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Glycols – Method for the determination of diethylene glycol, ethylene glycol and propylene glycol in workplace air using gas chromatography

Air Monitoring Method – Translation of the German version from 2018

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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 diethylene glycol, ethylene glycol and propylene glycol 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 glycols 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

ethylene glycol; diethylene glycol; propylene glycol; air analysis; workplace measurement; hazardous substances; workplace monitoring; air sampling; GGP-Mini; glass fibre filter; activated charcoal tube; gas chromatography

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Glycols – Method for the determination of diethylene glycol, ethylene glycol and propylene glycol in workplace air using gas chromatography

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

Summary

The analytical method described here enables monitoring of Occupational Exposure Limits (OEL) or MAK values of ethylene glycol, diethylene glycol and propylene glycol in workplace air [1, 2]. Glycols occurring in the gaseous and particulate state can be simultaneously determined with this method. Sampling consists of 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 glycols 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 internal standard. The qualitative and quantitative determination is performed by means of gas chromatography using a flame ionisation detector (FID). Multiple-point calibrations are used for the quantitative evaluation according to the internal standard method.

Characteristics of the method

Precision:	Standard deviation (rel.):	s = 2.9 to 3.9%
	Expanded uncertainty:	U = 26 to 38%
	in the concentration range from 0.5 to 100 mg/m^3 depending on the glycol and for n = 6 determinations	

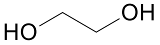
Limit of quantification:	Ethylene glycol	0.5 mg/m^3
	Diethylene glycol	0.5 mg/m^3
	Propylene glycol	0.5 mg/m^3
	at an air sample volume of 40 litres	
Recovery:	Ethylene glycol	84%
	Diethylene glycol	79%
	Propylene glycol	91%
Sampling recommendations:	Sampling period:	2 h
	Air sample volume:	40 L
	Flow rate:	20 L/h (0.33 L/min)

Description of the substances

Glycols

Glycols are divalent alcohols derived from ethylene glycol (1,2-diol). They are used as antifreeze agents due to their low freezing point (as low as −15 °C below that of water). In combination with water the freezing point is significantly lower and can reach −55 °C at the right mixture ratio. In industry glycols serve as solvents and additives for varnishes, paints and cleaning products. Furthermore, they are a component of brake fluid and more recently are used as a carrier substance for flavourings and to nebulise liquids in electronic cigarettes.

Ethylene glycol [107-21-1]



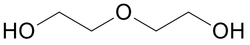
Synonyms: 1,2-Ethanediol, ethylene alcohol

Ethylene glycol is a clear, viscous liquid with a sweetish taste (molar mass 62.07 g/mol, boiling point 197 °C, melting point −16 °C, vapour pressure 5.3 Pa at 20 °C). It is miscible with water und polar organic solvents such as ethanol and acetone.

Ethylene glycol is used as an antifreeze agent for combustion engines and is marketed under the trade name of Glysantin®. Due to its hydrophilic properties it is used as an absorption agent for the removal of water vapour from natural and refinery gas. When mixed with water it is an effective de-icing agent for aircraft and traffic surfaces (e.g. runways) and is used at all commercial airports.

The OEL and MAK value for ethylene glycol is 26 mg/m^3 (10 ppm) [1, 2]. The short-term exposure limit is classified in Peak Limitation Category I with an excursion factor of 2. Furthermore, the following footnote applies to this substance: "*may occur simultaneously as vapour and aerosol*" [2]. Detailed information on the toxicity of ethylene glycol can be found in the toxicological-occupational health documentation of the MAK values [3, 4].

Diethylene glycol [111-46-6]



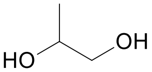
Synonyms: Ethylene diglycol, dihydroxy diethyl ether, diglycol

Diethylene glycol is a colourless and odourless liquid (molar mass 106.12 g/mol, boiling point 244 °C, melting point −6 °C, vapour pressure 0.008 hPa at 25 °C). It is completely miscible with water.

Diethylene glycol is used as the starting material for the synthesis of the polyester resins, morpholine and 1,4-dioxane. Mixed with water, diethylene glycol is used as an antifreeze agent.

