

Ethylene oxide – Method for the determination of ethylene oxide in workplace air using gas chromatography after thermal desorption

Air Monitoring Method

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Abstract

This analytical method is a validated measurement procedure for the determination of ethylene oxide [75-21-8] in workplace air averaged over the sampling period after personal or stationary sampling. A defined volume of air is drawn through two adsorption tubes packed with Chromosorb 106 and connected in series. For sampling the flow rate of the flow-regulated pump is set to 5 ml/min with an air sample volume of 200 ml (which corresponds to a sampling period of 40 min). For the following analysis the ethylene oxide is thermally desorbed and analysed by means of gas chromatography (GC) with a flame ionisation detector (FID). The quantitative evaluation is based on a calibration function obtained by means of a multiple-point calibration. The relative limit of quantification (LOQ) is 15 µg/m³ ethylene oxide for an air sample volume of 200 ml. The mean recovery was 100% and the expanded uncertainties were between 24 and 27% over the entire measurement range.

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This analytical method has been accredited by the accident insurance companies for the detection in workplace air of substances that are carcinogenic, mutagenic or toxic to reproduction.

This method has been tested and recommended for the determination of ethylene oxide at workplaces by the accident insurance companies.

Both personal and stationary sampling can be performed for measurements in order to evaluate work areas.

Name	Synonym	CAS No.	Molecular structure	Molar mass
Ethylene oxide	Oxirane	75-21-8	C ₂ H ₄ O	44.05

1 Summary

The mean concentration of ethylene oxide at the workplace over the sampling period can be determined with this method using personal or stationary sampling.

Measurement Principle: A pump draws a defined volume of air through two adsorption tubes connected in series and packed with 300 mg of Chromosorb 106. The deposited ethylene oxide is then thermally desorbed and after gas chromatographic separation it is determined using the flame ionisation detector (FID).

The calibration is performed using a certified test gas.

Limit of quantification: Absolute: 3.0 ng
Relative: 0.015 mg/m³ for an air sample volume of 200 ml

Measurement range: 0.015 mg/m³ to 3.27 mg/m³

Selectivity: Elevated values may be caused by interferences.

Advantages: Personal and selective measurements are possible.

Disadvantages: No indication of concentration peaks.

Apparatus: Pump
Flow meter
Adsorption tube packed with 300 mg of Chromosorb 106, gas chromatograph with a mass selective detector (MSD)
Thermal desorber, gas chromatograph with FID

2 Equipment and chemicals

2.1 Equipment

For sampling:

- Sampling pump, suitable for a flow rate of 5 ml/min, e.g. PP1, from Gilian, supplied by DEHA Haan & Wittmer, 71296 Heimsheim, Germany
- Flow meter, e.g. Gilibrator, from Sensidyne, St. Petersburg, FL 33716, USA
- Adsorption tubes made of stainless steel (6.3 mm × 90 mm, 5 mm inner diameter), packed with 300 mg of Chromosorb 106 (60–80 mesh) that is secured between two pieces of metal packing gauze, e.g. from Restek, 61348 Bad Homburg, Germany. Before use, the adsorption tubes packed with Chromosorb 106 are heated for 10 minutes in the thermal desorber at 120 °C and then tested for blank values. They are sealed with Swagelok caps for storage.

- Sealing caps (e.g. Swagelok with PTFE seals, PTFE caps)

For the analysis:

- Hamilton Microlab 900 syringe pump (diluter/dispenser), e.g. from Duratec Analysentechnik GmbH, 68766 Hockenheim, Germany
- Thermal desorber, gas chromatograph with flame ionisation detector (FID)

2.2 Chemicals

- Test gas, approx. 10 ppm ethylene oxide in nitrogen, e.g. from Air Liquide Deutschland GmbH, 47809 Krefeld, Germany

Gases for operation of the gas chromatograph:

- Helium, purity 99.996%
- Hydrogen, purity 99.999%
- Synthetic compressed air, free of hydrocarbons, dew point below -40°C

2.3 Test gases and calibration standards

A certified test gas with a concentration of 11.9 ppm (equivalent to 21.8 mg/m^3) is used for calibration and validation of the method. The required target concentrations of test gases 2 and 3 are prepared by dynamic mixing of this test gas with synthetic compressed air (DIN 2020). Adsorption tubes packed with Chromosorb 106 are connected to the suction side of the syringe injection pump and the volumes listed in Table 1 are drawn through the tubes. The resulting masses deposited onto the sample carriers and the concentrations in the air sample at an air sample volume of 200 ml are also listed in Table 1.

