

Amines – Determination of amines in workplace air using gas chromatography (headspace GC-MS)

Air monitoring method – Translation of the German version from 2024

Keywords

amines; air analyses; analytical method; workplace measurement; hazardous substance; headspace gas chromatography; mass spectrometry; headspace GC-MS; glass fibre filter; liquid extraction

R. Schmitt¹

W. Krämer¹

C. Kaus²

R. Hebisch^{3,*}

T. H. Brock^{4,*}

A. Hartwig^{5,*}

MAK Commission^{6,*}

¹ Method development, BASF SE, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany

² External verification, Institute for Occupational Safety and Health of the DGUV (IFA), German Social Accident Insurance (DGUV), Alte Heerstraße 111, 53757 Sankt Augustin, 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-Analge 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)

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Abstract

The working group “Air Analyses” of the German Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK Commission) developed and verified the presented analytical method. The analytical method described permits the determination of aliphatic amines in workplace air. The concentration range covers one tenth up to twice the currently valid occupational exposure limit value (OELV). Sampling is performed using a flow-regulated pump to draw a defined volume of air through a Millipore Aerosol Monitor type A system equipped with two glass fibre filters, which are acid-impregnated. The volumetric flow rate is 1 l/min and sampling time is 2 hours. The collected amines deposited on the filter are extracted with an aqueous solution and analysed by means of headspace gas chromatography with mass spectrometry. Quantitative determination is based on multiple-point calibrations with an internal standard. For an air sample volume of 120 litres, the relative limits of quantification are between 0.002 and 0.057 mg/m³. The measurement of the short-term exposure limit is also enabled. The recovery is between 95 and 104% and the expanded uncertainty is between 17 and 28% for a 2-hour sampling.

Method number	3
Application	Air analysis
Analytical principle	Headspace gas chromatography with mass spectrometry (headspace GC-MS)

1 Characteristics of the method

Precision:	Standard deviation (rel.): $s = 1.5\text{--}4\%$ Expanded uncertainty: $U = 17.3\text{--}27.5\%$ in the validated range and for $n = 6$ determinations
Limit of quantification:	0.002–0.057 mg/m ³ for an air sample volume of 120 l, a desorption volume of 5 ml, aliquots in a ratio of 1:20, an injection volume of 1 ml and a sampling period of 2 h
Recovery:	$\eta = 95\text{--}104\%$
Sampling recommendations:	Sampling period: 2 h Air sample volume: 120 l Volumetric flow rate: 1 l/min For short-term measurements: 15 min; 1 l/min

2 Description of the substance

Aliphatic amines are primary (e.g. *n*-butylamine, *sec*-butylamine, *tert*-butylamine, ethylamine, isobutylamine, isopropylamine, methylamine, *n*-propylamine, see [Figure 1](#)), secondary (e.g. diethylamine, diisopropylamine, dimethylamine, di-*n*-propylamine, methylisopropylamine, see [Figure 2](#)) or tertiary amines (e.g. *N*-ethyl-diisopropylamine, *N,N*-dimethyl-ethylamine, *N,N*-dimethylisopropylamine, *N,N*-dimethyl-*n*-propylamine triethylamine, trimethylamine, tri-*n*-propylamine, see [Figure 3](#)) that have alkyl substituents. Depending on the substitution, they occur as gaseous, liquid, oily, or solid substances with an unpleasant, in some cases fishy, odour. They are used in the production of tensides and pharmaceuticals, as flotation aids, bactericides, as corrosion and foam inhibitors and as additives (RÖMPP-Redaktion 2002). The method covers also benzylamine (see [Figure 1](#)), which is used for chemical synthesis, for the production of medicines, ammonium compounds and dyes and as an oil-soluble rust inhibitor (RÖMPP-Redaktion and Sefkow 2010).

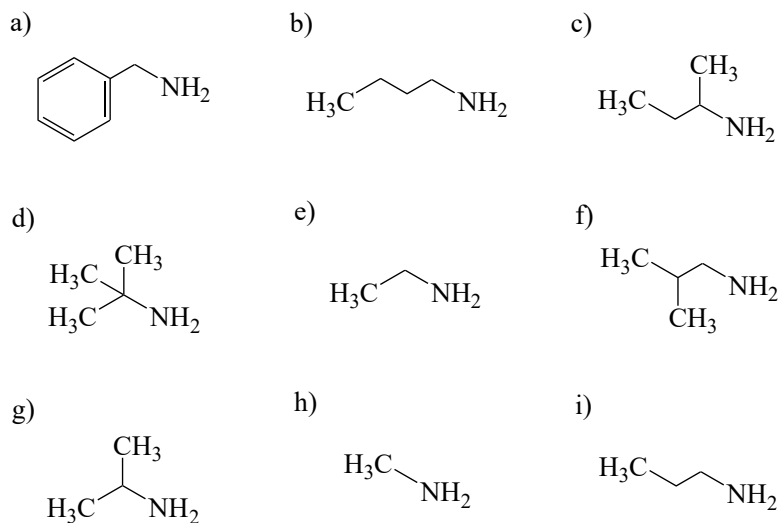


Fig. 1 Structural formulas of the investigated primary amines a) benzylamine, b) *n*-butylamine, c) *sec*-butylamine, d) *tert*-butylamine, e) ethylamine, f) isobutylamine, g) isopropylamine, h) methylamine and i) *n*-propylamine

