The MAK Collection for Occupational Health and Safety

Sampling and analysis of substances and substance mixtures which may occur simultaneously as vapours and particles in workplace air

Air Monitoring Methods, Conceptual Topics – Translation of the German version from 2018

D. Breuer[1], C.G. Dragan[2], R. Hebisch[3,*], R. Bartsch[4], Y. Giesen[1], W. Krämer[5], L. Nitschke[6], G. Nitz[7], K.-H. Pannwitz[8], M. Tschickardt[9], T.H. Brock[10,*], A. Hartwig[11,*], MAK Commission[12,*]

[1] *Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA), Alte Heerstraße 111, 53757 Sankt Augustin, Germany*

[2] *Helmholtz Zentrum München, Department CMA, Ingolstädter Landstraße 1, 85764 Neuherberg, Germany*

[3] *Head of the working group "Air Analyses" of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany*

[4] *Institute of Applied Biosciences, Department of Food Chemistry and Toxicology, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Building 50.41, 76131 Karlsruhe, Germany*

[5] *BASF SE, ESE/MA – Z 570, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany*

[6] *Bavarian Health and Food Safety Authority, Pfarrstraße 3, 80538 München, Germany*

[7] *Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany*

[8] *Dräger Safety AG & Co. KGaA, Revalstraße 1, 23560 Lübeck, Germany*

[9] *State Environmental Agency Rhineland-Palatinate, Kaiser-Friedrich-Straße 7, 55118 Mainz, Germany*

[10] *Head of the working group "Analytics", German Social Accident Insurance, Institution for the raw materials and chemical industry, Prevention - Department of Hazardous Substances, Biological Agents and Analytical Chemistry, Kurfürsten-Anlage 62, 69115 Heidelberg, Germany*

[11] *Chair of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Institute of Applied Biosciences, Department of Food Chemistry and Toxicology, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Building 50.41, 76131 Karlsruhe, Germany*

[12] *Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Kennedyallee 40, 53175 Bonn, Germany*

* *email: R. Hebisch (luftanalysen-dfg@baua.bund.de), T.H. Brock (analytik@bgrci.de), A. Hartwig (andrea.hartwig@kit.edu), MAK Commission (arbeitsstoffkommission@dfg.de)*

Keywords: vapour-aerosol mixture; workplace measurement; hazadous substances; air analyses; analytical method; requirements; combined sampling systems; sampling media; influence of temperature; particle size

Citation Note: Breuer D, Dragan CG, Hebisch R, Bartsch R, Giesen Y, Krämer W, Nitschke L, Nitz G, Pannwitz K-H, Tschickardt M, Brock TH, Hartwig A, MAK Commission. Sampling and analysis of substances and substance mixtures which may occur simultaneously as vapours and particles in workplace air. Air Monitoring Methods, Conceptual Topics – Tanslation of the German version from 2018. MAK Collect Occup Health Saf [Original edition. Weinheim: Wiley-VCH; 2018 Jul;3(3):1628-1662]. Corrected republication without content-related editing. Düsseldorf: German Medical Science; 2025. https://doi.org/10.34865/amsampmixe1918_w

Republished (online): 12 Dec 2025

Originally published by Wiley-VCH Verlag GmbH & Co. KGaA; https://doi.org/10.1002/3527600418.amsampmixe1918

Manuscript completed: 01 May 2017

Published (online): 26 Jul 2018

The commission established rules and measures to avoid conflicts of interest.

Sampling and analysis of substances and substance mixtures which may occur simultaneously as vapours and particles in workplace air

Air Monitoring Methods

D. Breuer[1], C.G. Dragan[2], R. Hebisch[3,*], R. Bartsch[4], Y. Giesen[1], W. Krämer[5], L. Nitschke[6], G. Nitz[3], K.-H. Pannwitz[7], M. Tschickardt[8], T.H. Brock[9,*], A. Hartwig[10,*], MAK Commission[11,*]

DOI: 10.1002/3527600418.amsampmixe1918

Abstract

Due to their physical properties semi-volatile substances can occur as particle/vapour mixtures in workplace air. Such mixtures are formed, e.g. as a result of mechanical processes such as the processing of metals or ceramics, during dipping processes in electroplating or during spraying processes. For that reason workplace air measurements must be carried out with a suitable sampling system for the collection of particles and vapours in workplace air. This report sets out the general principles of the physical behaviour of airborne aerosols and explains the different toxic effects of both phases by inhalation. Sampling strategies for collection of particle/vapour mixtures in workplace air using generally accepted combined sampling systems are described. In addition, several approved sampling heads and sampling systems such as GSP, GSP-Mini, GGP/GGP-U are presented. Influences on the measurement results such as temperature, humidity, sampling, transport and storage are discussed and the calculation of the expanded uncertainty when measuring these special kinds of substances is explained.

Joint Publication of the Analytical Subcommittee of the Chemistry Board of Experts of the Expert Committee Raw Materials and Chemical Industry of the German Social Accident Insurance and the working Group “Air Analyses” of the Permanent Senate Commission of the DFG for the Investigation of Health Hazards of Chemical Compounds in the Work Area.

Keywords

particle/vapour mixtures; particle; aerosol; sampling; sampling systems; sampling strategy; expanded measurement uncertainty; air analysis; workplace measurement; hazardous substances; workplace monitoring; air sampling

Author Information

[1] Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA), Alte Heerstr. 111, 53757 Sankt Augustin, Germany
[2] Cooperation Group “Comprehensive Molecular Analytics” (CMA), Helmholtz Zentrum München, P.O.Box 1129, 85758 Neuherberg, Germany
[3] Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany
[4] Department of Food Chemistry and Toxicology, Institute of Applied Biosciences, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Building 50.41, 76131 Karlsruhe, Germany
[5] BASF SE, ESE/MA – Z 570, 67056 Ludwigshafen, Germany
[6] Bavarian Health and Food Safety Authority, Pfarrstraße 3, 80538 München, Germany
[7] Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany
[8] Dräger Safety AG & Co. KGaA, Revalstr. 1, 23560 Lübeck, Germany
[9] State Environmental Agency Rhineland-Palatinate, Kaiser-Friedrich-Str. 7, 55118 Mainz, Germany
[10] German Social Accident Insurance, Institution for the Raw Materials And Chemical Industry, Prevention – Department of Hazardous Substances, Biological Agents and Analytical Chemistry, Kurfürsten-Anlage 62, 69115 Heidelberg, Germany
[11] Chair of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Department of Food Chemistry and Toxicology, Institute of Applied Biosciences, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Building 50.41, 76131 Karlsruhe, Germany

[*] Email: R. Hebisch (luftanalysen-dfg@baua.bund.de), T.H. Brock (analytik@bgrci.de), A. Hartwig (andrea.hartwig@kit.edu), MAK Commission (arbeitsstoffkommission@dfg.de)

Sampling and analysis of substances and substance mixtures which may occur simultaneously as vapours and particles in workplace air

Substances whose vapour pressures at room temperature are between 100 Pa and 0.001 Pa (boiling points between approx. 180 °C and 350 °C) are used for a wide range of activities. Characteristically these substances can simultaneously occur as vapours and as droplets (particles) in the workplace air. Such particle/vapour mixtures can be generated deliberately e.g. as a result of spraying liquid cleaning products or as part of a process.

The toxicological evaluation of a substance requires knowledge of whether the substance occurs primarily in the vapour or in the particulate phase and which part of the body it affects. While vapour can penetrate considerably deeper into the respiratory passages than inhalable particles, the local effect of a deposited droplet in the respiratory tract is generally greater than that of vapour.

The distribution ratio of a substance between the individual phases is influenced by environmental conditions such as air pressure, temperature and humidity. Generally, these conditions do not remain constant at workplaces in terms of space and over time, therefore the distribution ratio is continually changing. The fact that these substances occur simultaneously in the vapour and in the condensed phase (particles) must be taken into consideration when exposure by inhalation is investigated. This means that it is necessary to collect both phases simultaneously during sampling. Substances that can occur as vapour and as particles at the same time at the workplace are labelled accordingly in the "List of MAK and BAT Values of the DFG" as well as in the "Technical Rules for Hazardous Substances" (TRGS) in the TRGS 900 (OEL – Occupational Exposure Limits).

Contents

1 Introduction

Aerosols are defined as two-phase systems consisting of solid and/or liquid particles that are suspended in a carrier gas. The composition of an aerosol is constant in the case of thermodynamic equilibrium. A significant parameter for reaching thermodynamic equilibrium at a predefined temperature is the vapour pressure of the condensed phase. Thus solid substances, such as copper, have a very low vapour pressure and are in equilibrium with their environment (see Table 1). Liquid particles (droplets) generally have significantly higher vapour pressures, so that no equilibrium may occur between the condensed and vapour phase under real conditions. Reaching the equilibrium state is only possible in closed systems under ideal conditions.

Constant environmental conditions exist neither at workplaces nor in nature. This means that temperature and pressure are subject to temporal and local fluctuations. The cooling of aerosols leads to condensation of vapours and therefore to growth of existing droplets or formation of new droplets. Heating or dilution of an aerosol (e.g. through air movement) results in evaporation, which can lead to a droplet disappearing entirely. In the course of this process a continuous exchange of mass takes place between the droplets and the vapour phase.

With regard to their toxic effect, droplets and vapours differ significantly, whereby the local effect of a deposited droplet is generally more pronounced than that of vapour (see Sections 3.1 and 3.2). The reason for this is that the mass or concentration of a substance in a liquid (with respect to the area) is higher than in vapour. On the other hand, vapours can penetrate deeper into the respiratory tract than inhalable particles. It is therefore imperative to establish in which aggregate state a substance is present in the workplace atmosphere; whether it occurs predominantly in the droplet or in the vapour phase, when evaluating the exposure to substances in the workplace air that are harmful to health.

Organic substances, in particular, can be present simultaneously as vapour and droplets in the workplace air. In the case of volatile substances (Volatile Organic Compounds – VOCs), such as many solvents with a high vapour pressure, evapora-

Table 1 Examples of vapour pressures of solid and liquid substances

Substance	Physical state at 20 °C	Boiling point at normal pressure [°C]	Vapour pressure [hPa] $^{\text{Temperature in °C}}$
Acetone	liquid	56	233^{20}
Water	liquid	100	23.4^{20}
Toluene	liquid	111	29^{20}
Dimethylformamide (DMF)	liquid	153	5^{20}
Iodine	solid	184	0.039^{30}
Naphthalene	solid	218	0.04^{20}
Diethylene glycol	liquid	244	0.013^{20}
Dibutyl phthalate (DBP)	liquid	340	0.00016^{20}
Copper	solid	2562	0.00000075^{810}

tion takes place relatively rapidly. In substances such as these the droplet proportion can be disregarded, as experience has shown that most solvents in the workplace air occur only as vapour. Generally, measurement methods are employed, whereby the vapours are drawn through adsorption tubes and thus the analytes collected onto the adsorbent during sampling, when determining the air concentrations of volatile substances. The analytes are then analysed after desorption is complete [1].

