The MAK Collection for Occupational Health and Safety

Alkanolamines – Method for the determination of 11 alkanolamines in workplace air using ion chromatography (IC)

Air Monitoring Method – Translation of the German version from 2018

D. Breuer[1], M. Blaskowitz[1], P. Ansari Eshlaghi[2], R. Hebisch[3,*], T.H. Brock[4,*], A. Hartwig[5,*], MAK Commission[6,*]

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

[2] *External verification, Austrian Workers' Compensation Board (AUVA), Head office, Adalbert-Stifter-Straße 65, 1200 Wien, Austria*

[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: alkanolamines; air analyses; analytical method; workplace measurement; hazardous substance; ion chromatography; conductivity detection; IC; quartz fibre filter; liquid desorption

Citation Note: Breuer D, Blaskowitz M, Ansari Eshlaghi P, Hebisch R, Brock TH, Hartwig A, MAK Commission. Alkanolamines – Method for the determination of 11 alkanolamines in workplace air using ion chromatography (IC). Air Monitoring Method – Translation of the German version from 2018. MAK Collect Occup Health Saf [Original edition. Weinheim: Wiley-VCH; 2019 Jan;4(1):247–271]. Corrected republication without content-related editing. Düsseldorf: German Medical Science; 2025. https://doi.org/10.34865/am14143e1919_w

Republished (online): 30 Apr 2025

Originally published by Wiley-VCH Verlag GmbH & Co. KGaA; https://doi.org/10.1002/3527600418.am14143e1919

Manuscript completed: 01 May 2017

Published (online): 30 Jan 2019

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

Alkanolamines – Method for the determination of 11 alkanolamines in workplace air using ion chromatography (IC)

Air Monitoring Methods

D. Breuer[1], M. Blaskowitz[1], P. Ansari Eshlaghi[2], R. Hebisch[3,*], T.H. Brock[4,*], A. Hartwig[5,*], MAK Commission[6,*]

DOI: 10.1002/3527600418.am14143e1919

Abstract

This analytical method is a validated measurement procedure for the determination of 11 alkanolamines such as 2-aminoethanol, diethanolamine, triethanolamine, 2-amino-2-methyl-1-propanol, 2-(dimethylamino)ethanol, 2-(2-aminoethoxy)ethanol, methyl diethanolamine, 4-amino-1-butanol, (S)-3-amino-1,2-propanediol, 1-amino-2-propanol and 2-amino-2-methyl-1,3-propanediol in workplace air averaged over the sampling period after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a quartz fibre filter impregnated with methanesulfonic acid. The filter is positioned in a GSP sampling head which comply with the requirement of EN 481 for inhalable aerosols and EN 13936 for particle/vapour mixtures. After solvent extraction the sample solution is analysed by means of ion chromatography with a conductivity detector. The quantitative determination of the alkanolamines is based on calibration functions obtained by means of multiple-point calibrations. The limit of quantification for an individual alkanolamine is in the range from 0.087 to 0.58 mg/m^3.

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

Keywords

alkanolamines; cooling lubricants; 2-aminoethanol; diethanolamine; triethanolamine; 2-amino-2-methyl-1-propanol; 2-(dimethylamino)ethanol; 2-(2-aminoethoxy)ethanol; methyl diethanolamine; 4-amino-1-butanol; (S)-3-amino-1,2-propanediol; 1-amino-2-propanol; 2-amino-2-methyl-1,3-propanediol; air analysis; workplace measurement; hazardous substances; air sampling; workplace monitoring; measurement method; measuring procedure; GSP sampling head; ion chromatography; IC

Author Information

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

[2] Austrian Worker’ Compensation Board, Head office, Adalbert-Stifter-Str. 65, 1200 Wien, Austria

[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)

Alkanolamines – Method for the determination of 11 alkanolamines in workplace air using ion chromatography (IC)

Method number	2
Application	Air analyses
Analytical principle	Ion chromatography
Completed in	May 2017

Summary

The analytical procedure described here enables the Occupational Exposure Limit (OEL) or MAK values for 11 alkanolamines to be monitored in workplace air. These alkanolamines, which are used in cooling lubricants, include 2-aminoethanol, diethanolamine, triethanolamine, 2-amino-2-methyl-1-propanol, 2-(dimethylamino)ethanol, 2-(2-aminoethoxy)ethanol, methyl diethanolamine, 4-amino-1-butanol, (S)-3-amino-1,2-propanediol, 1-amino-2-propanol and 2-amino-2-methyl-1,3-propanediol [1, 2].

Sampling is carried out with a suitable pump drawing a defined volume of air through an acid-impregnated quartz fibre filter that is located in a GSP sampling head. Thus, the GSP sampling head used complies with the requirements set out in EN 481 [3] for inhalable aerosols and EN 13936 [4] for particle/vapour mixtures. As part of the sample preparation, the quartz fibre filter loaded with alkanolamines is extracted with methanesulfonic acid and the sample solution is analysed by means of ion chromatography and a conductivity detector. The quantitative determination is based on multiple-point calibrations with external standards.

Characteristics of the method

Precision:	Standard deviation (rel.):	s = 0.18 to 5.2%
	Expanded uncertainty:	U = 20.7 to 22.3%
	in the concentration range from 0.25 to 9.3 mg/m^3 and for n = 6 determinations	

Limit of quantification:	2-Aminoethanol (MEA):	0.25 mg/m^3
	Diethanolamine (DEA):	0.10 mg/m^3
	Triethanolamine (TEA):	0.50 mg/m^3
	2-Amino-2-methyl-1-propanol (AMP):	0.46 mg/m^3
	2-(Dimethylamino)ethanol (DMAE):	0.25 mg/m^3
	2-(2-Aminoethoxy)ethanol (DGA):	0.087 mg/m^3
	Methyl diethanolamine (MDEA):	0.25 mg/m^3
	4-Amino-1-butanol (4-AB):	0.25 mg/m^3
	(S)-3-Amino-1,2-propanediol (APD):	0.25 mg/m^3
	1-Amino-2-propanol (MIPA):	0.58 mg/m^3
	2-Amino-2-methyl-1,3-propanediol (AMPD):	0.25 mg/m^3

for an air sample volume of 60 L, a sample solution of 10 mL and an injection volume of 30 µL.

Recovery:	2-Aminoethanol (MEA):	95.0 to 100.5%
	Diethanolamine (DEA):	102.9 to 107.9%
	Triethanolamine (TEA):	97.0 to 104.6%
	2-Amino-2-methyl-1-propanol (AMP):	85.2 to 89.1%
	2-(Dimethylamino)ethanol (DMAE):	93.8 to 101.0%
	2-(2-Aminoethoxy)ethanol (DGA):	96.1 to 104.3%
	Methyl diethanolamine (MDEA):	92.2 to 102.2%
	4-Amino-1-butanol (4-AB):	88.4 to 97.8%
	(S)-3-Amino-1,2-propanediol (APD):	94.7 to 99.8%
	1-Amino-2-propanol (MIPA):	95.7 to 98.0%
	2-Amino-2-methyl-1,3-propanediol (AMPD):	94.0 to 101.3%

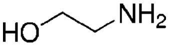
Sampling recommendations:	Sampling period:	2 h
	Air sample volume:	60 L
	Flow rate:	0.5 L/min (30 L/h)

Description of the substances

Alkanolamines Alkanolamines, also known as amino alcohols, comprise a chemical substance group, each member having two functional groups (a hydroxy and an amino group). The structure of the amino group can be primary, secondary or tertiary.

