assess the occupational exposure, the concentration of the hazardous substance in workplace air, in the form of a shift average value, needs to be compared with the relevant occupational exposure limit.

4.1 Type of measurement

There are several types of measurements associated with a specific sampling strategy. These are:

- Exposure measurements such as shift average (i.e., 8-hours TWA), short-term and monitoring measurements
- Worst-case measurements
- Measurements at the emission source
- Other measurements

For the report, it is necessary in each case to indicate the type of measurement according to the mentioned above.

4.1.1 Exposure measurements

Exposure measurements are measurements of hazardous substance concentrations in workplace air that detect one or several components and that describe the exposure at work, or in a working area, in terms of shift average or short-term values. They are also used in the process of occupational exposure assessment according to TRGS 402 [17].

Shift average values

To enable the shift average value to be obtained from exposure measurements, statistical methods were used for specifying the necessary sampling duration and corresponding minimum sample number that should be collected during a shift (Table 3).

Table 3. Sampling duration and minimum number of samples [17].

Sampling duration (averaging period)	Minimum sample number
10 sec	≥ 30
1 min	≥ 20
5 min	≥ 12
15 min	≥ 4
30 min	≥ 3
1 h	≥ 2
≥ 2 h	≥ 1

Before selecting the sampling duration, it should be verified by comparison with the limit of quantification, whether monitoring of the threshold limit value is feasible. The working range should be between 1/10 and 2-fold of the threshold limit value concentration.
In the case that several measuring values were obtained during a shift, a time-weighted shift average value (C_s) is calculated according to equation (3):

$$c_s = \frac{\sum c_i \cdot t_i}{\sum t_i} \tag{3}$$

where:
c_i is the concentration of substance i in the workplace air and
t_i is the sampling duration for measured value c_i

Exposure-free periods during a shift, if they occur, must also be included in the calculation of the shift average value according to equation (3) ($c_i = 0$). In addition, the conditions for short-term exposure limit values should be observed, which in the worst case result in excursions above the limit value, although the calculated shift average value is below the limit value. During sampling, breaks from work and other times at which the working area is left need to be accounted for by switching off the sampling pump.

Short-term exposure measurements

The aim of these measurements is to detect short-term increases in exposure. The exposure is to be assessed on the basis of a mean value that occurs during a time period of 15 minutes. The time interval between phases of increased exposure should last for at least one hour.

For substances for which the local irritant effect determines the threshold limit value, or respiratory allergens (short-term category I [19]), an excursion factor (EF) of 1 has been established that can be increased up to 8, specifically to the substance. In reasonable cases, a ceiling value can be established that is not to be exceeded by the momentary concentration of the corresponding substance occurring at the workplace [20]. However, phases of increased exposure are allowed four times per shift, which for substances of this category should not last for more than 15 minutes [19, 20]. Normally, the ceiling value can only be measured using direct-reading instruments, or with gas collection vessels and gas sample bags, due to the temporally constrained resolution. If such an equipment is unavailable, then enrichment methods can be used applying a maximum sampling duration of 15 minutes. In this case, however, a justification must be provided, explaining why an exposure above the permissible ceiling value may not occur.

For substances with systemic effects (short-term category II [19]), an excursion factor of 2 is established as the base value, which can also be increased up to a factor of 8. For substances belonging to this short-term category, the increased exposure is allowed to occur for a duration longer than 15 minutes, as long as the product of excursion time t_E and the actual excursion factor EF_{Real} is not greater than the product of the tabulated excursion factor multiplied by t = 15 minutes ($EF \times t$) [20].

The assessment of the compliance with increased short-term exposures places specific requirements with respect to the sampling technique, the choice of the sampling period during the shift and, not least, on the analysis, because of the shortened sampling duration. Therefore, for planning the measurement correctly, it is necessary to possess detailed knowledge of the work flow and the applied technology. In each case, it is to be examined when, where, how many times and for how long increased exposure peaks may occur. Besides these considerations, planning the measurement should involve as far as possible the inclusion of continuous measurement methods with sufficient time resolutions in order to obtain the required information on feasible measurement intervals (in case that collecting sampling procedures should be applied).

If the capacity of the analytical method used is insufficient, then several short-term sampling intervals should be accumulated in order to obtain sufficient amount of sample. Before sampling, it should be examined through a comparison with the limit of quantification, whether the short-term measurement can be performed between concentrations of one-half and two-times the corresponding limit concentration.

Monitoring measurements

The purpose of monitoring measurements is to check the observance of limit values when occupational exposure assessment has been completed. The time interval between the monitoring measurements depends on the results of the exposure measurement. The analytes (e. g. an indicator component), the measuring procedure and the sampling conditions will have been defined in the occupational exposure assessment.

Intervals for monitoring measurements are to be chosen according to TRGS 402 [17]. For mixtures of substances, the shift average values of each individual substance are used to calculate a substance index, and thereafter the sum of the substance indices (evaluation index) is compared with 1 [21].

4.1.2 Worst-case measurements

Worst-case measurements are performed in situations where markedly increased exposures are expected due to special exposure conditions. This may be the case e. g. when incoming orders make it necessary to increase the throughput of production up to the limit of capacity. If it is demonstrated that the threshold limit value is adhered to under such conditions, it can be assumed that the limit value in air is also adhered to under the usual conditions.

4.1.3 Measurements at the emission source

Measurements at the emission source are based on the same considerations as worst-case measurements. Similarly, if the threshold limit value is adhered to in the immediate vicinity of the emission source, then this can be concluded also for the entire working area, allowing thereby for a reduction of the measurement effort.

4.1.4 Other measurements

Data on specific individual activities, work flow, working techniques, as well as individual concentrations of substances can be obtained by performing specific measurements that are not intended to assess the entire working area or to calculate a shift average value. Such limited findings, however, can become necessary and valuable in determining the state-of-the-art or in the context of preliminary studies.

