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Method for the determination of 1,2-epoxybutane (1,2-butylene oxide)

Method tested and recommended by the Berufsgenossenschaften for the determination of 1,2-epoxybutane in working areas after discontinuous sampling.
For the assessment of working areas, both personal and stationary sampling are possible.

1 Sampling with a pump and adsorption on polymeric resin Amberlite XAD-4, gas chromatography after thermal desorption
"1,2-Epoxybutane-1-GC"
(Issue: November 1994)

2 Sampling with a pump and adsorption on activated carbon, gas chromatography after desorption.
"1,2-Epoxybutane-2-GC"
(Issue: November 1994)

IUPAC name: **CAS No.:**
1,2-Epoxybutane 106-88-7

1 Sampling with a pump and adsorption on polymeric resin Amberlite XAD-4, gas chromatography after thermal desorption

This method permits the determination of 1,2-epoxybutane concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a metal tube filled with XAD-4.
The adsorbed 1,2-epoxybutane is then desorbed by heating in a thermal desorber and determined by gas chromatography.

Technical data:

Quantification limit: 20 ng 1,2-epoxybutane per adsorption tube,
relative: 0.1 mg/m^3 1,2-epoxybutane for a 200 ml air sample.

Selecivity: The selectivity must be checked in each individual case.

Advantages: Personal sampling and selective determination possible.

Disadvantages: No indication of peak concentrations. Generally only one determination per adsorption tube is possible.

Apparatus: Pump,
gas meter or flow meter,
Adsorption tubes with XAD-4,
Thermal desorber,
Gas chromatograph with flame ionisation detector (FID),
Apparatus for calibration via the gas phase.

Detailed description of the method

Contents

1 Equipment and chemicals

1.1 Equipment

For sampling:

Pump with gas meter or flow meter, suitable for a flow rate of 1–10 ml/min,
e. g. SKC-PC Ex 224 from Analyt, Müllheim

Adsorption tubes with XAD-4 as collection phase:
The adsorption tubes are metal tubes filled with XAD-4 with an external diameter and length suited to the thermal desorber used. The length of the adsorption zone, which is enclosed by metal sieves, depends on the heating zone of the desorber. After the tube has been filled, it must be purified several times in the thermal desorber at 150 °C in a stream of helium. It is then closed.

Caps for closing the adsorption tubes

For sample preparation and analysis:

Thermal desorber

Gas chromatograph with flame ionisation detector

Evaluation unit

Apparatus for calibration via the gas phase [1], e. g. calibration station for thermal desorption from Axel Semrau GmbH & Co, Sprockhövel

1.2 Chemicals

1,2-Epoxybutane, e. g. from Merck, purity > 99 %, for synthesis,
Polymeric resin Amberlite XAD-4, 60–80 mesh (e. g. from Serva, Heidelberg),
Tenax TA, 60–80 mesh (e. g. from Chrompack, Frankfurt),
Gases for operating the gas chromatograph: Helium 4.6, (purity 99.996 %),
Hydrogen 5.0 (purity 99.999 %),
Purified or synthetic air

2 Sampling

Before sampling, the purified adsorption tube must be heated for about 15 minutes in the thermal desorber at 100 °C in a stream of helium and closed. For sampling, the adsorption tube is opened and connected to the pump. The pump and tube are carried by a person during working hours or used in a stationary position. The flow rate is set at 1 ml/min. With sampling for 200 minutes this corresponds to an air sample volume of 200 ml. After the end of sampling, the tube is closed.

3 Analytical determination

3.1 Sample preparation and analysis

The loaded adsorption tube is opened and placed in the thermal desorber. The adsorbed 1,2-epoxybutane is desorbed by heating in a stream of helium and collected in a cooling trap packed with Tenax TA. It is transferred from there to the GC column by flash-heating and then chromatographed. Quantitative evaluation is performed according to the external standard method using the peak areas or peak heights.

