

# Amines – Determination of *N,N*-dimethylethylamine, *N,N*-dimethylisopropylamine, *N,N*-dimethyl-*n*-propylamine and triethylamine in workplace air using ion chromatography (IC)

## Air monitoring method – Translation of the German version from 2024

### Keywords

amines; air analyses; analytical method; workplace measurement; hazardous substance; ion chromatography; conductivity detection; IC; impregnated quartz fibre filter; extraction

C. Kaus<sup>1</sup>  
W. Krämer<sup>2</sup>  
R. Schmitt<sup>2</sup>  
R. Hebisch<sup>3,\*</sup>

T. H. Brock<sup>4,\*</sup>  
A. Hartwig<sup>5,\*</sup>  
MAK Commission<sup>6,\*</sup>

<sup>1</sup> Method development, Institute for Occupational Safety and Health of the DGUV (IFA), German Social Accident Insurance (DGUV), Alte Heerstraße 111, 53757 Sankt Augustin, Germany

<sup>2</sup> External verification, BASF SE, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany

<sup>3</sup> 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

<sup>4</sup> 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

<sup>5</sup> 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

<sup>6</sup> 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](mailto:luftanalysen-dfg@baua.bund.de)), A. Hartwig ([andrea.hartwig@kit.edu](mailto:andrea.hartwig@kit.edu)), T. H. Brock ([analytik@bgrci.de](mailto:analytik@bgrci.de)), MAK Commission ([arbeitsstoffkommission@dfg.de](mailto:arbeitsstoffkommission@dfg.de))

### Citation Note:

Kaus C, Krämer W, Schmitt R, Hebisch R, Brock TH, Hartwig A, MAK Commission. Amines – Determination of *N,N*-dimethylethylamine, *N,N*-dimethylisopropylamine, *N,N*-dimethyl-*n*-propylamine and triethylamine in workplace air using ion chromatography (IC). Air monitoring method – Translation of the German version from 2024. MAK Collect Occup Health Saf. 2024 Sep;9(3):Doc075. [https://doi.org/10.34865/am12144eb9\\_3or](https://doi.org/10.34865/am12144eb9_3or)

Manuscript completed:  
22 Mar 2023

Publication date:  
30 Sep 2024

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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. This analytical method is a validated measurement procedure for the determination of *N,N*-dimethylethylamine [598-56-1], *N,N*-dimethylisopropylamine [996-35-0], *N,N*-dimethyl-*n*-propylamine [926-63-6] and triethylamine [121-44-8] in workplace air. The concentration ranges cover one tenth up to twice the currently valid occupational exposure limit values in Germany (OELV) of 6.1 mg/m<sup>3</sup> for *N,N*-dimethylethylamine, of 3.6 mg/m<sup>3</sup> for *N,N*-dimethylisopropylamine and of 4.2 mg/m<sup>3</sup> for triethylamine. For *N,N*-dimethyl-*n*-propylamine the same OELV as for trimethylamine was anticipated. For sampling, a defined volume of air is drawn through an acid-impregnated quartz fibre filter. The flow rate is set to 0.5 l/min and sampling duration is 2 hours (which corresponds to a sampling volume of 60 l). The amines are extracted with 10 mM methanesulfonic acid solution and subsequently analysed using ion chromatography with conductivity detection. The quantitative determination is based on a cubic calibration function. The limits of quantification are between 0.022 and 0.047 mg/m<sup>3</sup> based on

an air sample volume of 60 l and an extraction volume of 10 ml. The recoveries are between 77 and 86%. The expanded uncertainties for the validation range are between 13.2 and 16.8%.

<b>Method number</b>	2
<b>Application</b>	Air analysis
<b>Analytical principle</b>	Ion chromatography with conductivity detection (IC)

