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Glycol esters, glycol ethers – Method for the determination of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether in workplace air using gas chromatography

Air Monitoring Method – Translation of the German version from 2018

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Keywords: glycol ester; glycol ether; air analyses; analytical method; workplace measurement; gas chromatography; flame ionisation detection; GC-FID; glass fibre filter; activated charcoal

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Air Monitoring Methods

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Abstract

This analytical method is a validated measurement procedure for the determination and limit value monitoring of 1-ethoxy-2-propanol, 1-ethoxy-2-propyl acetate, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol and 2-(2-butoxyethoxy)ethanol in workplace air. With this method simultaneously airborne glycols in the gaseous state as well as particles are collected. Sampling is performed by drawing a defined volume of air through the sampling system GGP-Mini consisting of a glass fibre filter and a charcoal tube connected downstream using a suitable flow-regulated pump. The flow rate is set to 0.33 L/min with a recommended air sample volume of 40 L. The collected glycols are desorbed with a mixture of dichloromethane/methanol containing 1-hexanol as internal standard and then analysed by means of gas chromatography using FID. The quantitative evaluation is based on calibration functions obtained by means of multiple-point calibrations. The limit of quantification (LOQ) for the individual glycol esters or glycol ethers is 0.5 mg/m^3 based on an air sample volume of 40 L.

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 Deutsche Forschungsgemeinschaft for the Investigation of Health Hazards of Chemical Compounds in the Work Area.

Keywords

1-ethoxy-2-propanol; 1-ethoxy-2-propyl acetate; 2-(2-methoxyethoxy)ethanol; 2-(2-ethoxyethoxy)ethanol; 2-(2-butoxyethoxy)ethanol; glycol esters; glycol ethers; air analysis; workplace measurement; hazardous substances; workplace monitoring; air sampling; GGP-Mini; glass fibre filter; activated charcoal tube; gas chromatography

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Method number	1
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	October 2017

Summary

The analytical method described here enables monitoring of the Occupational Exposure Limits (OEL) or MAK values of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether in workplace air [1, 2]. Glycol esters and glycol ethers occurring in the gaseous and particulate state can be simultaneously determined with this method. Sampling is performed using a flow-regulated pump that draws a defined volume of air through a GGP-Mini sampling system with a 0.33 L/min intake cone, comprising a glass fibre filter and an activated charcoal tube connected downstream. Thus, airborne droplets are deposited on the filter, whereas gaseous glycol esters and glycol ethers are adsorbed onto the activated charcoal.

After sampling, the filter and activated charcoal are extracted together with a mixture of dichloromethane/methanol (7:3) in an ultrasonic bath and 1-hexanol is added as an internal standard (ISTD). The qualitative and quantitative determination is performed by means of gas chromatography and flame ionisation detector (FID). Multiple-point calibrations are used for quantitative evaluation according to the internal standard method.

Characteristics of the method

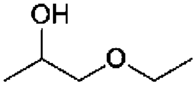
Precision:	Standard deviation (rel.):	s = 4.2 to 4.6%
	Expanded uncertainty:	s = 28 to 34%
	in the concentration range from 0.5 to 590 mg/m^3 depending on the glycol ester or glycol ether and for n = 6 determinations	
Limit of quantification:	Propylene glycol monoethyl ether	0.5 mg/m^3
	1-Ethoxy-2-propanol acetate	0.5 mg/m^3
	Diethylene glycol monomethyl ether	0.5 mg/m^3
	Diethylene glycol monoethyl ether	0.5 mg/m^3
	Diethylene glycol monobutyl ether	0.5 mg/m^3
	at an air sample volume of 40 litres	
Recovery:	Propylene glycol monoethyl ether	93%
	1-Ethoxy-2-propanol acetate	85%
	Diethylene glycol monomethyl ether	78%
	Diethylene glycol monoethyl ether	83%
	Diethylene glycol monobutyl ether	79%
Sampling recommendations:	Sampling period:	2 h
	Air sample volume:	40 L
	Flow rate:	20 L/h (0.33 L/min)

Description of the substances

Glycol esters and glycol ethers

Glycol esters and glycol ethers are substance groups of organic chemicals, which have ethylene glycol or diethylene glycol as a basic unit. They are primarily used as solvents, as they have advantageous solvent properties due to their high boiling points.

