

The MAK Collection for Occupational Health and Safety

Benzyl alcohol – Method for the determination of benzyl alcohol in workplace air using gas chromatography after thermal desorption

Air Monitoring Method – Translation of the German version from 2018

M. Tschickardt¹, W. Krämer², R. Schmitt², R. Hebisch^{3,*}, T.H. Brock^{4,*}, A. Hartwig^{5,*}, MAK Commission^{6,*}

¹ Method development, State Environmental Agency Rhineland-Palatinate, Kaiser-Friedrich-Straße 7, 55118 Mainz, Germany

² External verification, BASF SE, ESE/MA – Z 570, Carl-Bosch-Straße 38, 67056 Ludwigshafen, 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 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

⁵ 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

⁶ 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: benzyl alcohol; air analyses; analytical method; workplace measurement; hazardous substance; thermal desorption gas chromatography; flame ionisation detection; mass spectrometry; TD-GC-FID/MS; quartz fibre filter

Citation Note: Tschickardt M, Krämer W, Schmitt R, Hebisch R, Brock TH, Hartwig A, MAK Commission. Benzyl alcohol – Method for the determination of benzyl alcohol in workplace air using gas chromatography after thermal desorption. Air Monitoring Method – Translation of the German version from 2018. MAK Collect Occup Health Saf [Original edition. Weinheim: Wiley-VCH; 2019 Jul;4(3):1667–1682]. Corrected republication without content-related editing. Düsseldorf: German Medical Science; 2025. https://doi.org/10.34865/am10051e2019_w

Republished (online): 30 Apr 2025

Originally published by Wiley-VCH Verlag GmbH & Co. KGaA; <https://doi.org/10.1002/3527600418.am10051e2019>

Manuscript completed: 01 Mar 2018

Published (online): 25 Jul 2019

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



This work is licensed under a
Creative Commons Attribution 4.0 International License.

Benzyl alcohol – Method for the determination of benzyl alcohol in workplace air using gas chromatography after thermal desorption

Air Monitoring Methods

M. Tschickardt¹, W. Krämer², R. Schmitt², R. Hebisch^{3,*}, T.H. Brock^{4,*}, A. Hartwig^{5,*}, MAK Commission^{6,*}

DOI: 10.1002/3527600418.am10051e2019

Abstract

This analytical method is a validated measurement procedure for the determination of benzyl alcohol [100-51-6] in workplace air in a concentration range of one tenth up to twice the currently valid MAK value of 22 mg/m³. With this method simultaneously airborne benzyl alcohol in the gaseous state as well as particles are collected. Sampling is performed by drawing a defined volume of air through a quartz fibre filter located in the sampling head with an adsorption tube filled with Tenax TA[®] connected downstream using a suitable pump. The flow rate is set to 0.066 L/min with a recommended air sample volume of approx. 4 litres. The collected benzyl alcohol is thermally desorbed and then analysed by means of gas chromatography using two detectors, a FID for quantification and a MSD to recognise potential interferences. The quantitative determination is based on a calibration function obtained by means of a multi-point calibration. The limit of quantification is 0.24 mg/m³ based on an air sample of approx. 4 litres.

Keywords

benzyl alcohol; workplace measurement; hazardous substances; air analysis; workplace monitoring; glass fibre filter; Tenax TA[®]; gas chromatography; GC-FID; GC-MSD; thermal desorption; GGP-Mini

Author Information

¹ State Environmental Agency Rhineland-Palatinate, Kaiser-Friedrich-Str. 7, 55118 Mainz, Germany

² BASF SE, ESE/MA – Z. 570, 67056 Ludwigshafen, Germany

³ Head of the working group "Air Analysis" 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 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

⁵ 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

⁶ 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)

Benzyl alcohol – Method for the determination of benzyl alcohol in workplace air using gas chromatography after thermal desorption

Method number	1
Application	Air analysis
Analytical principle	Gas chromatography (thermal desorption)
Completed in	March 2018

Summary

The analytical method described here enables the determination of benzyl alcohol in workplace air from a tenth up to twice the currently valid OEL or MAK value of 22 mg/m³ (5 ppm) [1, 2]. Benzyl alcohol occurring in the gaseous and particulate state can be simultaneously determined with this method. Sampling is performed using a suitable sampling pump to draw a defined volume of air through an adsorption tube filled with Tenax TA®, which has a GGP-Mini type sampling head fitted with a quartz fibre filter connected upstream to capture the aerosol portion.