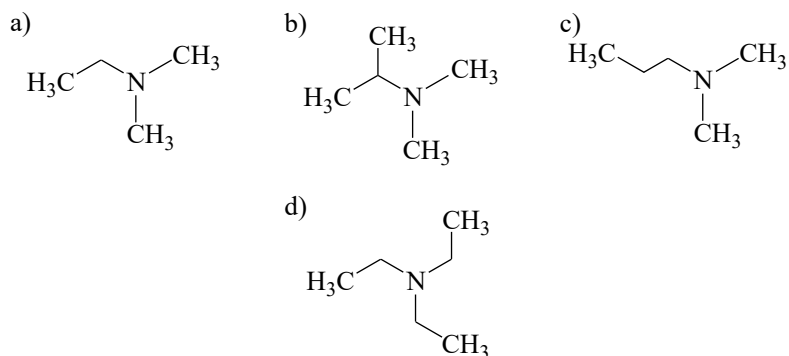
## 1 Characteristics of the method

<b>Precision:</b>	Coefficient of variation:	$V_x = 0.3\text{--}2.2\%$
	Expanded uncertainty:	$U = 13.3\text{--}16.2\%$
<b>Limit of quantification:</b>	<i>N,N</i> -Dimethylethylamine	0.034 mg/m <sup>3</sup>
	<i>N,N</i> -Dimethylisopropylamine	0.022 mg/m <sup>3</sup>
	<i>N,N</i> -Dimethyl- <i>n</i> -propylamine	0.030 mg/m <sup>3</sup>
	Triethylamine	0.047 mg/m <sup>3</sup>
	for an air sample volume of 60 l and an extraction volume of 10 ml	
<b>Recovery:</b>	<i>N,N</i> -Dimethylethylamine	84–86%
	<i>N,N</i> -Dimethylisopropylamine	80–82%
	<i>N,N</i> -Dimethyl- <i>n</i> -propylamine	77–85%
	Triethylamine	77–79%
<b>Sampling recommendations:</b>	Sampling period:	2 h
	Air sample volume:	60 l
	Volumetric flow rate:	0.5 l/min
	for short-term measurements:	15 min; 0.5 ml/min

## 2 Description of the substances

### *N,N*-Dimethylethylamine [598-56-1], *N,N*-dimethylisopropylamine [996-35-0], *N,N*-dimethyl-*n*-propylamine [926-63-6], triethylamine [121-44-8]

The aliphatic amines *N,N*-dimethylethylamine (DMEA), *N,N*-dimethylisopropylamine (DMIA), *N,N*-dimethyl-*n*-propylamine (DMPA) and triethylamine (TEA) (see [Figure 1](#)) are colourless to yellowish liquids with an odour of ammonia, fish and amines. All are volatile and form explosive mixtures with air. All of the listed amines induce adverse acute and chronic health effects (ECHA 2023 a, b, c, d).



**Fig. 1** Structural formulas of *N,N*-dimethylethylamine (DMEA), *N,N*-dimethylisopropylamine (DMIA), *N,N*-dimethylpropylamine (DMPA) and triethylamine (TEA)

DMEA is used, for example, as an adhesive and also as a curing agent in paper finishing (ECHA 2023 b). TEA serves as an alkaline solvent in organic synthesis and continues to be used in the manufacture of various plastics (ECHA 2023 d). All of the listed amines are utilised in foundries as catalysts for sand core production (cold-box method) (Wehde et al. 2008). Table 1 below offers an overview of other substance properties, the occupational exposure limit values (OELVs) and MAK values.

**Tab. 1** Substance data for *N,N*-dimethylethylamine (DMEA), *N,N*-dimethylisopropylamine (DMIA), *N,N*-dimethyl-*n*-propylamine (DMPA), triethylamine (TEA) (ECHA 2023 a, b, c, d)

Name	DMEA	DMIA	DMPA	TEA
CAS No.	598-56-1	996-35-0	926-63-6	121-44-8
Molar mass [g/mol]	73.14	87.16	87.16	101.19
Physical state at 20 °C	liquid	liquid	liquid	liquid
Density at 20 °C [g/cm <sup>3</sup> ]	0.66	0.713	0.701	0.73
Vapour pressure at 20 °C [kPa]	65.5 <sup>a)</sup>	18.99	17.25	7.2
Melting point [°C]	n. s.	-136	n. s.	-115
Boiling point at 1013 hPa [°C]	36.3	66.25	65.75	90
Flash point [°C]	-25	-24.8	n. s.	-15
Assessment criteria			4.2 mg/m <sup>3</sup> <sup>b)</sup>	
OELV, Germany (AGS 2023 b)				4.2 mg/m <sup>3</sup> , 1 ml/m <sup>3</sup>
MAK value, Germany (DFG 2023)	6.1 mg/m <sup>3</sup> , 2 ml/m <sup>3</sup>	3.6 mg/m <sup>3</sup> , 1 ml/m <sup>3</sup>	-	4.2 mg/m <sup>3</sup> , 1 ml/m <sup>3</sup>
Peak limitation category (excursion factor); =peak limitation= <sup>c)</sup> (AGS 2023 b; DFG 2023)	I (2); =2.5=	I (2)	-	I (2)