Propylene glycol monoethyl ether [1569-02-4]



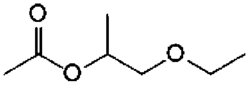
Synonyms: 1-Ethoxypropan-2-ol; propylene glycol ethyl ether; 2PG1EE

Propylene glycol monoethyl ether is a colourless liquid with a slight ether-like odour (molar mass 104.20 g/mol, boiling point 132 °C at 1013 hPa, melting point −100 °C, vapour pressure 10 hPa at 20 °C). It is miscible with water (36.6 g in 100 mL) and reacts very vigorously with strong oxidising agents. Propylene glycol monoethyl ether is used as a solvent in printing inks and synthetic resins as well as for the manufacture of paints.

The OEL or MAK value for propylene glycol monoethyl ether is 220 mg/m^3 (50 ppm) [1, 2]. The short-term exposure limit is classified in Peak Limitation Category II with an excursion factor of 2. Detailed information on the toxicity of propylene glycol monoethyl ether can be found in the toxicological-occupational health documentation of the MAK values [3].

1 mL/m^3 (ppm) ≙ 4.33 mg/m^3 1 mg/m^3 (ppm) ≙ 0.23 mL/m^3 (ppm)

1-Ethoxy-2-propanol acetate [54839-24-6]



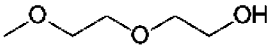
Synonyms: 2-Acetoxy-1-ethoxypropane; 2PG1EA

1-Ethoxy-2-propanol acetate is a colourless liquid with a slight ester-like odour (molar mass 146.18 g/mol, boiling point 150 to 160 °C, melting point < −70 °C, vapour pressure 2.03 hPa at 25 °C). It is miscible with water at 69.6 g/L. It is an important solvent in the paint and coatings industry.

The OEL or MAK value for 1-ethoxy-2-propanol acetate is 300 mg/m^3 (50 ppm) [1, 2]. The short-term exposure limit is classified in Peak Limitation Category II with an excursion factor of 2. Detailed information on the toxicity of 1-ethoxy-2-propanol acetate can be found in the toxicological-occupational health documentation of the MAK values [4].

1 mL/m^3 (ppm) ≙ 6.07 mg/m^3 1 mg/m^3 (ppm) ≙ 0.16 mL/m^3 (ppm)

Diethylene glycol monomethyl ether [111-77-3]



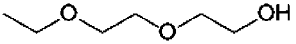
Synonyms: 2-(2-Methoxyethoxy)ethanol; methyldiglycol; DEGME

Diethylene glycol monomethyl ether is a clear, poorly volatile liquid with a slight ether-like odour (molar mass 120.15 g/mol, boiling point 193 °C, melting point approx. −65 °C, vapour pressure 0.3 hPa at 20 °C). It is completely miscible with water. At the workplace it can occur as a particle/vapour mixture in air. When mixed with air, vapours of diethylene glycol monomethyl ether can form an explosive mixture (flash point 87 °C, ignition temperature 215 °C). Diethylene glycol monomethyl ether is added as an antifreeze agent to kerosene. Furthermore, it is used as an additive in enamels and as a solvent for printing paste, stamping ink, leather paint products and ballpoint pen ink.

The OEL for diethylene glycol monomethyl ether is 50 mg/m^3 (10 ppm) for the sum of vapours and aerosols [1].

1 mL/m^3 (ppm) ≙ 4.88 mg/m^3 1 mg/m^3 (ppm) ≙ 0.20 mL/m^3 (ppm)

Diethylene glycol monoethyl ether [111-90-0]



Synonyms: Carbitol; 2-(2-ethoxyethoxy)ethanol; DEGEE

Diethylene glycol monoethyl ether is a clear liquid with a sweetish-musty to fruity odour (molar mass 134.18 g/mol, boiling point 202 °C, melting point −76 °C, vapour pressure 0.13 hPa at 20 °C). It is miscible with water and soluble in alcohols, ethers, ketones as well as in aliphatic and aromatic hydrocarbons. At the workplace it can occur as a particle/vapour mixture in air. When mixed with air, vapours of diethylene glycol monoethyl ether can form an explosive mixture (flash point 90 °C, ignition temperature 190 °C). Diethylene glycol monoethyl ether is used as a poorly volatile solvent. It is also used as a surfactant. It is added as a solvent to varnishes, stamping inks, leather paint products, wood stains, printing pastes and printing inks.