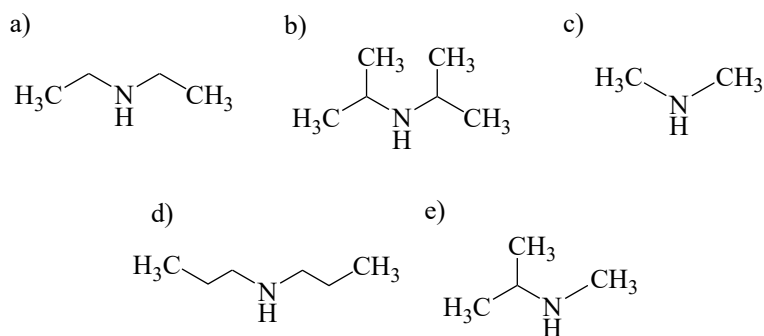


Fig. 2 Structural formulas of the investigated secondary amines a) diethylamine, b) diisopropylamine, c) dimethylamine, d) di-*n*-propylamine and e) methylisopropylamine

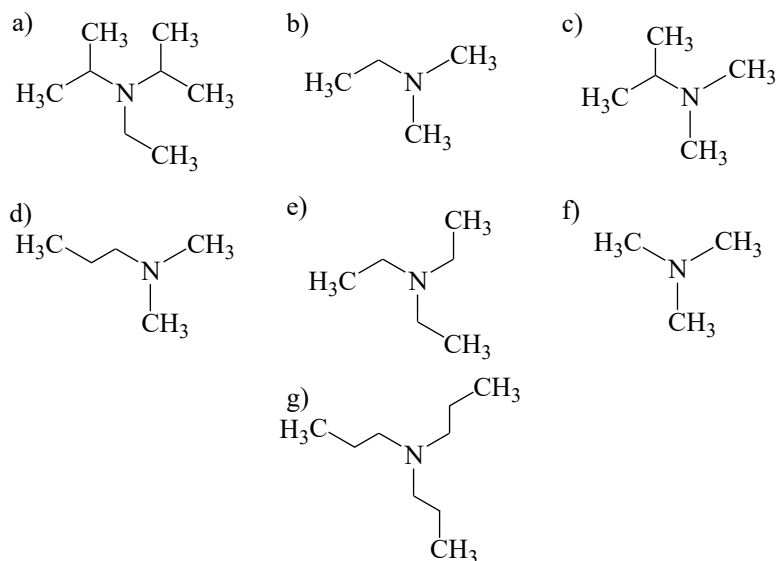


Fig. 3 Structural formulas of the investigated tertiary amines a) *N*-ethyldiisopropylamine, b) *N,N*-dimethylethylamine, c) *N,N*-dimethylisopropylamine, d) *N,N*-dimethyl-*n*-propylamine, e) triethylamine, f) trimethylamine and g) tri-*n*-propylamine

The MAK values and occupational exposure limit values (OELVs) as well as the peak limitation categories and excursion factors of the substances are listed in Tables 1 to 3 together with their physicochemical properties.

Tab. 1 Substance data and criteria of assessment for the investigated primary amines (ECHA 2023 a, b, h, k, l, q, r)

Name	Primary amines						
	Benzylamine	<i>n</i> -Butylamine	<i>sec</i> -Butylamine ^{a)}	<i>tert</i> -Butylamine	Ethylamine	Isobutylamine	Isopropylamine
CAS No.	100-46-9	109-73-9	13952-84-6	75-64-9	75-04-7	78-81-9	75-31-0
Molar mass [g/mol]	107.15	73.14	73.14	73.14	45.08	73.14	59.11
Physical state at 20 °C	liquid	liquid	liquid	liquid	gas	liquid	liquid
Density at 20 °C [g/cm ³]	0.981	0.737	0.722	0.69 ^{d)}	–	0.729	0.687
Vapour pressure at 20 °C [kPa]	0.06	10.2	22.13	49.6 ^{e)}	139.7 ^{e)}	15.9	63.1
Melting point [°C]	10	–47	n. s.	–68	n. s.	–82	–90
Boiling point at 1013 hPa [°C]	185	77	61.6	45.2	16.45	67.5	32
Flash point [°C]	65	–7.5	–17.5	–38	n. s.	–16.5	–37
Criteria of assessment	5.0 mg/m ³ ^{b)}						
OELV, Germany (AGS 2023) / MAK value, Germany (DFG 2023)	–	6.1 mg/m ³	6.1 mg/m ³	6.1 mg/m ³	9.4 mg/m ³	6.1 mg/m ³	12 mg/m ³
Peak limitation category (excursion factor), =momentary value= ^{e)} (AGS 2023; DFG 2023)	–	I(2); =2.5=	I(2); =2.5=	I(2); =2.5=	I; =2= / I(2)	I(2); =2.5=	I; =2= / I(2)

a) racemate

b) A valid MAK value or OELV is currently not available for this amine. The method was developed based on the assessment criterion of 5.0 mg/m³.

c) at 25 °C

d) at 24 °C

e) momentary value as a multiple of the MAK value or OELV

n. s.: not stated

Tab. 2 Substance data and criteria of assessment for the investigated primary and secondary amines (ECHA 2023 c, d, e, g, m, n, p)

