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Method for the determination of epichlorohydrin in workplace air using gas chromatography after thermal desorption

Air Monitoring Method

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Keywords: epichlorohydrin; air analysis; analytical method; workplace measurement; hazardous substances; thermal desorption gas chromatography; flame ionisation detection; TD-GC-FID; Tenax TA

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Abstract

This analytical method is a validated measurement procedure for the determination of epichlorohydrin [106-89-8] in workplace air averaged over the sampling period after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through an adsorption tube filled with Tenax TA using a suitable flow-regulated pump. The flow rate is set to 20 mL/min with a recommended air sample volume of 1.2 L (which corresponds to a sampling period of 60 min). After thermal desorption at 280 °C the sample is analysed by means of GC with a flame ionisation detector (FID). The quantitative determination is based on a calibration function obtained by means of a multiple-point calibration. The relative limit of quantification (LOQ) is 0.39 mg/m^3 epichlorohydrin for an air sample volume of 1.2 L. The mean recovery was 95% and the expanded uncertainty for epichlorohydrin was 16.1% over the entire measurement range.

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

DGUV Information 213-508; epichlorohydrin; air analysis; analytical method; workplace measurement; hazardous substances; gas chromatography; thermal desorption; GC-FID; Tenax TA

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German Social Accident Insurance
Expert Committee Raw Materials and Chemical Industry
Subcommittee Hazardous Substances

Analytical Subcommittee of the Chemistry Board of Experts[1)]

Recognised analytical procedures for the determination of carcinogens, mutagens or substances toxic to reproduction

Order number: DGUV Information 213-508, Method 02 Issued: April 2019

This method has been tested and recommended for the determination of epichlorohydrin in the workplace air by the German Social Accident Insurance.

Both personal and stationary sampling can be performed for risk assessment at work.

Sampling is performed by drawing a defined volume of air through an adsorption tube filled with Tenax TA. After thermal desorption, analysis is carried out by gas chromatography with a flame ionisation detector (FID).

Name	CAS number	Molar mass
Epichlorohydrin, 1-chloro-2,3-epoxypropane	106-89-8	92.53

Summary

This analytical method describes the determination of the mean concentration of epichlorohydrin in workplace air averaged over the sampling period after personal or stationary sampling.

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Principle:	A pump draws a defined volume of air through an adsorption tube packed with 200 mg of Tenax TA. The deposited epichlorohydrin is then thermally desorbed and, after gas chromatographic separation, it is determined using the flame ionisation detector (FID). Calibration is carried out using test gases or methanolic solutions that contain epichlorohydrin.
Limit of quantification:	Absolute: 0.047 µg Relative: 0.039 mg/m³ for an air sample volume of 1.2 L
Measurement range:	0.039 mg/m³ to 16.7 mg/m³ for an air sample volume of 1.2 L
Selectivity:	Excessively high values are possible due to interferents; interference can be eliminated by the use of a mass spectrometer if necessary.
Advantages:	Personal and selective measurements are possible.
Disadvantages:	No indication of concentration peaks.
Apparatus:	Pump, flow meter, adsorption tubes packed with 200 mg of Tenax TA, thermal desorber, gas chromatograph with FID (MSD if necessary).

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

- Sampling pump, suitable for a flow rate of 5 to 40 mL/min (e.g. PP1, from Gilian, supplied by DEHA Haan & Wittmer, 71296 Heimsheim, Germany)
- Flow meter (e.g. Gilibrator, from Gilian)
- Adsorption tubes made of stainless steel (6.3 mm x 90 mm, 5 mm inner diameter), packed with 200 mg of Tenax TA that is held in position between two pieces of metal packing gauze (e.g. PerkinElmer LAS, 63110 Rodgau, Germany). Before use, the adsorption tubes are heated for 10 minutes in the thermal desorber at 280 °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)
- ¼ inch Swagelok screw fitting with PTFE cones to connect two adsorption tubes

For analysis:

- Piston pipette (e.g. Microman M1000, from Gilson International, 65555 Limburg an der Lahn, Germany)
- Microlitre syringes with volumes of 5 and 10 µL (e.g. from Hamilton, supplied by Duratec, 68766 Hockenheim, Germany)
- Volumetric flasks 50 mL, 100 mL
- Dynamic test gas apparatus
- Syringe pump (diluter/dispenser) (e.g. Microlab M, from Hamilton, supplied by Duratec, 68766 Hockenheim, Germany)
- Thermal desorber, gas chromatograph with flame ionisation detector (FID) and optional mass selective detector (MSD)
- Optional Graphpack-3D/2 eluate flow splitter, Order No. GC 08194-40, from Gerstel, 45473 Mülheim an der Ruhr, Germany
- Optional test gas 20 ppm of 4-bromofluorobenzene in nitrogen (internal standard for MS quantification)

1.2 Chemicals

- Epichlorohydrin, purity ≥ 99.9% (e.g. from Merck, 64293 Darmstadt, Germany)
- Methanol, purity ≥ 99.9% (e.g. from Merck)

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
- Nitrogen, purity 99.999%

1.3 Solutions

Epichlorohydrin stock solution:

Solution of 22.9 g of epichlorohydrin/L of methanol.