The OEL value for diethylene glycol monoethyl ether is 35 mg/m^3 (6 ppm) [1] and the MAK value is 50 mg/m^3 [2]. The short-term exposure limit is classified in Peak Limitation Category I with an excursion factor of 2. Furthermore, the following footnote applies to this substance: "*may occur simultaneously as a vapour and aerosol*". Detailed information on the toxicity of diethylene glycol monoethyl ether can be found in the toxicological-occupational health documentation of the MAK values [5].

1 mL/m^3 (ppm) ≙ 5.57 mg/m^3 1 mg/m^3 (ppm) ≙ 0.18 mL/m^3 (ppm)

Diethylene glycol monobutyl ether [112-34-5]

Synonyms: Butyldiglycol; butoxydiglycol, 2-(2-butoxyethoxy)ethanol; diethylene glycol butyl ether; DEGBE

Diethylene glycol monobutyl ether is a high-boiling, colourless and odourless liquid (molar mass 162.23 g/mol, boiling point 231 °C, melting point −68 °C, vapour pressure 0.027 hPa at 20 °C). It is completely miscible with water. Diethylene glycol monobutyl ether is used as a solvent in paints and varnishes e.g. in textile processing and serves as an intermediary product in the chemical industry. Furthermore, it is also found in domestic detergents and brewing chemicals.

The OEL or MAK value for diethylene glycol monobutyl ether is 67 mg/m^3 (10 ppm) [1, 2]. The short-term exposure limit is classified in Peak Limitation Category I with an excursion factor of 1. Furthermore, the following footnote applies to this substance: "*may occur simultaneously as vapour and aerosol*". Detailed information on the toxicity of diethylene glycol monobutyl ether can be found in the toxicological-occupational health documentation of the MAK values [6–8].

1 mL/m^3 (ppm) ≙ 6.74 mg/m^3 1 mg/m^3 (ppm) ≙ 0.15 mL/m^3 (ppm)

Contents

1 General principles

The analytical method described here enables monitoring of the Occupational Exposure Limits (OEL) or MAK values of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether in workplace air [1, 2]. Glycol esters and glycol ethers occurring in the gaseous and particulate state can be simultaneously determined with this method. Sampling is carried out using a flow-regulated pump that draws a defined volume of air through a GGP-Mini sampling system with a 0.33 L/min intake cone, comprising a glass fibre filter and an activated charcoal tube connected downstream. Thus, airborne droplets are deposited on the filter and gaseous glycol esters and glycol ethers are adsorbed onto the activated charcoal.

After sampling, the filter and activated charcoal are extracted together with a mixture of dichloromethane/methanol (7:3) in an ultrasonic bath and 1-hexanol is added as an internal standard (ISTD). The qualitative and quantitative determination is performed by means of gas chromatography and flame ionisation detector (GC-FID). Multiple-point calibrations are used for quantitative evaluation according to the internal standard method.

2 Equipment, chemicals and solutions

2.1 Equipment

2.1.1 Devices for sampling

- Pump for personal air sampling, suitable for a flow rate of 20 L/h (0.33 L/min), e.g. Personal Air Sampler Gil Air 5 (from Gilian), supplied by DEHA Haan & Wittmer, 71296 Heimsheim, Germany
- GGP-Mini sampling system with intake cone for 0.33 L/min, supplied by Analyt-MTC GmbH, 79379 Müllheim, Germany
- Silicone adaptor for GGP-Mini sampling system with intake cone for 0.33 L/min, supplied by Carnacon, 67574 Osthofen, Germany
- Glass fibre filter, MN 85/90 BF, ∅ 13 mm, e.g. from Macherey and Nagel, supplied by LABC-Labortechnik Zillger KG, 53773 Hennef, Germany, Article Number 4060013
- Activated charcoal tubes, Dräger BIA type, from Dräger Safety AG & Co. KGaA, 23560 Lübeck, Germany, Article Number 6400744
- Flow meter, e.g. TSI, supplied by DEHA Haan & Wittmer
- Screw-capped vials, 10 mL with dedicated screw-caps
- Disposable tweezers, e.g. from LABC-Labortechnik Zillger KG, Article Number 130-0061186