In order to reduce the undesired release of organic substances at workplaces, volatile substances have been increasingly replaced with less volatile substances, so-called Semi-Volatile Organic Compounds (SVOCs) in recent years [2]. At room temperature these have a lower vapour pressure and thus vaporise significantly more slowly. Unlike volatile substances, droplets can appear in the workplace air over a longer period of time, so that these must not be disregarded during sampling [3]. Raynor [4] describes the appearance of such two-phase systems in nature as well as at the workplace. A significant evaporation of the particle phase was observed in measurements of SVOC aerosols, which led to a distinct underestimation of the particle mass collected on the filter.

It was shown that droplets of particle/vapour mixtures are polydisperse in workplace air and are not in thermodynamic equilibrium. This means that aerosols are subject to constant change in real environments. Sampling methods used for the measurement of hazardous substances in the workplace air are predominantly procedures in which the substance to be investigated is collected onto a carrier during sampling. The ratio of vapour to droplets is not constant due to climatic and technical ambient conditions. The influences are therefore not easily predicted, as they may change in the course of the measurement e.g. the room temperature. Particle size distribution can also be influenced by ambient conditions during material processing such as the rate of rotation of metalworking machinery or the formation of bubbles on open liquid surfaces.

In the following sections examples are used to show, which specific attributes must be taken into account when measuring particle/vapour mixtures and which sampling systems are suitable according to the current state of technology. Furthermore, interrelationships with regard to climatic boundary conditions, such as e.g. temperature, air pressure and relative humidity are discussed. One section provides information on toxic effects of particle/vapour mixtures and also addresses possible health risks that can arise from these types of mixtures.

2 Theoretical principles

An aerosol is a two-phase system of solid and/or liquid particles suspended in a gas. In general, SVOC aerosols are not stable over time. This includes e.g.:

- The concentration,
- the proportion of a substance in the particle or gas phase,
- the particle size distribution in mixtures as well as
- the chemical composition of the aerosol in the case of multi-component systems.

The aerosol concentration can vary spatially and over time. The concentration of an airborne substance is highest at the source of the emission. This value can be e.g. reduced by

- dilution by the ambient air,
- sedimentation of particles as well as
- sorption of gases onto surfaces.

Depending on the process used to generate the aerosol, vapours, for example, can form new droplets by means of condensation or airborne particles already present might act as cloud condensation nuclei and may continue to grow by encasing themselves with condensed vapours. On the other hand, airborne droplets can evaporate, whereby a time-dependent reduction in size of the droplets can be observed. If particles collide with one another, this can lead to a change in the particle size distribution. In this case, the number of particles is generally reduced, resulting in the mean size of particles being increased; however, the entire particle mass remains constant.

The measurement of the particle/vapour composition of SVOC aerosols is significantly dependent on the sampling conditions. The exact proportions of the droplet or vapour phase of a SVOC substance is often difficult to determine. Numerous investigations were carried out in recent years on the subject of the dynamics and sampling of SVOC aerosols [5, 6, 7, 8, 9, 10, 11].

In the following sections the influence of different parameters such as vapour pressure, temperature, particle size distribution, particle number and relative humidity on the particle/vapour composition will be described in detail.

2.1 Calculations regarding the evaporation dynamics of aerosol particles

As aerosols formed from SVOCs behave in a dynamic manner, it makes sense to illustrate the factors influencing droplet evaporation and vapour condensation by means of models. Model calculation gives a better understanding of the behaviour of airborne particle/vapour mixtures at the workplace and serves as risk assessment for the measurement.

In a closed system both fractions of a substance consisting of liquid and vapour constantly strive for equilibrium. In this case the liquid/vapour equilibrium varies with the temperature and the pressure of the system. Figure 1 shows the temperature-dependence of the liquid/vapour equilibrium of n-hexadecane at 1013 hPa as an example. It shows that in the closed system the vapour portion increases with the temperature. Thus the liquid particle phase evaporates below the saturation limit over time, while above the saturation limit the particle and gas phase coexist in a dynamic equilibrium.

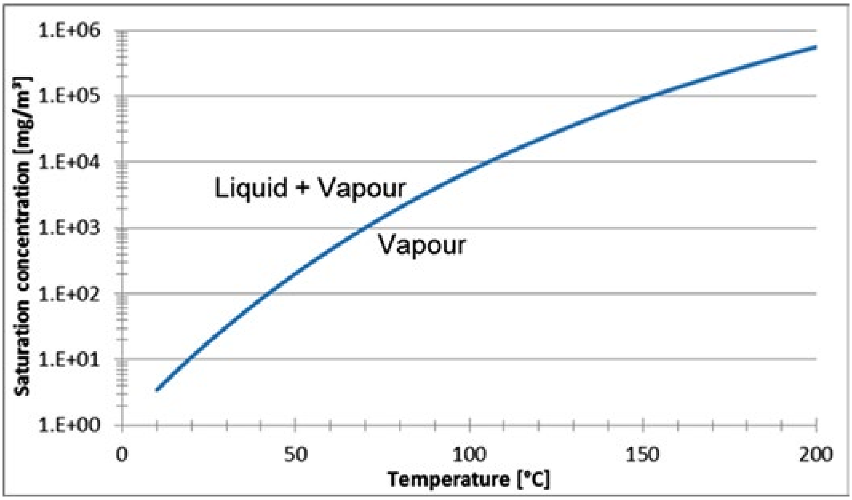


Figure 1 Vapour pressure curve of n-hexadecane as a function of the temperature [12]

If the aerosols are not in a state of equilibrium, then a substance interchange between the particle and gas/vapour phase takes place. The mass flow between both phases can be expressed using the Maxwell's equation [13] based on Equation (1):

$$\phi_p = \frac{\partial m}{\partial t} = 2\pi \cdot d_p \cdot D_j (c_p - c_l) \tag{1}$$

where:

Φp is the temporal evaporation mass flow of a particle in µg/s
m is the particle mass (droplet mass) in µg
t is the time in s
d_p is the particle diameter (droplet diameter) in µm
D_j is the diffusion coefficient of the substance j in the ambient air in cm²/s
c_p is the vapour concentration at the particle surface (droplet surface) in mg/m³
c_l is the vapour concentration in the ambient air in mg/m³
$\partial m/\partial t$ is the temporal variation of the particle mass (droplet mass) in µg/s

In order to determine the lifetime τ_p of a droplet at constant conditions (e.g. droplet diameter $d_{p,0}$ at the time t = 0) by means of Equation (1) by integration over time an exact solution can be calculated using Equation (2).

$$\tau_p = \frac{\rho_p \cdot d^2{}_{p,0}}{8 D_j \cdot (c_p - c_l)} \tag{2}$$

where:

$d_{p,0}$	is the droplet diameter at the time $t = 0$ in µm
τ_p	is the lifetime of a droplet in s
ρ_p	is the density of the particle solution in kg/m^3

The mixing process with the ambient air is modelled as an entry of the saturated aerosol with the vapour concentration $c_{l,0}$, the particle number concentration $C_{n,0}$ and the particle size $d_{p,0}$ into particle-free air with the dilution factor f according to Equation (3) (at the time $t = 1$).

$$f \cdot \left(c_{l,0} + C_{n,0} \cdot \rho_p \cdot \frac{\pi}{6} d_{p,0}^3 \right) = c_{l,1} + C_{n,1} \cdot \rho_p \cdot \frac{\pi}{6} d_{p,1}^3 \tag{3}$$

where:

f	is the dilution factor (dimensionless)
$c_{l,0}$	is the vapour concentration in the ambient air at the time $t = 0$ in mg/m^3
$C_{n,0}$	is the particle number concentration at the time $t = 0$ in 1/cm^3
$c_{l,1}$	is the vapour concentration in the ambient air at the time $t = 1$ in mg/m^3
$C_{n,1}$	is the particle number concentration at the time $t = 1$ in 1/cm^3
$d_{p,1}$	is the droplet diameter at the time $t = 1$ in µm

Equation (3) permits the calculation of the particle limit number concentration $C_{n,0}$ at the time t = 0, at which all particles at the time $t = 1$ have just evaporated ($d_{p,1} = 0$) and the substance concentration in air $c_{l,1}$ is equivalent to the saturation concentration of the gas phase $c_{l,sat}$ according to Equation (4).

The dynamics of the droplet evaporation are compensated due to the conservation of mass by the increase in the vapour concentration according to Equation (5):

$$C_{n,0} = c_{l,sat} \frac{6}{\pi \cdot \rho_p \cdot d_{p,0}^3} \tag{4}$$

$$\frac{\partial c_l}{\partial t} = C_n \cdot \phi_p \tag{5}$$

where:

$c_{l,sat}$	is the vapour concentration in the air in case of steam saturation in mg/m^3
C_n	is the particle number concentration in 1/cm^3
$\partial c_l/\partial t$	is the temporal change of the vapour concentration in the air in mg/(m^3 · s)

Two fundamental *scenarios* can be simulated using model calculations.

In *scenario 1* the vapour concentration in the air c_l is not influenced by the evaporation mass flow Φ_p (one single droplet in an infinite air volume). In *scenario 2* the aerosol concentration remains overall constant, however, Φ_p increases the vapour concentration (one cloud of droplets in a closed, finite air volume). In the first case the evaporation dynamic of a single droplet is calculated without interaction with the surroundings, while in the second case the vapour concentration does not only depend on the ambient temperature, but also on the number, size and evaporation rate of the droplets.