Alkanolamines react with fatty acids to form salts of low alkalinity (skin-friendly) which exhibit good emulsifying properties. They serve as emulsifiers e.g. in creams, lotions and shaving foams as well as those used in the textile, leather and petroleum industries. Cooling lubricants mixed with water used for metalworking purposes contain alkanolamines as emulsifiers, but also for the regulation of the alkalinity of a cooling lubricant [5]. Furthermore, aqueous solutions of ethanolamines are used as absorption agents for carbon dioxide and hydrogen sulphide in gas scrubbing processes.

2-Aminoethanol (MEA) [141-43-5]



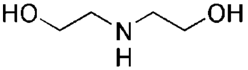
Synonyms: monoethanolamine, ethanolamine, aminoethanol, 2-aminoethyl alcohol

2-Aminoethanol is a colourless liquid with an odour similar to ammonia. It has an oily consistency (molar mass 61.08 g/mol, boiling point 172 °C, flash point 85 °C, melting point 10 °C, vapour pressure 0.5 hPa at 20 °C). It is miscible with water, whereby its aqueous solution is strongly alkaline.

The OEL or MAK value for 2-aminoethanol is 0.51 mg/m^3 (0.2 ppm) [1, 2]. The short-term value is assigned to Peak Limitation Category I (2) and MEA has the footnote "*The substance can occur simultaneously as a vapour and an aerosol*". Detailed information on the toxicity of 2-aminoethanol can be found in the toxicological-occupational health documentation of the MAK values [6, 7].

1 mL/m^3 (ppm) ≙ 2.54 mg/m^3 1 mg/m^3 ≙ 0.39 mL/m^3 (ppm)

Diethanolamine (DEA) [111-42-2]



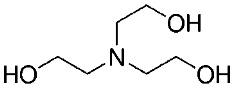
Synonyms: 2,2′-iminodiethanol; 2,2′-dihydroxydiethylamine; diethylamine; 2,2′-iminobisethanol

Diethanolamine is a colourless, hygroscopic solid with an odour similar to ammonia (molar mass 105.14 g/mol, boiling point 269 °C, flash point 138 °C, melting point 28 °C, vapour pressure < 0.01 hPa at 20 °C). It is soluble in water (954 g/L at 20 °C) and miscible with acetone and ethanol. In industry diethanolamine is used as a hardener for epoxy resins and serves as a catalyst for the production of polyurethanes. Furthermore, it is an intermediate product in the production of detergent base materials, accelerating admixtures to cement, insecticides as well as drilling and cutting oils. Moreover, it is used as an absorption agent for hydrogen sulphide (H_2S) and carbon dioxide (CO_2) in chemical processes.

The MAK value for diethanolamine is 1 mg/m^3 [2]. The short-term value is assigned to Peak Limitation Category I (1). DEA is ascribed the footnote "*The substance can occur simultaneously as a vapour and an aerosol*". Detailed information on the toxicity of diethanolamine can be found in the toxicological-occupational health documentation of the MAK values [8].

1 mL/m^3 (ppm) ≙ 4.37 mg/m^3 1 mg/m^3 ≙ 0.23 mL/m^3 (ppm)

Triethanolamine (TEA) [102-71-6]



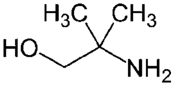
Synonyms: 2,2′,2″-nitrilotriethanol; tris(2-hydroxyethyl)amine; tri(hydroxyethyl)amine

Triethanolamine is a colourless to yellowish, hygroscopic liquid with a viscous consistency (molar mass 149.19 g/mol, boiling point 360 °C, flash point 179 °C, melting point 21 °C, vapour pressure < 0.01 hPa at 20 °C). It is miscible with water, ethanol and glycerine. It is also soluble in chloroform and acetone. Triethanolamine is used as a basic component of soaps and cosmetics, as a wetting agent for textiles as well as a plasticiser in the leather industry. Furthermore, it is used as a corrosion inhibitor and serves as an intermediate product for the production of soaps, dispersing agents and water-soluble herbicides.

The MAK value for diethanolamine is 1 mg/m³ [2]. The short-term value is assigned to Peak Limitation Category I (4). Detailed information on the toxicity of TEA can be found in the toxicological-occupational health documentation of the MAK values [9, 10].

1 mL/m³ (ppm) ≙ 6.20 mg/m³ 1 mg/m³ ≙ 0.16 mL/m³ (ppm)

2-Amino-2-methyl-1-propanol (AMP) [124-68-5]



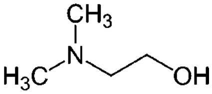
Synonyms: aminomethylpropanol; 2-amino-2-methylpropanol

2-Amino-2-methyl-1-propanol is a colourless solid with an amine-like odour (molar mass 89.14 g/mol, boiling point 165 °C, flash point 81 °C, melting point 30 °C, vapour pressure < 0.01 hPa at 20 °C). It is readily soluble in water. 2-Amino-2-methyl-1-propanol is used for the production of pigments and medicinal products.

The OEL or MAK value for AMP is 3.71 mg/m³ (1 ppm) [1, 2]. The short-term value for AMP is assigned to Peak Limitation Category II (2) with the footnote "*The substance can occur simultaneously as a vapour and an aerosol*". Detailed information on the toxicity of 2-amino-2-methyl-1-propanol can be found in the toxicological-occupational health documentation of the MAK values [11].

1 mL/m³ (ppm) ≙ 3.70 mg/m³ 1 mg/m³ ≙ 0.27 mL/m³ (ppm)

2-(Dimethylamino)ethanol (DMAE) [108-01-0]

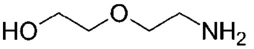


Synonyms: 2-dimethylaminoethanol; dimethylethanolamine; *N,N*-dimethylethanolamine

2-(Dimethylamino)ethanol is a colourless liquid with an odour similar to ammonia (molar mass 89.14 g/mol, boiling point 131 °C, flash point 31 °C, melting point < −10 °C, vapour pressure 5.6 hPa at 20 °C). It is miscible with water and ethanol. 2-(Dimethylamino)ethanol serves as an intermediate product or starting material for the production of pigments, emulsifiers, anti-corrosion agents and aids for the textile industry. Moreover, it is used as an aid for dispersing pigments in water-based varnishes. An OEL or MAK value for DMAE does not exist.

1 mL/m³ (ppm) ≙ 3.70 mg/m³ 1 mg/m³ ≙ 0.27 mL/m³ (ppm)

2-(2-Aminoethoxy)ethanol (DGA) [929-06-6]



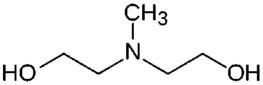
Synonyms: diethylene glycol amine; 2-(2-hydroxyethoxy)ethylamine

2-(2-Aminoethoxy)ethanol is a colourless to slightly yellowish liquid with an amine-like odour (molar mass 105.14 g/mol, boiling point 218–224 °C, flash point 127 °C, melting point < −11 °C, vapour pressure < 0.1 hPa at 20 °C). It is miscible with water. 2-(2-Aminoethoxy)ethanol, better known by the trade name of Diglycolamine®, is used in stripping solutions for demetallisation as well as an emulsifier in cooling lubricants and for gas scrubbing processes.