The OEL and MAK value for diethylene glycol is 44 mg/m^3 (10 ppm) [1, 2]. The short-term exposure limit is classified in Peak Limitation Category II with an excursion factor of 4. Furthermore, the following footnote applies to this substance: *"may occur simultaneously as vapour and aerosol"*. Detailed information on the toxicity of diethylene glycol can be found in the toxicological-occupational health documentation of the MAK values [5].

Propylene glycol [57-55-6]



Synonyms: 1,2-Propanediol, 1,2-dihydroxypropane, methyl ethyl glycol (MEG)

Propylene glycol is a hygroscopic, colourless and odourless liquid with a viscous consistency (molar mass 76.10 g/mol, boiling point 188 °C, melting point −60 °C, vapour pressure 0.11 hPa at 20 °C). It is miscible with water as well as polar organic solvents such as ethanol, acetone, chloroform and diethyl ether. Due to its hygroscopic properties propylene glycol aerosols act as condensation seeds in air for mist droplets from the ambient humidity.

As a result of its solubilising and emulsifying properties, propylene glycol is used as a carrier substance and carrier solvent for colorants, antioxidation agents, emulsifiers and enzymes amongst other things. Furthermore, it is contained in many body care products, such as skin creams, tooth pastes and deodorants, as a plasticiser. In addition, it is used as a humectant in nearly all tobacco products. Propylene glycol is approved in the EU, under the designation of E1520, as a food additive for chewing gums and dietary supplements in the form of capsules or tablets.

The List of MAK and BAT Values includes propylene glycol in Section II b [2]. Furthermore, the following footnote applies to the substance: *"may occur simultaneously as vapour and aerosol"*. Detailed information on the toxicity of propylene glycol can be found in the toxicological-occupational health documentation of the MAK values [6].

Contents

1 General principles

The analytical method described here enables monitoring of Occupational Exposure Limits (OEL) or MAK values of ethylene glycol, diethylene glycol and propylene glycol in workplace air [1, 2]. The glycols listed above can be simultaneously determined in the gaseous and particulate state with this method. For sampling a flow-regulated pump draws a defined volume of air through a GGP-Mini sampling system with a 0.33 L/min intake cone, consisting of a glass fibre filter and an activated charcoal tube connected downstream. Thus, airborne droplets are deposited on the filter, whereas gaseous glycols 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 internal standard. The qualitative and quantitative determination is performed by means of gas chromatography using a 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, 52313 Düren, Germany, 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, 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
- Diethylene glycol, purity≥ 99.0% (GC), e.g. Sigma-Aldrich 32160
- Ethylene glycol, purity ≥ 99.5% (GC), e.g. Fluka 03750
- Propylene glycol, purity ≥ 99.5% (GC), e.g. Sigma-Aldrich 82280

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:

The masses of the investigated glycols listed in Table 1 are weighed exactly to the nearest 0.1 mg into a 5 mL volumetric flask. The volumetric flask is then filled to the mark with dichloromethane/methanol (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 flask.

Calibration solutions:

The 10 calibration standard solutions are prepared by pipetting aliquots of 1 to 10 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 flask are then filled to the mark with dichloromethane/methanol (7:3) and 0.4 µL of 1-hexanol as an internal standard (ISTD) is dosed into each volumetric flask.

The calibration solutions have to 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) an appropriately equipped GGP-Mini sampling system with an intake cone for 0.33 L/min is connected to the pump.

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

Table 1 Concentration of the glycols in the stock solution

Glycol	Mass [mg/5 mL]	Concentration [µg/µL]
Ethylene glycol	56.8	11.4
Diethylene glycol	51.8	10.4
Propylene glycol	55.3	11.1

Table 2 Calibration solutions to determine the performance characteristics

Calibration solution No.	Volumes of stock solution [µL]	Ethylene glycol [µg/5 mL]	Diethylene glycol [µg/5 mL]	Propylene glycol [µg/5 mL]
1	1	11.4	10.4	11.1
2	2	22.7	20.7	22.1
3	3	34.1	31.1	33.2
4	4	45.4	41.4	44.2
5	5	56.8	51.8	55.3
6	6	68.2	62.2	66.3
7	7	79.5	72.5	77.4
8	8	90.9	82.9	88.5
9	9	102	93.2	99.5
10	10	114	104	111