If the droplets do not consist of a single substance, but of a substance mixture, then the vapour concentration $c_{p,j}$ of an individual substance j changes over the droplet surface with the molar mixture ratio. The saturation vapour pressure of a substance j is determined using Raoult's law for ideal mixtures. According to this law the vapour concentration of the substance j is reduced on the droplet surface of a mixture ($c_{p,j}$) consisting of i components by a factor R (see Equation (6)).

$$R = \frac{n_j}{\sum_{i=1}^{j} n_i} = \frac{c_{p,j}}{c_{p,j,sat}} \tag{6}$$

where:

R is the factor of the Raoult's law (dimensionless)
$c_{p,j}$ is the vapour concentration of the substance j at the surface of a droplet from i components in mg/m^3
$c_{p,j,sat}$ is the vapour concentration at the surface of a droplet consisting of a single compound j in mg/m^3
$n_j/\Sigma n_i$ is the molar mixing proportions of the substance j in a mixture with i components (dimensionless)

If a volatile substance evaporates from a particle surface, then the thermal energy necessary to achieve this is extracted from the droplet. Therefore, the enthalpy of vaporisation of a droplet has a significant influence on the rate of evaporation, as the droplet temperature is reduced through this process. Due to the decrease in temperature in the droplet, heat is transferred from the surroundings to the droplet surface. This heat transfer can be described as in Equation (1) (see Equation (7)).

$$\frac{\partial q}{\partial t} = 2\pi \cdot d_p \cdot \kappa_l \cdot (T_p - T_l) \tag{7}$$

where:

$\partial q/\partial t$ is the temporal change of the heat content (q) of the droplet in W
κ_l is the thermal conductivity of the air in W/(m · K)
T_p is the temperature of a droplet at the surface in K
T_l is the temperature of ambient air in K

The heat transfer and vapour transport are linked as follows (see Equation (8)).

$$\frac{\partial q}{\partial t} + H\frac{\partial m}{\partial t} = 0 \tag{8}$$

where:

H	is the specific heat of evaporation of the particle liquid in kJ/kg
$\partial m/\partial t$	is the temporal change of the particle mass (droplet mass) in µg/s

In a stationary case a solution can be calculated as follows using Equation (9) for this equation:

$$\kappa_l(T_p - T_l) = H \cdot D_j(c_p - c_l) \tag{9}$$

If the droplets are significantly smaller than 1 µm, then a correction for the vapour transport and heat transfer is necessary. The Fuchs correction factor (f_F) is used in this case as stipulated in Equation (10) according to Davies [14], whereby Kn is calculated using Equation (11).

$$f_F = \frac{1 + Kn}{1 + 1{,}71\ Kn + 1{,}333\,Kn^2} \tag{10}$$

$$Kn = \frac{\lambda}{d_p} \tag{11}$$

where:

f_F	is the Fuchs correction factor (dimensionless)
Kn	is the Knudsen number (dimensionless)
λ	is the mean free path of the air molecules in µm

A second correction, using the Kelvin equation, is necessary to take the curvature of the droplet surface into account (see Equation (12)). The vapour pressure at the droplet surface is therefore increased by the factor f_K.

$$f_K = \exp\left(\frac{4\sigma_p \cdot M_p}{R \cdot T \cdot \rho_p \cdot d_p}\right) \tag{12}$$

where:

f_K	is the Kelvin correction factor (dimensionless)
σ_p	is the surface tension of the particle liquid in kg/s²
M_p	is the molecular weight of the particle liquid in g/mol
R	is the universal gas constant ($R = 8{,}314$ J/(mol · K))
T	is the absolute temperature in K

2.2 Parameters that influence the particle/vapour ratio

The parameters, that influence the particle/vapour ratio, are described in the example below on the basis of the work of Dragan and Karg [6, 11].

2.2.1 Influence of the volatility of a substance

Depending on the substance-specific volatility (vapour pressure) of a substance, lifetimes from 0.01 to 100 seconds are possible for single particles with a diameter of 1 µm (e.g. for *n*-alkanes, such as *n*-dodecane with a boiling point of 216 °C to eicosane with a boiling point of 343 °C). The simulation illustrated in Figure 2 shows that by increasing the chain length by two carbon atoms a particle prolongs its lifetime by approximately a factor of 10. This means that aerosols made up of poorly volatile substances can linger in a condensed state for a considerably longer period of time.

2.2.2 Influence of the temperature

The vapour pressure of a substance or substance mixture is significantly influenced by the ambient temperature. A rise in temperature leads to a higher saturation concentration. As an example the vapour pressure of *n*-hexadecane doubles for a temperature increase from 20 to 26.5 °C. This results in different evaporation times for the same aerosol particles, as illustrated in Figure 3.

2.2.3 Variation of the particle mass at different temperatures

The particle/vapour ratio of an aerosol can vary markedly depending on the temperature. Thus it was possible to show by means of experiments that the lower the temperature, the smaller the vapour portion and vice versa. In a series of experiments a newly generated aerosol of *n*-hexadecane with a total concentration of approx. 19 mg/m^3 was subjected to different temperatures in a flight tube. Figure 4

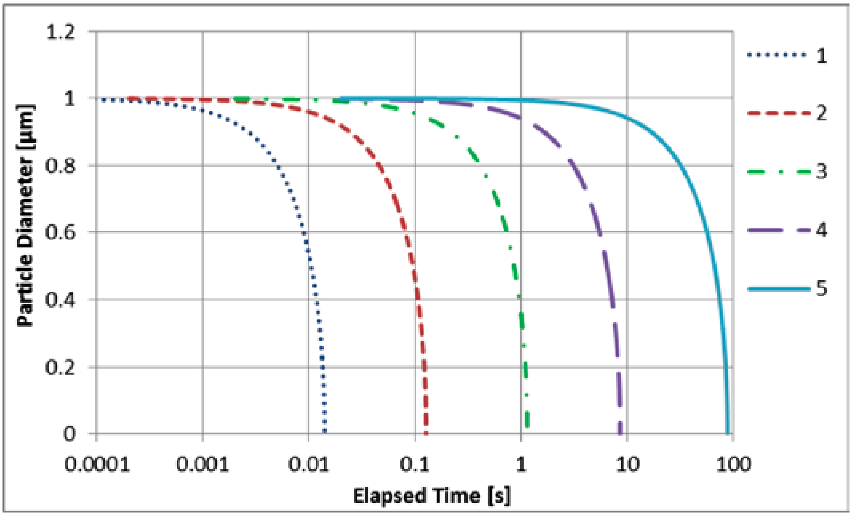


Figure 2 Model calculation for the evaporation of different particles of *n*-alkanes (initial diameter of 1 µm at 25 °C) in an unsaturated gaseous phase (1: dodecane, 2: tetradecane, 3: hexadecane, 4: octadecane, 5: eicosane)

shows the result of the changes in the particle mass concentration in the flight tube at the beginning (blue line) and after three seconds dwell time (red line), depending on the ambient temperature (green line). After a flight time of three seconds at a temperature of 11 °C the vapour proportion is approx. 10%. By increasing the temperature from 11 °C to approx. 35 °C the vapour proportion rises to 80%, whereas the particle portion decreases from 90% to 20%. With regard to the particle mass concentration after three seconds evaporation, this means that the vapour concentration at a temperature of 15 °C is approx. 2 mg/m³ and rises significantly with a further increase in the temperature; at 25 °C the vapour concentration is approx. 5 mg/m³ and at 30 °C approx. 7 mg/m³.

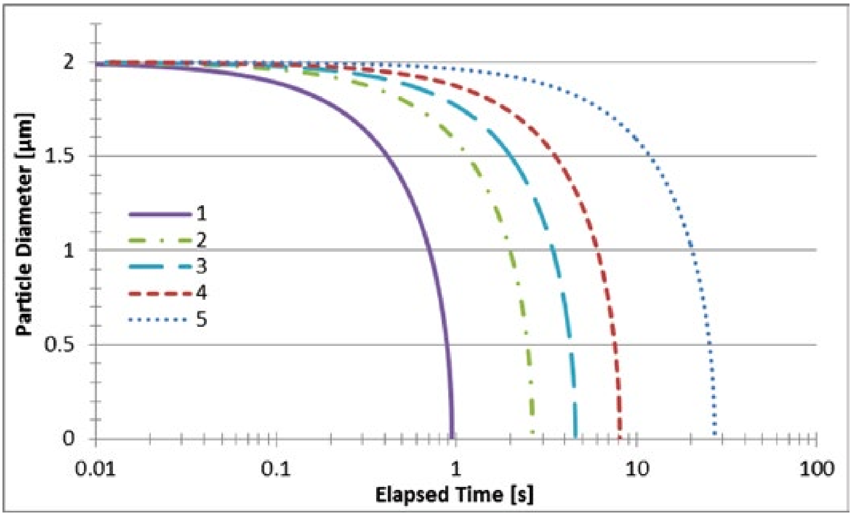


Figure 3 Model calculation for the evaporation process of *n*-hexadecane particles (initial diameter of 2 µm) at temperatures from 10 °C up to 40 °C
(evaporation at: 1: 40 °C; 2: 30 °C; 3: 25 °C; 4: 20 °C; 5: 10 °C)

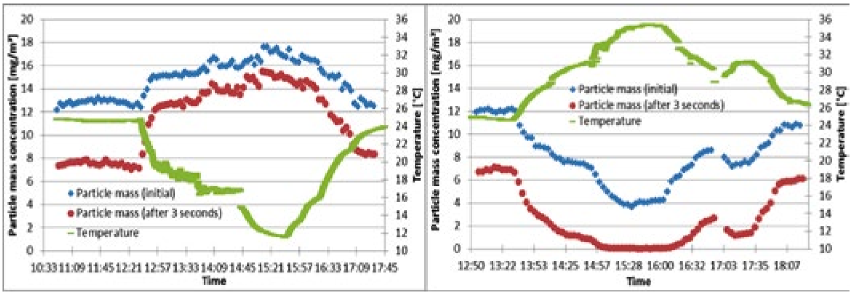


Figure 4 Behaviour of the particulate mass concentration of a *n*-hexadecane aerosol as a function of the temperature

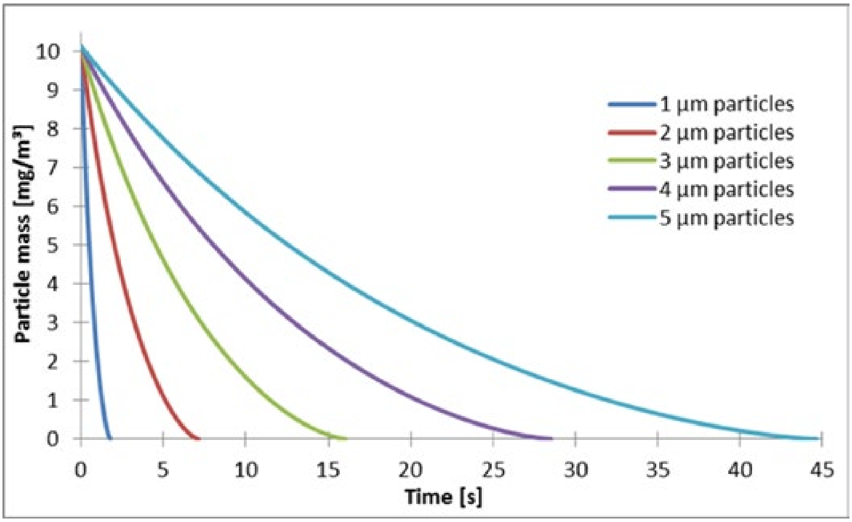


Figure 5 Model calculation for the dynamic evaporation process of a *n*-hexadecane aerosol (identical initial concentration) with various particle diameters at 25 °C

2.2.4 Influence of the particle diameter

In the case of a predefined total particle volume, small particles have a greater total surface than larger ones. As the evaporation flow per area unit remains constant, while the surface/volume quotient increases with decreasing particle size, small particles evaporate significantly faster, even at an initially identical particle mass concentration. Figure 5 shows how particle evaporation is dependent on the particle size.

This effect could also be experimentally determined with regard to the particle size distribution. Figure 6 shows that after a dwell time of three seconds in a flight tube [11] the 1 µm particles shrink considerably more rapidly that those with a diameter of 2 µm (shift of the particle size distribution to smaller diameters).