The OEL or MAK value for diglycolamine is 0.87 mg/m³ (2 ppm) [1, 2]. The short-term value for DGA is assigned to Peak Limitation Category I (1) with the footnote "*The substance can occur simultaneously as a vapour and an aerosol*". Detailed information on the toxicity of 2-(2-aminoethoxy)ethanol can be found in the toxicological-occupational health documentation of the MAK values [12].

1 mL/m³ (ppm) ≙ 4.37 mg/m³ 1 mg/m³ ≙ 0.23 mL/m³ (ppm)

Methyl diethanolamine (MDEA) [105-59-9]



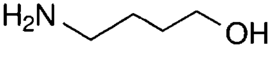
Synonyms: 2,2′-(methylimino)diethanol; *N*-methyldiethanolamine; *N*-methyl-2,2′-iminodiethanol

Methyl diethanolamine is a colourless liquid with an amine-like odour (molar mass 119.16 g/mol, boiling point 243 °C at 1013 mbar, flash point 137 °C, melting point < −21 °C, vapour pressure < 0.0013 hPa at 20 °C). It is miscible with water, short-chain alcohols, esters, acetone, benzene and chlorinated hydrocarbons and it is not miscible with diethyl ether and aliphatic hydrocarbons. Methyl diethanolamine is used as a catalyst in the production of polyurethane. Furthermore, MDEA is an intermediary product in the production of aids for the textile industry, pigments, insecticides, pharmaceuticals as well as emulsifiers and it is also used as an absorbent of hydrogen sulphide in gas scrubbing processes.

An OEL or MAK value for methyl diethanolamine does not exist. MDEA is assigned to Section II b in the List of MAK and BAT Values with the footnote "*The substance can occur simultaneously as a vapour and an aerosol*". Detailed information on the toxicity of methyl diethanolamine can be found in the toxicological-occupational health documentation of the MAK values [13].

1 mL/m³ (ppm) ≙ 4.95 mg/m³ 1 mg/m³ ≙ 0.20 mL/m³ (ppm)

4-Amino-1-butanol (4-AB) [13325-10-5]

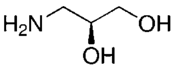


Synonyms: 4-aminobutane-1-ol; 4-aminobutanol

4-Amino-1-butanol is a colourless, air-sensitive, hygroscopic liquid (molar mass 89.14 g/mol, boiling point 206 °C, flash point 104 °C, melting point 16 to 18 °C, vapour pressure 0.06 hPa at 25 °C). An OEL or MAK value for 4-AB does not exist.

1 mL/m^3 (ppm) ≙ 3.70 mg/m^3 1 mg/m^3 ≙ 0.27 mL/m^3 (ppm)

(S)-3-Amino-1,2-propanediol (APD) [61278-21-5]

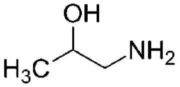


Synonym: (S)-3-3-aminopropane-1,2-diol

(S)-3-Amino-1,2-propanediol is a colourless solid (molar mass 91.11 g/mol, boiling point 267 °C, flash point 113 °C, melting point 54 to 56 °C, vapour pressure 0.0015 hPa at 25 °C). An OEL or MAK value for APD does not exist.

1 mL/m^3 (ppm) ≙ 3.79 mg/m^3 1 mg/m^3 ≙ 0.26 mL/m^3 (ppm)

1-Amino-2-propanol (MIPA) [78-96-6]



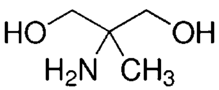
Synonyms: 1-aminopropane-2-ol; isopropanolamine

1-Amino-2-propanol is a colourless liquid with an odour similar to ammonia (molar mass 75.11 g/mol, boiling point 159 °C, flash point 71 °C, melting point 1.4 °C, vapour pressure 1.93 hPa at 20 °C). It is miscible with water as well as being soluble in ethanol and benzene. MIPA is used as a corrosion inhibitor in cooling lubricants. Furthermore, it is an intermediary product in the production of pigments and medicinal products as well as esters, amides and salts of long-chain fatty acids that are used as detergents and oil-in-water emulsifiers.

The OEL for 1-amino-2-propanol is 5.8 mg/m^3 (2 ppm) [1]. The short-term value of MIPA is assigned to Peak Limitation Category I (2) with the footnote "*The substance can occur simultaneously as a vapour and an aerosol*". Detailed information on the toxicity of 1-amino-2-propanol can be found in the toxicological-occupational health documentation of the MAK values [14].

1 mL/m^3 (ppm) ≙ 3.12 mg/m^3 1 mg/m^3 ≙ 0.32 mL/m^3 (ppm)

2-Amino-2-methyl-1,3-propanediol (AMPD) [115-69-5]



Synonyms: 2-amino-2-methylpropane-1,3-diol; aminoglycol

2-Amino-2-methyl-1,3-propanediol is a solid (white powder) (molar mass 105.14 g/mol, boiling point 151 °C at 13 mbar, melting point 100–110 °C, vapour pressure 0.0087 hPa at 25 °C). An OEL or MAK value for AMPD does not currently exist.

1 mL/m^3 (ppm) ≙ 4.37 mg/m^3 1 mg/m^3 ≙ 0.23 mL/m^3 (ppm)

Contents

1 General principles

The analytical procedure described here enables the Occupational Exposure Limit (OEL) or MAK value for 11 alkanolamines to be monitored in workplace air. These alkanolamines, which are used in cooling lubricants, include 2-aminoethanol, diethanolamine, triethanolamine, 2-amino-2-methyl-1-propanol, 2-(dimethylamino)ethanol, 2-(2-aminoethoxy)ethanol, methyl diethanolamine, 4-amino-1-butanol, (S)-3-amino-1,2-propanediol, 1-amino-2-propanol and 2-amino-2-methyl-1,3-propanediol [1, 2].

Sampling is carried out with a suitable sampling pump drawing a defined volume of air through an acid-impregnated quartz fibre filter that is located in a GSP sampling system. Thus, the sampling head used complies with the requirements set out in EN 481 [3] for inhalable aerosols and EN 13936 [4] for particle/vapour mixtures. As part of the sample preparation the quartz fibre filter loaded with alkanolamines is extracted with methanesulfonic acid and the sample solution is analysed by means of ion chromatography and a conductivity detector. The quantitative evaluation is based on multiple-point calibrations with external standards.

2 Equipment, chemicals and solutions

2.1 Equipment

2.1.1 Equipment for sampling

- Pump, suitable for a flow rate of 30 L/h (0.5 L/min)
- Gas meter
- PGP sampling system with a GSP sampling head including an intake cone for a flow rate of 0.5 L/min and a cartridge for a quartz fibre filter (suitable for collection of the inhalable fraction according to EN 481 [3])
- Quartz fibre filter, ∅ 37 mm (e.g. Merck Millipore, AQFA03700)
- Silicone tube for connecting the pump with the sampling system

2.1.2 Equipment for sample preparation and determination

- Screw cap vials made of HDPE, nominal volume: 20 mL with internal cone and wide opening (17 mm), height 60 mm
- Volumetric flasks made of polymethylpentene (PMP), 25, 50, 100 and 1000 mL
- Adjustable piston pipettes, nominal volume 0.01 µL to 5 mL
- Disposable syringes, 2, 5 and 10 mL with compatible cannulae
- Syringe filter units for the filtration of aqueous samples for ion chromatography, ∅ 37 mm, pore size 0.45 µm
- Autosampler vials made of HDPE with screw caps and slit PTFE septa, nominal volume: 1.5 mL
- Ultrasonic bath
- Ultrapure water system
- Ion chromatograph with column thermostat and conductivity detector
- Data evaluation unit
- Tweezers

Note:
The equipment used must be thoroughly cleaned before use (if necessary in the dishwashing machine).