Tab.1 Test gas concentrations and calibration standards

Test gas	1	2	3			
Dilution factor	1	40	122			
Concentration [mg/m^3] at 20°C and 1013 hPa	21.8	0.544	0.179			
Volume [ml]	Mass per sample carrier and concentration in the air sample					
	m [ng]	c [mg/m^3]	m [ng]	c [mg/m^3]	m [ng]	c [mg/m^3]
1			0.54	0.003		
5			2.72	0.014		
10	218	1.09			1.79	0.009
20	436	2.18			3.58	0.018
25			13.6	0.068		
30	654	3.27			5.37	0.027
40					7.16	0.036
50			27.2	0.136	8.95	0.045
60					10.8	0.054
70					12.5	0.063

Tab. 1 (continued)

Test gas	1	2	3			
Dilution factor	1	40	122			
Concentration [mg/m ³] at 20 °C and 1013 hPa	21.8	0.544	0.179			
Mass per sample carrier and concentration in the air sample						
Volume [ml]	m		c		m	
	[ng]	[mg/m ³]	[ng]	[mg/m ³]	[ng]	[mg/m ³]
80					14.3	0.072
90					16.1	0.081
100			54.4	0.272	17.9	0.090
200			109	0.544		

3 Sampling

Pre-treated adsorption tubes are used for sampling (see Section 2.1). The sealing caps are removed at the beginning of sampling and two adsorption tubes arranged in series are connected to the sampling pump. The recommended sampling period is 40 minutes at a flow rate of 5 ml/min, which is equivalent to an air sample volume of 200 ml (DIN 2014). The important parameters for the determination of the concentration (sample volume, temperature, air pressure and relative humidity) are documented in a sampling record.

The pump and the adsorption tubes are either worn by a person while performing their activities or stationary sampling is carried out. On completion of sampling, Swagelok screw fittings are used to seal both ends of the loaded adsorption tubes.

Before and after sampling, the flow rate must be tested for constancy using a comparable sample carrier. If the deviation from the adjusted flow rate is greater than 5%, it is advisable to discard the sample (see DGUV Information 231-500 “General Part”, Section 3 (DGUV 2015)).

4 Analytical determination

4.1 Sample preparation and analysis

After the thermal desorber and gas chromatograph have been prepared, the calibration and analytical samples are measured. The adsorption tubes are fitted with desorption caps and heated in the thermal desorber, whereby the components are transferred by means of a carrier gas into a cold trap packed with Tenax TA. After complete desorption from the adsorption tube, the cold trap is heated, so that the substance mixture reaches the separation column.

The thermal desorber is set to the following instrumental conditions:

Apparatus:	Turbomatrix ATD (from PerkinElmer LAS, 63110 Rodgau, Germany)	
Purge drying phase:	Temperature:	Room temperature
	Duration:	1 min
	Flow rate:	50 ml of helium/min ^{a)}
Desorption temperature:	120 °C	
Desorption period:	10 min	
MSD valve temperature:	150 °C	

Temperature of the transfer line:	150 °C
Transfer line:	1.5 m of deactivated blank capillaries, Inner diameter: 0.32 mm
Cold trap (adsorption):	-30 °C
Cold trap (injection):	280 °C
Cold trap filling:	20 mg of Tenax TA (60 to 80 mesh)
Heating rate:	40 °C/s
Heating period:	1 min
Carrier gas:	Helium
Carrier gas pressure:	200 kPa ^{b)}
Split (before the cold trap):	closed (input split)
Flow over the cold trap:	30 ml/min (desorption flow)
Split (after the cold trap):	closed (output split)

^{a)} Depending on the apparatus used, the direction of purging can be selected to be in the same direction or in the opposite direction to that of sampling, in this case the tubes were purge dried in the same direction as that of sampling.