2.2.5 Influence of the particle number concentration

The evaporation of aerosol particles can lead to a considerable mass transfer of particles into the vapour phase, whereby the vapour phase becomes increasingly saturated. As vapour concentration in the air increases the evaporation flow is reduced, whereby the lifetime of the particles is prolonged. However, if the saturation concentration in the vapour phase has been reached, then the state of equilibrium has been achieved and the particle size remains constant.

The lifetime of a particle is considerably prolonged, if a significant proportion of the mass is added in particle form. Figure 7 shows the influence of an increased particle number on the evaporation dynamics in a limited air volume. In this example the lifetime of a single hexadecane droplet with a diameter of 1 µm is approximately one second. Up to a concentration of 45,000 particles per cm^3 the lifetime

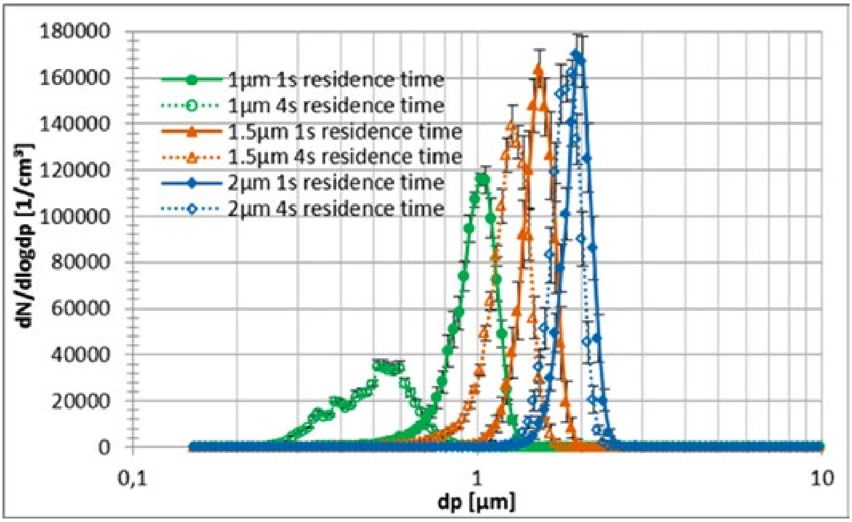


Figure 6 Particle size distribution (initial and after a dwell time of 3 seconds) for the evaporation of *n*-hexadecane particles with various particle diameters at 25 °C

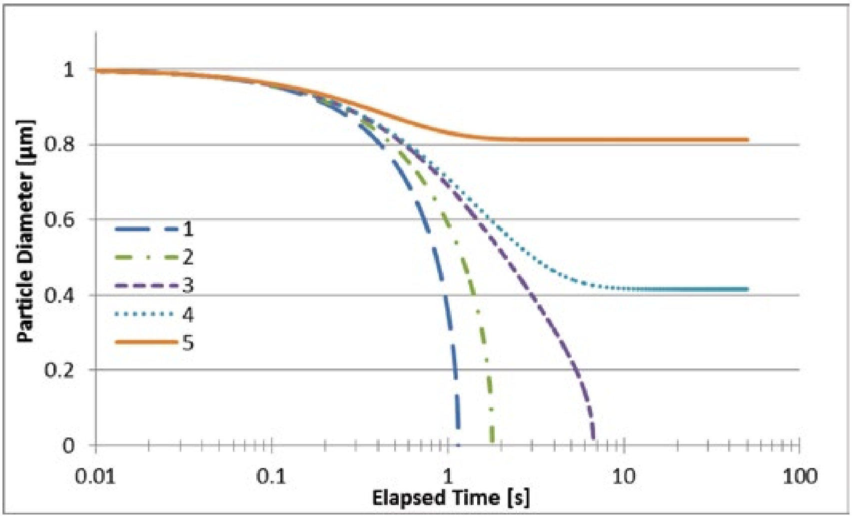


Figure 7 Model calculation for the evaporation process of *n*-hexadecane particles as a function of the particle number concentration [particles/cm³] (1: 1; 2: 25,000; 3: 45,000; 4: 50,000; 5: 100,000)

increases to approx. 7 seconds. At an even higher concentration (>50,000 particles per cm³) the saturated vapour pressure concentration is reached, which means that the particles can no longer evaporate and remain in the air as shrunken droplets.

2.3 Conclusions

Model calculations and measurements with monodisperse droplet aerosols show that substances with boiling points in the range of approx. 180 to 350 °C take different times to evaporate depending on the droplet size, and the dwell time of the droplet in the air can be only a few seconds up to several minutes. The phase composition of an aerosol changes with the dwell time in the sampling area, i.e. the mass ratio of vapour to particle does not remain constant. This means that during sampling only the simultaneous collection of the vapour and particle phase ensures that the workplace concentration of such a substance is correctly sampled. Therefore it is not possible to determine the workplace concentration of a substance with the properties described above by separate collection of the particle and vapour phases at the workplace.

3 Effects of vapour and particles when inhaled

In the case of substances that can occur simultaneously as vapour and particles, the particles generally showed a higher local toxic potential than the vapour. Reasons for this could be a greater deposition and retention as the result of impaction in the respiratory tract as well as a high local concentration around the deposited particles.

3.1 Substances with systemic effects

Substances with systemic effects are assigned to Peak Limitation Category II in the List of MAK and BAT Values [15].

If the systemic effects are considered critical in the derivation of a MAK value, the assumption that vapours and particles have the same potency can be justified. In this case, however, possible differences in the deposition and the retention in the respiratory tract of vapour and particle are neglected. The MAK value then applies to the sum of vapour and particle (inhalable fraction).

3.2 Substances with local effects

Substances with local effects are assigned to Peak Limitation Category I in the List of MAK and BAT Values [15].

If local effects are considered critical when a MAK value is derived, the situation is more difficult. In toxicological inhalation studies to test aerosols (dusts or mists) that are carried out according to the OECD test guidelines a respirable fraction is used, in order to ensure that the substance also reaches the lungs as a potential target organ. If the lung actually proves to be the target organ, then the MAK value is derived for the respirable fraction. However, if the upper respiratory tract rather than the lung is the target organ, the MAK value is established for the inhalable fraction.

Animal studies have shown that for some substances particles cause stronger effects than the vapour. Therefore, it can be assumed that after impaction onto the respiratory tract tissues particles cannot be subsequently exhaled in contrast to vapour. While vapour is distributed relatively evenly on the epithelial tissue, particles can be clustered in high local concentrations. In such cases a MAK value can only be assigned to the vapour phase or otherwise separate limit values are derived for the particle and vapour phase (see examples below). However, the markedly dynamic behaviour of particle/vapour mixtures makes it difficult to consider each phase separately.

3.3 Examples

N-Ethyl-2-pyrrolidone [16, 17]

Due to the vapour pressure of 18 Pa for N-ethyl-2-pyrrolidone (NEP) at 20 °C the vapour saturation concentration is approx. 840 mg/m^3. A MAK value was determined only for the vapour phase of NEP at 5 mL/m^3 (ppm) or 23 mg/m^3 (based on the local effect), as data from animal studies showed that droplets elicit a stronger local effect on the mucous membranes of the nose than vapour.

The MAK value was assigned on the basis of a 90-day study in rats, with concentrations of NEP of 30, 60 and 200 mg/m^3. NEP was exclusively present as a vapour; particles were metrologically undetectable. Conversely, a small particle proportion was detectable in a previous 28-day study at concentrations of 80, 200 and 400 mg/m^3. The MAK value was derived for the vapour based on the no-effect concentration of 60 mg/m^3. In the 28-day study with only a marginally higher concentration of 80 mg/m^3 effects on the mucous membranes of the nose of the animals were still detectable, despite a shorter exposure period. Clinically relevant irritating effects were visible in the animals at a concentration of 200 mg/m^3 in the 28-day study, which were not observed in the 90-day study at 200 mg/m^3. It is assumed that the reason for the discrepancies in these results is that the particle phase caused the local effects.

A MAK value for the particle fraction could not be established. Therefore, measurement of the sum of the vapour and particle fraction in the case of NEP is actually not conclusive from a toxicological point of view, as particles may be contained in the total concentration of 23 mg/m^3 and therefore it is not certain that compliance with this concentration will preclude local effects. As the adverse effects appeared at 80 mg/m^3, but with decreasing concentration in the air the ratio between vapour and particles shifts further towards the vapour fraction, the occurrence of aerosols in equilibrium at concentrations at the level of the MAK value is less probable and consequently also the risk of adverse effects to health is no longer posed. For this reason a measurement of the sum of vapour and particles appears sufficient.

Di-n-butyl phthalate [18]

The MAK value for di-n-butyl phthalate (DnBP) was established on the basis of the vapour saturation concentration of 1 mg/m^3 (calculated from the vapour pressure of 9.7 x 10^{-5} hPa at 25 °C) at 0.05 mL/m^3 (ppm) or 0.58 mg/m^3. It is assumed that the key adverse effect is caused by particles coming into contact with the larynx and nose. Setting the MAK value at 0.58 mg/m^3 should ensure that no particles or droplets occur at the workplace. However, the MAK value lies only marginally below the lowest used aerosol concentration of 1.18 mg/m^3, which is the LOAEC (Lowest Observable Adverse Effect Concentration). Compliance with the limit value, the sum of vapour and particles for DnBP, cannot rule out negative health effects with certainty, as the particle proportion, which is actually critical remains unknown by determining the sum.

Note:
Investigations into the particle/vapour ratio of DnBP aerosols in a flight tube showed that at a concentration of approx. 1.2 mg/m^3 (twice the MAK value) at room temperature only a small proportion of vapour was present, whereas a rise in temperature (35 °C) resulted in the vapour proportion increasing to approx. 30% (see Method No 3 “phthalates” 2017*)*

Hydrotreated light petroleum distillates [19]

Separate MAK values were established for the vapour and particle fraction of *hydrotreated light petroleum distillates* (boiling point range 150–290 °C, C_9–C_{16}). The MAK value for the vapour phase was set at 50 mL/m^3 (ppm) or 350 mg/m^3 in order to avoid effects on the central nervous system (CNS). In animal studies with the military fuel JP-8 (Jet Propellant 8) (C_9–C_{16}) no local effects in the lungs of rats were detected at vapour concentrations of up to 1000 mg/m^3, while the first indications of damage to the lungs of mice and rats could be observed from exposure to JP-8 (boiling point range 150–290 °C) aerosol at distinctly lower concentrations. However, a MAK value could not be derived from this data. As, unlike in the case of the vapour, the target organ for the particle phase was shown to be the lungs, the MAK value for the particle fraction for *hydrotreated light petroleum distillates* was determined as 5 mg/m^3 R (respirable fraction) by analogy with pharmaceutical white oil (target organ here are the lungs) [20]. The MAK value for white oil was established with a study using a mineral oil aerosol (C_{25}–C_{30}) and applied to the particle fraction for *hydrotreated light petroleum distillates*, as the lungs are a plausible target organ for hydrocarbons in the particle phase. The reasons for the different toxicity of the vapour and particle phases of long-chained hydrocarbons in the lungs are not known. The number of carbon atoms of the individual components of mineral oils is greater than 16. Furthermore, they have a low vapour pressure, so that the particle fraction of mineral oil can be measured without losses, unlike the aerosols of *hydrotreated light petroleum distillates*. It was observed that in the particle phase of JP8 (approx. 1600 mg/m^3) only aliphatic compounds with number of C-atoms > 12 are detectable [21]. Therefore, it must be assumed that the toxicity of the aerosols of JP8 fuel is due to hydrocarbons with chain lengths of C_{12}–C_{16}. These accumulate in the particle phase, while at the same time their concentration decreases in the vapour phase [22]. Due to the relatively high vapour pressure of the C_{12}–C_{16} hydrocarbons the particle fraction can currently not be reliably measured. However, this problem is only relevant to workplaces where exposure to hydrocarbons in aerosol form occurs. At such workplaces the sum of the vapour and particle fractions could be measured on condition that the total concentration may not exceed 50 mg/m^3, as the particle proportion was approximately 10% (5–16%) [21, 23] in the aerosols of jet fuels S8 (boiling point range 127–288 °C) and JP-8. In this case the particles were respirable.