2.2 Chemicals

The alkanolamines used should have at least p.a. purity and must be sourced from two different manufacturers in each case. The alkanolamines from one manufacturer are used for calibration, while the alkanolamines from the other manufacturer are used for checking the accuracy of the calibration.

- Methanesulfonic acid (MSA), purity ≥ 99.5% (density: 1.481 g/mL)
- 2-Aminoethanol (MEA), purity ≥ 99.0%
- Diethanolamine (DEA), purity ≥ 98.0%
- Triethanolamine (TEA), purity ≥ 99%
- 1-Amino-2-propanol (MIPA), purity ≥ 98.0%
- 2-Amino-2-methyl-1-propanol (AMP), purity ≥ 99.0%

- 2-Amino-2-methyl-1,3-propanediol (AMPD), purity ≥ 99.5%
- Methyl diethanolamine (MDEA), purity ≥ 99%
- Diethylaminoethanol (DEAE), purity ≥ 99.5%
- 2-(2-Aminoethoxy)ethanol (DGA), purity 98%
- 2-Amino-1-butanol (2-AB), purity 97%
- 4-Amino-1-butanol (4-AB), purity ≥ 98%
- 1,1′-Iminodipropane-2-ol (Diisopropanolamin, DIPA), purity ≥ 98.0%
- (2)-3-Aminopropanediol (APD), purity 98%
- 2-(Dimethylamino)ethanol (DMAE), purity ≥ 99.5%

2.3 Solutions

The eluent for the ion chromatographic separation of the alkanolamines is prepared directly in the IC unit by means of reagent-free ion chromatography (RFIC) and an EGC (eluent generator cartridge) III MSA (methanesulfonic acid) cartridge.

Eluent for the preparation of the measurement solutions and for the extraction of the loaded quartz fibre filters:	Methanesulfonic acid (MSA) 20 mmol/L

A pipette is used to transfer 1380 µL (~1.9319 g) of methanesulfonic acid into a 1000 mL volumetric flask made of PMP. The flask is then filled to the mark with ultrapure water and shaken.

The eluent must be freshly prepared every working day.

Impregnation solution for the quartz fibre filters:	Methanesulfonic acid (MSA) 313 mmol/L

2070 µL (~3.027 g) of methanesulfonic acid (MSA) are placed into a 100 mL volumetric flask made of PMP using a pipette. The volumetric flask is then filled to the mark with ultrapure water and shaken.

The impregnation solution can be used for up to a maximum of 2 weeks when stored at room temperature.

2.4 Calibration standards

Stock solutions

Standards supplied by both manufacturers are used for the preparation of individual stock solutions of the investigated alkanolamines for calibration and control.

Individual stock solutions:	DEA and DGA

125 mg of diethanolamine (DEA) and 2-(2-aminoethoxy)ethanol (DGA) are each weighed exactly to the nearest 0.1 mg into 50 mL volumetric flasks (PMP). The volumetric flasks are then filled to the mark with ultrapure water and shaken. The concentration of DEA and DGA is 2.5 g/L in each case.

Individual stock solutions: MEA, TEA, AMP, DMAE, MDEA, 4-AB, APD, MIPA, AMPD

250 mg of MEA, TEA, AMP, DMAE, MDEA, 4-AB, APD, MIPA and AMPD are each weighed exactly to the nearest 0.1 mg into 50 mL volumetric flasks (PMP). The volumetric flasks are then filled to the mark with ultrapure water and shaken. The concentration of MEA, TEA, AMP, DMAE, MDEA, 4-AB, APD, MIPA and AMPD is 5 g/L in each case.

Cumulative stock solution **A** (30 °C): contains only APD

1250 µL of (S)-3-amino-1,2-propanediol (APD) are pipetted into a 50 mL volumetric flask (PMP), into which approximately 30 mL of ultrapure water have been previously placed. The volumetric flask is then filled to the mark with ultrapure water and shaken. The concentration of APD is 125 mg/L.

Cumulative stock solution **B** (40 °C): contains DEA, DGA, DMAE, MIPA, AMPD

1250 µL each of DEA, DGA, DMAE, MIPA and AMPD from the 11 individual stock solutions are pipetted into a 50 mL volumetric flask (PMP), into which approximately 20 mL of ultrapure water have been previously placed. The volumetric flask is then filled to the mark with ultrapure water and shaken. The concentrations of DEA and DGA are each 62.5 mg/L and the concentrations of DMAE, MIPA and AMPD are 125 mg/L each.

Cumulative stock solution **C** (60 °C): contains MEA, TEA, AMP, MDEA, 4-AB

1250 µL each of MEA, TEA, AMP, MDEA and 4-AB from the 11 individual stock solutions are pipetted into a 50 mL volumetric flask (PMP), into which approximately 20 mL of ultrapure water have been previously placed. The volumetric flask is then filled to the mark with ultrapure water and shaken. The concentration of MEA, TEA, AMP, MDEA and 4-AB are 125 mg/L in each case.

The stock solutions can be used for at least 12 months when stored in the refrigerator at 4 °C.

Calibration solutions

Ten calibration solutions are prepared in 25 mL volumetric flasks (PMP) using the cumulative stock solutions **A**, **B** and **C** by means of suitable dilutions with ultrapure water as follows:

From the cumulative stock solutions **A**, **B** and **C** volumes in 100 µL steps (from 100 µL for standard 1 up to 1000 µL for standard 10) are pipetted into 25 mL volumetric flasks (PMP), into which approximately 10 mL of eluent have been previously placed in each case. The volumetric flasks are then filled to the mark with eluent (20 mmol/L of methanesulfonic acid) and shaken. The concentrations of the alkanolamines in the calibration solutions are shown in Table 1.

The calibration solutions can be used for at least 2 weeks when stored at room temperature.

2.5 Pre-treatment of the quartz fibre filters

For the purpose of filter impregnation enough of the impregnation solution (313 mol/L methanesulfonic acid) is placed onto a watch glass to ensure that the quartz fibre filter becomes completely saturated. The quartz fibre filter is then dried at room temperature for at least 12 hours (overnight). When drying is complete the impregnated filter is inserted into the filter holder and sealed with the designated sealing caps until sampling is carried out. An impregnated filter is useable for a maximum of two weeks.

3 Sampling and sample preparation

3.1 Sampling

Sampling is carried out as stipulated in EN 13936 [4] resulting in the total sum of vapour and droplets for an alkanolamine. A defined volume of air is drawn through the impregnated quartz fibre filter by means of a flow-regulated pump at a flow rate of 0.5 L/min. In this case the sampling head must comply with the specifications set out in EN 481 [3] for inhalable aerosols. The recommended sampling period is two hours. The pump and the sampling system are either worn by a person during working hours or stationary sampling is carried out. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to discard the measurement [15]. 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. In order to stabilise the loaded quartz fibre filter, it is transferred immediately after sampling into a screw cap vial filled with 10 mL of the eluent (methanesulfonic acid, 20 mmol/L). The sample vial is then sealed with the designated cap and shaken briefly. The stabilised quartz fibre filter must be delivered to the analytical laboratory without delay.