2.1.2 Devices for sample preparation and analysis

- Ceramus dispenser, 2 to 10 mL, e.g. from Hirschmann Laborgeräte GmbH, 74246 Eberstadt, Germany
- Volumetric flasks, 5 mL, e.g. from Duran Group GmbH, 55122 Mainz, Germany
- Microlitre syringes, 1, 2, 5, 10, 25, 50, 100, 250 and 500 µL, e.g. from Hamilton, 64739 Höchst, Germany
- Disposable syringes, nominal volume of 2 mL with disposable cannulae with Luer Lock (0.9 x 40 mm), e.g. from B. Braun Melsungen AG, 34212 Melsungen, Germany
- Disposable filters, MINISART SRP 15, pore size 0.45 µm, e.g. from Sartorius AG, 37075 Göttingen, Germany, Order No. 17559Q
- Autosampler vials made of glass (LABC-Labortechnik Zillger KG, Article Number 11090356) with screw caps, e.g. from CS-Chromatographie-Service GmbH, 52379 Langerwehe, Germany
- Ultrasonic bath with inserts, e.g. from SONOREX, BANDELIN electronic GmbH & Co. KG, 12207 Berlin, Germany
- PerkinElmer Clarus 500 gas chromatograph with flame ionisation detector (FID) and autosampler
- StabilWax separation column: 60 m; ID 250 µm, film thickness 0.5 µm, e.g. from Restek, 61348 Bad Homburg, Germany
- Data evaluation system, PerkinElmer TotalChrom Client/Server Version 6.3.2

2.2 Chemicals

- Methanol, p.a., purity ≥ 99.9%, e.g. Merck 1.06009
- Dichloromethane, p.a., purity ≥ 99.8%, e.g. Merck 1.06050
- 1-Hexanol, for synthesis, purity ≥ 98.0% e.g. Merck 804393
- Propylene glycol monoethyl ether, purity ≥ 90.0%
- 1-Ethoxy-2-propanol acetate, purity ≥ 99.0%
- Diethylene glycol monomethyl ether, purity ≥ 99.0%, e.g. Sigma-Aldrich 579548
- Diethylene glycol monoethyl ether, purity ≥ 98.0%, e.g. Fluka 32230
- Diethylene glycol monobutyl ether, purity ≥ 98.0%, e.g. Fluka 32250

Gases for operation of the gas chromatograph:

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

2.3 Solutions

Stock solution:
Using a 50 µL syringe, 30 µL of each of the substances listed in Table 1 are dosed into a 5 mL volumetric flask, into which approximately 50 mL of the dichloromethane/methanol mixture (7:3) have been previously placed. The volumetric flask is then filled to the mark with the dichloromethane/methanol mixture (7:3) and shaken.

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

Calibration solutions:
The 10 calibration standard solutions are prepared by pipetting aliquots of 2 to 11 µL of the stock solution (see Table 2) in each case into 5 mL volumetric flasks, into which approx. 2 mL of dichloromethane/methanol (7:3) have been previously placed. The volumetric flasks are then filled to the mark with dichloromethane/methanol (7:3) and 0.4 µL of 1-hexanol (ISTD) is dosed into each volumetric flask.

The calibration solutions must be freshly prepared each working day.

3 Sampling and sample preparation

3.1 Sampling

Suitable flow-regulated pumps are used for sampling. In order to adjust the flow rate to 20 L/h (0.33 L/min) a correspondingly equipped GGP-Mini sampling system with an intake cone for 0.33 L/min is connected to the pump in the same manner as for sampling.

