1-Chloro-2,3-epoxypropane (Epichlorohydrin)

Method number	1
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	June 1982

Summary

Defined air volumes are drawn through an activated carbon tube by use of a sampling pump. The adsorbed epichlorohydrin is eluted with acetone and determined by means of a gas chromatograph equipped with an electron capture detector.
A calibration curve where the epichlorohydrin concentrations of the calibration standards are plotted versus the obtained peak areas serves for the quantitative evaluation.

Precision:	Standard deviation (rel.) $s = 2.7$ % Mean variation $u = 6.9$ % at a concentration of 1.3 mL/m^3 epichlorohydrin in air and $n = 6$ determinations
Detection limit:	0.013 mL/m^3 epichlorohydrin in air (corresponding with 0.05 mg/m^3), referring to a sample volume of 20 L
Recovery rate:	$\eta = 0.96$ (96 %)
Sampling recommendation:	Sampling time: 1 h Sample volume: 20 L

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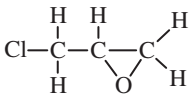

is a liquid (b. p. 116–117 °C, molecular weight 92.5 g · mole^{-1}, density 1.18 g · mL^{-1}) which is miscible with ether, alcohol, tetrachloromethane and benzene. Epichlorohydrin is little soluble in water and reacts very slowly to form chlorodihydroxypropane.

Epichlorohydrin is mainly used for the production of epoxide resins and as an intermediate in organic syntheses.
Epichlorohydrin is classified in the MAK values list (1982) into group III A 2 of substances which have clearly proved to be carcinogenic from animal tests. Moreover it is also suspect having a carcinogenic risk for human beings. The now valid TRK value (1982) is 3 mL/m^3. The uptake into the human body occurs by the respiratory tract. Additionally, epichlorohydrin strongly acts as a local irritant with nephrotoxic, neurotoxic effects. At present, two case studies exist to test the carcinogenic effect on human beings. Both studies did not show clear evidence [1].

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Contents

1 General principles

Defined air volumes are drawn through an activated carbon tube by use of a sampling pump. The adsorbed epichlorohydrin is eluted with acetone and determined by means of a gas chromatograph equipped with an electron capture detector.

A calibration curve where the epichlorohydrin concentration of the calibration standards are plotted versus the obtained peak areas serves for the quantitative evaluation.

2 Equipment, chemicals and solutions

2.1 Equipment

Gas chromatograph equipped with electron capture detector, compensation recorder and if necessary storage integrator
Glass tube (length 10 cm, outer diameter 0.7 cm), filled with about 0.5 g of activated carbon (e.g. of Auer Co., Berlin, Order No. 5085-823)
Membrane pump, conveying capacity about 20–25 L/h
Gas meter
Thermometer
Barometer
10 mL Volumetric flasks with ground glass stoppers
10 mL Funnel

2.2 Chemicals

1-Chloro-2,3-epoxypropane (Epichlorohydrin), purity ≥ 98 %
Acetone, analysis grade

2.3 Solutions

Stock solution
20 µL of epichlorohydrin are transferred into a 10 mL volumetric flask and diluted up to the mark with acetone (2.36 mg/mL). The solution is stable for one week in a refrigerator. Every day the calibration standards containing about 1–20 µg/mL epichlorohydrin in acetone are freshly prepared by dilution of the stock solution with acetone:

Volume of the stock solution	Final volume of the calibration standards	Epichlorohydrin	
		Weight in 10 mL Acetone	Concentration
µL	mL	µg	µg/mL
5	10	11.8	1.18
20	10	47.2	4.72
50	10	118.0	11.80
80	10	188.8	18.88

3 Sample collection and preparation

By means of a flow stabilized pump or a gas meter controlled pump the sample air is drawn through the collection phase with a flow rate of 20–25 L/h. Two activated carbon tubes have to be connected in series in case of higher ambient temperature (> 30 °C), higher air humidity (> 80 % humidity) and more than the fourfold of the limit value of the pollutant.
The decisive parameters for the determination of concentration like sample volume, temperature in the gas meter and ambient pressure have to be determined at the measuring location.
Loaded tubes can be stored up to two weeks without sample loss, but it is recommended to close the tubes with plastic caps. To elute the adsorbed epichlorohydrin the end of the activated carbon tube which was directed to the suction pump is connected with a 10 mL funnel. A volume of 10 mL acetone is pipetted into the funnel and for about five minutes drawn through the layer of the activated carbon into a 10 mL volumetric flask at the other end of the tube. After the elution is completed the volumetric flask is diluted with acetone up to the mark of 10 mL.