3.2 Sample preparation

Complete extraction of the collected alkanolamines is achieved by ultrasonic treatment of the sample vial with the loaded quartz fibre filter, which has been stabilised in methanesulfonic acid, in the ultrasonic bath for 15 minutes. Then it is left to cool to room temperature for approx. 30 minutes. The entire sample solution (≥ 8 mL) is then drawn into a disposable syringe with a cannula and filtered through a syringe filter unit into a new sample vial made of HDPE, whereby the first millilitres are discarded. The filtered sample solution can be pipetted directly into an autosampler vial and analysed.

Table 1: Concentrations of the 10 calibration standards (Std)

Alkanolamine	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10
	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]
MEA	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
DEA	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5
TEA	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
MIPA	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
AMP	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
AMPD	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
MDEA	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
DGA	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5
4-AB	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
APD	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
DMAE	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0

4 Operational parameters for ion chromatography

The characteristics of the method were determined under the operating conditions listed below.

Programmes 1, 2 and 3

Ion chromatograph:	Dionex ICS-2000, from Thermo Fisher Scientific with conductivity detector and autosampler
Column:	Dionex IonPac™ CS16, from Thermo Fisher Scientific Length: 250 mm, internal diameter: 3 mm, particle size: 5.5 µm
Guard column:	Dionex IonPac™ CG16, from Thermo Fisher Scientific Length: 50 mm, internal diameter: 3 mm, particle size: 5.5 µm
Eluent-Generator Cartridges (EGC):	Dionex EGC III MSA, from Thermo Fisher Scientific
Suppressor:	Dionex™ AERS™ 500, 2 mm, from Thermo Fisher Scientific
Electronic suppression:	approx. 0.1 µS/cm
Polarity:	positive
Injection volume:	30 µL

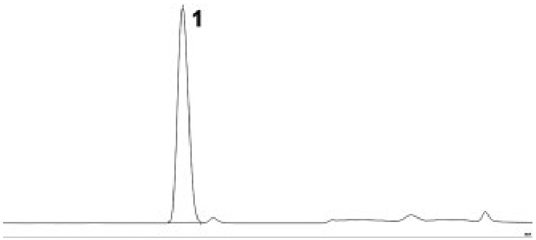
	Programme 1	**Programme 2**	**Programme 3**
Eluent:	7 mM MSA	20 mM MSA	5 mM MSA
Flow rate:	0.5 mL/min	0.36 mL/min	0.5 mL/min
Pressure:	approx. 2060 psi	approx. 2150 psi	approx. 1910 psi
Temperature of the column and in the measuring cell:	30 °C	40 °C	60 °C
Suppressor current:	11 mA	22 mA	8 mA

It should be noted that as part of the separation conditions at the end of an analytical run the concentration of the eluent must be increased to 40 mM for approx. 10 minutes in order to ensure that all sample residues are rinsed from the column. During the rinsing step the suppressor current is 59 mA for programmes 1 and 3 and 43 mA for programme 2. The separation system is then equilibrated with the respective initial concentrations for 20 minutes. Figures 1, 2 and 3 show examples of the ion chromatograms of the alkanolamine cumulative standards **A, B** and **C** under the conditions described above.

The concentrations of the investigated alkanolamines are approx. 2.5 and 1.25 mg/L for DEA and DGA, respectively. Interfering substances, such as lithium, generally occur in concentrations of approx. 0.6 mg/L and sodium, ammonium and potassium cations at concentrations of approx. 1.2 mg/L. Furthermore, the following concentrations of simple amines can occur: methylamine ~1.8 mg/L, dimethylamines ~1.6 mg/L and trimethylamine ~4.4 mg/L.

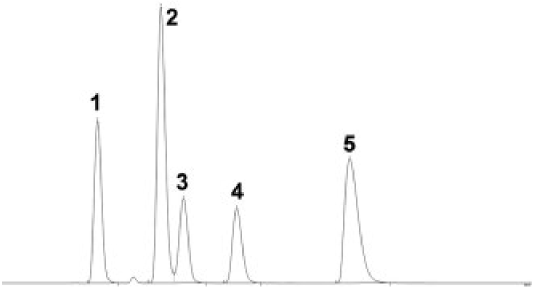
5 Analytical determination

30 µL of the prepared sample solution are injected into the 150 µL sample loop of the ion chromatograph by means of the autosampler and analysed under the conditions stated in Section 4. If the determined concentrations are above the calibration range, then appropriate dilutions of the samples are prepared with the eluent and the measurement is repeated.



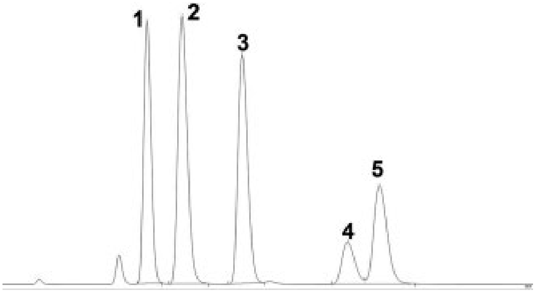
1 (S)-3-Amino-1,2-propanediol (APD) 10.9 min

Figure 1 Ion chromatogram of cumulative stock solution A (for working conditions see programme 1 in Section 4)



1	2-Amino-2-methyl-1,3-propanediol (AMPD)	10.9 min
2	1-Amino-2-propanol (MIPA)	13.7 min
3	Diethanolamine (DEA)	14.7 min
4	2-(2-Aminoethoxy)ethanol (DGA)	17.1 min
5	2-(Dimethylamino)ethanol (DMAE)	22.1 min

Figure 2 Ion chromatogram of cumulative stock solution B (for working conditions see programme 2 in Section 4)



1	2-Aminoethanol (MEA)	25.2 min
2	2-Amino-2-methyl-1-propanol (AMP)	27.5 min
3	4-Amino-1-butanol (4-AB)	31.5 min
4	Triethanolamine (TEA)	38.5 min
5	Methyl diethanolamine (MDEA)	40.7 min

Figure 3 Ion chromatogram of cumulative stock solution C (for working conditions see programme 3 in Section 4)

6 Calibration

The calibration solutions described in Section 2.4 are used to obtain the calibration functions. 30 µL of the calibration solutions are injected into the ion chromatograph in each case and analysed in the same manner as the sample solutions. The resulting peak areas are plotted versus the corresponding concentrations of the calibration standards. The calibration functions are linear or of the second order in the investigated concentration range.

Control samples must be analysed each working day to check the calibration functions. Calibrations previously carried out must be performed anew if the analytical conditions change or the quality control results indicate that this is necessary.

7 Calculation of the analytical result

The sum of vapour and aerosol must be calculated in order to obtain the concentration of an alkanolamine according to EN 13963 [4], as this value is independent of the ratio of the vapour/aerosol mixture and is not influenced by parameters, such as the room temperature. The data evaluation unit calculates the concentration of the alkanolamines in the measurement solution to give the concentration of the investigated alkanolamines in the workplace air as the sum of the vapour and aerosol concentrations.