^{b)} This is equivalent to a column flow rate of 22 ml/min for the selected conditions.

4.2 Operating conditions for chromatography

Apparatus:	Gaschromatograph Clarus 680 with flame ionisation detector (from PerkinElmer LAS)	
Column:	Material:	Fused silica capillary
	Stationary phase:	Porabond U
	Length:	25 m
	Inner diameter:	0.53 mm
	Film thickness:	20 µm
Detector temperatures:	300 °C	
Detector gases:	Hydrogen (45 ml/min), synthetic air (450 ml/min)	
Temperature program:	2 min at 40 °C, with 5 °C/min up to 170 °C, 1 min	

5 Evaluation

5.1 Calibration

The calibration samples prepared according to [Section 2.3](#) are analysed as described in [Section 4](#). The calibration function is obtained by plotting the resulting peak areas of the FID signal versus the respective loaded masses (see [Table 1](#)). The calibration curve is linear in the investigated concentration range and should be regularly checked during routine analysis. A control sample of known concentration must be analysed in each analytical series for this purpose. This control sample can be a calibration sample of known concentration in the medium measurement range.

5.2 Calculation of the analytical result

Based on the determined peak areas, the corresponding mass m in μg per sample is obtained from the calibration curve. The corresponding mass concentration (c) is calculated according to the following Equation (1):

$$c = \frac{m}{V \times \eta} \quad (1)$$

where:

- c is the mass concentration of ethylene oxide in the ambient air in mg/m^3
- m is the mass of ethylene oxide in the analytical sample in μg
- V is the air sample volume in l (calculated from the flow rate and the sampling period)
- η is the recovery (see Section 6.1), here it is equal to 1

6 Reliability of the method

6.1 Precision and recovery

The precision in the lowest measurement range as well as the recovery for five concentrations (see Table 2) was determined according to DIN EN 482 (DIN 2021). For this purpose an ethylene oxide test gas with a content of $21.8 \text{ mg}/\text{m}^3$ was dynamically mixed with various air streams at a relative humidity of $50\% \pm 5\%$.

The syringe pump is used to draw six samples in each case with test gas aliquots of 200 ml through the adsorption tubes at a flow rate of 25 ml/min and at an ambient temperature of $21^\circ\text{C} \pm 2^\circ\text{C}$. The preparation and analytical determination were carried out as described in Section 4.

Tab. 2 Characteristics of the method for the determination of ethylene oxide, air sample volume of 200 ml (n=6)

Test gas	1	2	3	4	5
Dilution factor	550	180	108	59.9	11.2
Theoretical concentration [mg/m^3]	0.0400	0.121	0.202	0.364	1.95
Actual concentration [mg/m^3]	0.0449	0.124	0.185	0.357	1.90
Recovery [%]	112	103	91.6	97.9	97.1
Relative standard deviation [%]	1.3	2.4	3.0	1.4	1.4

The mean value of the recovery is 100.3% and can be equated to 1. A relative humidity of 50% does not have an influence. The precision is 3% at most.

6.2 Breakthrough volume

Two experimental series were performed to determine the breakthrough volume.

In the case of the first experimental series a test gas with a concentration of $1.0 \text{ mg}/\text{m}^3$ and a relative humidity of $50\% \pm 5\%$ was prepared and air sample volumes of 100 to 500 ml at an ambient temperature of $21^\circ\text{C} \pm 2^\circ\text{C}$ were drawn through three adsorption tubes connected in series and these were then immediately analysed (see Table 3).