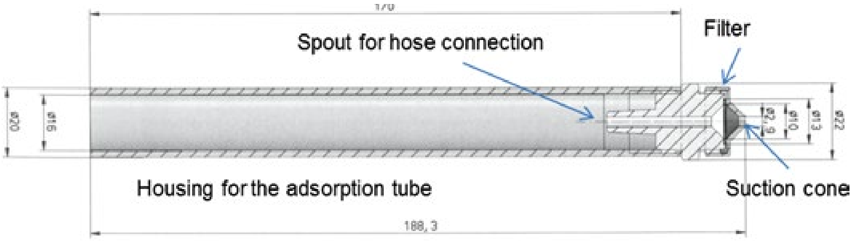


Figure 1 Schematic set-up of the sampling system GGP-Mini [7]

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 should be drawn through the sampling system at a pre-selected flow rate of 20 L/h 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 [8]. The important parameters for the determination of the concentration in air (sample volume, temperature, air pressure, 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 withdrawn using tweezers and transferred into the designated screw-capped vial, which is then sealed. The loaded sample carriers (filter and charcoal tube) must be delivered to the analytical laboratory as rapidly as possible.

Note:
Sampling should preferably be carried out at a medium humidity as the recovery of diethylene glycol was influenced by low or high humidities (see Section 8.3*).*

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 sample vial is sealed and the sample solution is extracted for 10 minutes in the ultrasonic bath. Immediately afterwards, the sample extract is filtered through a disposable filter into a separate vial in order to separate the filter and the adsorbent (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 Gas chromatograph Clarus 500 with 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:	250 °C	
Detector gases:	Hydrogen (45 mL/min), synthetic air (450 mL/min)	
Rate of heating:	$50\ ^{\circ}\mathrm{C}\ (5\ \mathrm{min}) \xrightarrow{15\ ^{\circ}\mathrm{C}/\mathrm{min}} 200\ ^{\circ}\mathrm{C}\ (15\,\mathrm{min})$	
Carrier gas:	Helium (280 kPa)	
Injection volume:	2 µL	

5 Analytical determination

For the analytical determination 2 µL each of the sample solution that have been prepared as described in Section 3.2 are 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 glycols.

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 dichloromethane/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.

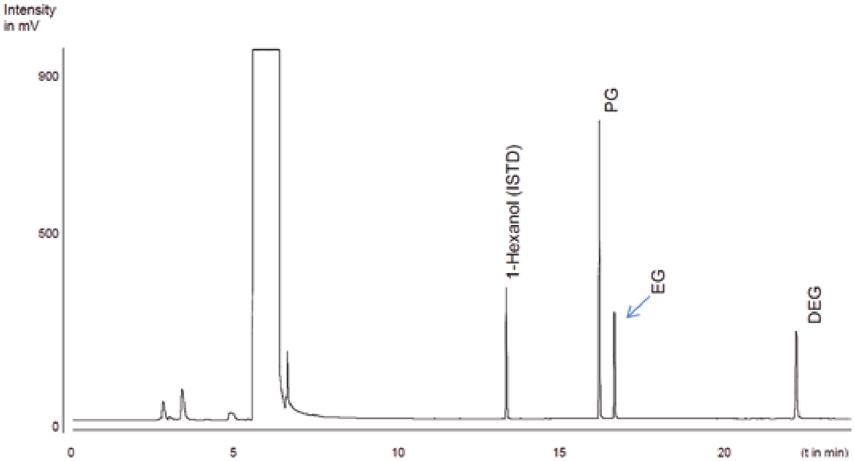


Figure 2 Chromatogram of the investigated glycols, i.e. ethylene glycol (EG), diethylene glycol (DEG) and propylene glycol (PG) (for chromatographic conditions see Section 4)

Table 3 Calibration solutions used for routine calibration

Calibration solution No.	Stock solution [µL]	DEG [µg/5 mL]	EG [µg/5 mL]	PG [µg/5 mL]
1	2	20.7	22.7	22.1
2	10	104	114	111
3	25	–	–	276
4	50	518	568	553
5	80	–	–	884
6	100	–	1136	1106
7	125	1295	1420	–
8	150	1554	1704	–
9	200	–	–	–
10	350	3626	–	–