4.2 Type of sampling

A distinction can be made between personal and stationary sampling. Since the objective is to assess workers' exposure to hazardous airborne substances, personal air sampling should be given preference.
As personal air sampling occurs in the breathing zone of the worker, it should be ensured that both the sampling and the work of the employee can be performed normally and unimpeded, so that the exposure can best be described.
If personal air sampling is not possible, it should be considered whether a stationary measurement can be conducted and, if possible, realized at the workers' breathing zone (usually at approximately 1.5 m in height, and as close to the worker as possible).
In practice, however, it has been demonstrated in some cases that stationary sampling delivers different results than simultaneously conducted personal air sampling. The reasons for such effects can be:

- Workers do not stay at the same place during the entire sampling period,
- The measured concentration depends on the distance from the emission source, and
- The local concentration is influenced by air currents.

4.3 Performance of the sampling

4.3.1 Documentation of the sampling conditions

Measurements of hazardous substance concentrations in workplaces are usually performed under the aspect of assessing the current exposure conditions. However, they also serve for long-term documentation of the exposure situation at workplace, so that a reliable database is provided in case of, e.g., any occupational incidents or diseases that may occur at a later time. Therefore, it is important that sampling conditions are documented in a comprehensive and comprehensible manner [17, 22].
Regarding the conditions during sampling, the following information is indispensable:

- All hazardous substances that are used or that occur at the workplace should be listed, taking also into account dermal absorption. Furthermore, all other substances should be considered additionally, as they, e.g., can have an influence on the sampling and analytical determination. If the measurement is restricted only to specific hazardous substances, it is important to give reasons why other compounds were regarded irrelevant, or to what extent they can be included in the assessment.
- Description of the working area and activity:
  - Definition of the working area (in terms of space, organization and/or activities)
  - Location of workplaces (e.g., outdoors, in closed areas, or partially open)
  - Description, type and/or purpose of the working procedure
  - Connections with further, in particular adjacent, working areas as far as they may have an influence on the exposure
  - Spatial conditions (ground plan), drawings, images
  - Area and height of the premises
  - Details of windows, doors or other areas via which air can be exchanged
- Type of plant and working material:
  - Type, year of construction, number, production conditions, working method
  - Power rating, production parameters, operating times, known emission sources
- Description of the working procedure:
  - Working process, times of exposure, working hours and peak exposures
  - Number of employees/number of workplaces in the working area
  - Personal protective measures/equipment
  - Organizational preventive measures
- Technical protective measures:
  - Measures against emissions (e.g., process engineering measures, local exhaust ventilation, encapsulation)
  - Ventilation
  - Air flow control
- Sampling procedures:
  - Stationary or personal
  - Sampling equipment used (collection medium, sampling pump)
- Sampling
  - Assignment of samples to a place/employee
  - Duration of sampling and volumetric air flow

- Ambient data/environmental data (indoors and outdoors)
- Description of working and operating conditions at the time of measurement

4.3.2 Possible sampling errors

During the measurement of gases and vapours in workplace air, sampling can contribute substantially to measurement errors.
Apart from methodical errors such as sampling site and time, failure to measure all relevant substances, or sampling incorrectly performed, there are a number of other possible errors related to sampling. Therefore, the following points should be checked during sampling:

- Leak-tightness of the system must be ensured (e. g., pumps, tubing, filter holder, sampling head)
- Operability of the pumps (e. g., capacity of the battery, adjustment setting conduct drift)
- Possible contamination during sampling and transport

Errors like these can be avoided by use of technically appropriate sampling procedures that entail proper handling, cleaning and maintenance of sampling devices, as well as the processing of blank samples. Sampling errors related to the system (e. g., volume flow and sampling duration) are discussed in chapter 7.1.
Threshold limit values are related to a temperature of 20 °C and an atmospheric pressure of 1013 hPa. In the German Workplaces Ordinance [22], ambient temperatures between 12 °C and 26 °C are designated, depending on the heaviness of work. In practice, however, higher or lower temperatures occur. In Germany, the atmospheric pressure is normally between 950 and 1050 hPa. Deviations from standard temperature and air pressure conditions are usually small. In worst case, deviations in sampling volume of approximately 10 %, can occur (e. g., in underground mining). Therefore, the sampling volume should be corrected in relation to pressure and temperature when necessary, in order to minimize the total measurement error. It should also be taken into account that the pre-set flow rate of the sampling pumps can be affected by changes in ambient conditions during sampling (e. g., increase of temperature during a shift). The experience has shown that it can help to initialize the sampling pump for several minutes at ambient conditions before commencing the sampling.

5 Transport and storage of samples

After sampling at the workplace, the transport of the sample to the laboratory for analysis and its storage has to proceed in a manner that the substance remains unchanged, or stays in a form, which can be analysed further.
The analytical determination in the laboratory should be carried out as quickly as possible, because there is a possibility, even for chemically stable compounds, that the substance undergoes changes during a longer storage period.

The most favourable storage conditions, as well as the certified storage duration, should be ascertained for each sample individually and documented in the standard operation procedure.

5.1 Transport of samples

The collected sample must be sealed appropriately and transported immediately to the laboratory as described in the following:

- Sampling tubes are sealed tightly using suitable caps or stoppers. They further should be transferred into a container to prevent damage during transport.
- Suitable transport cassettes should be used for filters to ensure that a loss of the collected substance cannot occur.
- Washing bottles and impingers should be sealed with suitable caps and packaged break-proof to prevent damage during transportation.
- Suitable transport containers should be used in particular if the transport of samples to the analytical laboratory is carried out by post or other parcel services.
- The transport container should resist far as possible harmful environmental and/or other external influences (e. g., increased temperatures, strong mechanical forces, etc.).
- Upon opening the samples in the laboratory, it should be checked that no damage has occurred in terms of, e. g., whether the sealing caps of the sampling tubes have become unfixed, or if visible precipitations in the filter cassette have taken place.