1 mL of epichlorohydrin is weighed exactly to the nearest 0.1 mg into a 50 mL volumetric flask. The volumetric flask is then filled to the mark with methanol, shaken and placed in the refrigerator for storage.

This solution is used to generate a test gas from which calibration standards are abstracted.

Epichlorohydrin calibration solutions:

The calibration standards solutions (see Table 1) are prepared by adding volumes of 50, 5 and 0.5 mL of the stock solution into three 100 mL volumetric flasks, into which methanol has been previously placed, and then filling the flasks to the mark with methanol.

These solutions are used for liquid spiking of the calibration standards.

Table 1 Concentrations of epichlorohydrin in the calibration solutions in g/L

Calibration solution	**I**	**II**	**III**
Epichlorohydrin [g/L]	11.45	1.145	0.1145

The stock and calibration solutions are stable for at least 3 months when stored at +4 °C to +8 °C.

1.4 Calibration standards

In the case of thermal desorption processes it is advisable to calibrate with test atmospheres. One option for preparing test gases is continuous injection (see Figure 1) [1]. Should such apparatus not be available, then the preparation of the calibration samples is carried out by injection of methanolic solutions into adsorption tubes.

Preparation using test gas:

The stock solution (see Section 1.3) is continuously injected at a rate of 120 µL/h into a basic gas flow of 500 mL/min in a dynamic test gas facility. The desired concentration is then adjusted by means of a diluting stream of gas (in this case 695 mL/min). Adsorption tubes packed with Tenax TA are connected to the suction side of the syringe pump and aliquots of this calibration gas are drawn through the tubes in the range of 1 to 500 mL. This results in the test gas concentrations and corresponding calibration masses shown in Table 2 at a total flow rate of 1195 mL/min.

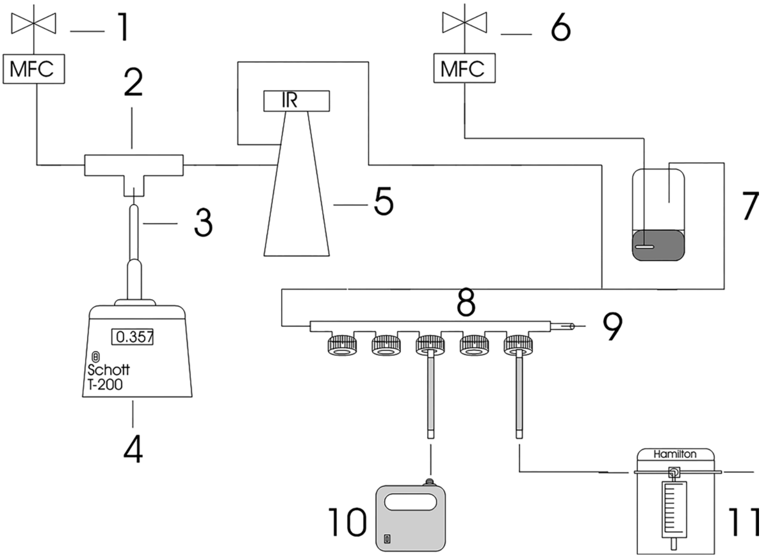

Figure 1 Dynamic test gas facility

1	Basic gas control	**7**	Humidifier
2	Injector	**8**	Test gas distributor
3	Piston	**9**	Test gas excess
4	Piston burette	**10**	Sampling pump
5	IR cuvette or buffer vessel	**11**	Syringe pump (diluter/dispenser)
6	Dilution gas control		

Table 2 Test gas concentration and calibration masses

Component	Epichlorohydrin
Concentration [mg/m^3]	38.4
Sample volume [mL]	Mass per sample [µg]
1	0.0384
5	0.192
10	0.384
25	0.960
50	1.920
100	3.840
150	5.760
200	7.680
500	19.200

Preparation using solutions:

Aliquots of the calibration solutions **I**, **II** and **III** (see Section 1.3, Table 1) are applied to the gauze in the adsorption tube in the direction of sampling and immediately transferred through the adsorbent using nitrogen for the purpose of calibration by means of direct injection of the solutions. In this case a nitrogen flow rate of 30 mL/min over a period of 20 minutes is sufficient. The resulting calibration masses in the spiked samples are shown in Table 3.