Immediately before sampling, the fused glass ends of the activated charcoal tubes are opened and the collection tube is connected to the sampling head containing the glass fibre filter. The arrow must be pointing towards the pump. The other end

Table 1: Concentrations of glycol esters and glycol ethers in the stock solution

Substance	Dosing volume [µL]	Concentration [µg/µL]
Propylene glycol monoethyl ether (2PG1EE)	30	5.4
1-Ethoxy-2-propanol acetate (2PG1EA)	30	5.9
Diethylene glycol monomethyl ether (DEGME)	30	6.2
Diethylene glycol monoethyl ether (DEGEE)	30	5.9
Diethylene glycol monobutyl ether (DEGBE)	30	5.8

Table 2: Calibration solutions to determine the performance characteristics of the method

No.	Volumes of stock solution	2PG1EE	2PG1EA	DEGME	DEGEE	DEGBE
	[µL]	[µg/5 mL]	[µg/5 mL]	[µg/5 mL]	[µg/5 mL]	[µg/5 mL]
1	2	10.8	11.8	12.4	11.9	11.5
2	3	16.2	17.7	18.5	17.8	17.3
3	4	21.6	23.6	24.7	23.8	23.0
4	5	26.9	29.5	30.9	29.7	28.8
5	6	32.3	35.4	37.1	35.6	34.6
6	7	37.7	41.3	43.3	41.6	40.3
7	8	43.1	47.2	49.4	47.5	46.1
8	9	48.5	53.1	55.6	53.5	51.8
9	10	53.9	59.0	61.8	59.4	57.6
10	11	59.3	64.9	68.0	65.3	63.4

of the activated charcoal tube is connected to a pump. The schematic set-up of the sampling system is illustrated in Figure 1.

The pump and the sampling system are either worn by a person while carrying out their activities or stationary sampling is carried out. An air sample volume of 40 litres is drawn through at a pre-selected flow rate of 20 L/min and a sampling period of two hours. After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to discard the measurement [10]. The important parameters for the determination of the concentration in air (sample volume, temperature, air pressure and relative humidity) are documented in a sampling record.

Immediately after sampling, the activated charcoal tube is sealed with the caps designated for this purpose. The sampling head of the GGP-Mini is unscrewed; the glass fibre filter is removed using tweezers and transferred into the designated screw-capped vial, which is then sealed. Both the loaded sample carriers (filter and charcoal tube) must be delivered to the analytical laboratory as rapidly as possible.

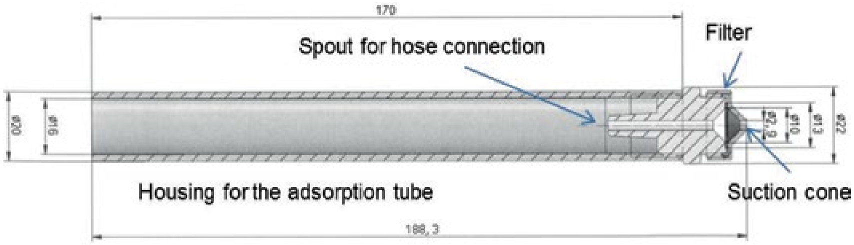


Figure 1 Schematic set-up of the GGP-Mini sampling system [9]

Note:
Sampling should preferably be carried out at room temperature and at a medium humidity, as the recovery for individual substances was altered at low temperatures and humidities (see Section 8.3 and Section 8.4).

3.2 Sample preparation

The activated charcoal tube is opened and the contents are transferred in their entirety into the screw-capped vial into which the loaded glass fibre filter has been previously placed. The loaded sample carriers (filter and activated charcoal) are then covered with 5 mL of dichloromethane/methanol (7:3) and 0.4 µL of 1-hexanol (internal standard) is added. The screw-capped vial is sealed and the sample solution is extracted for 10 minutes in the ultrasonic bath. Immediately after this, the sample extract is filtered through a disposable filter into a separate vial in order to separate the filter and activated charcoal from the sample solution. Part of the sample solution is transferred into an autosampler vial with a micro insert for analysis.

4 Operating conditions for chromatography

Apparatus:	PerkinElmer Clarus 500 gas chromatograph with FID and autosampler	
Column:	Material:	Fused silica
	Stationary phase:	StabilWax (Crossbond polyethylene glycol)
	Length:	60 m
	Inner diameter (ID):	0.25 mm
	Film thickness:	0.50 µm
Injector temperature:	200 °C	
Detector:	Flame ionisation detector (FID)	
Detector temperature (FID):	250 °C	

Rate of heating:	50 °C (5 min) $\xrightarrow{10\,°\text{C/ min}}$ 200 °C (4 min)
Carrier gas:	Helium 5.0 (280 kPa)
Split:	10 mL/min
Injection volume:	1 µL

5 Analytical determination

For the analytical determination 1 µL of each of the sample solutions prepared as described in Section 3.2 is injected into the gas chromatograph and analysed in a duplicate determination under the conditions stated in Section 4. If the measured concentrations are above the calibration range, then suitable dilutions must be prepared and the analysis must be repeated. Figure 2 shows an example of a chromatogram of the investigated glycol esters and glycol ethers.