5.2 Storage of samples

As mentioned previously, sample analysis in the laboratory should take place as quickly as possible after the sampling. However, specific conditions in the laboratory may sometimes require that the samples are stored for several days or even weeks. In such cases, the sample must be stored in a manner that changes in state are prevented to the furthest extent possible. In this respect, it is recommended to carry out storage experiments in order to obtain information on the maximum storage duration.

- If the analytes are stable, the samples can be stored over several weeks, or even longer. In many cases, the laboratory refrigerator serves well for the storage, because the sample is kept safe as far as possible from environmental influences (e. g., light and thermal fluctuations).
- Storage experiments should be carried out by applying different concentrations of the sample, because normally losses of the analyte have stronger effects on the analytical results at lower concentrations than at higher ones.

The following proceeding is suggested as an example for a four weeks' storage experiment.

1. Preparation of 14 samples each at two different concentrations. The two differing concentrations should lie within the range of 1/10 and 1/5 of the occupational exposure limit and near the occupational exposure limit.

2. Experiments should be planned so that they reflect as closely as possible the treatment of the samples as it may occur later on. For example, if the samples were prepared for postal delivery, they should not be stored in a refrigerator from the first day, but from the third day onwards.
3. Experiments using each two samples of both series should be performed on the day of sample preparation, then on the next day, after three days, and further after 7, 14, 21, and 28 days.
4. The deviation of the calculated concentrations from the initial value must not be greater than the single standard deviation ($\pm$ s) obtained from the determination of repeatability.
5. If changes in concentration were observed during storage, then the nature and extent of it must be exactly determined. Additionally, the maximum storage duration should be documented and correction factors, if employed, calculated.

5.3 Chemically unstable substances

Numerous substances are chemically unstable and cannot be transported or stored in their original form over a longer time period. In the following, several possibilities of stabilizing these substances, allowing for appropriate transport and/or storage, are described:

– Highly reactive substances, such as isocyanates or aldehydes, are already chemically bound during sampling and thereby converted into chemically more stable forms (derivatization), which significantly enhances the storage duration.
– If losses occur during transportation and/or storage after a short time, then the sample can be stabilized by immediately transferring it into an appropriate eluent after sampling.
– Immediate cooling of the samples can also significantly increase their stability, which in particular is recommended for volatile samples. For doing so, the samples should be transferred into suitable transport containers to allow for cooling over a longer time period. After delivering to the laboratory, the samples should be immediately placed in the refrigerator or freezer, depending on the recommended storage temperature for the substance of interest.

6 Analytical determination of gases and vapours

The analytical methods usually applied for determination of substances in gaseous form are the following:

– Gas chromatography (GC),
– High Performance Liquid Chromatography (HPLC),

– Ion chromatography (IC),
– Spectrophotometry in the ultraviolet-visible range (UV/VIS)
– Infrared spectroscopy (IR)

Chromatographic methods have the advantage that, even if the sample matrix is complex, it is possible to determine exactly the single substances by choosing a suitable analytical separation column.

6.1 Determination without enrichment

6.1.1 Gas collection vessels and gas sample bags

For the analysis of gases and vapours collected without enrichment, a gas-tight syringe is normally used for sampling from the collection device. While with using gas chromatography afterwards, the gas sample is directly injected into the column, it is also possible to just shake out the analyte by applying an absorption liquid, or to transfer the analyte (e. g., with nitrogen as flushing gas) into a gas cuvette for infrared spectroscopy. A selection of DFG methods for sampling without enrichment is given in Table 4.

Table 4. DFG methods referring to sampling without enrichment [24].

Substance of interest	Reference	Analytical method
Fluorochlorohydrocarbons	Method No. 1, Vol. 2	Gas collection vessel/GC
Methylbromide	Method No. 1, Vol. 3	Gas collection vessel/GC
Isopropyl alcohol	Method No. 1, Vol. 7	IR and gas collection vessel/IR
Carbon disulfide	Method No. 1, Vol. 5	Gas collection vessel/GC
Styrene	Method No. 2, Vol. 8	IR and gas collection vessel/IR

The calibration is carried out using test gases, or with especially prepared gaseous calibration standards that are processed in the same way as the air samples.
As the gas sample after sampling in gas vessels may suffer losses due to adsorption on the surface area and/or leakages at seals and septa, it must be checked for each substances whether such storage effects have occurred. Attention should be paid additionally on the failure-free function of the sample syringe, as leaky pistons and blocked needles can lead to erroneous results.

6.1.2 Direct-reading instruments

Direct-reading instruments are available for both personal and stationary measurements (cf. chapter 3.2.3). If installed permanently on location, these instruments can be applied for continuous monitoring of workplaces. This enables, e. g., to operate adequately an installed air-conditioning system.

Direct-reading instruments are available for the following substances [2]: ammonia, arsine, boron trifluoride, bromine, carbon dioxide, carbon monoxide, chlorine, chlorine dioxide, chlorine trifluoride, diborone, fluorine, formaldehyde, germanium tetrahydride, hydrazine, hydrogen bromide, hydrogen chloride, hydrogen cyanide, hydrogen fluorine, hydrogen peroxide, hydrogen selenide, hydrogen sulfide, iodine, nitrogen dioxide, nitrous oxide, ozone, phosgene, phosphorus trichloride, phosphine, phosphorus oxychloride, sulfur dioxide, sulfur hexafluoride, and tetrachloroethene.