4 Operating conditions for gas chromatography

Column:	Material: Steel	
	Length: 2 m	
	Internal diameter: 2 mm (1/8 inch tube)	
Column packing:	10 % SP 1000 on Supelcoport 80–100 mesh	
Detector:	Electron capture detector (^{63}Ni)	
Temperatures:	Column:	100 °C
	Injector block:	150 °C
	Detector:	210 °C
Purging gas:	95 % Argon + 5 % methane	(60 mL/min)
Carrier gas:	Nitrogen:	(20 mL/min)
Injection volume:	5 µL	

5 Analytical determination

Volumes of 5 µL each of the eluent are injected several times into the injector block of the gas chromatograph and the obtained peak areas are determined. Analysis and calibration have to be carried out in one single operation.

6 Calibration

Volumes of 5 µL each are taken from the calibration standards (cf. Sect. 2.3) and analyzed by means of gas chromatography in the same way as the sample. To obtain the calibration curve the peak areas of epichlorohydrin are determined and plotted versus the used concentrations. The calibration factor is automatically determined if computing integrators are applied. To check the calibration factor calibration standards of comparable concentrations are injected in regular changes with the samples.

7 Calculation of the analytical results

The epichlorohydrin concentrations (µg per 10 mL acetone) corresponding with the determined peak areas are taken from the calibration curve. At the same volume of the eluent the read off value corresponds with the epichlorohydrin concentration in µg (X). The concentration by weight ρ (mg of epichlorohydrin per m^3 ambient air) is calculated by the following equation:

$$\rho = \frac{X}{V_z \cdot \eta} \cdot \frac{273 + t_g}{273 + t_a}$$

At 20°C and 1013 mbar:

$$\rho_0 = \rho \cdot \frac{273 + t_a}{293} \cdot \frac{1013 \text{ mbar}}{p_a}$$

The corresponding concentration σ – independent of the state parameters pressure and temperature is:

$$\sigma = \rho_0 \cdot \frac{24.1 \text{ L} \cdot \text{mole}^{-1}}{92.5 \text{ g} \cdot \text{mole}^{-1}} = \rho \cdot \frac{273 + t_a}{p_a} \cdot \frac{1013 \text{ mbar}}{293} \cdot \frac{24.1 \text{ L} \cdot \text{mole}^{-1}}{92.5 \text{ g} \cdot \text{mole}^{-1}}$$

$$\sigma = \rho \cdot \frac{273 + t_a}{p_a} \cdot 0.901 \cdot \frac{\text{mbar} \cdot \text{mL}}{\text{mg}}$$

At $t_a = 20\,^{\circ}\text{C}$ and $p_a = 1013$ mbar:

$$\sigma = \rho \cdot 0.261 \frac{\text{mL}}{\text{mg}}$$

Legend:

X Epichlorohydrin concentration by weight in the eluent in µg
V_z Read off sample volume in L

η Recovery rate
t_g Temperature in the gas meter in °C
t_a Temperature of the ambient air in °C
p_a Pressure of the ambient air in mbar
ρ Epichlorohydrin concentration in the ambient air in mg/m^3 referring to t_a and p_a (as mentioned above)
ρ_0 Epichlorohydrin concentration in the ambient air in mg/m^3 referring to 20 °C and 1013 mbar
σ Epichlorohydrin concentration in the ambient air in mL/m^3

8 Reliability of the method

8.1 Precision

Six times a volume of 8.5 µL each of a solution of 100 µL epichlorohydrin in 10 mL of acetone corresponding with 100.3 µg of epichlorohydrin was injected into a gas collecting tube which was warmed up to 80 °C by use of heating wires. Applying a flow rate of 20–25 L/h purified air was drawn through the gas collecting tube and two serially connected activated carbon tubes. After the preparation of the tubes and the analysis according to Sect. 3 and 5 a mean value of 96 µg was obtained. The standard deviation (rel.) was s = 2.7 %. The mean variation u was calculated as 6.9 %.