6 Calibration

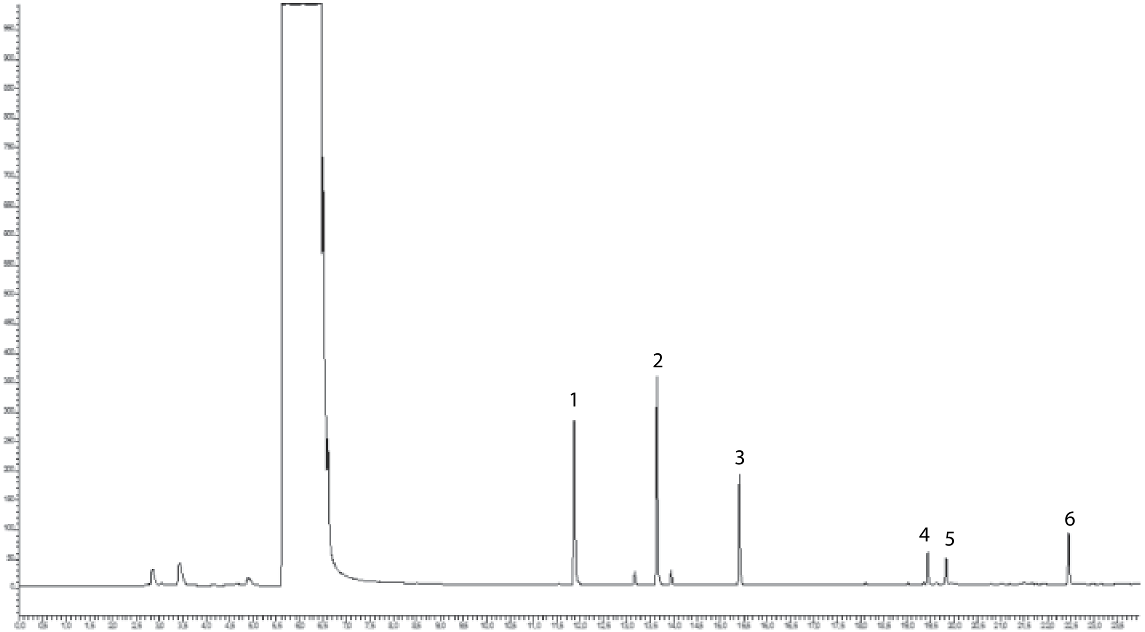
The calibration samples prepared according to Section 2.3 are analysed as described in Sections 4 and 5. Routine calibration is carried out by dosing aliquots of the stock solution (volumes listed in Table 3), into a mixture of dichlormethane/methanol (7:3).

The calibration functions are obtained by plotting the measured peak area ratios versus the respective concentration ratios.

The calibration functions are linear in the investigated concentration range and should be regularly checked during routine analysis. A control sample of medium concentration must be analysed in each analytical series as a control.

Table 3: Calibration solutions used for routine calibration

No.	Stock solution	2PG1EE	2PG1EA	DEGME	DEGEE	DEGBE
	[µL]	[µg/5 mL]	[µg/5 mL]	[µg/5 mL]	[µg/5 mL]	[µg/5 mL]
1	3	16.2	18	19	18	18
2	10	54	59	62	59	58
3	50	270	300	310	290	290
4	100	540	590	6208	590	580
5	200	1080	1180	1240	1190	1150
6	400	2160	2360	2470	2380	2300



1	Propylene glycol monoethyl ether (2PG1EE)
2	1-Ethoxy-2-propanol acetate (2PG1EA)
3	Diethylene glycol monomethyl ether (DEGME)
4	Diethylene glycol monoethyl ether (DEGEE)
5	Diethylene glycol monobutyl ether (DEGBE)

Figure 2 Chromatogram of the investigated glycol esters and glycol ethers (see Section 4 for the chromatographic conditions)