6.2 Determination after enrichment by adsorption

By using direct-reading instruments, the results are obtained immediately during the sampling. In contrary, samples collected involving enrichment and/or chemical reactions must be subsequently prepared for analysis in order to assess correctly the exposure.
In case the enrichment takes place via adsorption, then the following treatment step is normally thermal desorption or the use of liquid desorption agents. When using thermal desorption, the entire sample is transferred directly into the analytical instrument. By solvent desorption using a solvent or a mixture of solvents, a liquid sample is obtained, of which (after the required contact time has been maintained) an aliquot is taken and then injected into the analytical instrument.

6.2.1 Thermal desorption

The preparation of thermal desorption tubes takes place in the thermal desorber; an extraction step is not needed. The adsorption tubes are heated in a compatible thermal desorber, whereupon the collected substances are transferred into a cold trap using a carrier gas. When desorption is complete, the cold trap is heated abruptly and thereby transferring the sample onto the GC column for subsequent separation.
As an example, the conditions of currently used thermal desorption as recommended for determining solvent vapours are shown in Table 5.
After set-up of the thermal desorber and gas chromatograph, the calibration standards and the samples can be analysed. As an option, thermal desorption can also take place into gas cuvettes, using FTIR-spectrometry for the analytical determination afterwards [25]. A selection of DFG methods that involve adsorption and thermal desorption is shown in Table 6.

Table 5. Recommended parameters for thermal desorption of typical solvents using two adsorbents.

Adsorbent	Tenax TA™	XAD 4, Chromosorb 106™
Desorption temperature	280 °C	170 °C
Desorption time	10 min	5 min
Temperature of the transfer line	200 °C	200 °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™	
Carrier gas	Helium	
Input split	40 mL/min (input split)	
Desorb flow	10 mL/min (desorb flow)	
Output split	30 mL/min (output split)	

Table 6. Selection of DFG methods involving adsorption and thermal desorption [24].

Substance of interest	Reference	Adsorbent	thermal desorption coupled with
Lacquer aerosols	Method No. 3, Vol. 8	Tenax GR™	GC
Furfuryl alcohol	Method No. 3, Vol. 8	Tenax TA™	GC
Styrene	Method No. 3, Vol. 5	Tenax TA™	GC
Chlorinated biphenyls (PCBs)	Method No. 2, Vol. 8	Tenax TA™	GC/MS
Solvent mixtures	Method No. 2, Vol. 6	Tenax TA™, XAD-4, Chromosorb 106™	GC
2-Butenal	Method No. 2, Vol. 9	Chromosorb 106™	GC/MS
Dicyclopentadiene	Method No. 1, Vol. 9	Chromosorb 106™	GC/MS
Halogenated anaesthetics	Method No. 2, Vol. 9	XAD-4	GC
Nitrous oxide	Method No. 2, Vol. 10	Molecular sieve 5Å	FTIR
Nitrous oxide	Method No. 3, Vol. 9	Molecular sieve 5Å	GC/ECD

6.2.2 Solvent desorption

For solvent desorption, mainly sampling tubes that are filled with activated charocal and silica gel are used. After sampling, the content of the tubes is separated as to the collection phase and the control phase. Both phases are separately transferred into glass vessels and covered with a desorption agent. Normally, an internal standard is added. The substances that were adsorbed are now desorbed by the solvent. The efficiency of the desorption process must be validated according to EN 482 [26], for which the influence of humidity during sampling should be considered in particular.

During the analytical determination, the following two procedures are mainly applied:

a) Injection of the desorption solution

After desorption, the desorption solvent is separated from the adsorbent and transferred to adequate vessels in order to exclude that a new sorption process takes place and thereby leading to erroneous results in terms of low recovery of the analyte.
Subsequently, an aliquot of the sample is analysed with, e. g., gas chromatography or a spectrophotometry. For analytical determination, liquid desorption agents such as carbon disulfide, diethyl ether, or mixtures of two or three solvents, have proven their reliability. Additionally, ion chromatography, e. g., can be used to analyse aqueous extracts.

b) Headspace analysis

After the entire sample, consisting of the adsorbent and desorption agent, is brought to an adequate temperature, an aliquot of the sample's headspace is taken and injected into a gas chromatograph. There is no need to separate the adsorbent from the desorption agent. The boiling point of the desorption agent, however, must be accordingly high. Mainly desorption agents such as benzyl alcohol, dimethylacetamide, N,N-dimethyl formamide and dimethylphthalate (DMP) are used during analysis. Some DFG methods for adsorption and liquid desorption are shown in Table 7.

Table 7. Selection of DFG methods using adsorption and liquid desorption for the analysis of substances [24].

Substance to be determined	References	Adsorbent	Eluent	Analytical method
Tetrahydrofuran	Method No. 1, Vol. 3	Activated carbon	Dioxane	GC
Acetamide	Method No. 1, Vol. 8	Activated carbon	Methanol/CS_2	GC
Acrylates	Method No. 1, Vol. 3	Activated carbon	CS_2	GC
Benzene	Method No. 4, Vol. 5	Activated carbon	CS_2	GC
Lacquer aerosols	Method No. 3, Vol. 8	Activated carbon	CS_2	GC
Solvent mixtures	Method No. 1, Vol. 6	Activated carbon	CS_2	GC
1,1,1-Trichloro ethane	Method No. 1, Vol. 3	Activated carbon	CS_2	GC
Lacquer aerosols	Method No. 2, Vol. 8	Activated carbon	ternary mixture (dichloromethane/ CS_2/methanol)	GC
Solvent mixtures	Method No. 3, Vol. 6	Activated carbon	ternary mixture (dichloromethane/ CS_2/methanol)	GC
Solvent mixtures	Method No. 4, Vol. 6	Activated carbon	DMF	Headspace/ GC
Chlorinated biphenyls	Method No. 1, Vol. 2	Florisil	n-Hexane	GC/ECD
2-Butenal	Method No. 1, Vol. 2	Silica gel	Acetone	GC
2-Chloroethanol	Method No. 1, Vol. 3	Silica gel	Acetone	GC
Solvent mixtures	Method No. 2, Vol. 6	Activated carbon	Diethyl ether	GC