Name	Primary amines		Secondary amines				
	Methyl-amine	<i>n</i> -Propyl-amine	Diethyl-amine	Diisopropyl-amine	Dimethyl-amine	Di- <i>n</i> -propylamine	Methylisopropyl-amine
CAS No.	74-89-5	107-10-8	109-89-7	108-18-9	124-40-3	142-84-7	4747-21-1
Molar mass [g/mol]	31.06	59.11	73.14	101.19	45.08	101.19	73.14
Physical state at 20 °C	gas	liquid	liquid	liquid	gas	liquid	liquid
Density at 20 °C [g/cm ³]	–	0.72	0.71	0.72	–	0.74	0.703
Vapour pressure at 20 °C [kPa]	314	33	31.6 ^{a)}	9.333	168.8	2.68 ^{a)}	37.6 ^{a)}
Melting point [°C]	–93	–83	–50	n. s.	–92.2	n. s.	n. s.
Boiling point at 1013 hPa [°C]	–6.5	47.2	55.5	83	7	109.3	50.67
Flash point [°C]	0	–35	–25.95	–13.45	–55	7	–30.5
Criteria of assessment		5.0 mg/m ^{3 b)}		5.0 mg/m ^{3 b)}		5.0 mg/m ^{3 b)}	5.0 mg/m ^{3 b)}
OELV, Germany (AGS 2023) / MAK value, Germany (DFG 2023)	6.4 mg/m ³	–	6.1 mg/m ³	–	3.7 mg/m ³	–	–
Peak limitation category (excursion factor), =momentary value= ^{c)} (AGS 2023; DFG 2023)	I(2); =2.5=	–	I(2); =2.5=	–	I(2)	–	–

a) at 25 °C

b) A valid MAK value or OELV is currently not available for this amine. The method was developed based on the assessment criterion of 5.0 mg/m³.

c) momentary value as a multiple of the MAK value or OELV

Tab. 3 Substance data and criteria of assessment for the investigated tertiary amines (ECHA 2023 f, i, j, o, s, t, u)

Name	Tertiary amines						
	<i>N</i> -Ethyl-diiso-propylamine	<i>N,N</i> -Dimethyl-ethylamine	<i>N,N</i> -Dimethylisopropylamine	<i>N,N</i> -Dimethyl- <i>n</i> -propylamine	Triethyl-amine	Trimethyl-amine	Tri- <i>n</i> -propylamine
CAS No.	7087-68-5	598-56-1	996-35-0	926-63-6	121-44-8	75-50-3	102-69-2
Molar mass [g/mol]	129.25	73.14	87.16	87.16	101.19	59.11	143.27
Physical state at 20 °C	liquid	liquid	liquid	liquid	liquid	gas	liquid
Density at 20 °C [g/cm ³]	0.754	0.66	0.713	0.701	0.73	–	0.756
Vapour pressure at 20 °C [kPa]	1.425	65.5 ^{a)}	18.99	17.25	7.2	190	4.3
Melting point [°C]	n. s.	n. s.	–136	n. s.	–115	–117	n. s.
Boiling point at 1013 hPa [°C]	128.33	36.3	66.25	65.75	90	2.9	156
Flash point [°C]	12	–25	–24.8	–20	–15	–6.66	33
Criteria of assessment	5.0 mg/m ^{3 b)}			5.0 mg/m ^{3 b)}			5.0 mg/m ^{3 b)}
OELV, Germany (AGS 2023) / MAK value, Germany (DFG 2023)	–	6.1 mg/m ³	3.6 mg/m ³	–	4.2 mg/m ³	4.9 mg/m ³	–
Peak limitation category (excursion factor); =momentary value= ^{c)} (AGS 2023; DFG 2023)	–	I(2); =2.5=	I(2)	–	I(2)	I(2); =2.5=	–

a) at 25 °C

b) A valid MAK value or OELV is currently not available for this amine. The method was developed based on the assessment criterion of 5.0 mg/m³.

c) momentary value as a multiple of the MAK value or OELV

n. s.: not stated

3 General principles

This analytical method is used to determine certain volatile amines (see [Tables 1 to 3](#)) in the workplace air in a concentration range from 0.1 times to twice the currently valid OELV for each amine (AGS 2023). An assessment criterion of 5 mg/m³ is assumed for substances that do not have a valid MAK value or OELV. As the method was being developed, the criteria of assessment for methylamine, diethylamine and *N,N*-dimethylethylamine were lowered from 12, 15 and 20 mg/m³. The criteria of assessment that are now valid were not taken into consideration for the validation of the method described here.

Samples are taken by drawing a defined volume of air from the breathing zone through a Millipore type A aerosol monitor using a suitable sampling pump. The amines are bound and retained on two acid-impregnated glass fibre filters that are separated by a supporting sieve. After sampling, the amines are desorbed using demineralised water. Potassium carbonate solution is then added to an aliquot of this solution and the amines are determined and quantified by headspace gas chromatography with mass spectrometry (headspace GC-MS).