Note:
The examples described above imply that the aim of the measurement of substances, which can be simultaneously present in the workplace air as vapour and particles, should include accurate collection of the vapour and particle portions. However, this is metrologically not possible due to the specific physical properties of such substances.

- Due to the dynamic behaviour only the sum of the vapour and particle portions can be measured reliably, if the particle portion is collected as an inhalable fraction in its entirety.
- In the case of substances that can simultaneously occur as vapours and particles, limit values that have been determined exclusively for one phase (vapour or particles) are metrologically not presentable.
- In the case of substances that can simultaneously occur as vapours and particles, limit values that have been determined for a certain particle fraction (thoracic or respirable) that only represent one part of the entire particle fraction are metrologically not presentable.

4 Regulations

Compliance with normative guidelines as well as the stipulations found in the technical regulations is essential when determining particle/vapour mixtures. This applies to all substances that appear in the List of MAK and BAT Values [15] as well as the TRGS 900 [24] that have been marked as substances that can occur simultaneously in vapour and particle form. All substances with a vapour pressure in the range of 100 to 0.001 Pa or with a boiling point in the range of approx. 180 to 350 °C were thus labelled. The particle phase must always be collected as the inhalable dust fraction according to EN 481 [25].

For substances that can simultaneously occur in vapour and particle phases the technical regulations require that the sum of both of these phases is determined and assessed on the basis of the corresponding OEL or another applicable assessment standard.

Note:
In order to derive suitable protective measures it can be useful to determine both phases separately.

4.1 Normative requirements

If workplace measurements are carried out to determine the exposure to substances that occur as particle/vapour mixtures, then the methods used must meet the specifications set out in EN 13936 [26]. In addition, the requirements for the sampling apparatus and collection media for the capture of the vapour and particle phase that have been described in the relevant publications of this collection of methods [27] also apply.

Furthermore, the recovery of the measurement procedure, which is determined from the combined results of the collection substrate for airborne particles and the collection substrate for vapour, must be at least 90%.

The requirement according to EN 482 Table 1 [28] must be fulfilled for the expanded uncertainty of the entire measurement procedure, including the measurement of airborne particles and vapour. If the workplace measurements are carried out in areas with a risk of explosions, then the requirements stipulated in EN 50014 [29] must be met.

4.2 Technical regulations for hazardous substances

Sampling of particle/vapour mixtures can be carried out as stationary or personal sampling. However, personal sampling is preferable according to TRGS 402 [30].

In order to ensure the most comprehensive and representative evaluation of an exposure situation for particle/vapour mixtures, the requirements and procedures described in TRGS 402 [30] as well as EN 689 [31].must be met. This ensures an objective assessment of the activities by comparing the determined concentrations of particle/vapour mixtures with the respective evaluation criteria. Workplace measurements of particle/vapour mixtures can serve different objectives in terms of the measurement strategy, such as:

- Exposure measurements (shift mean, short-term or control measurements)
- Measurements in the most unfavourable cases (worst case measurements)
- Measurements at the source of emission
- Other measurements

When planning a measurement it is particularly important to consider changes resulting from activities (see Section 6) with regard to the temporal and spatial distribution of substances between the vapour and particle phase, which can additionally complicate the exposure evaluation. Therefore, comprehensive documentation of the sampling conditions and activities carried out is absolutely necessary. In particular this should take into consideration whether

- Employees are present at different locations during sampling. Thus different exposure patterns may clearly emerge with regard to the particle/vapour mixtures than would be the case if exposure were to vapours or particles alone.
- The concentration and distribution between the phases is significantly dependent on the distance to the source of emission.
- The local concentration of the vapour and particle phases is influenced to a varying degree by air currents.

5 Sampling of particle/vapour mixtures: Examples of sampling systems

Active collection methods are used for sampling substances that can occur in the workplace air simultaneously as vapour and droplets or as vapour and solids. For this purpose sampling systems are used that ensure the simultaneous collection of the inhalable fraction according to EN 481 [25] and of the vapours. Generally, in these sampling systems the particles are initially deposited onto a filter, then adsorption of the vapours takes place on a suitable adsorbent.

The requirements on sampling systems for the collection of particle/vapour mixtures are defined in EN 13936 [26]. Notwithstanding the above, the measurement procedure must independently fulfil the requirements according to EN 482 as well as – if applicable – comply with EN 1076 [32], EN 13205-1 [33] and EN 13890 [34].

Pumps used for active sampling must meet the requirements set out in EN ISO 13137 [35]. In this case it is important to consider that by configuring the collection phase in series an increased counter pressure can occur. Sampling systems that have been designed for personal sampling are presented and described below.

5.1 Sampling systems with one collection phase

Sampling systems with only one collection phase are generally based on chemical reactions. In this case vapours and particles are deposited together onto a collection phase. Suitable are e.g. washing bottles with an absorption solution or impregnated filters.

5.1.1 Absorber B 70

The Absorber B 70 [36, 37] is a washing bottle that collects gases and vapours as well as the inhalable dust fraction of droplet aerosols and dusts at a flow rate of 70 L/h (see Figure 8). The absorption liquid must be suitable for the substances and substance mixtures to be collected.

5.1.2 GSP sampling head with impregnated filter

The GSP sampling head was developed for the collection of inhalable aerosols [36]. The schematic set-up of the GSP head is illustrated in Figure 9. An impregnated filter can be inserted into the filter cassette for sampling particle/vapour mixtures. The impregnation must be suitable for the substances and substance mixtures to be collected (see Table 2).

5.2 Sampling systems with several collection phases

Sampling systems with several collection phases are generally based on filtration and adsorption. In this case, vapours and particles are deposited onto two or more collection phases. Suitable are e.g. filters and adsorption tubes connected in series. Particles are thus deposited on the filter, whereas vapours are adsorbed onto the adsorbent connected downstream.

The collected particles can – depending on the vapour pressure – partially or even completely evaporate in the further process of sampling. The vapours are then also adsorbed onto the adsorbent connected downstream. The particle and vapour proportions analytically determined after sampling is complete do not generally reflect the distributions present at the workplace. For this reason the evaluation at the workplace can only be based on the sum of the concentration of vapour and particles.

Figure 8 Absorber B 70

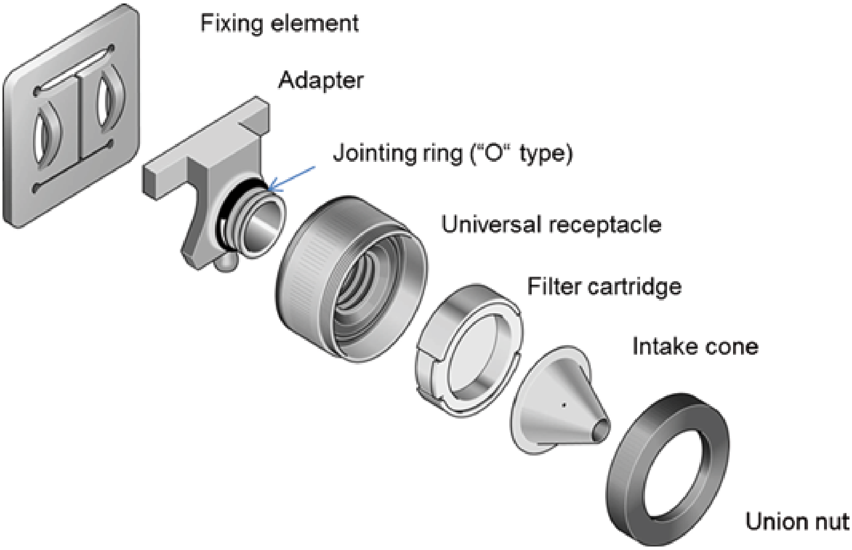


Figure 9 Schematic structure of the GSP sampling head

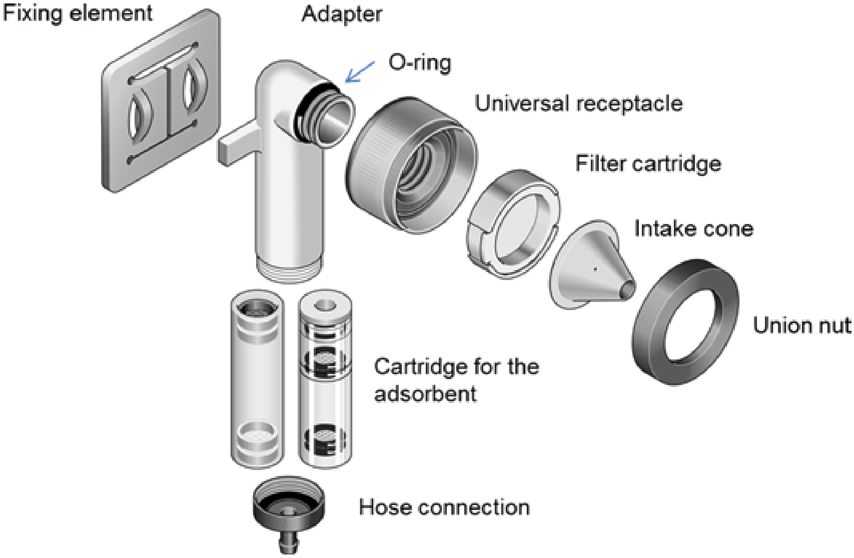


Figure 10 Schematic structure of the GGP systems with a glass or plastic cardridge for the adsorbent [38]

5.2.1 GGP/GGP-U sampling system (inhalable dust/vapour sampling)

The GGP sampling system is suitable for personal sampling to measure airborne substances that occur in particulate as well as in vapour form (e.g. mineral oils, lacquer aerosols and cooling lubricants) at the workplace. A filter cassette that is equipped with a suitable filter material (37-mm filter) to function as a dust collection element is positioned behind the intake cone. Thereafter there is a cartridge that is filled with suitable adsorption material. The GGP system is designed for a flow rate of 3.5 L/min as standard. Other flow rates are possible when the flow resistance of the entire system, including suitable intake cones, is taken into consideration (see Table 2). Substances occurring in the particulate and vapour state are collected simultaneously according to the definition of total dust and deposited onto the filter in the first instance during sampling. Particles already deposited onto the filter can evaporate completely or partially from the filter over time, so that they are adsorbed onto the adsorbent in the cartridge connected downstream. It must be ensured that the adsorbent is suitable for the respective analyte. The GGP system is schematically presented in Figure 10.