Determination of the alkanolamines by means of ion chromatography is based on first-order and second-order calibration functions generated by the data evaluation unit, which permit the concentration of the individual alkanolamines to be calculated. Taking the dilution and the air sample volume into consideration, the concentration of the individual alkanolamines in the workplace air is calculated from the concentrations of alkanolamines in the sample solution determined by analysis.

A first-order calibration function is calculated according to Equation (1) as follows:

$$F = b \times \rho_{\mathrm{alkanolamine(solution)}} + a \tag{1}$$

A second-order calibration function is calculated according to Equation (2) as follows:

$$F = c^2 \times \rho_{\mathrm{alkanolamine(solution)}} + b \times \rho_{\mathrm{alkanolamine(solution)}} + a \tag{2}$$

where:

F	is the peak area of an alkanolamine
a	is the ordinate intercept of the calibration function
b	is the slope of the calibration function in L/mg
c	is a constant in $(\mathrm{L/mg})^2$
$\rho_{\mathrm{alkanolamine(solution)}}$	is the mass concentration of an alkanolamine in the sample solution in mg/L

Taking the elution and sample volumes as well as (if necessary) the recovery and dilution into account, the concentration of an alkanolamine in the air samples is calculated using Equation (3) as follows:

$$\rho_{\mathrm{alkanolamine(air)}} = \frac{\rho_{\mathrm{alkanolamine(solution)}} \times \eta \times F_E \times F_{\mathrm{dilution}}}{V_{\mathrm{Air}}} \tag{3}$$

where:

$\rho_{\mathrm{alkanolamin(air)}}$	is the mass concentration of an alkanolamine in the air in $\mathrm{mg/m^3}$
V_{air}	is the air sample in $\mathrm{m^3}$

η	is the recovery (see Section 8.2)
F_E	is the conversion factor of the elution volume in the measuring sample in L (0.010 L)
$F_{dilution}$	is the dilution factor

8 Reliability of the method

The characteristics of the method were calculated according to EN 482 [16], EN 1076 [17], EN 13963 [4] and DIN 32645 [18] as well as determined with the help of a software developed by the IFA [19].

8.1 Precision and expanded uncertainty

Concentrations of the 11 alkanolamines were spiked onto impregnated quartz fibre filters in the minimum measurement range (0.1 of the OEL (Occupational Exposure Limit value); once and two times the OEL) to determine the precision. Clean laboratory air with humidities in the ranges of 10 to 30%, 40 to 60% and 70 to 90% was then drawn through the filters for 2 hours at a flow rate of 0.5 L/min (30 L/h). The filters were then prepared and analysed in the same manner as the analysis samples (see Sections 3.2, 4 and 5).

The expanded uncertainty was estimated taking all relevant influencing factors into consideration as stipulated in EN 482 [16]. The resulting characteristics, such as relative standard deviation and expanded uncertainty, are listed in Table 2.

8.2 Recovery

The recoveries of the alkanolamines were evaluated in the course of the determination of the precision in the minimum measurement range. Three filters were loaded per concentration. The results can be found in Table 3.

Recoveries in the range of 95 to 105% were determined for the majority of the alkanolamines. In order to elicit whether humidity has an influence on the recovery, higher and lower humidities were checked at the limits of the minimum measurement range in each case.

8.3 Limit of quantification (LOQ)

The limits of quantification of the alkanolamines were determined from 10-point calibrations in concentration ranges of 0.5 to 5 mg/L and 0.25 to 2.5 mg/L for DGA and DEA according to DIN 32645 [18]. For all alkanolamines the concentrations of one tenth of the OEL could be validated as the LOQ from the sum of vapour and aerosol based on an air sample volume of 60 L and a sample solution of 10 mL. The LOQ for the alkanolamines are shown in Table 4. A fictional OEL of 2.5 mg/m^3 was assumed for the alkanolamines for which no OEL currently exists.

Table 2: Standard deviation (rel.) and expanded uncertainty *U* for *n* = 6 determinations

Alkanolamine	Concentration [mg/m³]	Standard deviation [%]	Expanded uncertainty U [%]
2-Aminoethanol (MEA)	0.25	1.1	20.6
	2.5	0.38	20.0
	5.0	0.47	20.0
Diethanolamine (DEA)	0.1	0.94	19.7
	1.1	0.45	19.7
	2.2	0.50	19.7
Triethanolamine (TEA)	0.5	0.91	20.1
	5.0	1.3	20.5
	10.0	0.35	20.7
1-Amino-2-propanol (MIPA)	0.55	0.30	19.4
	5.7	0.64	19.5
	11.5	0.47	19.7
2-Amino-2-methyl-1-propanol (AMP)	0.46	0.52	19.8
	4.6	0.72	19.8
	9.3	0.48	19.8
2-Amino-2-methyl-1,3-propanediol (AMPD)	0.25	0.82	20.2
	2.5	0.41	19.8
	5.0	0.82	19.8
Methyl diethanolamine (MDEA)	0.26	0.98	20.6
	2.6	1.4	20.2
	5.2	0.42	20.4
2-(2-Aminoethoxy)ethanol (DGA)	0.09	0.50	20.7
	0.9	0.18	21.0
	1.7	0.56	20.6
4-Amino-1-butanol (4-AB)	0.25	0.88	21.3
	2.5	0.81	21.3
	4.8	0.34	21.3
(S)-3-Amino-1,2-propanediol (APD)	0.25	1.3	20.1
	2.6	0.62	20.8
	5.3	0.69	20.6
2-(Dimethylamino)ethanol (DMAE)	0.25	0.59	20.2
	2.5	0.40	19.8
	5.0	0.55	19.9

Table 3: Mean recoveries of the 11 alkanolamines for n = 6 determinations

Alkanolamine	Mean recovery [%]		
	0.1 OEL*	1 OEL	2 OEL
2-Aminoethanol (60 °C) (MEA)	94.9	100.5	98.7
Diethanolamine (40 °C) (DEA)	103.7	107.9	106.3
Triethanolamine (60 °C) (TEA)	99.3	104.6	102.6
1-Amino-2-propanol (40 °C) (MIPA)	97.2	97.3	97.0
2-Amino-2-methyl-1-propanol (60 °C) (AMP)	85.7	89.1	87.8
2-Amino-2-methyl-1,3-propandiol (40 °C) (AMPD)	94.8	100.5	100.0
Methyl diethanolamine (60 °C) (MDEA)	95.1	102.2	99.1
2-(2-Aminoethoxy)ethanol (40 °C) (DGA)	97.1	104.3	103.0
4-Amino-1-butanol (60 °C) (4-AB)	89.3	97.8	95.8
(S)-3-Amino-1,2-propanediol (30 °C) (APD)	98.0	94.7	95.2
2-(Dimethylamino)ethanol (40 °C) (DMAE)	94.6	101.0	99.8