The analysis is carried out by means of gas chromatography with a flame ionisation detector (FID) after thermal desorption. At the same time a mass selective detector (MSD) is used, which can be useful for identification and quantification in the case of chromatographic interferences. A multiple-point calibration with calibration standards of known concentration is carried out for quantitative evaluation. There is a linear relationship between the peak area and the concentration.

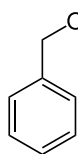
Characteristics of the method

Precision:	Standard deviation (rel.):	$s = 0.8$ to 1.2%
	Expanded uncertainty:	$U = 26.3$ to 26.4%
	in the concentration range of the limit of quantification up to twice the limit value and $n = 6$ determinations	

Limit of quantification:	0.24 mg/m ³ for an air sample volume of 4 L		
Recovery:	$\eta > 0.95$ (> 95%)		
Sampling recommendations:	Sampling time:	60 min	
	Air sample volume:	4 L	
	Volumetric flow rate:	4 L/h	

Description of the substances

Benzyl alcohol [100-51-6]



Synonyms: Phenylmethanol, Phenylcarbinol, E 1519

Benzyl alcohol is a colourless liquid with an oily consistency (molar mass 108.14 g/mol, boiling point 206 °C at 1013 mbar, melting point –15 °C, vapour pressure 2.7 hPa at 20 °C, density 1.04 g/cm³). It has a mild aromatic, almond-like odour. It is moderately soluble in water (39 g/L at 20 °C); it is however, readily soluble in most organic solvents. It occurs at approx. 6% in jasmine essential oil and is furthermore a natural component of clove and wallflower essential oils. Benzyl alcohol is sensitive to light and air; in the presence of oxygen in air it is auto-oxidized to benzaldehyde.

Benzyl alcohol is used as a solvent in water-based varnishes and as a paint stripper. Furthermore, it is used as a precursor for the production of a variety of esters and as a preservative in cosmetics and pharmaceutical products. Benzyl alcohol can be used as food additive to produce flavours and is marked by the food additive code number E 1519. The flavourings produced using benzyl alcohol may only be used in limited amounts (up to 100 mg/L) in liqueurs, flavoured beverages and cocktails. Chocolate, biscuits, cakes and other confectioneries may have up to 250 mg/kg added.

The OEL and MAK value for benzyl alcohol is 22 mg/m³ (5 ppm) [1, 2]. The short-term exposure limit is classified in Peak Limitation Category I with an excursion factor of 2. Furthermore, the following footnote applies to the substance: “*may occur simultaneously as vapour and aerosol*”. Detailed information on the toxicity of benzyl alcohol can be found in the toxicological-occupational health documentation of MAK values [3, 4].

$$1 \text{ mL/m}^3 (\text{ppm}) \triangleq 4.497 \text{ mg/m}^3$$

$$1 \text{ mg/m}^3 \triangleq 0.222 \text{ mL/m}^3 (\text{ppm})$$

Contents

1	General principles	1670
2	Equipment, chemicals and solutions	1671
2.1	Equipment	1671
2.2	Chemicals	1671
2.3	Preparation of the sampling system	1672
2.3.1	Adsorption tubes	1672
2.3.2	Quartz fibre filters	1672
2.4	Solutions	1673
2.5	Calibration standards	1673
3	Sampling and sample preparation	1674
4	Operating conditions for chromatography	1674
5	Analytical determination	1675
6	Calibration	1676
7	Calculation of the analytical result	1676
8	Reliability of the method	1677
8.1	Precision and expanded uncertainty	1677
8.2	Recovery and influence of the air humidity	1677
8.3	Influence of the temperature	1678
8.4	Limit of quantification	1678
8.5	Capacity of the sampling system	1678
8.6	Storage stability	1678
8.7	Interference	1679
9	Discussion	1679
	References	1680
	Appendix	1681

1 General principles

The analytical method described here enables the determination of benzyl alcohol in workplace air from a tenth up to twice the currently valid OEL or MAK value of 22 mg/m³ (5 ppm) [1, 2]. Benzyl alcohol in the gaseous and particulate state can be simultaneously determined with this method. Sampling is carried out using a suitable sampling pump to draw a defined volume of air through a sampling system consisting of a sampling head (GGP-Mini) fitted with a quartz fibre filter and an adsorption tube filled with Tenax TA[®] connected downstream. Thus, droplets are deposited on the filter, whereas the gaseous portions are adsorbed onto the Tenax TA[®]. Deposited droplets that evaporate from the filter during sampling are collected downstream in the tenax tube.