Table 7 (continued)

Substance to be determined	References	Adsorbent	Eluent	Analytical method
Pentachlorophenol	Method No. 1, Vol. 2	Silica gel	Potassium carbonate solution	GC
Urea herbicides	Method No. 1, Vol. 3	Silica gel	Methanol	HPLC/UV
Volatile inorganic acids	Method No. 1, Vol. 6	Silica gel	Sodium carbonate solution	IC
Aliphatic amines	Method No. 1, Vol. 10	Silica gel	Sulfuric acid	GC/HS
Methanol	Method No. 2, Vol. 1	Silica gel	H_2O	GC
Solvent mixtures (alcohols and 2-butanone)	Method No. 6, Vol. 6	Silica gel	H_2O	Headspace-GC
Azinphos-methyl	Method No. 1, Vol. 6	Tenax TA™	Acetonitrile	HPLC/UV
Gelatinous explosives	Method No. 1, Vol. 8	Tenax TA™	Methanol	HPLC/UV
Methabenzthiazuron	Method No. 1, Vol. 6	Tenax TA™	Methanol	HPLC/UV
Fenthion	Method No. 1, Vol. 6	Tenax TA™	n-Butyl acetate	GC/MS
Parathion	Method No. 1, Vol. 6	Tenax TA™	n-Butyl acetate	GC/NPD
Atrazine	Method No. 1, Vol. 8	XAD-2	Acetone	HPLC/UV
Polycyclic aromatic hydrocarbons (PAH)	Method No. 3, Vol. 8	XAD-2	Toluene	GC/MS
Halogenated anaesthetics	Method No. 2, Vol. 9	Activated carbon	Toluene	GC
Metal-working fluids	Method No. 1, Vol. 5	GFF/XAD-2	Tetrachloroethene	FTIR
Polycyclic aromatic hydrocarbons (PAH)	Method No. 2, Vol. 8	Teflonfilter/ XAD-2	Acetonitrile/ methanol	HPLC/DAD/ Fluorescence

6.3 Determination after enrichment by absorption or reaction

Gases and vapours enriched by absorption or reaction can principally be analysed as described in chapters 6.1 and 6.2. For the analysis of reaction products of the substance to be determined, it must be ensured that a unique stoichiometric correlation exists between the analyte of interest and the reaction product. Furthermore, different gases and vapours to be determined should not form the same reaction products due to problems that arise in the simultaneous determination of these substances, which could affect negatively the assessment of exposure.

If the reaction or absorption takes place in a liquid medium, the preferred analytical method normally is spectrophotometry in visible or UV-range. Additionally, reagent solvents in reaction samplers can be used and analysed in the laboratory. Some DFG methods that apply absorption and reaction samplers are listed in Table 8.

Table 8. Selection of DFG methods using absorption and reaction sampler [24].

Substance to be determined	Reference	Absorption in/ Derivatisation with:	Eluent	Analytical method
Aldehydes (n-C_1-C_4, glutaraldehyde)	Method No. 1, Vol. 2	2,4-dinitrophenyl-hydrazine (DNPH) on fiber glass filters	Acetonitrile	HPLC
Aldehydes (n-C_1-C_9, glutaraldehyde)	Method No. 2, Vol. 5	2,4-dinitrophenyl-hydrazine (DNPH) on silica gel	Acetonitrile	HPLC
Alkanolamines	Method No. 1, Vol. 8	Na-octane-sulfonate (filter)	Na-octane-sulfonate-solution/ phosphoric acid	IC
Ammonia	Method No. 2, Vol. 9	PTFE-filter/ H_2SO_4-impregnated activated carbon	Sulfuric acid	IC
Ammonia	Method No. 1, Vol. 2	Sulfuric acid		Photometry
N-Methyl-2-pyrrolidone	Method No. 1, Vol. 1	Acetone		GC
Organotin compounds	Method No. 1, Vol. 3	Ion exchanger	Diethyl ether in hydrochloric acid	GC
Ozone	Method No. 1, Vol. 3	Indigocarmine solution		Photometry
Phosphine	Method No. 1, Vol. 5	With $Hg(CN)_2$ impregnated silica gel	potassium permanganate solution	Photometry
2-Propenal	Method No. 1, Vol. 2	DNPH on fiber glass filters	Acetonitrile	HPLC
Sulfur dioxide	Method No. 2, Vol. 8	KOH (activated carbon)	Alkaline H_2O_2-solution	IC
Tetraethyl orthosilicate	Method No. 1, Vol. 1	2-Propanol		GC
Hydrogen peroxide	Method No. 1, Vol. 8	Potassium titanium oxide oxalate-2-hydrate/oxalic acid		Photometry

7 Sources of errors

Even under consideration of all known possible errors, every analytical result essentially includes a measurement error. Therefore, the analyst according to EN ISO/IEC 17025 [27] is required to determine the measurement uncertainty. For this purpose, the "guide to the expression of uncertainty in measurements (GUM)" [28] has been developed. In Annex C of EN 482 [26] possible error sources involved in measurement of hazardous substances are listed. The measurement of such substances at workplaces consists of the following four sub-steps:

– Sampling
– Transport and storage of the sample
– Sample preparation
– Analysis and calculation of the result

Each of these sub-steps can contain numerous sources of error. The following tries to identify the most significant possibilities of errors that can occur. As a rule, each error possesses random and systematic components.