n. s.: not stated

<sup>a)</sup> at 25 °C

<sup>b)</sup> Valid MAK or OELV values are currently not available for DMPA. The method was developed based on the DNEL (derived no-effect level established in compliance with REACH) of 4.2 mg/m<sup>3</sup> (IFA 2022)

<sup>c)</sup> momentary value as a multiple of the MAK value or OELV

### 3 General principles

This method is used to quantitatively determine the concentrations of the short-chain aliphatic amines DMEA, DMIA, DMPA and TEA in the workplace air. It is suitable for making determinations according to the Technical Rules for Hazardous Substances 402 (TRGS 402) (AGS 2023 a) and fulfils the requirements set forth by DIN EN 482 (DIN 2021 a) and DIN EN ISO 22065 (DIN 2021 b).

This analytical method can be used to determine the concentrations of certain aliphatic amines in the workplace air in a range from one tenth to twice the currently valid MAK values, OELV or assessment criteria. The assessment criteria used for validation are listed in Table 1.

Samples are taken by drawing a defined volume of air through a quartz fibre filter impregnated with methanesulfonic acid (MSA) using a suitable flow-regulated pump. After desorption with a solution of methanesulfonic acid and ion chromatography (IC), the analytes are identified by conductivity detection. Quantitative determination is based on multiple-point calibrations with external standards.

## 4 Equipment, chemicals and solutions

### 4.1 Equipment

For sampling:

- Pump for personal sampling suitable for a flow rate of 0.5 l/min (e.g. GilAir Plus, from DEHA Haan & Wittmer GmbH, 71296 Heimsheim, Germany)
- Air volume flow meter (e.g. TSI Flowmeter 4146, from TSI GmbH, 52068 Aachen, Germany)
- GSP sampling head with an intake cone for a flow rate of 0.5 l/min for personal sampling systems for hazardous substances (e.g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- Silicon tube
- Quartz fibre filter, Ø 37 mm (e.g. Millipore, Art. No. AQFA03700, from Merck KGaA, 64293 Darmstadt, Germany)
- Filter capsules for personal sampling systems for hazardous substances, plastic, for 37-mm filters with covers (e.g. GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- Plastic tweezers
- 15-ml narrow-neck bottle made of polyethylene (PE)

For sample preparation and analytical determination:

- Volumetric flasks made of glass, nominal volumes 10 to 1000 ml
- Variable positive displacement pipettes, nominal volumes 0.1 to 5 ml
- 10-ml disposable syringes, Luer-Lock connector, with disposable cannulas
- 1.5-ml short-thread autosampler vials made of polypropylene (PP)
- Screw caps with silicon PTFE (polytetrafluoroethylene) septum and 6-mm hole for vials
- Ultrasonic bath
- Ultrapure water system for the preparation of ultrapure water ( $\rho \geq 18.2 \text{ M}\Omega \times \text{cm}$  at 25 °C) (e.g. Millipore-Q-Gradient with Elix 3UV, from Merck Chemicals GmbH, 64293 Darmstadt, Germany)
- Ion chromatograph with conductivity detector (e.g. Dionex Integriion HPIC, from Thermo Fisher Scientific GmbH, 63303 Dreieich, Germany)

- Pre-column and analytical column for cation exchange, suitable for separating amines (e.g. Thermo Scientific Dionex IonPac CG16 (ID 3 mm, L 50 mm) & Dionex IonPac CS16 (ID 3 mm, L 250 mm), from Thermo Fisher Scientific GmbH, 63303 Dreieich, Germany)