After sampling, the filter is withdrawn from the sampling head and pushed into the end of the adsorption tube facing the sampling head. Sample preparation is performed by means of thermal desorption, whereby the thermal desorption is carried out in the opposite direction of flow to that during sampling. After thermal desorp-

tion, benzyl alcohol is determined by gas chromatography with a flame ionization detector (FID). At the same time a mass selective detector (MSD) is used, which can be useful for identification and quantification in the case of chromatographic interferences. A multiple-point calibration with calibration standards of known concentration is carried out for quantitative evaluation. There is a linear relationship between the peak area and the concentration.

2 Equipment, chemicals and solutions

2.1 Equipment

- Pump, suitable for a flow rate of 66 mL/min (e.g. Pocket Pump, from Analyt-MTC Messtechnik GmbH, 79379 Müllheim, Germany)
- Aerosol monitor for collecting the inhalable aerosols, e.g. GGP-Mini type sampling head with intake cone for 0.066 L/min (e.g. from Analyt-MTC Messtechnik GmbH)
- Quartz fibre filter, Munktell MK 360, Ø = 37 mm (e.g. from Binzer & Munktell Filter GmbH, 35088 Battenberg, Germany)
- Filter punch, Ø = 13 mm
- Muffle furnace
- Adsorption tubes made of stainless steel (6.3 mm x 90 mm, inner diameter of 5 mm), e.g. from PerkinElmer LAS, 63110 Rodgau, Germany
- Gauze loading rig (e.g. from PerkinElmer LAS, Order No. L4070023)
- Metal sieve for stainless steel tubes (e.g. from PerkinElmer LAS, Order No. L4071034)
- Retaining spring for metal packing gauze (e.g. from PerkinElmer LAS, Order No. L4071123)
- Gas chromatograph with thermal desorber, flame ionisation detector (FID), mass selective detector (MSD) and evaluation system
- Sealing caps (e.g. Swagelok with PTFE seals, PTFE)
- Capillary column e.g. DB-624: 30 m, film thickness of 1.4 µm; inner diameter of 0.25 mm, e.g. from Agilent, 76337 Waldbronn, Germany
- Gas meter or stopwatch and soap bubble flowmeter
- Analytical balance
- Volumetric flasks, nominal volume 100 mL
- Positive displacement pipette, Microman type, 1 to 10 µL, from Gilson, 65555 Limburg, Germany
- Tweezers

2.2 Chemicals

- Benzyl alcohol, p.a., purity ≥ 99.5%, e.g. from Merck, 64293 Darmstadt, Germany
- Methanol, p.a., purity ≥ 99.5%, e.g. from Merck
- Tenax TA® (35–60 mesh), e.g. from Agilent Technologies, 64289 Darmstadt, Germany

1672 Air Monitoring Methods

Gases for operation of the gas chromatograph/thermal desorber:

- Helium 5.0 (carrier gas)
- Purified or synthetic air (free of hydrocarbons, dew point better than -40°C)
- Hydrogen 5.0
- Nitrogen 5.0

2.3 Preparation of the sampling system

The sampling system – consisting of a filter and an adsorption tube connected downstream – is prepared as follows before use:

Adsorption tubes filled with Tenax TA[®] (75 mg Tenax TA[®] 35–60 mesh) are not commercially available and must be prepared and conditioned in the laboratory. The quartz fibre filters are conditioned in the muffle furnace at 500°C for four hours prior to sampling.