A further possibility is to use the GSP sampling head and connect it by means of a suitable tube material to commercially available – pre-filled – glass or steel tubes. In this case, the opening diameter of the intake cone must be taken into consideration when selecting the flow rate.

Table 2 Types of sampling systems for the collection of particle/vapour mixtures

Sampling head	Volume flow [L/min]	Volume flow [L/h]	DFG Method
GSP [36]	0.5; 1; 2; 3.5; 10	30; 60; 120; 210; 600	Method 2 “Lacquer aerosols“ 2003
GSP with impregnated filter	1.0	60	Methode 1 “Alkanolamines” 2000
AMS	3.5	210	Method 1 “Lacquer aerosols“ 2000
GGP [37; 38]	3.5	210	Method ”Cooling lubricants, immiscible with water and vapours“ 2015
GGP [38]	1.0	60	Method 3 “Phthalates” 2017
GGP-U [37]	0.5; 1	30; 60	Method “Butylated hydroxytoluen” 2012
Mini GGP [9; 37]	0.066; 0.333; 0.5	4; 20; 30	Benzyl alcohol Meth. No. 1 (*in print*) 2-Phenoxyethanol Meth. No. 1 (*in print*) Method “Glykole” 2018 Method “Glykolester, Glykolether” 2018
GSP sampling head with adsorption tubes	2.0	120	Method 3 “Chlorinated biphenyls (PCB)“ 2016
Absorber B 70 [36; 37]			
SILPP: Filter cartridge and passive sampler type „ATD“	2.5[1]	150	Method 1 “Lacquer aerosols“ 2000

[1] dependent on the opening diameter of the used cartridge

The GGP-U sampling system is designed for lower air flow rates. Depending on the opening diameter of the intake cone, air samples can be drawn through the GGP-U system at a flow rate of 0.5 or 1.0 L/min. Instead of the cartridge, a cylinder can be connected downstream and up to three commercially available types of adsorption tubes connected in parallel can be used (see Figure 11). It must be ensured that the adsorbent is suitable for the respective analyte.

5.2.2 GGP-Mini sampling head

The GGP-Mini sampling system was developed on the basis of experience with the GSP sampling head (see Figure 12). Three different intake cones with flow rates of 0.066; 0.333 and 0.5 L/min are available for use. The particles are deposited onto 13 mm filters, while the vapour phase is collected onto commercially available adsorption tubes.

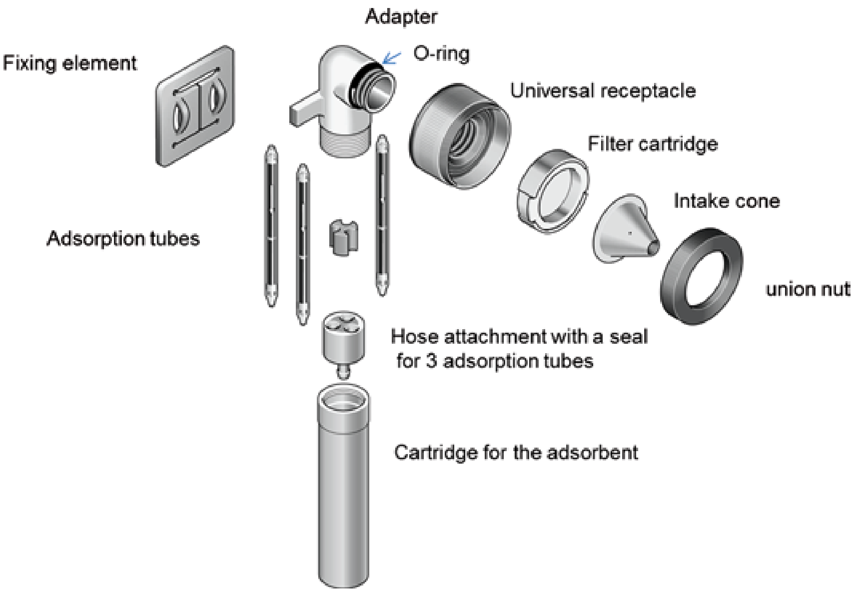


Figure 11 Schematic structure of the GGP systems – GGP-U for I-dust (inhalable dust) and sampling of gaseous substances [37]

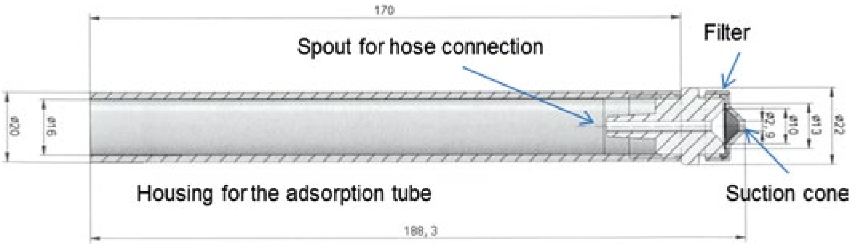
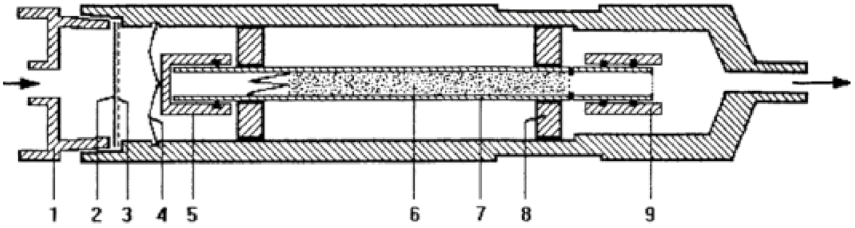


Figure 12 Schematic illustration of the GGP-Mini sampling system [37]

5.2.3 Sampling systems for lacquer aerosols

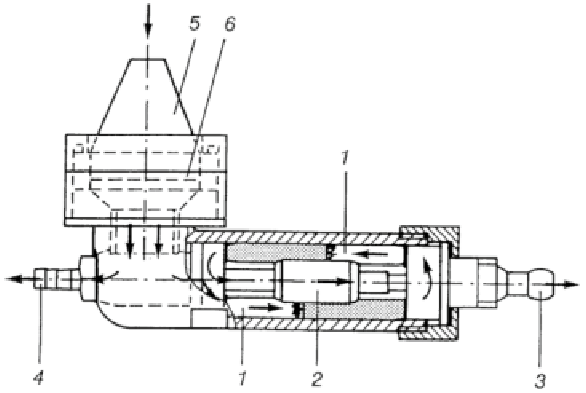
Lacquer aerosols are multiple substance systems, consisting of lacquer droplets, solid lacquer particles as well as vaporous solvents. Their generation in spray-paint work is process-dependent and their occurrence in the workplace air in very variable concentrations depending on the type of lacquer system used and the processing conditions.

Sampling systems for the measurement of lacquer aerosols must be capable of collecting solid and liquid particles as well as solvent vapours in one working step. In order to implement this requirement the ’SILPP’ (Simultane Lösemittel- und Partikel-Probenahme, simultaneous sampling of solvents and particles) sampling system was developed (see Figure 13).



1	Sampling head	6	Adsorbent
2	Glass fibre filter	7	Thermal desorption tube
3	Filter carrier	8	Star-shaped brackets
4	Tension spring	9	Diffusion cap
5	Sealing cap		

Figure 13 Sampling system for the simultaneous solvent/particle sampling (SILPP) (http://www.patent-de.com/pdf/DE29707940U1.pdf)



1	Collection tube (type NIOSH 6 x 70 mm, activated carbon: 100/50 mg)	2	Adapter housing for collection tubes in series
3	Pump connection for absorbers, volume flow: 0.5 L/min	4	Pump connection, volume flow: 3 L/min
5	Intake cones for 3.5 L/min	6	Universal receptacle for filter cartridge

Figure 14 Schematic illustration of the AMS measuring system for lacquer aerosols

For sampling a conditioned filter and a baked out 'ATD' type adsorption tube are inserted into the sampling head and locked in place. The adsorption tube is fitted with a passive collection cap. During sampling the air to be investigated is drawn through the sampling system, whereby the particles are deposited onto the filter. The particulate components of lacquer aerosols are thus deposited as an inhalable fraction as described by EN 481 [25]. After sampling is complete, clean air is drawn through the sampling system for approx. 5 minutes in order to ensure that the solvent, which adheres to the deposited particles, evaporates completely. It then reaches the adsorption tube by diffusion, to be collected there (passive collection).

A further sampling system for the simultaneous collection of the components of lacquer aerosols is the AMS measurement systems for lacquer aerosols (see Figure 14).

Table 3 Examples of activities, during which particle/vapour mixtures may arise at the workplace

Activities	Examples	Substances	Industries/trades/ occupational groups
Cleaning work	Cleaning surfaces by wiping and spraying	Liquid cleaning products, tensides	Health care system, cleaning businesses
	Blasting of surfaces	Blasting abrasives and surface components	Building trade, metal working
Spraying	Pest control	Insecticides	Pest controllers
	Plant protection	Plant protection products	Agriculture, plant nurseries
	Animal husbandry	Disinfectants e.g. cyanamide, dicyandiamide	Agriculture, animal breeding
Foam applications	Pest control	Rodenticides	Pest controllers
	Disinfection	Disinfectants	Food industry
Surface coating	Electroplating	Inorganic acids, metals and their compounds	Electroplating industry
	Spray painting	Solid pigments, solvents of varying volatility	Painters, paint shops, joinery, furniture industry, automotive production and maintenance
	Rolling, pouring	Bitumen	Road building, roofing trade, building industry
	Painting with bushes or rollers	Paints, lacquers	Painting trade
	Impregnation of garments		Textile industry, leather goods industry

Table 3 (continued)

Activities	Examples	Substances	Industries/trades/ occupational groups
Wood preservation	Impregnation, immersion, adjustment	PAHs, metals (e.g. wood preservatives containing Cu, Cr)	Impregnation companies for railway sleepers, hot/cold adjustment
	Applying antifouling agents by brushing, rolling, or spraying	Cu and Sn compounds	Shipyard, shipbuilders
	Timber treatment after infestation (in situ)	e.g. Permethrin, quaternary ammonium compounds	Pest controllers
Disinfection work	Disinfection of surfaces by wiping, spraying	Aldehydes (e.g. glutaraldehyde)	Health care system
	Disinfection of food containers		Food industry
Mechanical processing	Drilling, turning, grinding, lapping, honing	Cooling lubricants, oil mists, metal dusts	Metal working and processing industry
Extraction of natural resources	Drilling	Oil mists	Oil industry (e.g. oil drilling rigs)
Assembling materials	Gluing	Isocyanates	Automotive industry, joinery, furniture industry
Production	Manufacture of grinding disks	Naphthalene	Ceramic industries
Nebulising	Plant protection	Plant protection products	Agriculture, market gardens
	Concerts, theatrical performances	Glycols/water	Entertainment industry, theatres
	Pest control	Insecticides	Pest controllers
	Disinfection	Disinfectants	Disinfectors, Pest controllers

6 Workplaces, at which particle/vapour mixtures may occur: Examples and applications

Particle/vapour mixtures can occur during many activities. It is necessary to differentiate between whether a substance is simultaneously present as vapour and in particulate form or whether different substances occur in both these phases. Examples of such activities and the corresponding workplaces are listed in Table 3. In this case the release of particle/vapour mixtures can be specifically influenced (e.g. due to spraying) or process-related through gas development and an associated emission of substances (e.g. when charging lead-acid batteries). Equally, the release of aerosols is possible due to energy input as a result of conducting the activity such as e.g. when applying paint with a roller.