## 4.2 Chemicals

- Methanesulfonic acid (MSA),  $\geq 99\%$  (e.g. from Merck KGaA, 64271 Darmstadt, Germany)
- Methanesulfonic acid, cartridge for the generation of MSA eluents (e.g. Thermo Scientific Dionex EGC 500, from Thermo Fisher Scientific GmbH, 63303 Dreieich, Germany)
- *N,N*-Dimethylethylamine (DMEA),  $\geq 99\%$  (e.g. from Merck KGaA, 64271 Darmstadt, Germany)
- *N,N*-Dimethylisopropylamine (DMIA),  $\geq 99\%$  (e.g. from Merck KGaA, 64271 Darmstadt, Germany)
- *N,N*-Dimethyl-*n*-propylamine (DMPA),  $\geq 97\%$  (e.g. from Pfaltz & Bauer Inc., Waterbury, CT, USA)
- Triethylamine (TEA),  $\geq 99\%$  (e.g. Merck KGaA, 64271 Darmstadt, Germany)
- Certified standard solution, amines (matrix water), as single-component or multi-component standards, 1000 mg/l, for the calibration (e.g. custom-made, from Neochem GmbH, 55294 Bodenheim, Germany)
- Certified standard solution, amines (matrix methanol), as single-component or multi-component standards, 1000 mg/l, for the accuracy assessment (e.g. from LGC Standards GmbH, 46485 Wesel, Germany)

Amines in pure form are required only when the loading experiments are carried out with a test gas or no standard solutions are available.

## 4.3 Solutions

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

**Extraction solution:** (20 mmol MSA/l in water):

1380  $\mu$ l of MSA ( $\geq 99\%$ ) are pipetted into a 1000-ml volumetric flask. The volumetric flask is then filled to the mark with ultrapure water and shaken. The extraction solution is freshly prepared every week.

**Impregnation solution:** (313 mmol MSA/l in water):

2070  $\mu$ l of MSA ( $\geq 99\%$ ) are pipetted into a 100-ml volumetric flask. The volumetric flask is then filled to the mark with ultrapure water and shaken. The impregnation solution is stable for 14 days.

**Multi-component stock solution:** (1000 mg/l):

This solution is needed only if the calibration is not carried out with certified standard solutions (see [Section 4.2](#)).

About 100 mg each of DMEA, DMIA, DMPA and TEA are weighed into a 100-ml volumetric flask using an analytical balance. The volumetric flask is then filled to the mark with extraction solution and shaken.

The multi-component stock solution is stable for at least 4 months if stored in the refrigerator.

## 4.4 Calibration and control solutions

**Calibration solutions:** (2.0–20.0 mg/l):

To prepare the calibration solutions, first extraction solution is placed into a 25-ml volumetric flask (see [Section 4.3](#)). A certified standard solution (see [Section 4.2](#)) is then added by pipette in the amounts given in [Table 4](#). The flask is then filled with extraction solution and shaken.

As an alternative, the ten calibration solutions are prepared by following the same procedure as described above but beginning with the multi-component stock solution.

**Tab. 2** Pipetting scheme for the preparation of the calibration solutions

Calibration solution	Volume of standard solution [ $\mu$ l]	Concentration of DMEA, DMIA, DMPA and TEA [mg/l]
1	50	2.0
2	100	4.0
3	150	6.0
4	200	8.0
5	250	10.0
6	300	12.0
7	350	14.0
8	400	16.0
9	450	18.0
10	500	20.0

**Control samples:** (10 mg/l):

To check for precision within an analytical series, a control sample is prepared using a standard with a concentration in the middle of the calibrated range. The control solution is prepared in the same manner as calibration solution 5.

If stored in the refrigerator, the calibration and control solutions are stable for at least 4 months.

**Samples for accuracy assessments:** (5, 10 and 18 mg/l):

The control samples used to assess the accuracy of the calibration are prepared with commercially available certified standard solutions for the respective amines (see [Section 4.2](#)). The samples used to assess accuracy are prepared in the same manner as calibration solutions 2, 5 and 9.

The samples used for accuracy assessments should be prepared fresh every working day.

## 5 Sampling and sample preparation

### 5.1 Preparation of the sample carriers

The quartz fibre filters must be impregnated before they can be used as a collection medium. For this purpose, the filters are completely immersed in impregnation solution and then dried at room temperature for at least 12 hours.

The prepared sample carriers can be used for two weeks.

The batch of quartz fibre filters intended for use must be checked for blank values.