– Systematic errors, e. g., are a reduced recovery during sample preparation, an error in the volume of the volumetric flask, or measurement deviations of an instrument that measures the air flow. If such errors cannot be avoided, they can be taken into account by applying adequate correction factors. In case of a correction, then only the random component of the systematic error needs to be considered.
– Random errors are variations in the analytical results caused by, e. g., repeating several times the same steps during sample preparation, or by fluctuations in the air flow of sampling pumps. Such errors cannot be accounted for by means of correction factors. However, it is possible to estimate the extent of the random error by assuming a Gaussian distribution, if the measurements were repeated sufficiently.

According to EN 482 [26], the expanded uncertainty U during the measurement of the hazardous substance must not exceed:

0.1 – 0.5 of the threshold limit value: 50 %
0.5 – 2 of the threshold limit value: 30 %

When calculating the uncertainty according to equation 4, all significant error sources need to be considered.
The combined random standard uncertainty is calculated by:

$$u_{c_r} = \sqrt{u_{s_r}^2 + u_{a_r}^2} \tag{4}$$

where:
u_{cr} is the combined random standard uncertainty,
u_{sr} is the random sampling uncertainty,
u_{ar} is the random analytical uncertainty.

The calculation of the combined non-random standard uncertainty is followed according to equation (5):

$$u_{c_{nr}} = \sqrt{u_{s_{nr}}^2 + u_{a_{nr}}^2} \tag{5}$$

where:
u_{cnr} is the combined non-random standard uncertainty,
u_{snr} is the non-random sampling uncertainty,
u_{anr} is the non-random analytical uncertainty.

The combined standard uncertainty u_c is calculated according to equation (6):

$$u_c = \sqrt{u_{c_{nr}}^2 + u_{c_r}^2} \tag{6}$$

The expanded uncertainty U is calculated according to equation (7):

$$U = 2 \times u_c \tag{7}$$

where:
u_c is the standard uncertainty
2 is the coverage factor

When developing the method, the coverage factor in turn is calculated from the number of degrees of freedom (for experiments independent from each other). Normally the factor lies between "3" and "2". The factor reaches nearly "2" according to the method development as outlined in the guidelines of EN 482 [26] (or those of the DFG), which requires that numerous, independent experiments are to be performed.
Figure 2 gives an overview on the most important error sources that need to be regarded during the measurement of vaporous hazardous substances.
Each uncertainty components as shown in Figure 2 are in turn subject to numerous further individual components and should be considered when estimating the uncertainty. The following describes in more detail the single uncertainty components.

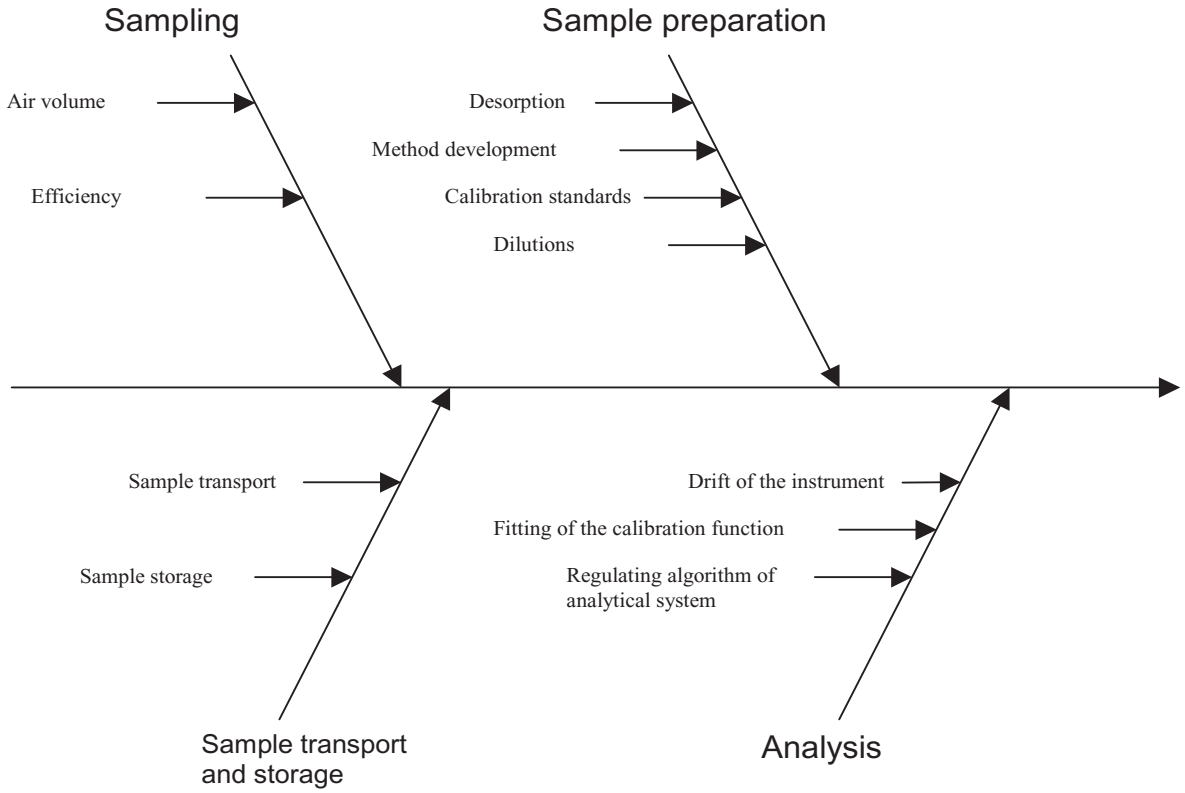

Fig. 2. Possible error sources regarding the determination of the overall analytical uncertainty.