Table 3 Calibration masses when calibrating by liquid spiking [µg]

Spiked volumes [µL]	Calibration solution	Mass per sample [µg]
0.5	**III**	0.057
1	**III**	0.115
2	**III**	0.229
5	**III**	0.573
10	**III**	1.15
2	**II**	2.29
5	**II**	5.73
10	**II**	11.5
2	**I**	22.9

These calibration samples are equivalent to the concentrations shown in Table 4, based on an air sample volume of 1.2 L.

Table 4 Concentrations of epichlorohydrin in the calibration samples for liquid spiking in mg/m^3 (based on an air sample volume of 1.2 L)

Spiked volumes [µL]	Calibration solution	Epichlorohydrin [mg/m^3]
0.5	**III**	0.048
1	**III**	0.096
2	**III**	0.191
5	**III**	0.478
10	**III**	0.958
2	**II**	1.91
5	**II**	4.78
10	**II**	9.58
2	**I**	19.1

2 Sampling

Pre-treated adsorption tubes are used for sampling (see Section 1.1). The sealing caps are removed and the adsorption tube is connected to the sampling pump. The recommended sampling period is 60 minutes at a flow rate of 20 mL/min, which is equivalent to an air sample volume of 1.2 L. Different sampling times for shorter or longer periods, such as 30 minutes or 4 hours, are possible. However, the flow rate must be adjusted for the desired sampling period. The important parameters for the determination of the concentration (sample volume, temperature, air pressure and relative humidity) are documented in the sampling record.

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

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 repeat the measurement (see DGUV Information 213-500 “General Part”, Section 3 [5]).

3 Analytical determination

3.1 Operational parameters for thermal desorber

The adsorption tubes are fitted with desorption caps and transferred to the autosampler. The Tenax tubes are heated in the thermal desorber, whereby the substances 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 epichlorohydrin reaches the separation column.

The following instrumental conditions are adjusted for the thermal desorber:

Apparatus: Turbomatrix 650 (PerkinElmer LAS)
Desorption temperature: 280 °C
Desorption time: 10 min
Valve temperature: 220 °C
Temperature of transfer line: 200 °C
Transfer line: 1.5 m of deactivated blank capillaries, ID 0.32 mm
Cold trap (adsorption): −30 °C
Cold trap (injection): 280 °C
Cold trap filling: 20 mg of Tenax TA
Heating rate: 40 °C/s
Carrier gas: Helium
Carrier gas flow: 1.7 mL/min
Split (before the cold trap): 90 mL/min (input split)
Flow over the cold trap: 10 mL/min (desorption flow)
Split (after the cold trap): 10 mL/min (output split)
Purge drying phase: 1 min at room temperature at 50 mL/min

Optional (for MS quantification)
Gas dosing loop:

Volume:	5 mL
Filling period:	2 min
Equilibration time:	2 min
Flooding time:	2 min
Rinse flow:	50 mL/min

3.2 Operational parameters for gas chromatography

GC operational conditions

Apparatus:	Clarus 600 gas chromatograph with flame ionisation detector (FID), Clarus 600T mass selective detector (MSD) (optional for ensuring identification and quantification), PerkinElmer LAS
Column:	Material: Fused silica capillary Stationary phase: DB-624 (6% cyanopropylphenylpolysiloxane and 94% dimethylpolysiloxane) Length: 30 m Inner diameter: 0.25 mm Film thickness: 1.4 µm
Detector temperature:	320 °C
Detector gases:	Hydrogen (45 mL/min), synthetic air (450 mL/min)
Rate of heating:	10 min at 35 °C, increased by 10 °C/min up to 240 °C, 10 min

MS operational conditions

Eluate flow splitter:	Graphpack-3D/2-eluate flow splitter, split ratio: 1 : 1 (FID/MSD)
Temperatures:	Ion source: 180 °C Transfer line: 200 °C
Type of ionisation:	Electron impact (EI)
Ionisation energy:	70 eV
Mass range:	35–520 amu

4 Evaluation

4.1 Calibration

The calibration standards prepared according to Section 1.4 are analysed as described in Sections 3. The calibration function is obtained by plotting the measured peak areas of the FID signal versus the respective loaded masses (see Tables 2 or 3). The calibration function is linear in the investigated concentration range and should be regularly checked during routine analysis. A reference standard of known concentration must be analysed in each analytical series for this purpose.