### 5.2 Sampling

Samples are collected by stationary or personal sampling. The samples taken by personal sampling are collected within the breathing zone. The inlet of the sampling head must remain unobstructed during sampling.

Samples are collected by inserting an impregnated quartz fibre filter into the sampling head of the GSP sampling system and connecting a flow-regulated pump. The pump is used to draw an air sample through the filter at a flow rate of 0.5 l/min. The recommended sampling time is two hours, which is equivalent to an air sample volume of 60 l. The loaded sample carrier is removed from the sampling head immediately after the sample is collected. Tweezers are used to transfer the carrier into a narrow-neck bottle filled with 10 ml of extraction solution.

The flow rate must be checked for constancy after sampling. If the deviation from the adjusted flow rate is larger than  $\pm 5\%$ , the measurement should be repeated (DIN 2023). The filter cassette with the loaded filter is sealed with its cover and transported to the laboratory.

A field blank should be included in each series of samples. 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 prepared and analysed in the same manner as the samples.

### 5.3 Sample preparation

In the laboratory, the narrow-neck bottle is treated in an ultrasonic bath for 15 minutes at room temperature. The supernatant solution is removed using a disposable syringe with cannula, filtered into another vessel via a syringe filter and then transferred into an autosampler vial. The filtered solution is stored until the analysis of the sample has been completed in case the measurement needs to be repeated or the sample needs to be diluted. The autosampler vial is closed with a screw cap and analysed in duplicate under the conditions described in [Section 6](#).

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

<b>Apparatus:</b>	Dionex Integration HPIC with eluent generator
<b>Pre-column:</b>	Dionex Ion Pac AG CG16, ID 3 mm, L 50 mm
<b>Separation column:</b>	Dionex Ion Pac AS CS16, ID 3 mm, L 250 mm
<b>Column temperature:</b>	60 °C
<b>Autosampler temperature:</b>	20 °C
<b>Detector:</b>	conductivity detector
<b>Suppressor:</b>	Cation Dynamically Regenerated Suppressor CDRS 600, 2 mm
<b>Suppressor current:</b>	58 mA
<b>Mobile phase:</b>	55 mM MSA isocratic
<b>Flow rate:</b>	0.36 ml/min
<b>Injection volume:</b>	30 µl
<b>Run time:</b>	35 min

Under the given conditions, the retention time of DMEA was about 10.2 min, of DMIA about 13.2 min, of DMPA 15.0 min and of TEA 18.0 min.

## 7 Analytical determination

For the analytical determination, 30 µl of each of the samples prepared as described in [Section 5.3](#) are injected into the ion chromatograph and analysed in duplicate under the conditions given in [Section 6](#). If the resulting concentrations lie above the calibration range, suitable dilutions are prepared and analysed.

The control sample that was prepared for the assessment of precision (see [Section 4.4](#)) is analysed before and after running each series of samples. A new standard must be used if the results obtained with the control sample deviate by more than 5% from the nominal value. The analysis is carried out again with the new standard. If the results deviate again from the nominal value, a new calibration must be performed.

The prepared field blanks are analysed in the same manner as the analytical samples.

Figure 2 shows an example of an ion chromatogram of two calibration solutions (2 mg/l and 20 mg/l) with all amines described in this method.