* OEL = Occupational Exposure Limit

Table 4: Limits of quantification (LOQ) for the 11 alkanolamines

Alkanolamine	LOQ = 0.1 OEL*	LOQ = 0.1 OEL
	[mg/m³]	[mg/L]
2-Aminoethanol (60 °C) (MEA)	0.25 (EU)**	1.50
Diethanolamine (40 °C) (DEA)	0.10	0.60
Triethanolamine (60 °C) (TEA)	0.50	3.00
1-Amino-2-propanol (40 °C) (MIPA)	0.58	3.48
2-Amino-2-methyl-1-propanol (60 °C) (AMP)	0.46	2.76
2-Amino-2-methyl-1,3-propanediol (40 °C) (AMPD)	0.25	1.50
Methyl diethanolamine (60 °C) (MDEA)	0.25	1.50
2-(2-Aminoethoxy)ethanol (40 °C) (DGA)	0.087	0.52
4-Amino-1-butanol (60 °C) (4-AB)	0.25	1.50
(S)-3-Amino-1,2-propanediol (30 °C) (APD)	0.25	1.50
2-(Dimethylamino)ethanol (40 °C) (DMAE)	0.25	1.50

* OEL = Occupational Exposure Limit; ** European Union

8.4 Capacity of the quartz fibre filters

The impregnation of the quartz fibre filters was tested – based on the worst-case scenario – assuming that all alkanolamines included in the development of the method have a concentration equivalent to twice the OEL. This is equivalent to a substance content of 0.0783 mmol per alkanolamine. Furthermore, 500 µL of the impregnation solution contains 0.160 mmol of MSA. Pre-treatment of the filters involves the filters being completely soaked in impregnation solution and thus absorbing at least 500 µL of MSA solution.

As no irregularities were observed during the recovery experiments (concentrations of twice the OEL for a 2-hour sampling period and a sample volume of 60 L), it can be assumed that the impregnation is sufficient in the measurement range.

8.5 Storage stability

Storage stability was determined by spiking impregnated quartz fibre filters in a dynamic test gas facility at a relative humidity of between 70 to 90% with concentrations of alkanolamines equivalent to one tenth and twice the OEL. The spiked filters were then transferred into screw cap vials made of HDPE and covered with eluent. The vials were sealed with the designated caps and shaken briefly. The screw cap vials were initially stored at room temperature for seven days and then in the refrigerator at 4 °C. One sample was removed on the 1st, 3rd, 7th, 21st and 28th day respectively and analysed in a duplicate determination. No changes in concentration were detected over the investigated time period. The alkanolamine APD was the only exception. Its recovery decreased by approx. 91% at low concentrations within 14 days and remained at this level until the end of the experiment (28 days).

If loaded samples have to be stored for some time prior to analysis by means of ion chromatography, then a recovery of 0.909 (90.9%) should be used in the calculation of the results for APD. This recovery is valid for the concentration range of 0.25 to 1.5 mg/m^3.

8.6 Influence of the humidity

The influence of the humidity was checked for alkanolamine concentrations in the lower and upper minimum measurement range (one tenth and twice the OEL) at relative humidities of 10 to 30%, 40 to 60% as well as 70 to 90%. For this purpose 60 litres of air were drawn through a filter spiked with alkanolamines over a time period of 2 hours at a flow rate of 0.5 L/min. In this case, the relative humidities used were generated in a dynamic test gas facility. Immediately after the filters had been spiked and the air had been drawn through them, the filters were prepared and analysed in the same manner as the analysis samples (see Sections 3.2, 4 and 5). There was no evidence that the humidity exerted any influence.

8.7 Blank values

For the purpose of checking the blank values, quartz fibre filters were impregnated and left to dry overnight at room temperature. Filter extraction was then carried out in 10 mL of methanesulfonic acid (20 mmol/L) in the same manner as the analysis samples and the filters were subsequently treated in the ultrasonic bath for 15 minutes. The complete sample solution was then filtered through a syringe filter unit and analysed by means of ion chromatography using programme 2 (40 °C) (see Section 4).

No alkanolamine blank values were detectable. However, cation blank values were detected, such as sodium, potassium and ammonium ions that do not interfere with the determination in the low concentrations that were present. Therefore, it should be ensured when purchasing new quartz fibre filters that they have low blank values for sodium, potassium and ammonium ions. For control purposes at least two non-impregnated filters from each packet of every new filter batches has to be checked for blank values. The filters are subjected to the entire analytical procedure (see Sections 3.2, 4 and 5).

8.8 Interference

Under certain conditions the 11 alkanolamines can interfere with one another, so that sufficient chromatographic separation and subsequent quantification of individual alkanolamines proves impossible. If, in the worst case, all 11 alkanolamines are present in the same sample, then some of the alkanolamines may be determined only qualitatively. Furthermore, additional alkanolamines that may be present in the sample, such as 2-amino-1-butanol (2-AB) [96-20-8] and diisopropanolamine (DIPA) [110-97-4], can coelute with the alkanolamines present. It is advisable to use the three eluent programmes in order to ensure a sufficient chromatographic peak separation.

Thus, for instance, 2-amino-2-methyl-1-propanol (AMP) can be quantitatively determined only in the absence of 1-amino-2-propanol (MIPA). However, in the case that both alkanolamines are present in the same sample, then only qualitative determination of AMP is possible. A further option for quantitative determination of AMP is measurement with eluent programme 1 (30 °C) (see Section 4). In this case, however, no 2-aminoethanol (MEA) must be present in the sample. Yet, practical experience has shown that MEA occurs in most samples and therefore its presence does not enable a quantitative determination of AMP.

Investigations have shown that interference can occur not only due to alkanolamines, but also due to the presence of sodium, potassium and ammonium ions, which e.g. can originate from the water used in cooling lubricant emulsions when cooling lubricants mixed with water are used or are formed during processing. High concentrations of ammonium ions have frequently been observed, resulting in very strong interference. Potassium ions also cause interference, but occur in relatively low concentrations in samples compared with ammonium ions. Sodium ions are readily separated in the concentrations encountered to date and do not cause interference. Moreover, contamination of the sample solution with amines, such as methylamine, dimethylamine and trimethylamine, can interfere with the separation properties of the alkanolamines.

9 Discussion

The analytical procedure described here enables the quantitative determination of selected alkanolamines in the workplace air in concentration ranges from one tenth up to twice their OEL or MAK values. An acid-impregnated filter has proved suitable for use as a sampling system. The sampling system used in the measurement procedure fulfilled the requirements for sampling of particle/vapour mixtures set out in EN 13936 [4].

10 Appendix: Precision and accuracy by means of comparative measurements

The precision and comparability of the analytical method presented here were checked by comparative measurements by the IFA (Institute for Occupational Safety and Health of the German Social Accident Insurance) and the AUVA (Austrian Workers' Compensation Board). For this purpose, real samples were collected in two manufacturing companies (metal-working with cooling lubricants mixed with water and the manufacture of microchips) and they were prepared and analysed for comparison with the analytical procedure described here (IFA) and the preferred method of the AUVA (see Tables 5 and 6). Furthermore, comparative measurements using samples from the IFA were carried out.

The comparative measurements for the alkanolamine 2-amino-2-methyl-1-propanol (AMP) were carried out as an example. Additionally, the alkanolamines 2-aminoethanol (MEA), triethanolamine (TEA), 2-(2-aminoethoxy)ethanol (DGA), 2-(dimethylamino)ethanol (DMAE) and methyl diethanolamine (MDEA) could be used as a reference in the method comparison based on the IFA samples. The results of the comparative measurements of routine samples of the AUVA, including the recoveries, are listed in Table 7.