3.2 Instrumental operating conditions

The method was characterized under the following experimental conditions:

Apparatus: Thermal desorber ATD 400 from Perkin Elmer GmbH, Überlingen,
Gas chromatograph 2000 with FID from Perkin Elmer GmbH, Überlingen

Desorption conditions:

Temperatures: Desorption furnace: 100 °C,
Transfer line: 70 °C,

Cooling trap:	Filling:	40 mg Tenax TA, 60–80 mesh,
	Temperatures:	–30 °C (adsorption)
		300 °C (injection)
Desorption flow rate:	45 ml/min,	
Desorption time:	10 min.	
GC conditions:		
Column:	Material:	Quartz capillary,
	Length:	27.5 m,
	Internal diameter:	0.32 mm
	Stationary phase:	Poraplot Q from Chrompack, Frankfurt
Temperatures:	Furnace:	150 °C, isothermal,
	Detector:	200 °C
Split (at injection):	10 ml/min	
Carrier gas:	Helium, 200 kPa	
Detector gases:	Hydrogen, 30 ml/min	
	Synthetic air, 300 ml/min	

4 Evaluation

4.1 Calibration

Calibration is performed via the gas phase. A test gas can be produced e. g. according to the continuous injection procedure [1]. For this, a solution of 1,2-epoxybutane in methanol is injected into an injector through which air is flowing. By dilution with synthetic air, concentrations are produced in the range from 0.5 to 2.0 mg/m^3. Known volumes of the test gas are drawn through the adsorption tubes and analysed as described in Section 3.
The calibration curve is obtained by plotting the determined peak areas or peak heights against the 1,2-epoxybutane weights in ng. The curve is linear in the range from 0.1 to 2.0 mg/m^3.

4.2 Calculation of the analytical result

The weight of 1,2-epoxybutane in the sample corresponding to the peak area (height) is calculated using the calibration curve.
The 1,2-epoxybutane concentration by weight in the air sample is calculated in mg/m^3 according to equation (1):

$$c_w = \frac{w}{V} \tag{1}$$

Where:
c_w Concentration of 1,2-epoxybutane in the air sample in mg/m^3

w Weight of 1,2-epoxybutane in the sample in ng
V Air sample volume in ml

For 20 °C and 1013 hPa the concentration by volume in ml/m^3 is calculated according to the following equation (2):

$$c_V = 0.33 \cdot c_w \tag{2}$$

5 Reliability of the method

5.1 Accuracy

The relative standard deviation of the procedure was determined with 3 test gas concentrations (produced acc. to [1] and n = 6 determinations) in the range from 0.5 to 2 mg/m^3. The humidity of the air was about 40 %.

Concentration mg/m^3	Relative standard deviation %
0.51	0.7
1.14	1.0
1.97	1.9

5.2 Quantification limit

The quantification limit is 20 ng 1,2-epoxybutane per adsorption tube. This corresponds to a relative quantification limit of 0.1 mg/m^3 for a 200 ml air sample.

5.3 Selectivity

The selectivity of the procedure depends above all on the type of column used. In practice the column named has proved reliable. In case of interfering compounds, a column with a different separation phase must be used.

6 Discussion

The performance of the pump and the air sample volume are set so that about 2/3 of the breakthrough volume is not exceeded [2].

At a concentration of about 2 mg/m^3, 20 °C and with a tube filling of 450 mg Amberlite XAD-4 resin the breakthrough volume is 1000 ml.
The water vapour in humid air(up to 90 % relative humidity) hardly displaces 1,2-epoxybutane from the surface of the collection phase.
In the temperature range from 20 °C to 25 °C there was no loss of 1,2-epoxybutane from loaded adsorption tubes within 8 days after sampling. This was determined with a test gas with 40 % relative humidity and a concentration of 2 mg/m^3.

7 References

[1] *VDI 3490* (January 1981) Prüfgase – Herstellung durch kontinuierliche Injektion. Blatt 8
[2] *Tschickardt M* (1989) Routineeinsatz des Thermodesorbers ATD-50 in der Gefahrstoffanalytik. Angewandte Chromatographie, Bodenseewerk Perkin Elmer GmbH, Überlingen. Vol 48

2 Sampling with a pump and adsorption on activated carbon, gas chromatography after desorption

This method permits the determination of 1,2-epoxybutane concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a glass tube filled with activated carbon. The adsorbed 1,2-epoxybutane is then desorbed with a mixture of dichloromethane/carbon disulfide/methanol and determined by gas chromatography.

Technical data:

Quantification limit: absolute: 8 ng 1,2-epoxybutane,
relative: 0.5 mg/m^3 1,2-epoxybutane for a 20-litre air sample, 2.5 ml of desorption solution and 2 µl injection volume.