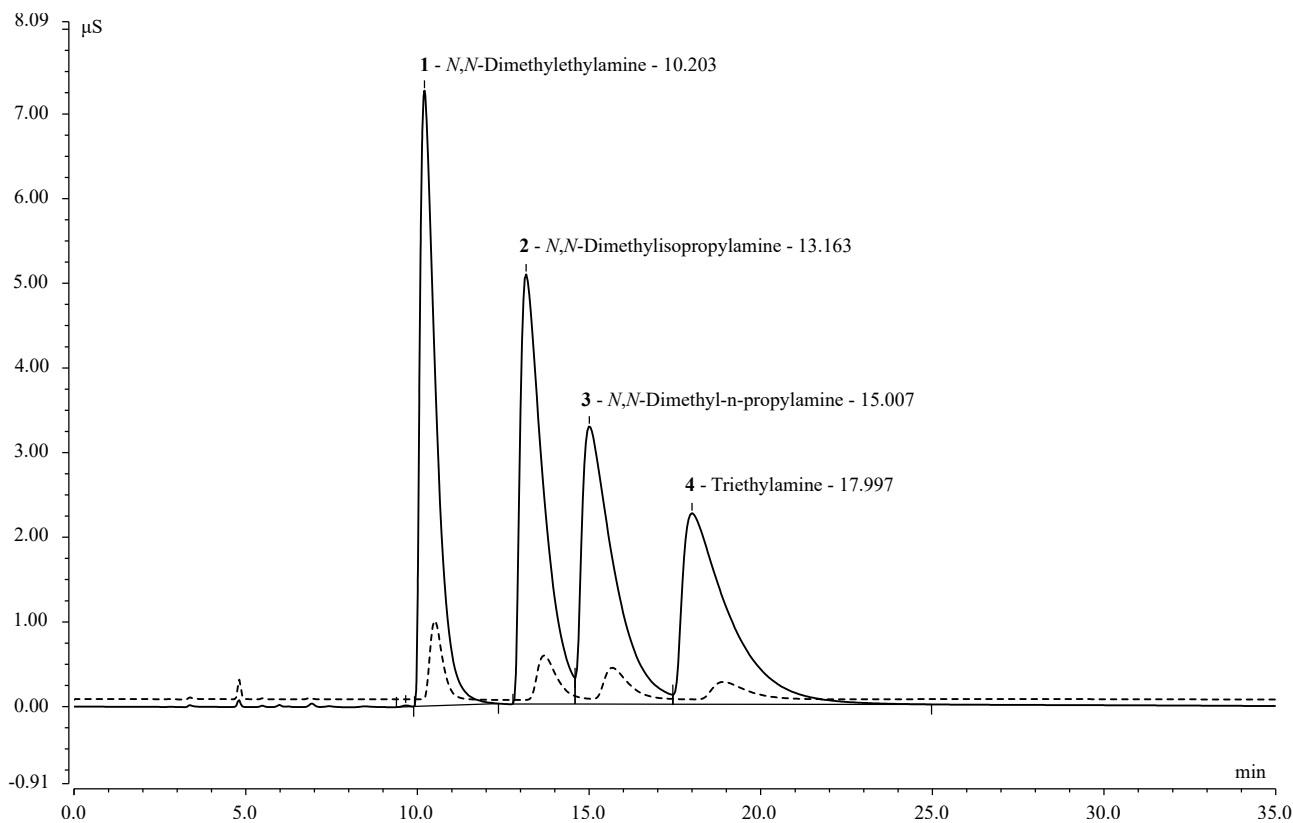


Fig. 2 Example of an ion chromatogram of the calibration standards with the aliphatic amines DMEA, DMIA, DMPA and TEA in concentrations of 2 mg/l (dashed) and 20 mg/l (solid)

## 8 Calibration

The calibration standards described in Section 4.4 are used to derive the calibration functions. 30  $\mu$ l of each of the calibration solutions are injected into the injection loop and analysed as described in Sections 6 and 7. The resulting peak areas are plotted against the respective concentrations. A suitable software programme is used to derive the calibration function. Under the given conditions, this is equivalent to a second-order polynomial (see Section 9).

To assess accuracy, three samples (see Section 4.4) are measured directly after each calibration and analysed. These samples contain analytes in concentrations that are approximately in the lower third, in the middle and in the upper third of the range of the respective calibration. The calibration is considered accurate if the concentration of the standard solution used to assess accuracy deviates by at most  $\pm 5\%$  from the nominal concentration.

In the examined concentration range, the calibration functions are generally second-order polynomials and should be checked regularly as part of routine analysis (see Section 6). A new calibration must be performed if the analytical conditions change or the results of the quality control indicate that this is necessary.