4 Equipment, chemicals and solutions

4.1 Equipment

For sampling:

- Pump for personal sampling, flow rate 10.0 l/min (e.g. Gilian PP1 or Gilian PP5, supplied by DEHA Haan & Wittmer GmbH, 71296 Heimsheim, Germany)
- Filter holder, Ø 25 mm (e.g. Millipore Type A Aerosol Monitor, Order No. M000025A0, from Merck KGaA, 64293 Darmstadt, Germany)
- Volumetric flow meter (e.g. Gilibrator, supplied by DEHA Haan & Wittmer GmbH, 71296 Heimsheim, Germany)
- Glass fibre filters, Ø 25 mm (e.g. Munktell MG160, from Ahlstrom-Munksjö Oyj, FI-00101 Helsinki, Finland)

For sample preparation and the analytical determination:

- Ultrasonic bath (e.g. from Bandelin electronic GmbH & Co. KG, 12207 Berlin, Germany)
- Volumetric flasks 10 ml, 50 ml, 500 ml
- Beaker, 1 l
- Automatic piston pipette (e.g. HandyStep, from Brand GmbH + Co. KG, 97877 Wertheim, Germany)
- Gas-tight syringe, 2.5 ml (e.g. from Gerstel GmbH & Co. KG, 45473 Mülheim an der Ruhr, Germany)
- Headspace vials, 10 ml with cap with septum
- Gas chromatograph with mass spectrometer and headspace injector with autosampler (e.g. Agilent 6890 Plus with Agilent MSD 5973, from Agilent Technologies Deutschland GmbH, 76337 Waldbronn, Germany, and MPS 2 headspace sampler, from Gerstel GmbH & Co. KG, 45473 Mülheim an der Ruhr, Germany)
- Separation column (e.g. Restek Rtx-5 Amine, inner diameter (ID) 0.32 mm, length (L) 30 m, film thickness 5 µm, from Restek GmbH, 61348 Bad Homburg, Germany)

4.2 Chemicals

- Amines, purity/content see [Table 4](#) (e.g. from Sigma-Aldrich Chemie GmbH, 82024 Taufkirchen, Germany)
- Diethyl-d₁₀-amine, 98% (e.g. from Sigma-Aldrich Chemie GmbH, 82024 Taufkirchen, Germany)

- Sulphuric acid, $c = 0.25$ mol/l (e.g. from Merck KGaA, 64293 Darmstadt, Germany)
- Sulphuric acid, 98% (e.g. from Merck KGaA, 64293 Darmstadt, Germany)
- Potassium carbonate anhydrous, p.a. (e.g. J.T. Baker, from Thermo Fisher Scientific GmbH, 63303 Dreieich, Germany)
- Polyethylene glycol (PEG) 400 (e.g. Art. No.: 202398, from Sigma-Aldrich Chemie GmbH, 82024 Taufkirchen, Germany)
- Demineralised water

4.3 Solutions

The following solutions were prepared with the chemicals listed in [Section 4.2](#):

Potassium carbonate solution: (1 g K_2CO_3 /l in water)

About 600 ml of water are placed into a 1-l beaker. 600 g of potassium carbonate are dissolved in the water by stirring.

Impregnation solution: (0.5 mol sulphuric acid/l in water with 1% PEG 400):

200 ml of demineralised water are placed into a 250-ml volumetric flask and 6.9 ml of 98% sulphuric acid are added by pipette. 2.5 ml of PEG 400 are then added, the volumetric flask is filled to the mark with demineralised water and shaken.

The impregnation solution is stable for about a year.

Internal standard solution: (402 mg diethyl- d_{10} -amine/l in water)

Several millilitres of demineralised water are placed into a 100-ml volumetric flask. 50 μ l of diethyl- d_{10} -amine (density 0.804 g/ml), weighed to the nearest 0.1 mg, are pipetted into the flask. The flask is then filled with demineralised water and shaken.

Calibration stock solutions:

Several millilitres of sulphuric acid in a concentration of 0.25 mol/l are placed into a 20-ml volumetric flask. The amines are pipetted into the flask in the volumes given in [Table 4](#), weighed to the nearest 0.1 mg. The flasks are then filled to the mark with demineralised water and shaken.

Validation stock solutions:

The validation stock solutions containing amines in concentrations of about 9 to 47 mg/ml are prepared by dissolving the substances (see [Table 4](#)). For this purpose, several millilitres of methanol are placed into a 10-ml volumetric flask. The amines are added, weighed to the nearest 0.1 mg. Methanol must be used for some of the amines because they are not completely soluble in water at higher concentrations. However, the validation stock solutions for ethylamine, isopropylamine, methylamine, diethylamine and *N,N*-dimethylethylamine are prepared using only water without the addition of methanol (see note under [Table 4](#)). The volumetric flasks are then filled to the mark with water and shaken.

Tab. 4 Purity of the substances used, the volumes and sample weights for the preparation of the calibration and validation stock solutions and the resulting concentrations

Substance	Purity	Calibration stock solution, 20 ml			Validation stock solution, 10 ml	
		Amine volume [μ l]	Amine weight [mg]	Concentration ^{a)} [mg/ml]	Amine weight [mg]	Concentration ^{a)} [mg/ml]
Primary amines						
Benzylamine	99.0	30	34.5	1.71	287.1	28.43
<i>n</i> -Butylamine	99.0	60	35.1	1.74	125.8	12.45
<i>sec</i> -Butylamine	99.0	60	33.8	1.68	123.1	12.06
<i>tert</i> -Butylamine	99.5	60	28.6	1.42	118.3	11.77

Tab. 4 (continued)