2.3.1 Adsorption tubes

Adsorption tubes made of stainless steel are filled with 75 mg Tenax TA[®] (35–60 mesh) and the adsorbent is slightly compressed by tapping. It is important to ensure that the adsorbent is not compressed too much. The individual tubes are fitted into the gauze loading rig and a metal packing gauze is carefully pushed to the end of the adsorbent layer. Then a spring is pushed up to the gauze, in order to prevent the gauze falling out of the tube (see Figure 1). The flow resistance must be checked before an adsorption tube is used for the first time. This should not exceed 30 hPa at a flow rate of 1 L/min.

Before their first use, the adsorption tubes filled with Tenax TA[®] are conditioned for approx. 20 minutes in the thermal desorber at 300°C and then tested for blank values. Then they are sealed with suitable caps for storage. The tubes can be re-used after analysis is complete.

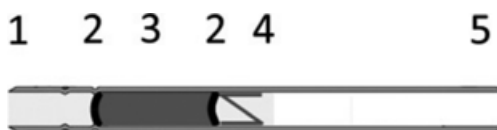


Figure 1 Schematic illustration of the adsorption tubes used

- | | |
|-------------------------------------|-----------------------|
| 1 Connection to the pump | 4 Spring for fixation |
| 2 Retention gauze for the adsorbent | 5 Sampling opening |
| 3 Adsorbent Tenax TA [®] | |

2.3.2 Quartz fibre filters

The quartz fibre filters are conditioned at 500°C for four hours in the muffle furnace, whereby the background of thermally desorbable compounds is reduced to a minimum.

2.4 Solutions

Stock solution: Benzyl alcohol (51.6 g/L)

5.0 mL of benzyl alcohol are pipetted into a 100 mL volumetric flask and weighed. The volumetric flask is then filled to the mark with methanol and shaken.

Calibration solutions:

The calibration solutions are prepared by diluting the stock solution with methanol in a ratio of 1:10 (Calibration Solution I) or 1:100 (Calibration Solution II) (Table 1).

Table 1 Concentration of the stock solution and calibration solutions

Substance	Stock solution	Calibration solution I	Calibration solution II
	[g/L]	[µg/µL]	[µg/µL]
Benzyl alcohol	51.6	5.16	0.516

The prepared solutions can be stored in the refrigerator at approx. 4 °C for at least 6 months. The date of preparation must be noted on the volumetric flask.

2.5 Calibration standards

For the purpose of calibration, aliquots of 1 to 10 µL of the calibration solutions (see Table 1) are applied to the adsorption tubes filled with Tenax TA®. Clean air or nitrogen is then drawn through the adsorption tubes at a flow rate of 30 mL/min for 10 minutes in order to remove the excess methanol solvent. The spiked adsorption tubes contain the calibration masses shown in Table 2.

Table 2 Calibration standards

Solution	Dosing volume	Spiked mass	Concentration at an air sample volume of 4 L
	[µL]	[µg]	[mg/m³]
Calibration solution II	1	0.516	0.129
	5	2.58	0.645
	10	5.16	1.29
Calibration solution I	2.5	12.9	3.22
	5	25.8	6.45
	7.5	38.7	9.67
	10	51.6	12.9
Stock solution	2.5	129	32.2
	5	258	64.5

3 Sampling and sample preparation

The GGP-Mini type sampling head is fitted with a prepared quartz fibre filter and an intake cone suitable for the flow rate of 0.066 L/min. An adsorption tube filled with Tenax TA® is connected to the tube connection of the sampling head and sampling pump [5]. The connection between the sampling head and adsorption tube is established using a short section of Viton® tube.

The definition of an inhalable dust is fulfilled by this sampling system [6, 7]. The schematic set-up of the sampling system is illustrated in Figure 2.

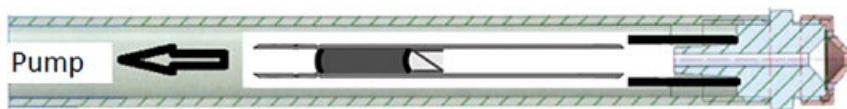


Figure 2 Schematic illustration of the sampling system consisting of a GGP-Mini sampling head and an adsorption tube connected downstream

The pump and the sampling system are either worn by a person while performing their activities or stationary sampling is carried out. Air from the breathing zone is sampled. The opening of the adsorption tube should be freely accessible. An air sample volume of 4 litres is achieved, at a pre-selected flow rate of 0.066 L/min and a sampling time of 60 minutes. The important parameters for the determination of the concentration in air (sample volume, temperature, air pressure and relative humidity) are documented in the sampling record.