7.1 Sampling

7.1.1 Air volume

There are three devices need when determining the air sample volume: a sampling pump, a flow rate measurement device, and a chronometer (clock).
The sampling pump should be in conformation with the requirements according to EN 1232 [9], which means that the flow rate of the pump remains within $\pm 5\,\%$ range of the pre-set value. This deviation normally cannot be corrected. Here, the rectangular probability distribution $A/\sqrt{3}$ is used to calculate the uncertainty (u) of the pump's flow rate according to equation (8):

$$u_{\text{pump flow}} = (5/\sqrt{3})\ \% \tag{8}$$

The uncertainty of the flow rate measurement device divides to random and non-random components. Information on the latter can be obtained, e. g., from calibration certificates. Here as well, a rectangular probability distribution can be assumed. For most of the measurement devices used (rotameters with 30 cm in length, mass flow meters, bubble flow or dry piston flow meters), the non-random uncertainty component is less than 2% (cf. Annex C of EN 482 [26]). The random uncertainty component derives from reading the flow rate measurement device and normally is also significantly below 2%.
To date, very precise chronometers are commercially available with practically no deviation over the measurement period. Errors therefore may mainly result from inaccurate readings. During long-term measurements accompanied with sampling durations of more or equal than 2 h, a false reading of even a minute contributes to the uncertainty by 0.48% deviation only. In these cases, the error resulting from time measurements can be neglected.
The situation, however, is different for short-term measurements. For time measurements of 15 minutes, the false reading of one minute would contribute to the uncertainty by 3.8%. Therefore, if the registration is not performed accurately within seconds, an error in the sampling duration for short term measurements cannot be neglected.

7.1.2 Efficiency of sampling

The process of sampling gases and vapours can be considered efficient, as long as the breakthrough volume of the substance under investigation is not exceeded.
When applying reaction samplers, the capacity of the sampler must be ascertained prior to use. In addition, the application range of the sampler must be identified and documented.
Ambient parameters (e. g., humidity and temperature) may have an influence on the sampling efficiency. These parameters are, however, difficult to estimate and, therefore, a dynamic test gas stand should be used preferably to analyse vaporizable substances, because this technique provides a possibility to take ambient parameters into account.

For methods developed without the option of using test gases, ambient parameters should be estimated and considered in the calculation of uncertainty.

7.2 Transport and storage of samples

During developing the analytical method, the time period in which the sample has to be transported to the laboratory and additionally the storage conditions should be ascertained (cf. chapter 5). Although most substances are not subject to particular transport and storage conditions, so they can be analysed without having to expect significant losses, others possess chemical reactive characteristics and, thus, are suspects to restricted storage.
For substances that are storable without losses over a described period, it is not necessary to consider an uncertainty component for transport and storage. For those, however, with restricted storage stability, the following needs to be taken into account and documented:

- The time period in which the sample remains stable (in this case, no uncertainty component is needed), or
- The loss of an analyte occurring during transport and storage over time, as well as the beginning of the analytical determination (the value can be corrected as non-random deviation; only the random deviation needs to be accounted for).

7.3 Sample preparation

Most of the uncertainty components in this area are determined within the scope of method development. As normally the same materials and devices are used in the laboratory during method development and application (e. g., volumetric flask, analytical balance, pipettes, calibration standards, solvents, analytical instruments, etc.), there is no need to determine the uncertainty for each of these components separately.
If a method is adopted from another laboratory, then obviously the specified conditions and materials do not apply. Here, the uncertainty components need to be determined for the new laboratory, and all uncertainty components of the method have to be recalculated.

7.3.1 Desorption

The desorption rate can be determined from spiked samples at different concentrations. Deviations from the reference concentration can be corrected as non-random deviation, taking the random variation of this uncertainty component into account.

7.3.2 Method development

If test gases (single or mixture) are applied during method development for determining the performance characteristics, then it must be considered that the test gas conditions can contribute to the uncertainty components. However, by using dynamic test gases, there should be no problem to keep the random error (related to the reference concentration) well below $\pm$ 3 % during test gas production. In addition, when using test gases, there is no need to determine the desorption rate, as it is included in the recovery rate, which was established during sample preparation. Ordinarily, the use of a dynamic test gas stand should be preferred when developing the analytical method.
If the method development is performed with using spiked samples, then besides of the desorption rate (see chapter 7.3.1), the random and non-random components of the sample preparation are to be determined additionally. This involves also an estimation of all errors that possibly occur during sample preparation.

7.4 Other methods for determining the recovery

Interlaboratory round-robin tests can be used to determine non-random deviations of the analytical procedure. Another possibility is provided by employing certified reference materials. However, as interlaboratory round-robin tests cannot be easily organized and/or performed, and as reference materials are restrictively available, these two options are only seldom considered for routine applications.

7.5 Analysis

When performing the analytical determination, the conditions should be the same as for the development of the analytical procedure. Thereby, uncertainty components such as, e. g., the random uncertainty for the injection of the sample into the gas chromatograph, are already included in the uncertainty. The same is valid for the evaluation algorithm of the analytical instrument, if the parameters have not changed.
As analytical instruments are recalibrated from time to time, the contribution of the calibration to the uncertainty must be taken into account in each single case.

8 Quality management

Each laboratory performing chemical analyses should establish a quality management system (QM). One main task of a QM-system is to ensure the quality of the analytical process permanently by means of considering the following important aspects:

– Overall quality of the laboratory (including its facilities and equipments)
– Material control and traceability

- Validation of analytical procedures
- Quality assurance of analytical results
- Quality assurance of reports and of archiving analytical results
- Control of measurement and test equipment, inspections, and calibration of measurement devices
- Quality monitoring and documentation
- Statistical quality control

In addition to these internal measures, an external quality management system should be employed if this can be achieved. Most of these measures are known and well described in the literature [29]. In this respect, a particular importance pertains to statistical quality control measures. Furthermore, specific quality assurance measures according to EN 17025 [27] are required for accreditated laboratories.
The following describes measures for an external quality assurance. They are required elements of a quality management system.