Substance	Purity	Calibration stock solution, 20 ml			Validation stock solution, 10 ml	
		Amine volume [µl]	Amine weight [mg]	Concentration ^{a)} [mg/ml]	Amine weight [mg]	Concentration ^{a)} [mg/ml]
Ethylamine ^{b)}	70.0 ^{c)}	320	215.1	7.53	326.4	22.85
Isobutylamine	99.0	60	34.7	1.72	125.1	12.39
Isopropylamine ^{b)}	99.0	100	52.8	2.61	289.0	28.61
Methylamine ^{b)}	40.0 ^{c)}	650	474.2	9.48	784.7	31.39
<i>n</i> -Propylamine	99.0	60	38.5	1.89	122.2	11.98
Secondary amines						
Diethylamine ^{b)}	98.0	120	64.6	3.21	360.6	35.88
Diisopropylamine	99.5	60	30.0	1.49	122.7	12.15
Dimethylamine	41.2 ^{c)}	120	88.2	1.76	222.5	8.90
Di- <i>n</i> -propylamine	99.0	60	32.7	1.62	125.5	12.42
Methylisopropylamine	98.0	40	25.9	1.27	278.4	27.28
Tertiary amines						
<i>N</i> -Ethyl-diisopropylamine	98.0	40	29.2	1.43	297.1	29.12
<i>N,N</i> -Dimethylethylamine ^{b)}	99.0	100	48.3	2.34	479.3	47.45
<i>N,N</i> -Dimethylisopropylamine	99.7	50	28.8	1.48	93.0	9.02
<i>N,N</i> -Dimethyl- <i>n</i> -propylamine	99.9	60	33.8	1.68	120.4	11.99
Triethylamine	99.0	50	29.7	1.48	101.6	10.11
Trimethylamine	45.0 ^{c)}	120	91.8	1.29	428.7	12.00
Tri- <i>n</i> -propylamine	98.0	50	30.1	1.47	120.5	11.81

^{a)} The concentration is corrected by the purity of the amines used.

^{b)} The validation stock solution was prepared in several millilitres of water instead of methanol.

^{c)} Amines in gas form were tested as solutions in water.

The concentrations of the stock solutions for methylamine, diethylamine and *N,N*-dimethylethylamine were chosen based on the criteria of assessment of 12, 15 and 20 mg/m³, respectively, that were valid at the time the validation was performed. The concentrations of the stock solutions should be based on the criteria of assessment valid at the time of measurement.

5 Sampling and sample preparation

5.1 Preparation of the sample carriers

The glass fibre filters are impregnated prior to sampling. The filters are first immersed in impregnation solution and then dried on a large watch glass in a fume cupboard for at least 12 hours. 10 ml of impregnation solution are required to treat approximately 10 filters.

After preparation, the sample carriers are stable for six weeks.

The batch of glass fibre filters used must be checked for blank values.

5.2 Sampling

A Millipore filter holder is loaded with two impregnated filters that are separated by a spacer. To check the mean shift value, sampling is carried out over a period of about 2 hours at a flow rate of 1 l/min. This results in an air sample volume of 120 litres. Sampling can be carried out using either personal or stationary sampling procedures.

After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted volumetric flow rate is greater than $\pm 5\%$, the sample should be discarded (DIN 2023). The filter holders with the loaded filters are then sealed and transported to the laboratory.

Each series of samples should include a field blank. The only difference in the handling of this sample and the analytical samples is that an air sample is not drawn through the filter. The field blank is stored and processed in the same manner as the samples.

5.3 Sample preparation

Each loaded filter is transferred to a separate 10-ml headspace vial for desorption. After adding 5 ml of demineralised water to each sample, the vials are closed and treated for 30 minutes in an ultrasonic bath. The vials containing the filters must not be shaken, otherwise the filters will disintegrate and can only be removed by centrifuge! The amount of demineralised water can be adjusted for the determination of the short-term concentrations. The calculation must be corrected for any dilution used.

Solutions are placed into another 10-ml headspace vial in the following order:

1. 250 μ l of desorption solution
2. 25 μ l of internal standard solution
3. 5 ml of potassium carbonate solution

After adding the solutions, the vial is immediately closed with a cap with septum.

The field blank is prepared and analysed in the same manner as the collected samples.

A lab blank should also be determined.

6 Operating conditions

Apparatus:	Agilent 6890 Plus with Agilent 5973 inert MSD and Gerstel MPS 2 headspace sampler
Separation column:	Restek Rtx-5 Amine, ID 0.32 mm, L 30 m, film thickness 5 μ m
Temperature programme:	2 min at 20 °C, 10 °C/min up to 120 °C and 40 °C/min up to 200 °C, 2 min
Carrier gas:	Helium
Flow rate:	Constant 4.0 ml/min
Injector:	Split injection at a ratio of 1:5
Injector temperature:	150 °C
Injection volume:	1 ml
Sampler:	90 °C, 30 min, 750 rpm
Syringe temperature:	100 °C

Detector: Mass spectrometer

Spectrometric mode: Scan, 29–750 amu

7 Analytical determination

For the analytical determination, 1 ml of the gas in the headspace of each sample that was prepared as described in Section 5.3 is injected into the chromatograph and analysed under the conditions listed in Section 6. If the resulting concentrations lie above the calibration range, suitable dilutions are prepared and then analysed. In addition, the field blank and lab blank are analysed using the same procedure as for the samples.

8 Calibration

The calibration is carried out by placing a filter that has been impregnated as described in Section 5.1 into a 10-ml headspace vial. Calibration stock solution is pipetted onto the filter in the volumes listed in Table 7. The filters are then prepared and analysed as described in Sections 5, 6 and 7. The concentrations of the prepared calibration solutions are listed in Table 5. The spiked amounts are equivalent to concentrations in the air of 0.05 to 5.5 mg/m³ at an air sample volume of 120 l (see Table 5).