4.2 Calculation of the analytical result

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

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

where:

c	is the mass concentration of epichlorohydrin in the air in mg/m³
m	is the mass of epichlorohydrin in the analytical sample in µg
V	is the air sample volume in litres
η	is the recovery (see Section 5.1)

5 Reliability of the method

5.1 Precision and recovery

The precision in the minimum measuring range as well as the recovery for 5 concentrations (see Tables 5 and 6) were determined according to EN 482 [2]. For this purpose test gases were used that were generated with the stock solution prepared as described in Section 1.3.

The syringe pump is used to draw 6 samples of these gases in each case with test gas aliquots through the adsorption tubes packed with 200 mg of Tenax TA at a flow rate of 25 mL/min and at an ambient temperature of 23 °C. Then 1.2 L of clean air with a relative humidity of 80% was drawn through the tube. The preparation and analytical determination were carried out as described in Section 3.

Table 5 Test gas concentrations of epichlorohydrin during validation

Dosing rate of the stock solution	Gas flow rate	Test gas concentration	Test gas aliquot	Mass of epichlorohydrin	Epichlorohydrin concentration based on 1.2 L
[µL/h]	[mL/min]	[mg/m³]	[mL]	[µg]	[mg/m³]
60	4444	5.16	25	0.129	0.108
40	395	38.7	10	0.387	0.32
20	490	15.6	150	2.34	2.0
60	502	45.7	200	9.14	7.6
120	401	114	175	20.0	16.7

Table 6 Precision and recovery

Mass of epichlorohydrin	Epichlorohydrin concentration based on 1.2 L	Relative standard deviation	Recovery
[µg]	[mg/m^3]	[%]	[%]
0.129	0.108	7.3	91.3
0.387	0.32	2.1	92.7
2.34	2.0	0.43	99.1
9.14	7.6	0.53	95.1
20.0	16.7	0.32	98.7

The mean recovery is 95%.

5.2 Experiments to establish the breakthrough volumes

Two adsorption tubes were connected using a ¼ inch Swagelok screw fitting, the second tube served as a control layer. A total of 6 such tube combinations were prepared.

Breakthrough was tested for air sample volumes of 2.4 L and 3.6 L each for three tube combinations at a concentration of 16.7 mg/m^3 after spiking with 175 mL of test gas. In this process air was drawn through the tubes at a flow rate of 60 mL/min at a relative humidity of at least 80% and a temperature of 23 °C. The tubes were subsequently analysed (see Table 7).

Table 7 Results of the breakthrough tests

Volume drawn through [L]	Recovery from the analysis tube [%]	Recovery from the control tube* [%]
2.4	99.7	0.3
3.6	98.4	1.6

* based on the recovered total amount of epichlorohydrin

5.3 Limit of quantification

The limit of quantification (see Table 8) was determined as stipulated in DIN 32645 [3] according to the calibration line method with 10 calibration gas standards.

Table 8 Limit of quantification according to the calibration line method (P=95% and k=3)

Substance	Calibration gas concentrations [mg/m^3]	Mass range [µg]	Limits of quantification	
		from – to	absolute [µg]	relative* [mg/m^3]
Epichlorohydrin	5.2–45.7	0.016–0.228	0.047	0.039

*on the basis of an air sample volume of 1.2 L

5.4 Storage stability

Storage stability was determined by using six loaded sample carriers in each case with test gas concentrations of 0.108 and 7.6 mg/m^3 at a relative humidity of approx. 75%. The tubes were sealed with Swagelok caps and stored at room temperature. The investigations were carried out over the course of 2 and 4 weeks. The results are shown in Table 9. The tubes can be stored without losses for at least 4 weeks.

Table 9 Storage stability

Substance	Recovery			
	Storage period [weeks]	Concentration [mg/m^3]	η (n=3)	mean η
Epichlorohydrin	2	0.108	0.95	0.96
	4		0.97	
	2	7.60	0.96	
	4		0.94	

5.5 Selectivity

The selectivity depends above all on the type of separation column used. The specified column has proved successful in practice. Interference in determination can arise from substances with the same retention time. If the evaluation by the mass spectrometer (MSD) detects such interference, then the samples must be evaluated using the substance-specific individual masses.

5.6 Uncertainty

The expanded uncertainty (U) was determined taking all relevant influencing factors into consideration [2–6]. 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 16.1% over the entire measurement range (see Table 10).

Table 10 Expanded uncertainty

Epichlorohydrin concentration [mg/m^3]	0.108	0.323	1.97	7.6
U [%]	16.1	16.1	16.1	16.1

References

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