7 Calculation of the analytical result

The concentrations of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether in the workplace air are calculated from the concentrations of the substances in the measurement solution by the data evaluation unit. Taking the dilution, the recovery and the air sample volume into account, the concentrations of the substances in the measurement solution are used to calculate the concentrations of the glycol esters and glycol ethers in the workplace air according to Equation (1) as follows:

$$\rho = \frac{(A_Q - a)}{b \times V \times \eta} \times F \tag{1}$$

where:

ρ is the mass concentration of a glycol ester or glycol ether in the ambient air in mg/m^3

A_Q is the peak area quotient $\left(A_Q = \frac{A_{sample}}{A_{ISTD}}\right)$

a is the y-axis intercept

b is the slope of the graph in L/mg

V is the air sample volume in m^3 (calculated from the flow rate and the sampling period)

η is the recovery

F is the conversion factor of the mass to volume of the measured sample (in this case 0.005 L)

8 Reliability of the method

The characteristics of the method were calculated as stipulated in EN 482 [11], EN 1076 [12] and EN 13936 [13]. The limits of quantification of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether in the workplace air were calculated from the results of the respective 10-point calibrations according to DIN 32645 [14]. Furthermore, Appendix B 3.4.1 of EN 13890 [15] was taken into consideration for the particle fraction.

8.1 Precision and expanded uncertainty

A six-fold determination was carried out to ascertain the precision for the concentrations of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether listed in Table 4. The filters were spiked using microlitre syringes after connecting the sampling head upstream of the activated charcoal while the pump was in operation. For this purpose 40 litres of clean air were drawn through the sampling system at a flow rate of 20 L/h at room temperature. These

Table 4: Standard deviations (rel.) and expanded uncertainties *U (*for *n* = 6 determinations)

Substance	Concentration	Standard deviation (rel.)	Expanded uncertainty U
	[mg/m³]	[%]	[%]
Propylene glycol monoethyl ether	23	2.5	28
	230	4.8	29
	450	5.2	29
1-Ethoxy-2-propanol acetate	31	4.1	28
	310	9.2	28
	590	4.9	28
Diethylene glycol monomethyl ether	4.9	4.8	29
	54	3.5	29
	100	9.8	30
Diethylene glycol monoethyl ether	3.5	5.2	29
	37	4.0	29
	72	12	30
Diethylene glycol monobutyl ether	6.8	5.5	32
	69	5.1	31
	130	17	34

Table 5: Mean recoveries for n = 6 determinations

Substance	Validated working range	Mean recovery
	[mg/m³]	[%]
Propylene glycol monoethyl ether	0.5 to 440	93
1-Ethoxy-2-propanol acetate	0.5 to 600	85
Diethylene glycol monomethyl ether	0.5 to 100	78
Diethylene glycol monoethyl ether	0.5 to 70	83
Diethylene glycol monobutyl ether	0.5 to 130	79

experiments were carried out at a relative humidity of approx. 40%. The spiked sample carriers were prepared and analysed as described in Sections 3.2, 4 and 5. The results are documented in Table 4.

The expanded uncertainties of the investigated glycol esters and glycol ethers were calculated, taking all relevant influencing factors into consideration as stipulated in EN 482 [11]. The expanded uncertainty of the entire method consists principally of the sampling uncertainty contributions (e.g. air sample volume, deviation from the sampling convention) and the analytical preparation (scatter of the calibration function, fluctuations in the transfer as well as the reproducibility). The resulting characteristics, such as relative standard deviation and expanded uncertainty, are listed in Table 4.

8.2 Recovery

The recoveries of the concentrations of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether in the workplace air are calculated using the results of the precision experiments. The mean recoveries are constant in the investigated concentration range (see Table 5).

8.3 Influence of the relative humidity

The influence of the humidity was examined at concentrations of a tenth and twice the OEL of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether at relative humidities of approx. 20, 40 and 80%. No influence due to humidity could be detected for the substances 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether.

Lower humidities ≤ 30% can lead to lower recoveries of propylene glycol monoethyl ether.

8.4 Influence of the temperature

The influence of the temperature was examined at concentrations of a tenth and twice the OEL of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether at a temperature of 3 °C and a relative humidity of approx. 80%. A lower recovery could be determined for some substances at low temperatures.