Tab. 5 Concentrations of the calibration solutions and the corresponding concentrations in air at 1 l/min and 120 l air volume and a sampling period of 2 hours

Substance	Calibration solution							
	1	2	3	4	5	6	7	8
	Volume of calibration stock solution [µl]							
	5	10	20	30	40	50	60	70
	Concentration of calibration solution ^{a)} [mg/l], air concentration ^{b)} [mg/m ³]							
Primary amines								
Benzylamine	1.71	3.42	6.84	10.3	13.7	17.1	20.5	23.9
	0.071	0.142	0.285	0.427	0.570	0.712	0.855	0.997
<i>n</i> -Butylamine	1.74	3.48	6.96	10.4	13.9	17.4	20.9	24.4
	0.072	0.145	0.290	0.435	0.580	0.725	0.870	1.02
<i>sec</i> -Butylamine	1.71	3.42	6.84	10.3	13.7	17.1	20.5	23.9
	0.071	0.142	0.285	0.427	0.570	0.712	0.855	0.997
<i>tert</i> -Butylamine	1.42	2.84	5.69	8.53	11.4	14.2	17.1	19.9
	0.059	0.118	0.237	0.355	0.474	0.592	0.711	0.829
Ethylamine	7.53	15.06	30.11	45.17	60.23	75.29	90.34	105.4
	0.314	0.627	1.255	1.882	2.510	3.137	3.764	4.392
Isobutylamine	1.72	3.43	6.86	10.3	13.7	17.16	20.6	24.0
	0.071	0.143	0.286	0.429	0.572	0.715	0.858	1.00
Isopropylamine	2.61	5.22	10.5	15.7	20.9	26.1	31.3	36.6
	0.109	0.218	0.435	0.653	0.871	1.09	1.31	1.52
Methylamine	9.48	19.97	37.94	56.90	75.87	94.84	113.8	132.8
	0.395	0.790	1.581	2.371	3.161	3.952	4.742	5.532

Tab. 5 (continued)

Substance	Calibration solution							
	1	2	3	4	5	6	7	8
	Volume of calibration stock solution [µl]							
	5	10	20	30	40	50	60	70
	Concentration of calibration solution ^{a)} [mg/l], air concentration ^{b)} [mg/m ³]							
<i>n</i> -Propylamine	1.89	3.77	7.54	11.3	15.1	18.9	22.6	26.4
	0.079	0.157	0.314	0.472	0.629	0.786	0.943	1.10
Secondary amines								
Diethylamine	3.21	6.43	12.9	19.3	25.7	32.1	38.6	45.0
	0.134	0.268	0.535	0.803	1.07	1.34	1.61	1.87
Diisopropylamine	1.49	2.97	5.95	8.92	11.9	14.9	17.8	20.82
	0.062	0.124	0.248	0.372	0.496	0.620	0.743	0.867
Dimethylamine	1.76	3.53	7.06	10.6	14.1	17.6	21.2	24.7
	0.074	0.147	0.294	0.441	0.588	0.735	0.882	1.03
Di- <i>n</i> -propylamine	1.62	3.24	6.47	9.71	12.9	16.2	19.4	22.6
	0.067	0.135	0.270	0.404	0.539	0.674	0.809	0.944
Methylisopropylamine	1.27	2.54	5.08	7.62	10.2	12.7	15.2	17.8
	0.053	0.106	0.212	0.317	0.423	0.529	0.635	0.740
Tertiary amines								
<i>N</i> -Ethyl-diisopropylamine	1.43	2.86	5.72	8.58	11.4	14.3	17.2	20.0
	0.060	0.119	0.238	0.358	0.477	0.596	0.715	0.834
<i>N,N</i> -Dimethylethylamine	2.39	4.78	9.55	14.3	19.1	23.9	28.7	33.4
	0.100	0.199	0.398	0.597	0.796	0.995	1.194	1.39
<i>N,N</i> -Dimethylisopropylamine	1.40	2.80	5.59	8.39	11.2	14.0	16.8	19.6
	0.058	0.116	0.233	0.349	0.466	0.582	0.699	0.815
<i>N,N</i> -Dimethyl- <i>n</i> -propylamine	1.68	3.36	6.72	10.1	13.4	16.8	20.2	23.5
	0.070	0.140	0.280	0.420	0.560	0.700	0.840	0.980
Triethylamine	1.48	2.96	5.91	8.87	11.8	14.8	17.7	20.7
	0.062	0.123	0.246	0.369	0.493	0.616	0.739	0.862
Trimethylamine	1.29	2.57	5.14	7.71	10.3	12.8	15.4	18.0
	0.054	0.107	0.214	0.321	0.428	0.535	0.642	0.749
Tri- <i>n</i> -propylamine	1.47	2.95	5.90	8.85	11.8	14.7	17.7	20.6
	0.061	0.123	0.246	0.369	0.491	0.614	0.737	0.860

^{a)} The volume of the calibration stock solution was not taken into consideration for the calculation of the concentrations.

^{b)} concentrations at an air sample volume of 120 l and a desorption solution volume of 5 ml

The calculated peak area quotients (ratio of the peak areas of the individual amines to the peak area of the internal standard diethyl-*d*₁₀-amine) are plotted against the respective concentrations. The calibration curves are linear in the examined concentration ranges. A control sample in the middle concentration range must be analysed every working day to check the calibration function.