## 9 Calculation of the analytical result

The quantification is based on the relationship between the concentration and the peak area that is determined during calibration. To analyse the amines by ion chromatography, the concentration in the air at the workplace is calculated based on the second-order polynomial expressed as [Equation 1](#).

$$A = ac^2 + bc + d \quad (1)$$

The concentration of the respective amine in the air sample is calculated based on [Equation 2](#), taking into consideration the extraction volume and the air sample volume as well as, if applicable, the dilution.

$$\rho = \frac{c \times F \times f_d}{\eta \times V_{air}} \quad (2)$$

where:

- $A$  is the peak area
- $c$  is the mass concentration of the substance in the analytical sample in mg/l
- $a$  is the function coefficient
- $b$  is the function coefficient
- $d$  is the function coefficient
- $\rho$  is the mass concentration of the amine in the air sample in mg/m<sup>3</sup>
- $f_d$  is the dilution factor
- $F$  is the factor for conversion to the extraction volume of the analytical sample in l (in this case 0.01)
- $V_{air}$  is the air sample volume in m<sup>3</sup> (determined from the volumetric flow rate and the sampling time, in this case 0.060 m<sup>3</sup>)
- $\eta$  is the recovery

## 10 Reliability of the method

The characteristics of the method were determined according to DIN 32645 ([DIN 2008 a](#)), DIN EN 482 ([DIN 2021 a](#)) and DIN EN ISO 22065 ([DIN 2021 b](#)).

To determine the characteristics of the method, dynamic test gases were generated with amines. Samples were taken at different concentrations, different levels of relative humidity and different temperatures. The test gas contained all of the amines included in this method; the concentrations were dependent on their specific assessment criteria. A sample volume of 60 l of air was drawn through the sample carrier at a flow rate of 0.5 l/min. Unless specified otherwise, the test gas was loaded onto eight sample carriers for each experiment. The loaded filters were processed and analysed as described in [Section 5.3](#).

### 10.1 Recovery

To determine what effect exposure concentration has on the results, the impregnated filters were loaded with test gases containing different concentrations (see [Section 10](#)). The concentrations were chosen based on the specific assessment criteria for each analyte. In the concentration range of one tenth to twice the assessment criteria, the mean recovery was between 77% and 86% depending on the amine (see [Table 3](#)). This was taken into consideration for the calculation of the results (see [Equation 2](#)).

**Tab. 3** Results of the experiments carried out to determine the recovery

Compound	Recovery [%]			
	0.1 assessment criteria	0.5 assessment criteria	1 assessment criteria	2 assessment criteria <sup>a)</sup>
DMEA	86	86	87	84
DMIA	82 <sup>b)</sup>	82	83	80
DMPA	85	81	82	77
TEA	79 <sup>b)</sup>	80	81	77

<sup>a)</sup> for n = 7 determinations

<sup>b)</sup> The recovery was not calculated for 0.1 assessment criteria because this series was an outlier. The data for recovery at 0.3 assessment criteria was therefore used instead.

The recovery for samples prepared by spiking was > 90%. However, the loaded samples tested in the dynamic test gas stream more closely reflect the actual sampling situation; for this reason, the recovery from these experiments was used for the calculation of the results.

## 10.2 Repeatability

The coefficients of variation  $V_x$  for each concentration (see Table 4) were calculated from the standard deviations of the recovery experiments (see Section 10.1).

**Tab. 4** Coefficients of variation for the sampling results

Compound	Coefficient of variation [%]			
	0.1 assessment criteria	0.5 assessment criteria	1 assessment criteria	2 assessment criteria <sup>a)</sup>
DMEA	2.2	1.2	0.3	0.5
DMIA	0.7 <sup>b)</sup>	1.3	0.3	0.4
DMPA	1.9	1.2	0.3	0.5
TEA	0.7 <sup>b)</sup>	1.4	0.5	0.5

<sup>a)</sup> for n = 7 determinations

<sup>b)</sup> The coefficient of variation was not calculated for 0.1 assessment criteria because this series was an outlier in the recovery experiments. The coefficient of variation at 0.3 assessment criteria was therefore used instead.

## 10.3 Expanded uncertainty of the entire procedure

The expanded uncertainty of the method was determined based on the standard DIN EN ISO 22065 (DIN 2021 b). All steps of the method were taken into consideration such as sample collection, transport and storage, environmental influences as well as uncertainties arising from analysis. The combined, concentration-dependent uncertainties for the entire method were calculated by combining the contributions from all sources of uncertainty. The percentages listed in Table 5 for the expanded uncertainty for the entire method were obtained by multiplying the various uncertainties arising from sampling and analysis, etc., with the expansion factor  $k=2$ . The calculation was carried out using the Excel tool provided by IFA for the calculation of expanded uncertainty (IFA n.d.).