After sampling, the filter is removed from the sampling head, folded using tweezers and pushed into the end of the adsorption tube that faces towards the sampling head. Then the tube is sealed at both ends using Swagelok caps with PTFE seals until analysis.

4 Operating conditions for chromatography

Apparatus:	Clarus 600 gas chromatograph with flame ionisation detector (FID), Clarus 600T mass selective detector (MSD), PerkinElmer LAS	
Column:	Material:	Fused silica
	Stationary phase:	DB-624 (6% cyanopropylphenyl-polysiloxane and 94% dimethyl-polysiloxane)
	Length:	30 m
	Inner diameter (ID):	0.25 mm
Eluate flow splitter:	Film thickness (FT):	1.4 µm
	Graphpack-3D/2-eluate flow splitter, Order No. GC 08194-40, from Gerstel, Mülheim an der Ruhr, Germany	
	Split ratio:	1:1 (FID/MSD)

Detectors: Flame ionisation detector (FID) and mass selective detector (MSD)

Detector temperature (FID):

320 °C

Detector gases: Hydrogen (45 mL/min), synthetic air (450 mL/min)

Rate of heating: 10 min at 35 °C, increased by 10 °C/min up to 240 °C, 10 min

MS-operational conditions

Temperatures: Ion source: 180 °C

Transfer line: 200 °C

Type of ionisation: Electron impact (EI)

Pressure of the ion source:

3×10^{-6} kPa

Ionisation energy: 70 eV

Mass range: 35–520 amu

Under the conditions given here the retention time for benzyl alcohol is 23.6 minutes (see Table 7 in the Appendix).

5 Analytical determination

The adsorption tubes are heated in the thermal desorber in the opposite direction to that of sampling. The benzyl alcohol desorbed in this manner is transferred by means of a carrier gas into a cold trap packed with Tenax TA®. After complete desorption the cold trap is heated, so that the analyte is transferred to the separation column as a narrow substance plug.

The thermal desorber is set to the following instrumental conditions:

Conditions of the thermal desorption

Apparatus: Turbomatrix 650 (from PerkinElmer LAS)

Desorption temperature: 280 °C

Desorption duration: 20 min

Valve temperature: 220 °C

Temperature of the transfer line: 200 °C

Transfer line: 1.5 m deactivated non-loaded pre-column, (ID 0.32 mm)

Cold trap (adsorption): –30 °C

Cold trap (injection): 280 °C

Cold trap filling: 20 mg of Tenax TA® (Order No. M0413535)

Heating rate: 40 °C/s

Carrier gas: Helium

Carrier gas flow: 1.7 mL/min

Split (before the cold trap): 200 mL/min (input split)

1676 Air Monitoring Methods

Flow rate (through the cold trap): 10 mL/min (desorption flow)
Split (after the cold trap): 20 mL/min (output split)
Purge drying phase: 1 min at room temperature at 50 L/min

After the thermal desorber and gas chromatograph have been prepared, the calibration and analytical samples are measured. Should other thermal desorption devices be used, then the instrumental conditions must be adapted accordingly.

6 Calibration

The calibration samples prepared according to Section 2.5 are analysed as described in Sections 4 and 5. The calibration function is obtained by plotting the peak areas measured versus the respective loaded masses (see Table 2).

The calibration function is linear in the investigated concentration range and should be regularly checked during routine analysis. A calibration standard of known concentration must be analysed in each analytical series for this purpose.

7 Calculation of the analytical result

Based on the determined peak areas, the corresponding mass X in μg per sample is obtained from the respective calibration curve. The corresponding concentration by weight (ρ) is calculated according to Equation 1 below:

$$\rho = \frac{X}{V \times \eta} \quad (1)$$

Equation 2 below enables calculation of the value at 20 °C and 1013 hPa:

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

where:

- ρ is the mass concentration of benzyl alcohol in the ambient air at t_a and p_a in mg/m^3
- ρ_0 is the mass concentration of benzyl alcohol in mg/m^3 at 20 °C and 1013 hPa
- X is the mass of benzyl alcohol in the analytical sample in μg
- V is the air sample volume (calculated from the flow rate and the sampling period) in L
- η is the recovery
- t_a is the temperature during sampling at the sampling location in °C
- p_a is the air pressure at the sampling location during sampling in hPa

8 Reliability of the method

The characteristics of the method were calculated as stipulated in DIN EN 482 [8], DIN EN 1076 [9], DIN EN 13936 [6] and DIN 32645 [10]. The precision data and the influence of the humidity were determined in each case on the basis of a series of six sample measurements.