8.5 Limit of quantification

The limits of quantification of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether were calculated in the same manner as the calibration line method described in DIN 32645 [14] with a statistical certainty of $P = 95\%$ and $k = 3$.

The limit of quantification of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether is 0.5 mg/m^3 in each case based on an air sample volume of 40 litres. The results are listed in Table 6.

8.6 Capacity of the sampling system

Breakthrough experiments at concentrations of twice the OEL were carried out to determine the capacity of the sample carrier. In total six sample carriers with two adsorption tubes connected in series were loaded for these experiments. The exper-

Table 6: Variation coefficients and limits of quantification for *n* = 6 determinations

Substance	Validated working range	Variation coefficient	Limit of quantification
	[mg/m^3]	[%]	[mg/m^3]*
Propylene glycol monoethyl ether	0.5 to 440	4.2	0.5
1-Ethoxy-2-propanol acetate	0.5 to 600	4.3	0.5
Diethylene glycol monomethyl ether	0.5 to 100	4.6	0.5
Diethylene glycol monoethyl ether	0.5 to 70	4.5	0.5
Diethylene glycol monobutyl ether	0.5 to 130	4.3	0.5

* for an air sample volume of 40 L

iments were carried out at room temperature and a relative humidity of 80%. The sampling period was 2 hours at a flow rate of 20 L/h. No breakthrough to the second tube could be detected.

An experiment involving sampling for 3 hours and two adsorption tubes connected in series was unfortunately impossible due to the high dosing volume, as the pumps were not able to maintain the flow rate of 20 L/h.

However, a maximum sampling period of 2 hours has been validated up to a concentration of twice the limit value by means of the experiment described above. Should the concentration or the sampling period exceed these parameters, then the measured value must be limited accordingly.

8.7 Storage stability

Tests on storage stability of sample carriers loaded with propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether were carried out over a time period of four weeks. For this purpose two experimental series with concentrations of a tenth and twice the OEL or MAK value were performed. The sample carriers were spiked at room temperature and a relative humidity of approx. 80 to 90%. The sample carriers were then stored at room temperature.

Over a period of three weeks no losses could be detected, therefore storage stability over a period of 21 days is ensured.

8.8 Interference

On account of the low specificity of flame ionisation detectors, interference is principally possible due to components with the same retention time. Interference from possible blank values occurring for propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether caused by the desorption agent, the original substances or the internal standard must be ruled out during the preliminary stages.

9 Discussion

The analytical method described here enables the determination of propylene glycol monoethyl ether, 1-ethoxy-2-propanol acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether in workplace air in concentration ranges of one tenth to twice the currently valid OEL or MAK values. Furthermore, the analytical method is suitable for monitoring compliance with the peak limits (short-term exposure limits).

Sampling with the GGP-Mini sampling system ensures that the airborne aerosol fraction is always captured in its entirety [16].

The analytical method described here was checked by spiking five sample carriers in the laboratory of the examiner of the method (BGN – *German Social Accident Insurance Institution for the foodstuffs industry and the catering trade*) with defined amounts of glycol esters and glycol ethers, but the masses were unknown to the laboratory of the developer of the method (IFA – *Institute for Occupational Safety and Health of the German Social Accident Insurance*). These samples were subsequently prepared and analysed in the laboratory of the developer of the method as described in Sections 3.2, 4 and 5. A sixth sample carrier served as the field blank value. Loading with spiking masses of 0.2 to 0.7 times the Occupational Exposure Limit resulted in recoveries of 94% for propylene glycol monoethyl ether to 117% for diethylene glycol monomethyl ether. The exact results can be found in Table 7.

It was not possible to conduct actual comparative measurements, as no comparative laboratory was available.

Table 7: Results of testing the measurement method

Substance	Set value	Actual value	Recovery
	[µg]	[µg]	[%]
Propylene glycol monoethyl ether	1911	1805	94
1-Ethoxy-2-propanol acetate	1804	2080	115
Diethylene glycol monomethyl ether	508	592	117
Diethylene glycol monoethyl ether	997	986	99
Diethylene glycol monobutyl ether	1139	1168	103

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