8.2 Recovery rate

The completeness of the epichlorohydrin adsorption on the activated carbon tubes was tested by use of the same experimental equipment. The mean recovery in the first tube was 96 %. Up to an applied weight of 1 mg no epichlorohydrin could be detected on the second tube.

8.3 Detection limit

Under the experimental conditions as mentioned the detection limit for epichlorohydrin was 0.13 mL/m^3 at a sample volume of 20 L. A check-up of the method by use of another experimental equipment lead to a detection limit lowered by the factor ten.

8.4 Specificity

Under the analysis conditions for the gas chromatography as mentioned before the following substances interfere with the method.
1,3-Dichloropropene
1,3-Dichloropropane
1,2-Dichloroethane

The following substances do not interfere up to the concentrations as indicated:
Tetrachloroethene (1.14 µg/mL)
Trichloromethane (1.04 µg/mL)
Dichloromethane (0.98 µg/mL)
Tetrachloromethane (1.06 µg/mL)
1,1,1-Trichloroethane (1.24 µg/mL)
1,1,2-Trichloroethane (1.10 µg/mL)
2,2,2-Trichloroethanol (1.17 µg/mL)
Trichloroethene (1.12 µg/mL)
1,1,1-Trichlorotrifluoroethane (1.01 µg/mL)
1,1,2-Trichlorotrifluoroethane (1.07 µg/mL)
1,1,2,2-Tetrachloroethane (1.15 µg/mL)
Acetonitrile (1.0 µL/mL)
Benzene (1.0 µL/mL)
Butanol (1.0 µL/mL)
Isobutylmethylketone (1.0 µL/mL)
Cyclohexane (1.0 µL/mL)
Diethylether (1.0 µL/mL)
Dioxane (1.0 µL/mL)
Acetic acid ethylester (1.0 µL/mL)
Ethanol (1.0 µL/mL)
n-Hexane (1.0 µL/mL)
n-Heptane (1.0 µL/mL)
Methanol (1.0 µL/mL)

9 Discussion of the method

The described method permits the rapid and accurate determination of airborne epichlorohydrin concentrations in the range of the TRK value.
The application of this method leads to personal or workplace typical values. A specific measurement is possible. Although peak concentrations are detected they cannot be determined.
The loaded tubes can be stored up to two weeks without sample losses. For that purpose they should be kept closed with plastic caps and stored at dark, cool and dry places.

Apparatus: Gas chromatograph F22 and integrator M2 of Perkin-Elmer Co.

10 References

[1] Technische Regeln für gefährliche Arbeitsstoffe TRgA, Anhang zur TRgA 102 "Begründung zu den TRK-Werten", Ziff. 5: "TRK-Wert für Epichlorhydrin (1-Chlor-2,3-epoxypropan): 10.8 mg/m^3 (3 ppm)". Edition September 1982. Bek. des BMA vom 10. Mai 1982 – IIIb 4–35 125–5, Bundesarbeitsblatt 9/1982, S. 95 (S. 97).

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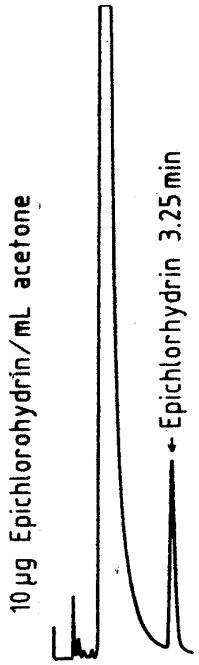

Fig. 1. Gas chromatogram of an epichlorohydrin solution in acetone (10 µg/mL). The retention time is 3.25 min; for gas chromatographic conditions see Sect. 4.