Good correlation was found between the measurement results of the IFA and AUVA samples. Based on the results obtained by the IFA the substance non-specific recoveries of the AUVA were in the range of 81 to 127%.

The results of the field tests are listed in Table 8, whereby the determined relative standard deviation of less than 5% was very good. Although measurements were carried out in two manufacturing companies, only the results of the one company (microchip manufacture) are shown, as no alkanolamines, other than 2-amino-2-methyl-1-propanol (AMP), were detected in the metal-working company and were therefore not quantified. In this case AMP was used to compare the measurement procedures with regard to sampling (sampling system) and the method of analysis. According to the safety data sheet for the water-mixed cooling lubricant used, DGA and TEA were also present in the cooling lubricant besides the alkanolamine AMP. Their concentrations, however, could not be determined. In the context of the field test, nine samples were collected with the sampling system used by the IFA (and presented here) and analysed with the method described here. For comparative measurements the AUVA collected eight samples with their own sampling system, which were then analysed and evaluated using the AUVA measurement procedure.

Table 5: Sampling and sample preparation – comparison of the results determined by IFA with those found by the AUVA

	IFA	AUVA
Sampling system:	GSP head with an intake cone for 0.5 L/min and a filter cartridge	Millipore capsule
Flow rate:	0.5 L/min	0.5 L/min
Sample preparation:	Elution in 10 mL of MSA (20 mmol/L)	Elution in 5 mL of MSA (20 mmol/L)

Table 6: Equipment and working conditions – comparison of the results determined by IFA with those found by the AUVA

	IFA	AUVA
Guard column:	IonPac CG16 (3 × 50 mm)	Metrohm C4 S-Guard/4.0
Column:	IonPac CS16 (3 × 250 mm); particle size: 5.5 µm	Metrosep C4 (4 × 250 mm); particle size: 5 µm
Eluent (20 mM Methanesulfonic acid (MSA)):	programme 1: 7 mmol/L programme 2: 20 mmol/L programme 3: 5 mmol/L	1.7 mmol/L HNO_3 + 0.7 mmol/L dipicolinic acid + 0.05 mmol/L 18-Crown-6
Flow rate:	programme 1: 0.50 mL/min programme 2: 0.36 mL/min programme 3: 0.50 mL/min	0.93 mL/min
Injection volume:	30 µL	20 µL
Alkanolamines:	MEA, DEA, TEA, AMP, MIPA, DMAE, MDEA, DGA, APD, AMPD, 4-AB	MEA, MIPA, DEA, AMP, DGA, TEA, MDEA,
Calibration standard: [mg/L]	0.50; 1.00; 1.50; 2.00; 2.50; 3.00; 3.50; 4.00; 4.50; 5.00 (for MEA, DEA and DGA concentrations were halved)	0.78; 1.56; 3.125; 6.25; 12.5; 25; 50; 100 (for DGA the concentration was halved)

Table 7: Results of the comparative measurements and recoveries (comparison of the IFA with the AUVA)

Alkanolamine	Number of comparative samples	Sample concentration (IFA)	Recovery (AUVA)
	n	[mg/m³]	[%]
MEA	10	0.24–1.9	81–116
TEA	3	0.50–2.4	86–106
DGA	3	0.13–0.19	83–115
DMAE	2	0.38–1.4	88–127
MDEA	3	0.46–1.5	89–100

Table 8: Comparative results of AMP from the plant of a chip manufacturer

Measuring station	Result IFA	Standard deviation (rel.)	Result AUVA	Standard deviation (rel.)	Recovery IFA/AUVA
	[mg/m^3]	[%]	[mg/m^3]	[%]	[%]
1	2.1[1]	2.8	1.5[1]	4.7	140
2	1.7[2]	2.9	1.4[3]	4.0	121

[1] Mean value from 3 individual measurements
[2] Mean value from 6 individual measurements
[3] Mean value from 5 individual measurements

The measured concentrations of AMP were higher in the method presented here (IFA) at both measurement locations than those determined by the AUVA. The differences can be explained by the fact that the requirements for particle/vapour mixtures set out in EN 481 [3] as well as EN 13936 [4] were not fulfilled by the sampling system used by the AUVA, therefore it is possible that larger particles were only partially captured.

References

[1] TRGS 900 (2006) Arbeitsplatzgrenzwerte. BArBl Heft 1/2006 S. 41–55 recently revised and supplemented: GMBl 2018, pp. 542–545 [No. 28] (07.06.2018), https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/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/10.1002/9783527818402

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

[4] 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

[5] Hartwig A (ed.) (2014) Komponenten von Kühlschmierstoffen, Hydraulikflüssigkeiten und anderen Schmierstoffen [MAK Value Documentation in German language]. Gesundheitsschädliche Arbeitsstoffe, Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten, 56. Lieferung. Wiley-VCH, Weinheim, https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb0215khsd0056

[6] Greim H (ed.) (2001) 2-Aminoethanol [MAK Value Documentation in German language]. Gesundheitsschädliche Arbeitsstoffe, Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten, 33. Lieferung. Wiley-VCH, Weinheim, https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb14143d0033

[7] Hartwig A and MAK Commission (2016) 2-Aminoethanol [MAK Value Documentation in German language]. The MAK Collection for Occupational Health and Safety, Vol. 1, No 1, Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb14143d0060/pdf

[8] Hartwig A (ed.) (2015) Diethanolamine [translation of German version 2007]. The MAK-Collection for Occupational Health and Safety Part I: MAK Value Documentations. Wiley-VCH, Weinheim, Germany,
https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb11142e4314

[9] Hartwig A and MAK Commission (2017) Triethanolamine [translation of German version 2010]. The MAK Collection for Occupational Health and Safety, Vol. 2, No 4. Wiley-VCH, Weinheim, Germany,
https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb10271kske4817

[10] Hartwig A and MAK Commission (2017) Triethanolamine. The MAK Collection for Occupational Health and Safety, Vol. 2, No 4. Wiley-VCH, Weinheim, Germany,
https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb10271kske6017

[11] Hartwig A (ed.) (2015) 2-Amino-2-methyl-1-propanol [MAK Value Documentation in German language]. Gesundheitsschädliche Arbeitsstoffe, Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten, 59. Lieferung. Wiley-VCH, Weinheim, Germany,
https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb12468kskd0059

[12] Hartwig A (ed.) (2014) 2-(2-Aminoethoxy)ethanol (Diglykolamin) [MAK Value Documentation in German language]. Gesundheitsschädliche Arbeitsstoffe, Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten, 56. Lieferung. Wiley-VCH, Weinheim, Germany,
https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb92906kskd0056

[13] Greim H (ed.) (1998) Methyldiethanolamine. Occupational Toxicants, Vol. 9, pp. 291–294. Wiley-VCH, Weinheim, Germany,
https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb10559kske0009

[14] Greim H (ed.) (1998) 1-Amino-2-propanol. Occupational Toxicants, Vol. 9, pp. 237–244. Wiley-VCH, Weinheim, Germany,
https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.mb7896kske0009

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

[16] 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

[17] 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

[18] DIN 32645 (2008) Chemical analysis – Decision limit, detection limit and determination limit under repeatability conditions – Terms, methods, evaluation. Beuth Verlag, Berlin, Germany

[19] Heckmann P and Breuer D (2014) 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