7 Calculation of the analytical result

The concentrations of ethylene glycol, diethylene glycol and propylene glycol in the workplace air are calculated from the concentrations of the substances in the measurement solution by the data evaluation unit. The concentrations of the substances in the measurement solution, taking the dilutions, the recovery and the air sample volume into account, are used to calculate the concentrations of the investigated glycols ethylene glycol, diethylene glycol and propylene glycol 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 in the air in mg/m^3

A_Q is the area ratio ($A_Q = \frac{A_{sample}}{A_{ISTD}}$)

a is the y-axis intercept

b is the slope of the graph in L/mg

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

η is the recovery

F is the extraction volume in L (here 0.005 L)

8 Reliability of the method

The characteristics of the method were calculated as stipulated in EN 482 [9], EN 1076 [10] and EN 13936 [11]. The limits of quantification of ethylene glycol, diethylene glycol and propylene glycol in the workplace air were calculated from the results of the respective 10-point calibrations according to DIN 32645 [12]. Furthermore, Appendix B 3.4.1 of EN 13890 [13] 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 ethylene glycol, diethylene glycol and propylene glycol listed in Table 4. The filters were spiked using microlitre syringes after connecting the sampling head upstream of the activated charcoal tube while the pump was in operation. For this purpose 40 litres of clean air was drawn through the sampling system at a flow rate of 20 L/h at room temperature. These experiments were carried out at a relative humidity of approx. 40 to 50%. 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 for the determination of the investigated glycols was calculated, taking all relevant influencing factors into consideration, as stipulated in EN 482 [9]. 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.

Table 4 Relative standard deviations and expanded uncertainties U for $n = 6$ determinations

Glycol	Concentration [mg/m^3]	Relative standard deviation [%]	Expanded uncertainty U [%]
Ethylene glycol	2.6	7.3	29
	27	3.0	29
	53	3.3	29
Diethylene glycol	4.4	6.1	38
	44	1.8	38
	88	3.8	38
Propylene glycol	5.0	8.3	27
	50	3.0	26
	100	3.0	26

Table 5 Mean recovery for $n = 6$ determinations

Glycol	Validated working range [mg/m^3]	Mean recovery [%]
Ethylene glycol	0.5 to 53	84
Diethylene glycol	0.5 to 88	79
Propylene glycol	0.5 to 100	91

8.2 Recovery

The recoveries of the concentrations of ethylene glycol, diethylene glycol and propylene glycol in the workplace air were calculated using the results of the precision experiments. The mean recoveries are constant in the investigated concentration range at medium relative humidities (see Table 5). The results show that the sum of the concentrations of vapour and droplets is independent of the temperature (see Section 8.4), but partially dependent on the relative humidity (see Section 8.3).

8.3 Influence of the relative humidity

The influence of the humidity was examined at concentrations of a tenth and twice the OEL of ethylene glycol, diethylene glycol and propylene glycol at relative humidities of approx. 30, 45 and 80%. No influence due to humidity could be detected for ethylene glycol and propylene glycol. In the case of diethylene glycol, deviations in the recovery appeared both at a low humidity (≤ 30%) as well as at a high humidity (≥ 70%), therefore it is advisable to carry out sampling at a medium relative humidity.

8.4 Influence of the temperature

The influence of the temperature was examined at concentrations of a tenth up to twice the OEL of ethylene glycol, diethylene glycol and propylene glycol at a temperature of 3 °C and a relative humidity of approx. 80%. No influence on the recovery could be detected due to temperature.

8.5 Limit of quantification

The limits of quantification of ethylene glycol, diethylene glycol and propylene glycol were calculated in the same manner as the calibration line method described in DIN 32645 [12] with a statistical certainty of $P = 95\%$ and $k = 3$.

The limit of quantification for the three glycols is 0.5 mg/m^3 based on an air sample volume of 40 litres. The results are listed in Table 6.