Tab.3 Breakthrough experiment with constant ethylene oxide concentration

Sample	1	2	3	4	5
Air sample volume [ml]	100	200	300	400	500
Loaded mass [ng]	98	196	294	392	490
Recovery [%]					
Tube 1	100	98	79	63	46
Tube 2	< LQ	2	21	38	47
Tube 3	< LQ	< LQ	< LQ	< LQ	6

LQ: Limit of quantification

In the case of the second experimental series, 10 ml of the undiluted test gas according to [Section 2.2](#) were drawn through three adsorption tubes arranged in series and they were then purged with air sample volumes of 100 to 500 ml at a relative humidity of $50\% \pm 5\%$ and an ambient temperature of $21\text{ °C} \pm 2\text{ °C}$. Analysis followed immediately (see [Table 4](#)).

Tab.4 Breakthrough experiment with constant ethylene oxide mass

Sample	1	2	3	4	5
Air sample volume [ml]	110	210	310	410	510
Loaded mass [ng]	212	212	212	212	212
Recovery [%]					
Tube 1	100	72	8	5	6
Tube 2	< LQ	28	92	86	26
Tube 3	< LQ	< LQ	< LQ	9	68

LQ: Limit of quantification

During the experiments to determine the breakthrough volume of the Chromosorb 106 batch used, it was discovered that when concentration peaks occur at the beginning of sampling at volumes as low as between 100 and 200 ml, ethylene oxide is detectable on the second tube connected in series (see [Table 4](#)). If the ethylene oxide concentration is approximately constant, then less than 5% of the total mass is found on the tube connected downstream for an air sample volume of 200 ml (see [Table 3](#)).

Therefore, two adsorption tubes connected in series must be used and an air sample of no more than 200 ml should be collected.

Experience has shown that the breakthrough volume is reduced when using porous polymers such as Chromosorb 106 for an increase of the sampling temperature of 10 °C by a factor of 2. This should be taken into consideration when sampling.

6.3 Limit of quantification

The limit of quantification was determined as stipulated in DIN 32645 (DIN 2008) according to the calibration line method with 10 test gas samples (air sample volumes of 10 to 100 ml) and resulted in a concentration of 0.179 mg/m^3 (see [Table 1](#)). The resulting absolute limit of quantification was 3.0 ng of ethylene oxide ($P=95\%$ and $k=3$) equivalent to a concentration of 0.015 mg/m^3 in air for an air sample volume of 200 ml.

6.4 Storage stability

Two experimental series were performed to determine the storage stability.

In the case of the first experimental series, air sample volumes of 200 ml of a test gas with a concentration of 0.12 mg/m³ and a relative humidity of 50% ± 5% at an ambient temperature of 21 °C ± 2 °C were drawn through six adsorption tubes. The tubes were sealed with Swagelok caps and stored at room temperature. In the case of the second experimental series, air sample volumes of 200 ml of a test gas with a concentration of 1.2 mg/m³ and a relative humidity of 50% ± 5% at an ambient temperature of 21 °C ± 2 °C were drawn through adsorption tubes. The tubes were sealed and stored in the same manner as in the first experimental series.

Analysis was carried out after a storage period of one week for both experimental series.

Tab.5 Storage stability

Storage period [weeks]	Concentration [mg/m ³]		η (n=6)
	supplied	analysed	
1	0.120	0.126	1.05
1	1.20	1.13	0.94

Loaded samples can be stored for at least one week at room temperature.

6.5 Selectivity

The selectivity depends above all on the type of separation column used. The specified column has proved successful in practice. Interference in the determination can arise from substances with the same retention time.

6.6 Uncertainty

The expanded uncertainty was determined taking all the relevant influencing factors into consideration as stipulated in DIN EN 482 (DIN 2021; IFA 2020). The uncertainty of the entire method and thus also of the analytical result consists principally of the uncertainty contributions of sampling (e.g. air sample volume) and the analytical preparation (complete desorption, scatter of the calibration function, fluctuations in the recovery and the reproducibility). The expanded uncertainties were 24 to 27% over the entire measurement range.

Tab.6 Expanded uncertainties

Ethylene oxide concentration [mg/m ³]	0.04	0.202	0.364	1.95
U (%)	27.0	25.7	24.4	24.4

Notes

Competing interests

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

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