The samples were prepared by spiking the filters with solutions (see Section 2.4; Table 1). The spiked filter was then immediately fitted into the sampling head. After attaching the intake cone, the sampling head was connected to the adsorption tube and humidified air was drawn through the sampling system. After sampling, the filter is folded using tweezers and pushed from the rear side into the adsorption tube. The sample is then analysed according to Sections 4 and 5. Storage stability was determined by directly spiking onto the adsorption tube.

8.1 Precision and expanded uncertainty

For the purpose of determining the precision three experiment series with benzyl alcohol concentrations in the range of one tenth to twice the MAK value were carried out. After spiking the filters and connecting a sampling head upstream of the adsorption tube, 4 litres of air with a relative humidity of 80% were drawn through the sampling system at room temperature (23 °C).

The expanded uncertainty was estimated as stipulated in EN 482 [8] and calculated according to [11] taking all relevant influencing factors into consideration. The expanded uncertainty of the entire method consists principally of the contributions of the sampling uncertainty (e.g. air sample volume, deviation from the sampling convention) and the analytical preparation (scatter of the calibration function, fluctuations in the transfer as well as the reproducibility). The resulting characteristics, such as relative standard deviation and expanded uncertainty, are listed in Table 3.

Table 3 Standard deviation (rel.), expanded uncertainty U and recovery for $n=6$ determinations

Spiked mass of benzyl alcohol	Concentration of benzyl alcohol at $V = 4 \text{ L}$ of air	Standard deviation (rel.)	Expanded uncertainty U	Recovery
[μg]	[mg/m^3]	[%]	[%]	[%]
10.3	2.6	1.2	26.4	96
103	25.8	0.8	26.3	96
258	64.5	1.2	26.4	94

8.2 Recovery and influence of the air humidity

The recoveries were calculated using the precision experiments (see Section 8.1). The mean recovery was 95%.

1678 Air Monitoring Methods

8.3 Influence of the temperature

The influence of the temperature during sampling was determined by conducting two experimental series. After spiking the filter with 5 µL of stock solution (see Section 2.4), equivalent to 258 µg of benzyl alcohol, and subsequent connection of the filter upstream of the adsorption tube four litres of air with a relative humidity of 50% were drawn through the sampling system at 5 °C and 40 °C (see Table 4).

There was no evidence that the temperature had any influence.

Table 4 Standard deviation (rel.) and recovery for $n = 3$ determinations

Spiked mass of benzyl alcohol	Temperature	Concentration of benzyl alcohol at $V = 4$ L of air	Standard deviation (rel.)	Recovery
[µg]	[°C]	[mg/m ³]	[%]	[%]
258	5	64.5	0.1	96
258	40	64.5	1.9	97

8.4 Limit of quantification

The limit of quantification was calculated in the same manner as the calibration line method described in DIN 32645 [10] with a statistical certainty of $P = 95\%$ and $k = 3$.

The limit of quantification was determined by spiking the filter with aliquots of 1 to 10 µL of calibration solution II (see Section 2.4; Table 1) and then pushing the filter into the end of the adsorption tube using tweezers. Nitrogen is then drawn through the adsorption tubes at a flow rate of 30 mL/min for 10 minutes in order to remove the excess methanol. For this purpose, the rear ends of the adsorption tubes were connected to the nitrogen supply. According to the calibration line method ($P = 95\%$, $k = 3$) the limit of quantification of benzyl alcohol is 0.24 mg/m³ (0.97 µg absolute) based on an air sample volume of four litres.

8.5 Capacity of the sampling system

The capacity of the sampling system is determined by spiking an adsorption tube with 5 µL of the stock solution (see Section 2.4), which is equivalent to 258 µg of benzyl alcohol. A second adsorption tube is then connected downstream and 12 litres of air are drawn through the combined tubes at room temperature (23 °C) and a relative humidity of 80%. No breakthrough was observed.