8.1 Audits

Audits are normally part of the accreditation procedure in order to examine systematically and independently quality-related activities of a laboratory. Thereby, it should be ascertained that all procedures are described satisfactorily, and the staff performing the analysis possesses sufficient competency to achieve the overall quality. The quality aims are not subject of the auditing. Audits are repeatedly performed at periodic intervals from accreditation bodies.
Furthermore, the laboratory is obliged to perform internal audits in order to verify whether the quality aims have been achieved.

8.2 Round-robin tests

Interlaboratory round-robin tests are conducted mainly for the following purposes:

- Evaluation of analytical methods within the scope of a standardization process
- Evaluation of the laboratory performance in routine analysis

Participation in round-robin tests is requested by accreditation bodies as a measure of external quality assurance. Carried out by an independent reference laboratory, they serve to evaluate the performance of a laboratory and to ensure that problems are recognized and solved in due course.
In principle, nearly identical samples are used and analysed under the same repeated conditions by all participating laboratories. After evaluation of the test results, characteristic data are obtained under comparative conditions.
Different organizations in Europe offer round robin tests for the measurement of hazardous substances in workplace air. More information is available from the European database on round robin tests (www.eptis.bam.de). The most important systems in Europe regarding “proficiency testing” are offered from:

– The British Health and Safety Laboratory (HSL); Workplace Analysis Scheme for Proficiency (WASP), and
– The BG-Institute for Occupational Safety and Health (BGIA) in Germany; round-robin tests for laboratories analysing hazardous substances.

While mostly prefabricated samples are used to perform interlaboratory round robin tests, some tests are also executed in which the participants actively take samples from a dynamic test gas stand [30, 31]. The advantage thereby is that the entire measurement procedure is taken into account.
The evaluation process after completion of round-robin tests is normally conducted according to ISO guide 43 [32, 33], in which the so-called "Z-score" (equation 9) is explained to serve as an assessment of quality. Therewith, the laboratory result deviating from the target value is standardized, by taking the permitted deviation into account (e. g., the standard deviation, or a maximum deviation predefined in advance).

$$Z = \frac{|\text{analytical result} - \text{target value}|}{\text{standard deviation}} \tag{9}$$

The quality criterion is fulfilled if the Z-score does not exceed the value of 2, values between 2 and 3 are considered "equivocal" and values above 3, "most equivocal".

9 References

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10 Appendix

Appendix 1: Pumps for personal air sampling.

Pump	Air flow [mL/min][1]	Supplier
SKC Universal 224-PCXR8	5–5000	2
SKC Universal 224-PCTX8	5–4000	2
SKC Sidekick 224–52TX	5–3000	2
SKC AIR-Lite	5–3000	2
SKC EXEC-Pump	5–3250	2
SKC Pocket-Pump	5–225	2
SKC Series 222	20–80 50–200	2
GSA SG350ex	20–350	4
GSA SG2500ex	50–3000	4
GSA SG 4000	20–4000	4, 5
ESCORT ELF	500–3000	5
Gilian HFS-513AUP	1–5000	1, 4, 5
Gilian LFS-113DC	1–350	1, 4, 5
Gilian GilAir 3 Ex	1–3000	1, 4, 5
Gilian GilAir 5 Ex	1–5000	1, 4, 5
GilAir 3500	20–3500	1
SP 330	20–3000	1
SP 350	20–4000	1
SP 530	20–3000	1
SP 730	20–3000	1
Buck VSS 1	1–600	6
Buck VSS 2	1–800 (800–5000)	6
ALPHA 1 (no longer in production)	5–5000	1, Service only
P 4000 (no longer in production)	20–4000	1, Service only
GSA 500, 501ex, 502ex (no longer in production)	10–1000	4, Service only
GSA 2000, 2001ex, 2002ex (no longer in production)	300–3000	4, Service only
GSA SG 4500 (no longer in production)	20–4000	4, Service only

1 According to manufacturer information

Appendix 2: Devices for adjusting and checking the air flow.

Device	Supplier
BIOS DryCal DC-1	1 (Service only), 2
BIOS DryCal DC-2	1, 2
Soap Bubble Flow Meter Gilibrator (Gilian Instrument Corp.)	1, 4
Mass flow Meter Series 358 (0–1 L/min)	1, 2
Drum Gas Meter TG05-PP-PP	3
Mass Flow Meters DFM+	2
BIOS DryCal DC-Lite	1, 2, 4, 5
Thermal Mass Flow Meters 4140	1
Thermal Mass Flow Meters FlowCal	1
MiniBuck M1	6
MiniBuck M5	6
Rotameter	1, 2, 4, 6

Suppliers for devices as shown in Appendices 1 and 2.

1 = DEHA Haan + Wittmer GmbH
Birkenstraße 31
71292 Friolzheim

2 = Analyt - MTC Messtechnik
GmbH & Co. KG
Klosterrunsstr. 18
79379 Müllheim

3 = Dr. Ing. Ritter
Apparatebau GmbH
Coloniastraße 19–23
44892 Bochum

4 = GSM Gesellschaft für Schadstoff-
messtechnik GmbH
Gut Vellbrüggen
41469 Neuss

5 = LMT Leschke
Messtechnik GmbH
Bergstraße 168
15230 Frankfurt/Oder

6 = Ravebo Supply B. V.
't Woud 2
NL-3230 AG Brielle

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