Furthermore, this can also apply to substances, even though no indication of their occurrence as particle/vapour mixture is given. Information to that effect, whether particle/vapour mixtures may also arise in certain industries/trades or activities, is provided in Table 3.

7 Estimation of the measurement uncertainty

7.1 Principal findings

The following information on the estimation of the uncertainty of the measurement method that is used in the determination of particle/vapour mixtures is based on EN 13936 [26]. This standard refers to the standards EN 1076 [32] for vapours and EN 13890 [34] for particles with regard to the respective assignment of individual uncertainty contributions. On these grounds, the estimation of the uncertainty for particle/vapour mixtures is composed of contributions from the uncertainty considerations for vapour und particles.

The following three cases must be differentiated for the estimation of the uncertainty:

Case A

During sampling a certain flow rate is drawn through e.g. an impregnated collection medium, whereby particles and vapours are collected together and then analysed.

Case B

During sampling a certain flow rate is drawn through two collection media arranged in series, whereby both fractions (vapour and particles) are collected separately and are then analysed together.

Cases A and B can be treated in the same manner. In this case, the uncertainty in terms of sampling is calculated according to EN 13890 [34] for the inhalable fraction. All further uncertainty contributions are determined as stipulated in EN 1076 [32].

Case C

During sampling a certain flow rate is drawn through two collection media arranged in series, whereby both fractions (vapour and particles) are collected separately and also analysed separately. Then the sum is formed from the determined measurement values for the different fractions.

In this case, the uncertainty in terms of sampling is also calculated according to EN 13890 [34] for the inhalable fraction. All further uncertainty contributions relate to the analytical steps and can be calculated according to EN 1076 [32] for organic substances, the substances deposited onto the filter as well as for the vapour fraction. However, they must be considered separately.

The expanded uncertainty U is calculated using Equation (13) as follows:

$$U = 2 \cdot u_c = 2 \cdot \sqrt{\sum_{i=1}^{n} u_i^2} \quad \text{alternative} \quad U = 2 \cdot u_c = 2 \cdot \sqrt{\sum_{i=1}^{n} u_i\left(y_i, x_i\right)^2} \qquad (13)$$

where:

U is the expanded uncertainty
u_c is the combined uncertainty
u_i is the contribution of the process step i to the uncertainty

Section 4 of Chapter 13 of this collection of methods (see Preliminary Remarks', Part III, Vol. 13, chapter "Quality assurance for workplace measurements" 2012) gives examples for the calculation of the expanded uncertainty U of particle/vapour mixtures.

7.2 Experimental tests with particle/vapour mixtures

All experiments are conducted in an identical manner in cases A, B and C described in Section 7.1.

It is advisable to use a dynamic system such as e.g. a flight tube (see Sections 2.2.3 and 2.2.4) for sampling, in which a particle/vapour mixture of known composition is present. If such a system is not available, then the following procedure is recommended for all experiments:

The sample carrier is connected to a suitable flow-regulated pump. After the pump has been switched on, the analyte is applied onto the aerosol sample carrier, which is usually a filter. In accordance with the recommended sampling conditions (flow rate and sampling period) purified and conditioned air (humidity, temperature) is then drawn through the sampling system.

7.3 Uncertainty associated with sampling, transport and storage

7.3.1 Uncertainty associated with sampling

Consideration of the uncertainty associated with respect to sampling should be approached in the same manner as in cases A, B and C. However, the uncertainty must be evaluated in relation to the air sample volume, which depends on the following uncertainty contributions:

Table 4 Examples of the presentation for the evaluation of measurement uncertainty

Uncertainty in connection with	Chapter 13 "Quality assurance for workplace measurements" 2012
Air sample volume • Calibration of the flow rate • Readings of the flow measuring device • Pump flow rate • Sampling period	Section 13.2.1.1.1 Pump-operated sampling
Sampling efficiency • Calibration of the test system of the sampling device • Estimation of the sampled concentration • Systematic deviation from the sampling convention	Section 13.2.1.3.2 Sampling devices for particles – estimation of the measurement uncertainty: Section "inhalable particles"

- Pump flow rate
- Calibration of the flow rate
- Display of the flow meter
- Sampling period

The additional uncertainty to take into consideration related to the sampling effectiveness depends on the sampling system used. The following must also be considered as uncertainty contributors.

- The calibration of the test system of the sampling device.
- The estimation of the sampled concentration.
- Systematic deviation from the sampling convention.

As particle/vapour mixtures are collected using a sampling system that captures the inhalable particle fraction, the predetermined estimated values can be used for the calculation as stipulated in EN 13890 [34]. The estimation of the uncertainty for the stated influencing factors is described in this collection of methods, "Preliminary Remarks', Part III, Vol. 13, chapter "Quality assurance for workplace measurements" 2012. The sections from this chapter are listed in Table 4, where the calculations can be found.

7.3.2 Uncertainty associated with transport and storage

The influence of transport and storage on the measurement results must always be checked in the case of vapours, whereas a recommendation is given for particles.

The storage must be checked with special care for substances that occur as particle/vapour mixtures in air. In particular, particles deposited on the filter can exhibit a noticeable volatility. It must be ensured that there is no loss of analyte during transport and storage. Losses during transport and storage can be avoided, if the loaded collection media are sealed tightly. Furthermore, it must be checked whether

- refrigerated transport and storage is necessary or

- immediately after sampling is complete it is necessary to stabilise the samples in a suitable extraction solution for transport and storage.

Once it has been ensured that no loss of analyte occurs due to the measures outlined above the uncertainty associated with the transport of the samples can be neglected. The influence of the storage on the recovery is investigated in a storage experiment as described in EN 1076 [32].

7.4 Uncertainty associated with the analysis

7.4.1 Recovery

The uncertainty in relation to the recovery can be determined by analysing spiked sample carriers.

For this purpose sample carriers are spiked at three different concentrations in the minimum measuring range (a tenth to twice the limit value) with at least six repetitions each. This should be carried out at 'normal' temperatures and humidities (approx. 20 °C, RH approx. 50%). Then the sample carriers are prepared and analysed in the same manner as the analysis samples, whereby the recoveries are determined from the results.

In order to calculate the uncertainty in relation to the recovery the uncertainty of the concentration must be taken into consideration. For this purpose all random and non-random deviations of volume measurement devices used for the preparation of the solutions, expressed as relative standard deviations, are added together. The purity of a substance that is used for the preparation of solutions must also be considered for this uncertainty component. Recoveries, that vary significantly (> ± 5%) from 100%, show evidence of a systematic deviation and must be taken into account when calculating the measurement result.

7.4.2 Influence of the relative humidity

Whether the relative humidity has an influence on the recovery, is investigated at the limits in the minimum measurement range at approx. 20 and approx. 80% relative humidity using at least six repetitions each. If the determined recoveries deviate significantly from those at the mean humidity, the influence must be included in the calculations as an uncertainty contribution.

7.4.3 Influence of the temperature

It must be ensured that no losses occur – especially of the collected particles. The influence of the temperature must always be checked, if the filter is transported and stored separately from the vapour collection medium and was not stabilised immediately after sampling.

If an influence of the temperature cannot be excluded, then experiments on sampling in the range of the upper concentration limit within the minimum measurement range at relative humidities of approx. 50% are carried out. The temperatures, at which experiments are conducted, should be based on the temperatures that can be anticipated in the practical application of the measurement procedure (e.g. 10 and 40 °C). The sampling experiments are conducted e.g. in a climate cabinet at a known temperature and humidity (see Section 7.3.1).

If an influence of the temperature is established, then further experiments should be carried out at the upper and lower limits of the minimum measurement range at low and high humidity. If the determined recoveries deviate significantly from those at the 'normal' temperature, the influence must be included in the calculations as an uncertainty contribution.

7.4.4 Uncertainty associated with the analytical precision

The uncertainty associated with the analytical precision is composed of the following uncertainty contributions:

- Uncertainty of the concentration of the calibration solutions,
- Uncertainty of the calibration function and
- Uncertainty due to drift of the measurement devices

The spiking concentrations with regard to the calibration concentrations described in Section 7.4.1 must also be taken into the uncertainty consideration.

The uncertainty contribution of the calibration function is expressed numerically by means of the coefficient of variation of the method. The uncertainty due to drift errors in the measurement devices refers to the tolerated deviation from the theoretical value of the contents of a control sample analysed every working day. The extent of the permissible deviation is specified by the user of the method. If the collection phases are analysed separately, then the uncertainty contributions must be considered separately for preparation and analysis.

7.5 Validation scheme for measurement procedures for the determination of particle/vapour mixtures

The validation scheme for gases and vapours (see "Preliminary Remarks", Part III, Vol. 13, Section 3.2.4 chapter "Quality assurance for workplace measurements" 2012) also applies in principle to particle/vapour mixtures. In contrast to spiking on a dynamic test gas facility, the sample carriers are spiked in such a manner that a defined volume of solution of known content of the substances of interest is applied to the sample carrier while the sampling pump is operating. Then a volume of air that corresponds to the standard sampling conditions is drawn through the sample carrier.

The influence of the temperature on the recovery must always be investigated (see Section 7.4).