8.6 Storage stability

Tests on storage stability of the loaded sampling systems were carried out over periods of two and four weeks. For this purpose, experimental series were prepared with 2.58 µg and 181 µg of benzyl alcohol – equivalent to 0.645 mg and 45.1 mg of benzyl alcohol per m³ at an air sample volume of 4 L.

The sample was dosed by applying aliquots in the μL range directly onto the Tenax TA[®] adsorbent in the adsorption tubes and then four litres of air with a relative humidity of 80% were drawn through the tubes. The tubes were sealed with Swagelok caps and stored at room temperature.

After one day as well as after two and four weeks three adsorption tubes were prepared and analysed according to Sections 4 and 5 in each case. The results are listed in Table 5. During the four-week period no losses could be detected, therefore storage stability over a period of four weeks is ensured.

Table 5 Recoveries of benzyl alcohol after a storage period of 2 and 4 weeks at room temperature.

Spiked mass of benzyl alcohol [μg]	Detected mass [μg] after a storage period of		
	1 day	2 weeks	4 weeks
2.58	2.25	2.35	2.29
181	180	181	183

8.7 Interference

On account of the low specificity of flame ionisation detectors, interference is principally possible due to components with the same retention time. The results of the mass selective detection are used to confirm the analytical results.

9 Discussion

Benzyl alcohol can be determined in workplace air in a concentration range of a tenth up to twice the currently valid MAK value with the analytical method described here. Furthermore, the analytical method is suitable for monitoring compliance with the peak limit.

The method described here was examined using two different concentrations. For this purpose, six sample carriers were each spiked with 25.59 μg and 51.17 μg of benzyl alcohol in the laboratory of the developer of the method (LfU – State Environmental Agency Rhineland-Palatinate) and that of the examiner of the method (BASF SE Environmental Analysis). Four litres of ambient air at an air humidity of approx. 55% were then drawn through the sample carriers. The sample carriers were sealed and exchanged between the laboratories, so that both laboratories each analysed three samples that had been spiked in-house and three spiked by the other laboratory. The analyses were carried out simultaneously in accordance with Sections 4 and 5 after five days. Recoveries of 90 to 96% were obtained. The exact results can be found in Table 6.

Sampling with the mini GGP sampling system ensures that the airborne aerosol portion is always captured in its entirety [12].

1680 Air Monitoring Methods

Table 6 Results of testing the measurement method for benzyl alcohol

	Laboratory 1 (LfU*)			Laboratory 2 (BASF**)	
	Theoretical concentration	Concentration found	Recovery	Concentration found	Recovery
	[mg/m ³]	[mg/m ³]	[%]	[mg/m ³]	[%]
Experiment series 1	6.40	5.91	92	5.74	90
Experiment series 2	12.8	12.1	95	12.3	96

* State Environmental Agency Rhineland-Palatinate

** BASF SE Environmental Analysis

References

- [1] TRGS 900 (2006) Arbeitsplatzgrenzwerte. BARBI Heft 1/2006 S. 41–55 zuletzt geändert und ergänzt: GMBI 2017 S. 368–370 [Nr. 20] (v. 8.6.2017), <http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-900.html>
- [2] DFG – Deutsche Forschungsgemeinschaft (2018) List of MAK and BAT Values 2018. Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area. Report No. 54. Wiley-VCH, Weinheim, Germany, <https://onlinelibrary.wiley.com/doi/book/10.1002/9783527818396>
- [3] Hartwig A, MAK Commission (2017) Benzyl alcohol. The MAK Collection for Occupational Health and Safety, Vol. 2, No. 3. Wiley-VCH, Weinheim, Germany, <https://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb10051kske6318>
- [4] Greim (ed.) (2006) Benzylalkohol [MAK Value Documentation in German language]. Gesundheitsschädliche Arbeitsstoffe, Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten, 40th Issue. Wiley-VCH, Weinheim, Germany, <http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb10051d0040/pdf>
- [5] EN ISO 16017-1 (2001) Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 1: Pumped sampling. Beuth Verlag, Berlin, Germany
- [6] 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
- [7] EN 481 (1993) Workplaces atmospheres; size fraction definitions for measurement of airborne particles; German version EN 481:1993. Beuth Verlag, Berlin, Germany
- [8] EN 482 (2015) Workplace exposure – General requirements for the performance of procedures for the measurement of chemical agents; German version EN 482:2012+A1:2015. Beuth Verlag, Berlin, Germany
- [9] 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
- [10] DIN 32645 (2008) Chemical analysis – Decision limit, detection limit and determination limit under repeatability conditions – Terms, methods, evaluation. Beuth Verlag, Berlin, Germany