Selectivity: Interfering components can lead to higher values. Generally interferences can be eliminated by selecting another type of analytical column.

Advantages: Personal sampling and selective determination possible.

Disadvantages: No indication of peak concentrations.

Apparatus: Pump,
gas meter or flow meter,
Adsorption tubes with activated carbon,
gas chromatograph with flame ionisation detector (FID).

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:
Pump with gas meter or flow meter
Adsorption tubes filled with activated carbon (standardized, consisting of two zones filled with about 300 mg and 700 mg of activated carbon and separated by porous polymeric material), e. g. from Dräger, activated carbon tubes type B.

For sample preparation and analysis:
Volumetric flasks, 5 ml, 10 ml, 100 ml
Vials with screw-caps with seals, 5 ml
Sample vials with crimp-caps
Disposable filter holder PTFE*-membrane, 0.45 µm
Crimper
Gas chromatograph with autosampler and flame ionisation detector (FID)
Evaluation unit

* Polytetrafluoroethylene.

1.2 Chemicals

1,2-Epoxybutane, purity > 99%
Cyclohexane, GC standard (internal standard)
Dichloromethane, analytical grade
Carbon disulfide, analytical grade
Methanol, analytical grade
Gases for gas chromatography: Helium
Hydrogen
Synthetic air.

1.3 Solution

Desorption solution: Dichloromethane, carbon disulfide and methanol are mixed in a 100 ml volumetric flask in the ratio 60 : 35 : 5 v/v/v.

Cyclohexane stock solution: Solution of 10 µl (= 7.78 mg at 20 °C) cyclohexane per ml desorption solution.
50 µl of cyclohexane is pipetted into a 5 ml volumetric flask containing a few millilitres desorption solution. The flask is filled to the mark with desorption solution and shaken.

1,2-Epoxybutane stock solution: Solution of 2.5 µl (= 2.09 mg at 20 °C) 1,2-epoxybutane per ml desorption solution.
25 µl of 1,2-epoxybutane is pipetted into a 10 ml volumetric flask containing a few millilitres desorption solution. The flask is filled to the mark with desorption solution and shaken.

Calibration solutions: Solutions of 41.8, 83.6, 125.4, 167.2, 209, 418, 627, 836, 1045 and 1254 µg 1,2-epoxybutane and 155.5 µg cyclohexane in 5 ml desorption solution.
A few millilitres of desorption solution are each placed in ten different 5 ml volumetric flasks. Volumes of 20, 40, 60, 80, 100, 200, 300, 400, 500 and 600 µl of the 1,2-epoxybutane stock solution are added. Then 20 µl of the cyclohexane stock solution is each added and the flasks are filled to the mark with desorption solution. With these solutions, a 20-litre air sample volume and 2.5 ml desorption solution, a concentration range of 1 to 30 mg/m^3 1,2-epoxybutane is covered.

2 Sampling

A tube filled with activated carbon is opened and connected to the pump. The pump and tube are carried by a person during working hours or used in a stationary position. The procedure was tested with flow rates of 10 l/hour for 2 hours and 2 l/hour for 8 hours sampling.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded activated carbon tube are placed in a 5 ml vial with screw-caps. After the addition of 2.5 ml desorption solution and 10 µl cyclohexane stock solution the vial is closed and left to stand for 30 minutes, during which time it is occasionally shaken. The supernatant sample solution is then filtered and transferred to a sample vial (sample solution). The vial is closed tightly.
To ensure that the desorption solution used and the activated carbon do not contain any interfering impurities, the filling of an unloaded activated carbon tube is desorbed with 2.5 ml desorption solution and 10 µl cyclohexane stock solution (blank solution).
2 µl of the sample solution and blank solution are injected into the gas chromatograph and the gas chromatograms are produced as described in Section 3.2. Quantitative evaluation is performed according to the internal standard method using the peak areas of 1,2-epoxybutane and cyclohexane.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph Perkin Elmer Autosystem with autosampler and flame ionisation detector	
Column:	Material:	Quartz capillary
	Length:	30 m
	Internal diameter:	0.25 mm,
	Stationary phase:	DB-5, cross-linked
	Film thickness:	0.5 µm
Temperatures:	Injector block:	100 °C
	Detector:	150 °C
	Furnace temperature programme:	
	Initial temperature:	40 °C, 4 minutes isothermal,
	Heating rate:	10 °C/min
	Final temperature:	80 °C, 2 minutes isothermal