References

[1] IFA Arbeitsmappe Messung von Gefahrstoffen (2017) Sachgruppe 9 – Messverfahren, Erich Schmidt Verlag, Berlin,
http://www.ifa-arbeitsmappedigital.de/sg/9/inhalt.html

[2] Zschiesche W, Behrens T, Brüning T, Giesen Y, van Gelder R, Breuer D (2014) Volatile organic compound reference materials suitable for practical use: Database analysis for the selection of hazardous substances. Poster presented at the 8th International Symposium on Modern Principles for Air Monitoring and Biomonitoring. 15.–19.06.2014, Marseille, Frankreich

[3] Breuer D (1999) Measurement of vapour – aerosol mixtures. J. Environ. Monit., Vol. 1, No. 4, pp. 299–305,
http://pubs.rsc.org/en/content/articlelanding/1999/em/a902081k/unauth

[4] Raynor P and Leith D (1999) Evaporation of accumulated multicomponent liquids from fibrous filters. Ann. Occup. Hyg., Vol. 43, No. 3, pp. 181–192,
http://annhyg.oxfordjournals.org/content/43/3/181.full.pdf

[5] Sutter B, Bémer D, Appert-Collin J-C, Thomas D, Midoux N (2010) Evaporation of liquid semi-volatile aerosols collected on fibrous filters. Aerosol Science and Technology, Vol. 44, No. 5, pp. 395–404,
http://www.tandfonline.com/doi/full/10.1080/02786821003674244

[6] Dragan GC, Karg E, Nordsieck H, Schnelle-Kreis J, Breuer D, Arteaga-Salas JM, Ferron GA, Zimmermann R (2014) Short-term evaporation of semi-volatile n-alkane aerosol particles: experimental and computational approach. Environmental Engineering and Management Journal (EEMJ), Vol. 13, No. 7, pp. 1775–1785,
https://www.researchgate.net/profile/Dietmar_Breuer/publication/292394754_Dynamic_behaviour_of_aerosols_from_semi_volatile_organic_compounds/links/56bafee508ae3af6847d9648.pdf

[7] Dragan GC, Breuer D, Blaskowitz M, Karg E, Schnelle-Kreis J, Arteaga-Salas JM, Nordsieck H, Zimmermann R (2015) An evaluation of the "GGP" personal samplers under semi-volatile aerosols: sampling losses and their implication on occupational risk assessment. Environ. Sci. Process Impacts, Vol. 17, No. 2, pp. 270–277,
http://pubs.rsc.org/en/content/articlehtml/2015/em/c4em00468j?page=search

[8] Breuer D, Dragan GC, Friedrich C, Möhlmann C, Zimmermann R (2015) Development and field testing of a miniaturized sampling system for simultaneous sampling of vapours and droplets. Environ. Sci. Process Impacts, Vol. 17, No. 2, pp. 278–287,
http://pubs.rsc.org/en/Content/ArticleLanding/2015/EM/C4EM00602J#!divAbstract

[9] Breuer D, Friedrich C, Möhlmann C, Dragan GC (2015) Das miniaturisierte Probenahmesystems GGP-Mini zur gleichzeitigen Erfassung von Dampf-Tröpfchen-Gemischen schwerflüchtiger Verbindungen – Ergebnisse von Labor- und Praxismessungen. Gefahrstoffe – Reinhaltung der Luft, Vol. 75, No. 10, pp. 390–394,
http://www.dguv.de/medien/ifa/de/pub/grl/pdf/2015_175.pdf

[10] Kohlmeier V, Dragan GC, Karg E, Schnelle-Kreis J, Breuer D, Forbes PBC, Rohwer ER, Zimmermann R (2015) Die Eignung von Multichannel-PDMS-Denudern zur Gas-Partikel-Trennung von SVOC. Gefahrstoffe – Reinhaltung der Luft, Vol. 75, No. 10, pp. 383–389,
http://www.dguv.de/medien/ifa/de/pub/grl/pdf/2015_174.pdf

[11] Karg E, Dragan GC, Ferron GA, Nordsieck H, Blaskowitz M, Friedrich C, Kohlmeier V, Möhlmann C, Schnelle-Kreis J, Stanglmaier S, Zimmermann R, Breuer D (2015) Dynamisches Verhalten von Aerosolen aus semivolatilen Komponenten. Gefahrstoffe – Reinhaltung der Luft, Vol. 75, No. 7/8, pp. 265–74,
http://www.dguv.de/medien/ifa/de/pub/grl/pdf/2015_135.pdf

[12] Ambrose D, Walton J (1989) Vapour pressures up to their critical temperatures of normal alkanes and 1-alkanols. Pure & Appl. Chem., Vol. 61, No. 8, pp. 1395–1403, http://www.iupac.org/publications/pac-2007/1989/pdf/6108x1395.pdf

[13] Maxwell JC (1890) The scientific papers of James Clerk Maxwell. Cambridge University Press, London, http://dx.doi.org/10.1017/CBO9780511698095

[14] Davies CN (1978) Evaporation of airborne droplets. In: Shaw DT (Ed.) Fundamentals of aerosol science. John Wiley & Sons, New York, pp. 135–164

[15] DFG – Deutsche Forschungsgemeinschaft (2017) List of MAK and BAT Values 2017. Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Report No. 53. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/book/10.1002/9783527812127

[16] Hartwig A and MAK Commission (2016) N-Ethyl-2-pyrrolidone [MAK Value Documentation, 2014]. The MAK Collection for Occupational Health and Safety, Vol. 1, No. 4, pp. 2588–2609, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb268791e5616/pdf

[17] Hartwig A and MAK Commission (2017) N-Ethyl-2-pyrrolidone (vapour) [MAK Value Documentation, 2016]. The MAK Collection for Occupational Health and Safety, Vol. 2, No. 2, pp. 357–368, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb268791e5617/pdf

[18] Hartwig A and MAK Commission (2013) Di-n-butylphthalate [MAK Value Documentation, 2013]. The MAK Collection for Occupational Health and Safety, Vol. 2, No. 1, pp. 1–72, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb8474yole4813/pdf

[19] Hartwig A and MAK Commission (2016) Distillates (petroleum), hydrotreated light [MAK Value Documentation, 2012]. The MAK Collection for Occupational Health and Safety, Vol. 1, No. 3, pp. 1791–1803, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb6474247yole5216/pdf

[20] Hartwig A and MAK Commission (2017) Distillates (petroleum), hydrotreated light [MAK Value Documentation, 2016]. The MAK Collection for Occupational Health and Safety, Vol. 2, No. 3, pp 1144–1169, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb6474247yole6017/pdf

[21] Dietzel KD, Campbell JL, Bartlett MG, Witten ML, Fisher JW (2005) Validation of a gas chromatography/mass spectrometry method for the quantification of aerosolized Jet Propellant 8. J Chromatogr A, Vol. 1093, No. 1-2, pp. 11–20, http://www.sciencedirect.com/science/article/pii/S0021967305015487

[22] Gregg SD, Campbell JL, Fisher JW, Bartlett MG (2007) Methods for the characterization of Jet Propellent-8: vapor and aerosol. Biomed Chromatography, Vol. 21, No. 5, pp. 463–472, http://onlinelibrary.wiley.com/doi/10.1002/bmc.776/pdf

[23] Wong SS, Thomas A, Barbaris B, Lantz RC, Witten ML (2009) Pulmonary evaluation of permissible exposure limit of syntroleum S-8 synthetic jet fuel in mice. Toxicol. Sci., Vol. 109, No. 5, pp. 312–320, http://www.ncbi.nlm.nih.gov/pubmed/19357071

[24] TRGS 900 (2006) Arbeitsplatzgrenzwerte. BArbBl. Version 1/2006, pp. 41–55, last amended and supplemented: GMBl 2017, pp. 919–922 [No. 50] from 30.11.2017, https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/TRGS-900.html

[25] EN 481 (1993) Workplaces atmospheres – size fraction definitions for measurement of airborne particles; German version EN 481:1993. Beuth Verlag, Berlin, Germany

[26] EN 13936 (2014) Workplace exposure – Procedures for measuring a chemical agent present as a mixture of airborne particles and vapour – Requirements and test methods; German version EN 13936:2014. Beuth Verlag, Berlin, Germany

[27] Hebisch R, Hartwig A, MAK Commission. Analytische Methoden zur Prüfung gesundheitsschädlicher Arbeitsstoffe. Band 1 Luftanalysen. Bearbeitet von der Arbeitsgruppe „Luftanalysen“ der Ständigen Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoff, Deutsche Forschungsgemeinschaft. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/book/10.1002/3527600418/topics

[28] EN 482 (2015) Workplace exposure - General requirements for the performance of procedures for the measurement of chemical agents; German version EN 482:2012, Beuth Verlag, Berlin, Germany

[29] EN 50014 (2000) Electrical apparatus for potentially explosive atmospheres – General requirements; German version EN 50014:1997 + Corrigendum:1998 + A1:1999 + A2:1999, https://www.beuth.de/de/norm/din-en-50014/15289853

[30] TRGS 402 (2010) Identification and assessment of the risks from activities involving hazardous substances: inhalation exposure. Version: February 2010, corrected: GMBl 2011 p. 175 [No. 9] (March 2011) (not up-to-date and inofficial version; mandatory is the current German version),
https://www.baua.de/EN/Service/Legislative-texts-and-technical-rules/Rules/TRGS/TRGS-402.html

[31] EN 689 (2016) Workplace exposure – Measurement of exposure by inhalation to chemical agents – Strategy for testing compliance with occupational exposure limit values; German and English version prEN 689:2016. Beuth Verlag, Berlin, Germany

[32] EN 1076 (2010) Workplace exposure – Procedures for measuring gases and vapours using pumped samplers – Requirements and test methods; German version EN 1076:2009. Beuth Verlag, Berlin, Germany

[33] EN 13205-1 (2014) Workplace exposure – Assessment of sampler performance for measurement of airborne particle concentrations – Part 1: General requirements; German version EN 13205-1:2014. Beuth Verlag, Berlin, Germany

[34] EN 13890 (2010) Workplace exposure – Procedures for measuring metals and metalloids in airborne particles – Requirements and test methods; German version EN 13890:2009. Beuth Verlag, Berlin, Germany

[35] ISO 13137 (2013) Workplace atmospheres – Pumps for personal sampling of chemical and biological agents – Requirements and test methods; German version EN ISO 13137:2013. Beuth Verlag, Berlin, Germany

[36] IFA Arbeitsmappe Messung von Gefahrstoffen (2017) Kennzahl 3010: Geräte zur Probenahme der einatembaren Staubfraktion (E-Staub). Erich Schmidt Verlag, Berlin,
http://www.ifa-arbeitsmappedigital.de/did/00301000/redirect/301/inhalt.html

[37] IFA Arbeitsmappe Messung von Gefahrstoffen (2017) Kennzahl 3040: Geräte zur Probenahme von Stoffen, die gleichzeitig partikel- und dampfförmig vorliegen. Erich Schmidt Verlag, Berlin,
http://www.ifa-arbeitsmappedigital.de/did/00304000/redirect/301/inhalt.html

[38] IFA Arbeitsmappe Messung von Gefahrstoffen (2017) Kennzahl 30514/5: Messstrategie für Kühlschmierstoffe und komplexe kohlenwasserstoffhaltige Gemische. Erich Schmidt Verlag, Berlin,
http://www.ifa-arbeitsmappedigital.de/q/0514%7C5/truncation/0/suche.html