**Tab. 5** Determination of the expanded uncertainty  $U$ 

Compound	Expanded uncertainty [%]			
	0.1 assessment criteria	0.5 assessment criteria	1 assessment criteria	2 assessment criteria <sup>a)</sup>
DMEA	15.1	14.9	15.0	15.0
DMIA	14.4 <sup>b)</sup>	14.5	14.4	14.4
DMPA	16.8	14.5	16.7	16.7
TEA	13.2 <sup>b)</sup>	13.4	13.2	13.2

<sup>a)</sup> for  $n=7$  determinations

<sup>b)</sup> The expanded uncertainty was not calculated for 0.1 assessment criteria because the series was an outlier in the recovery experiments. The expanded uncertainty at 0.3 assessment criteria was therefore used instead.

For the described method, the mean values for expanded uncertainty were 15.0% for DMEA, 14.4% for DMIA, 16.2% for DMPA and 13.3% for TEA in the analysed range from 0.1 or 0.3 times the limit value up to twice that value and a sampling period of 2 hours.

## 10.4 Influence of humidity

The influence of relative humidity on recovery was examined by loading filters with test gas at varying levels of relative humidity (20% and 80%). The experiment was carried out with two different concentrations. The concentrations were based on the respective assessment criteria and were equivalent to twice that value.

The relative humidity did not have a noticeable influence on recovery.

## 10.5 Influence of temperature

The influence of temperature on recovery was examined by loading filters with test gas at different temperatures (10 °C and 40 °C). The concentration was based on the respective assessment criteria and was equivalent to twice that value.

Temperature was found to influence recovery. At a temperature of 10 °C, the recovery was, on average, about 6% lower than the recovery at 40 °C. This effect was taken into consideration for the expanded uncertainty. It was not taken into consideration for the calculation of the results because temperatures at the workplace are usually around the standard room temperature or slightly higher.

## 10.6 Limit of quantification

The limit of quantification was determined using the blank value method according to DIN 32645 (DIN 2008 b)

To confirm the limit of quantification for the entire method, a sample was taken at one tenth of the assessment criteria. This concentration is considered verified if the value calculated for the limit of quantification using the blank value method is lower. This results in the values for the limit of quantification listed in Table 6 for an air sample volume of 60 l and 10 ml of extraction solution.

**Tab. 6** Limit of quantification for the method determined using the blank value method

Compound	Limit of quantification [mg/m <sup>3</sup> ] <sup>a)</sup>
DMEA	0.034
DMIA	0.022
DMPA	0.030
TEA	0.047

<sup>a)</sup> for an air sample volume of 60 l

## 10.7 Storage stability

To determine storage stability, several filters were loaded with two different concentrations and analysed at different time points after sampling. The concentrations were based on the respective assessment criteria and were equivalent to one tenth and twice that value. The filters were loaded at a temperature of 20 °C and a relative humidity of the test gas of 80%.

The loaded filters were covered with a layer of 10 ml of extraction solution, stored at room temperature and prepared and analysed on days 4, 7, 14 and 21 as described in Sections 5 and 6. The determinations for each concentration and test day were taken at least in replicates of three. The reference (day 0) was analysed in a replicate of six. The recovery for the amines remained unchanged at both examined concentrations.

Therefore, a storage stability of at least 21 days is confirmed for all amines examined in this method.

## 10.8 Interference

The ion chromatographic method is not specific to DMIA under the given working conditions because there is co-elution with *N,N*-diethylmethylamine (CAS No.: 616-39-7). Individual quantification is not possible if both substances occur at the same time. Other sources of interference are not known.

## 11 Discussion

The method described above is suitable for determining DMEA, DMIA, DMPA and TEA in the workplace air in a concentration range from one tenth to twice the assessment criteria of 6.1 mg/m<sup>3</sup> for DMEA, 3.6 mg/m<sup>3</sup> for DMIA and 4.2 mg/m<sup>3</sup> for DMPA and TEA. The method is also suitable for monitoring compliance with the short-term value.

Comparative experiments were carried out to compare the method described here with method 3, which is also included in this issue (Schmitt 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](http://www.dfg.de/mak/conflicts_interest)) ensure that the content and conclusions of the publication are strictly science-based.

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