Table 6 Variation coefficients for *n* = 6 determinations and limits of quantification (LOQ)

Glycol	Validated working range [mg/m^3]	Variation coefficient [%]	Limit of quantification [mg/m^3]*
Ethylene glycol	0.5 to 53	2.9	0.5
Diethylene glycol	0.5 to 88	3.9	0.5
Propylene glycol	0.5 to 100	3.9	0.5

* for an air sample volume of 40 L

8.6 Capacity of the sampling system

The breakthrough behaviour of the glycols listed above in combination with the sampling system used was determined by connecting a second activated charcoal tube downstream of the sampling system (combination of two activated charcoal tubes connected in series), switching on the pump and setting a flow rate of 20 L/h. The filter was then spiked with ethylene glycol, diethylene glycol and propylene glycol in concentrations of twice the OEL or MAK value and air was drawn through this sample carrier configuration for three hours at a relative humidity of approx. 80% at room temperature. No breakthrough was observed.

8.7 Storage stability

Tests on storage stability of loaded sample carriers were conducted over a period of four weeks. For this purpose 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 at a relative humidity of approx. 80%. The sample carriers were then stored at room temperature.

Over a period of three weeks no losses could be detected, therefore storage stability over 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 ethylene glycol, diethylene glycol and propylene glycol caused by 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 Occupational Exposure Limits (OEL) or MAK values for ethylene glycol, diethylene glycol and propylene glycol in workplace air in the concentration range of a tenth up to twice

Table 7 Results of the measurement procedure check

Glycol	Set value [µg]	Actual value [µg]	Recovery [%]
Ethylene glycol	583	642	110
Diethylene glycol	1229	1355	110
Propylene glycol	889	906	102

the OEL or MAK value. Furthermore, the analytical method is suitable for monitoring compliance with the peak limit (short-term exposure limits).

Sampling with the GGP-Mini sampling system ensures that the airborne aerosol fraction is always captured in its entirety [14].

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 masses of glycols, 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 in accordance with Sections 3.2, 4 and 5. A sixth sample carrier served as the field blank value. Loading with spiking masses of half to 0.7 times the OEL resulted in recoveries of 102% for propylene glycol and 110% for ethylene glycol and diethylene glycol. The exact results are shown in Table 7.

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

References

[1] TRGS 900 (2006) Arbeitsplatzgrenzwerte, BArbBl. Heft 1/2006 pp. 41-55, recently revised and supplemented: GMBl 2017 pp. 919-922 [No. 50] (30.11.2017), https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/TRGS-900.pdf?_blob=publicationFile&v=3

[2] DFG – Deutsche Forschungsgemeinschaft (2017) List of MAK and BAT Values 2017. Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Report No. 53. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/book/10.1002/9783527812127

[3] Greim H (ed.) (2000) Ethylenglykol [MAK Value Documentation in German language]. Gesundheitsschädliche Arbeitsstoffe, Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten, 30. Lieferung. Wiley-VCH, Weinheim, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb10721d0030/pdf

[4] Henschler D (ed.) (1992) Ethylene glycol. The MAK-Collection Part I: Occupational Toxicants, Vol. 4, pp 226-245. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb10721e0004/pdf

[5] Greim H (ed.) (2012) Diethylene glycol [translation of German version 1998]. The MAK Collection for Occupational Health and Safety, pp. 74–90. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb11146e0010/pdf

[6] Greim H (ed.) (2007) Propylenglykol [MAK Value Documentation in German language]. Gesundheitsschädliche Arbeitsstoffe, Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten, 42. Lieferung. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb5755kskd0042/pdf

[7] IFA Arbeitsmappe (2015) Kennzahl 3040: Geräte zur Probenahme von Stoffen, die gleichzeitig partikel- und dampfförmig vorliegen. Erich Schmidt Verlag, Berlin, Germany http://www.ifa-arbeitsmappedigital.de/did/00304000/redirect/301/inhalt.html

[8] 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

[9] 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

[10] 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

[11] 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

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

[13] EN 13890 (2010) Workplace exposure – Procedures for measuring metals and metalloids in airborne particles – Requirements and test methods; German version EN 13890:2009. Beuth Verlag, Berlin, Germany

[14] Breuer D, Friedrich C, Möhlmann C, Dragan GC (2015) Das miniaturisierte Probenahmesystem GGP-Mini zur gleichzeitigen Erfassung von Dampf/Tröpfchen-Gemischen schwerflüchtiger Verbindungen – Ergebnisse von Labor- und Praxismessungen. Gefahrstoffe – Reinhaltung der Luft Vol. 75(10), S. 390-294, http://www.dguv.de/medien/ifa/de/pub/grl/pdf/2015_175.pdf