A new calibration must be performed if the analytical conditions change or the results of the quality control measurements indicate that this is necessary.

9 Calculation of the analytical result

The corresponding mass X is determined in μg for each sample from the calibration function based on the peak areas. The corresponding value for the mass concentration (ρ) is calculated according to [Equation 1](#). [Equation 1](#) does not require correction if the recovery of $100 \pm 5\%$ is within the range of one tenth to twice the limit value.

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

The results are extrapolated to 20°C and 1013 hPa using [Equation 2](#).

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

where:

- ρ is the mass concentration of the substance in the air sample in mg/m^3 at t_a and p_a
- ρ_0 is the mass concentration of the substance in mg/m^3 at 20°C and 1013 hPa
- X is the mass of the substance in the analytical sample in μg
- V is the air sample volume in l (determined based on the volumetric flow rate and sampling period; in this case 120 l)
- η is the recovery
- t_a is the temperature during sampling in $^\circ\text{C}$
- p_a is the air pressure during sampling in hPa

The results obtained with each of the two loaded filters per sample are added together. Samples that contain amine concentrations outside of the calibration range must be diluted and then analysed again. Be aware that the calibration range does not always cover the upper limit.

10 Reliability of the method

The characteristics of the method were determined according to the standards DIN EN 482 (DIN 2021) and DIN 32645 (DIN 2008). The method has been fully validated.

10.1 Precision and recovery

The precision in the minimum measurement range according to DIN EN 482 (DIN 2021) and the recovery were analysed at three concentration levels in replicates of six (see [Table 6](#)). For this purpose, six Millipore type A aerosol monitors were connected to the pump via a six-port valve to individually adjust the flow to each sampler. A glass tube filled with a quartz wool plug was connected in front of each sampler using a short piece of PTFE tubing (to establish a direct connection).

To measure the concentrations at 0.1, 1 and 2 times the limit value, 5, 50 or 100 μl of each of the validation stock solutions were injected onto the quartz wool with a microlitre syringe. The mass of the injected substances was equivalent to the concentrations in air given in [Table 6](#) at an air sample volume of 120 l. Air was then drawn through each sampler for 2 hours at room temperature ($23\text{--}25^\circ\text{C}$) at a flow rate of 1 l/min. The relative humidity was 50–60%. The sample carriers were prepared and analysed as described in [Sections 5, 6 and 7](#).

The recovery listed in [Table 6](#) for each substance was obtained under the conditions described in [Section 6](#) at a volumetric flow rate of 1 l/min and a sampling period of 2 hours. The recovery was determined by comparing the measured

values with the results of the analysis of the reference solutions. The reference solutions were prepared by adding the corresponding amounts of validation stock solution to a corresponding amount of demineralised water. The mean recoveries were between 95.3 and 103.8%.

The relative standard deviations and their mean values are listed in Table 6 and were between 1.5 and 4.0%. The mean recoveries for the individual amines were between 95.3 and 103.8%.

Tab. 6 Validation concentrations and characteristics of the method

Substance	Validation concentrations ^{a)} [mg/m ³]			Recovery [%]				Relative standard deviation			
	c_1	c_2	c_3	η_1	η_2	η_3	η	s_1	s_2	s_3	s
Primary amines											
Benzylamine ^{b)}	0.592	5.922	11.844	95.8	96.6	95.3	95.9	4.5	4.7	2.7	4.0
<i>n</i> -Butylamine	0.519	5.189	10.379	95.9	100.2	101.1	99.1	1.4	2.7	3.5	2.5
<i>sec</i> -Butylamine	0.503	5.026	10.052	96.6	100.7	100.6	99.3	1.4	2.3	3.2	2.3
<i>tert</i> -Butylamine	0.491	4.905	9.811	99.7	101.4	100.0	100.4	2.0	2.0	3.1	2.4
Ethylamine	0.952	9.519	19.038	94.5	99.7	111.1	101.8	2.3	4.0	2.8	3.0
Isobutylamine	0.516	5.161	10.322	96.9	100.6	100.5	99.3	1.8	2.5	3.2	2.5
Isopropylamine	1.192	11.920	23.839	96.9	101.3	105.0	101.1	0.9	2.6	1.0	1.5
Methylamine ^{c)}	1.308	13.079	26.158	101.9	101.8	107.6	103.8	2.2	4.5	2.9	3.2
<i>n</i> -Propylamine ^{b)}	0.499	4.991	9.982	95.8	100.6	101.0	99.1	2.0	3.4	3.3	2.9
Secondary amines											
Diethylamine ^{c)}	1.495	14.949	29.897	98.8	100.3	102.8	100.6	1.8	2.6	0.8	1.7
Diisopropylamine ^{b)}	0.506	5.063	10.126	100.4	101.8	98.4	100.2	3.1	2.6	2.5	2.7
Dimethylamine	0.371	3.708	7.417	94.8	101.4	101.4	99.2	3.0	3.2	3.2	3.1
Di- <i>n</i> -propylamine ^{b)}	0.518	5.175	10.350	99.4	100.4	98.2	99.3	3.8	3.6	2.6	3.3
Methylisopropylamine ^{b)}	0.568	5.683	11.366	100.8	98.1	100.4	99.8	3.3	3.6	1.0	2.6
Tertiary amines											
N-Ethyl-diisopropylamine ^{b)}	0.607	6.066	12.132	95.8	100.0	100.7	98.8	4.9	3.2	2.2	3.4
<i>N,N</i> -Dimethylethylamine ^{c)}	1.977	19.769	39.538	101.9	103.4	103.8	103.0	3.6	3.5	1.3	2.8
<i>N,N</i> -Dimethylisopropylamine	0.376	3.757	7.513	99.3	101.3	98.6	99.7	3.5	2.0	2.5	2.7
<i>N,N</i> -Dimethyl- <i>n</i> -propylamine ^{b)}	0.499	4.995	9.990	99.8	101.7	98.2	99.9	3.5	2.0	2.4	2.6
Triethylamine	0.421	4.214	8.428	99.8	100.4	99.5	99.9	4.2	2.2	2.3	2.9
Trimethylamine	0.500	5.002	10.003	99.7	102.2	98.1	100.0	2.9	1.8	2.4	2.4
Tri- <i>n</i> -propylamine ^{b)}	0.492	4.920	9.839	102.0	100.9	98.1	100.3	4.9	2.1	3.5	3.5