- [11] Heckmann P, Breuer D (2017) Calculation of the expanded uncertainty according to IFA, <http://www.dguv.de/ifa/praxishilfen/praxishilfen-gefahrstoffe/software-berechnung-der-erweiterten-messunsicherheit-nach-ifa/index.jsp>
- [12] Breuer D, Friedrich C, Möhlmann C, Dragan GC (2015) Das miniaturisierte Probenahme-system GGP-Mini zur gleichzeitigen Erfassung von Dampf/Tröpfchen-Gemischen schwer-flüchtiger Verbindungen – Ergebnisse von Labor- und Praxismessungen. *Gefahrstoffe – Re-inhaltung der Luft* Vol. 75(10), pp. 390–294, http://www.dguv.de/medien/ifa/de/pub/grl/pdf/2015_175.pdf

Appendix

Table 7 Retention times of selected solvents (Separation column 30 m DB-624, for analytical conditions see Section 4)

Retention time [min]	Substance	CAS number
3.26	Methanol	67-56-1
4.48	Ethanol	64-17-5
5.22	Acetone	67-64-1
5.63	2-Propanol	67-63-0
6.03	Methyl acetate	79-20-9
6.66	<i>tert</i> -Butyl alcohol	75-65-0
7.86	n-Hexane	110-54-3
8.91	1-Propanol	71-23-8
10.49	2-Butanone	78-93-3
10.85	Ethyl acetate	141-78-6
11.27	Tetrahydrofuran	109-99-9
11.37	<i>sec</i> -Butyl alcohol	78-92-2
12.03	Cyclohexane	110-82-7
12.98	Isobutyl alcohol	78-83-1
13.26	Isopropyl acetate	108-21-4
13.64	<i>n</i> -Heptane	142-82-5
14.33	1-Propylene glycol 1-methyl ether	107-98-2
14.42	<i>n</i> -Butyl alcohol	71-36-3
14.69	Methylcyclohexane	108-87-2
15.26	Propyl acetate	109-60-4
16.46	4-Methyl-2-pentanone	108-10-1
16.72	Toluene	108-88-3
17.01	<i>n</i> -Octane	111-65-9

1682 Air Monitoring Methods

Retention time [min]	Substance	CAS number
17.06	Isobutyl acetate	110-19-0
17.86	2-Hexanone	591-78-6
18.10	<i>n</i> -Butyl acetate	123-86-4
18.18	Cyclopentanone	120-92-3
18.92	Ethylene glycol monomethyl ether acetate	110-49-6
19.20	Ethylbenzene	100-41-4
19.38	m+p-Xylene	108-38-3; 106-42-3
19.46	<i>n</i> -Nonane	111-84-2
19.51	Propylene glycol 1-methyl ether-2-acetate	108-65-6
19.98	o-Xylene	95-47-6
20.16	Ethylene glycol monoethyl ether acetate	111-15-9
20.33	Cyclohexanol	108-93-0
20.56	Cumene	98-82-8
20.61	Ethylene glycol monobutyl ether	111-76-2
20.67	Cyclohexanone	108-94-1
21.17	<i>n</i> -Propyl benzene	103-65-1
21.44	1,3,5-Trimethylbenzene	108-67-8
21.47	<i>n</i> -Decane	124-18-5
21.64	Diisobutyl ketone	108-83-8
21.99	1,2,4-Trimethylbenzene	95-63-6
22.62	1,2,3-Trimethylbenzene	526-73-8
23.58	Benzyl alcohol	100-51-6
23.61	Ethylene glycol monobutyl ether acetate	112-07-2
24.48	Nitrobenzene	98-95-3
25.20	Tetrahydronaphthalene	119-64-2
26.58	2-Phenoxyethanol	122-99-6