Injector:	Split ratio:	1:20
Carrier gas:	Helium, 1.5 ml/min	
Detector gases:	Hydrogen, 30 ml/min,	
	Synthetic air, 300 ml/min	
Make-up gas:	Helium, 30 ml/min	

4 Evaluation

4.1 Calibration

2 µl of each of the calibration solutions described in Section 1.2 is injected into the gas chromatograph. The calibration curve is obtained, and its linearity checked, by plotting the determined peak areas against the 1,2-epoxybutane weights in µg contained in the calibration solutions.
Using the peak areas of 1,2-epoxybutane and the internal standard cyclohexane, the calibration factor f is determined in the different calibration solutions according to equation (1):

$$f = \frac{A'_{is} \cdot w'}{A' \cdot w'_{is}} \tag{1}$$

Where:
f Calibration factor for 1,2-epoxybutane
A' Peak area for 1,2-epoxybutane from the corresponding calibration solution
A'_{is} Peak area for cyclohexane from the corresponding calibration solution
w' Weight of 1,2-epoxybutane in µg in 2.5 ml of the corresponding calibration solution
w'_{is} Weight of cyclohexane in µg in 2.5 ml of the corresponding calibration solution

The calibration factor is approximately the same for all dilutions. The mean value $\bar{f}$ should be used for calculating the analytical result.

4.2 Calculation of the analytical result

The 1,2-epoxybutane concentration by weight in the air sample c_w is calculated in mg/m^3 according to equation (2):

$$c_w = \frac{A \cdot w_{is} \cdot \bar{f}}{A_{is} \cdot V \cdot \eta} \tag{2}$$

For 20 °C and 1013 mbar the concentration by volume in ml/m^3 is calculated according to the following equation (3):

$$c_V = 0.33 \cdot c_w \quad (3)$$

Where:

c_w Concentration 1,2-epoxybutane in the air sample in mg/m^3
c_V Concentration of 1,2-epoxybutane in the air sample in ml/m^3 (ppm)
A Peak area for 1,2-epoxybutane from the sample solution
A_{is} Peak area for cyclohexane from the sample solution
w_{is} Weight of the cyclohexane in µg in 2,5 ml sample solution
V Air sample volume in l
$\bar{f}$ Mean calibration factor for 1,2-epoxybutane
η Recovery rate

5 Reliability of the method

5.1 Accuracy

To determine the relative standard deviation of the procedure, volumes of 5 µl, 10 µl, 50 µl and 100 µl of the 1,2-epoxybutane stock solution were injected into a gas collection vessel. Then laboratory air (40–50 % relative humidity) was drawn through the gas collection vessel and an activated carbon tube placed between the gas collection vessel and pump at a flow rate of 10 l/hour for 2 hours. The weights of 1,2-epoxybutane injected correspond to concentrations of 0.5 mg/m^3 to 10.5 mg/m^3 for a 20-litre air volume. With 6 individual measurements carried out as described, the relative standard deviations shown in the table were obtained.

Concentration mg/m^3	Relative standard deviation %
0.5	4.0
1.1	5.4
5.2	6.0
10.5	7.3

5.2 Quantification limit

The absolute quantification limit is 8 ng 1,2-epoxybutane. This corresponds to 10 µg per activated carbon tube or sample.
The relative quantification limit is 0.5 mg/m^3 = 0.177 ml/m^3 (ppm) for a 20-litre air sample, 2.5 ml desorption solution and 2 µl injection volume.

5.3 Selectivity

The selectivity of the procedure depends above all on the type of column used. In practice the column named has proved reliable. If there is interference, a column with a different separation phase must be used.

5.4 Recovery

Under the conditions described in Section 5.1 and a 20-litre air sample volume and flow rate of 10 l/hour the recovery rate was found to be >0.9.

6 Discussion

The shelf-life of 1,2-epoxybutane in the adsorbed state at room temperature is at least 14 days.
In addition to 1,2-epoxybutane, with this procedure also 1,2-epoxypropane can be determined. Under the gas chromatographic conditions described, complete separation is achieved.