^{a)} concentrations at an air sample volume of 120 l and a desorption solution volume of 5 ml

^{b)} A MAK value or OELV has not been established yet for this substance. For this reason, the validation was performed based on the assessment criterion of 5 mg/m³.

^{c)} The MAK value or OELV for this substance was lowered as the method was being developed. As a result, the validated range no longer fulfils the current requirements.

As the method was being validated, the criteria of assessment for methylamine, diethylamine and *N,N*-dimethylethylamine of 12, 15 and 20 mg/m³, respectively, were lowered to the current values. The validation described here is based on the previous criteria of assessment.

10.2 Expanded uncertainty

The expanded uncertainty was determined taking all relevant influencing parameters into consideration as stipulated in DIN EN 482 (DIN 2021). The main sources of uncertainty with respect to the results obtained by the method as a whole and thus also to the results of the analyses are uncertainties in the sampling procedure (e.g. air sample volume) and in the analytical procedure (e.g. complete desorption, scatter of the calibration function, fluctuations in recovery and reproducibility). The combined analytical uncertainty was calculated to be 10% and the expanded uncertainty for the entire method was between 17.3 and 27.5%.

10.3 Limit of quantification

As the method was being developed, the limit of quantification was calculated according to DIN 32645 (DIN 2008) using the calibration line method with a statistical certainty of $P = 95\%$ and $k = 2$. The absolute limit of quantification was between 0.19 and 68.8 μg . This is equivalent to a relative limit of quantification of 0.002 to 0.57 mg/m^3 of amine at an air sample volume of 120 l, a headspace vial with a volume of about 10 ml, a desorption solution volume of 5 ml, aliquots in the ratio of 1:20 and an injection volume of 1 ml. The exact values are shown in Table 7.

Tab. 7 Absolute and relative limits of quantification

Substance	Limit of quantification	
	absolute [μg]	relative ^{a)} [$\mu\text{g}/\text{m}^3$]
Primary amines		
Benzylamine	1.27	10.6
<i>n</i> -Butylamine	1.34	11.2
<i>sec</i> -Butylamine	1.54	12.8
<i>tert</i> -Butylamine	1.48	12.3
Ethylamine	8.18	68.2
Isobutylamine	2.53	21.1
Isopropylamine	1.57	13.1
Methylamine	68.8	573
<i>n</i> -Propylamine	2.88	24.0
Secondary amines		
Diethylamine	1.49	12.4
Diisopropylamine	1.56	13.0
Dimethylamine	3.76	31.3
Di- <i>n</i> -propylamine	0.82	6.8
Methylisopropylamine	0.52	4.3
Tertiary amines		
<i>N</i> -Ethyl-diisopropylamine	0.19	1.6
<i>N,N</i> -Dimethylethylamine	1.94	16.2
<i>N,N</i> -Dimethylisopropylamine	0.88	7.3
<i>N,N</i> -Dimethyl- <i>n</i> -propylamine	1.09	9.1
Triethylamine	0.83	6.9
Trimethylamine	0.62	5.2
Tri- <i>n</i> -propylamine	0.82	6.8

^{a)} concentrations at an air sample volume of 120 l and a desorption solution volume of 5 ml

10.4 Storage stability

The sample carriers loaded with amines can be stored for at least 14 days at room temperature.

11 Discussion

The method described here is used to determine primary, secondary and tertiary amines in the workplace air in a concentration range from one tenth to twice the currently valid OELV. The method is also suitable for monitoring compliance with the short-term value. The method was validated at room temperature (23 to 25 °C) and a relative humidity of 50 to 60%. If the conditions at the time of the measurement differ significantly from these conditions, the method must be validated for the actual conditions.

The criteria of assessment for methylamine, diethylamine and *N,N*-dimethylethylamine were lowered at the time the method was being developed. The validation described in this method is not based on the current criteria of assessment.

Comparative experiments were carried out to compare the method described here with method 2, which is also included in this issue (Kaus et al. 2024). The comparative experiments found good agreement between the values determined using the two methods.

Notes

Competing interests

The established rules and measures of the Commission to avoid conflicts of interest (www.dfg.de/mak/conflicts_interest) ensure that the content and conclusions of the publication are strictly science-based.

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