Method for the determination of chlorinated hydrocarbons in workplace air using gas chromatography

---

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

Analytical Subcommittee of the Chemistry Board of Experts*

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

Order number: DGUV Information 213-565 Method 02 Issued: October 2014

This method has been tested and recommended for the determination of chlorinated hydrocarbons in the air at workplaces by the German Social Accident Insurance.

Both personal and stationary sampling can be performed for the assessment of workplaces.

Sampling is carried out with a pump and adsorption on activated charcoal. Analysis is performed by gas chromatography after desorption.

The method is validated for following substances:

Name	CAS No.	Molar mass
Tetrachloroethylene	127-18-4	165,83
Carbon tetrachloride	56-23-5	153,82
1,1,1-Trichloroethane	71-55-6	133,42
1,1,2-Trichloroethane	79-00-5	133,42
Trichloroethylene	79-01-6	131,39
Trichloromethane	67-66-3	119,38

---

[*] Please direct correspondence to Berufsgenossenschaft Rohstoffe und chemische Industrie, Prävention, P.O. Box 101480, 69004 Heidelberg, Germany; analytik@bgrci.de

Summary

The analytical method describes the determination of the mean concentration of tetrachloroethylene, carbon tetrachloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, trichloroethylene and trichloromethane, abbreviated to chlorinated hydrocarbons (CHC) in this method, in the workplace air averaged over the sampling period after personal or stationary sampling.

Principle:	A defined air volume from the breathing zone is drawn through a tube containing activated charcoal by a sampling pump. The CHCs occurring in the gaseous state in the workplace air are adsorbed onto the activated charcoal layer. Then the adsorbed CHCs are desorbed with carbon disulphide and are determined by means of a flame ionisation detector (FID) after gas chromatographic separation onto two capillary columns of different polarity.
Limit of quantification:	Absolute: 0.6 ng to 3.9 ng per CHC Relative: 0.04 mg/m^3 to 0.24 mg/m^3 of CHC for 25 L of air sample volume, 1.5 mL desorption solution and an injection volume of 1 µL.
Selectivity:	Higher results are possible due to interfering substances; generally overlaps are recognised in the double capillary column technique used.
Advantages:	Personal and selective measurements are possible.
Disadvantages:	No indication of peak concentrations.
Apparatus:	Pump, flow meter, charcoal tubes, gas chromatograph with FID

Detailed description of the method

Contents

1 Equipment, chemicals and solutions 224
1.1 Equipment 224
1.2 Chemicals 225
1.3 Solutions 225
2 Sampling 227
3 Analytical determination 227
3.1 Sample preparation and analysis 227
3.2 Operating conditions for gas chromatography 228
4 Evaluation 229
4.1 Calibration 229

4.2	Calculation of the analytical result	229
5	Reliability of the method	229
5.1	Precision and recovery	230
5.2	Limit of quantification	231
5.3	Uncertainty	231
5.4	Storage stability	231
5.5	Comments	232
	References	232

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

- Adsorption tubes, containing activated charcoal (standardised, comprising two fillings of activated charcoal, 100 mg and 50 mg, separated from each other by porous polymer material), e.g. SKC charcoal tubes, NIOSH type, supplied by Analyt-MTC, 79379 Müllheim, Germany
- Tube holder
- Sampling pump, suitable for a flow rate of 50 mL/min, e.g. PP5, from Gilian, supplied by Haan & Wittner, 71296 Heimsheim, Germany
- Flow meter, e.g. Gilibrator, from Gilian

For sample preparation and analytical determination:

- Gas chromatograph with flame ionisation detector (FID), split/splitless-injector and capillary splitter after the precolumn
- Capillary columns of different polarity
- Microlitre syringe, 10 µL
- Screw-capped vials with cap and septum, 2 mL
- Autosampler vials, 1.5 mL with PP screw caps and PTFE-coated butyl rubber septa
- Ultrasonic bath
- Analytical balance
- Variable piston pipette
- Electronic microlitre syringe, e.g. eVol XR, from SGE, in Germany supplied by VWR International, 64295 Darmstadt, Germany
- Volumetric flasks, 10, 25 and 250 mL
- Short glass tubes, quartz wool and Teflon tube for the validation

1.2 Chemicals

- Tetrachloroethylene, purity 99.9%, e.g. from Honeywell, 30926 Seelze, Germany
- Carbon tetrachloride, purity 99.5%, e.g. from Sigma-Aldrich, 82024 Taufkirchen, Germany
- 1,1,1-Trichloroethane, purity 99%, e.g. from Sigma-Aldrich, Germany
- 1,1,2-Trichloroethane, purity 98.4%, e.g. from Sigma-Aldrich, Germany
- Trichloroethylene, purity 99.9%, e.g. from Sigma-Aldrich, Germany
- Trichloromethane, purity 99.8%, e.g. from Sigma-Aldrich, Germany
- *n*-Tetradecane, purity > 99% (internal standard (ISTD)), e.g. from Honeywell, Germany
- Carbon disulphide, purity 99.8%, e.g. from LGC Promochem, 46485 Wesel, Germany

Gases for operation of the gas chromatograph:

- Helium 5.0, purity 99.999% (carrier gas)
- Hydrogen 5.0, purity 99.999%
- Nitrogen 5.0, purity 99.999% (make-up gas)
- Synthetic air, free of hydrocarbons

1.3 Solutions

n-Tetradecane stock solution (ISTD):	Solution of 15.24 mg of *n*-tetradecane per mL of carbon disulphide. A pipette is used to add 200 µL of *n*-tetradecane (density 0.762 g/mL) into a 10 mL volumetric flask, which has been nearly completely filled with carbon disulphide. The flask is then filled to the mark with carbon disulphide and shaken.
Desorption solution:	Solution of 15.2 µg of *n*-tetradecane per mL of carbon disulphide. A pipette is used to add 250 µL of the *n*-tetradecane stock solution into a 250 mL volumetric flask, which has been nearly completely filled with carbon disulphide. The flask is then filled to the mark with carbon disulphide and shaken.
Stock solution I (S I):	Solution of approx. 16.1 mg of carbon tetrachloride per mL, approx. 14.0 mg of 1,1,2-trichloroethane per mL and approx. 15.1 mg of trichloromethane per mL in the desorption solution.

250 µL of 1,1,2-trichloroethane, carbon tetrachloride and trichloromethane are each pipetted into a 25 mL volumetric flask in that order and weighed exactly to the nearest 0.1 mg and filled to the mark with desorption solution.

Stock solution II (S II): Solution of approx. 16.0 mg of tetrachloroethylene per mL, approx. 13.2 mg of 1,1,1-trichloroethane per mL and approx. 14.6 mg of trichloroethylene per mL in the desorption solution.

250 µL of tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane are each pipetted into a 25 mL volumetric flask in that order and weighed exactly to the nearest 0.1 mg, the flask is then filled to the mark with desorption solution.

Calibration solutions: Two series of eight solutions each of the CHCs with concentrations of approx. 2 to 160 µg/mL.

Pipettes are used to add 2, 5, 10, 20, 40, 60, 80 or 100 µL of the respective CHC stock solution into eight 25 mL volumetric flasks into which several millilitres of the desorption solution have already been placed.

Based on an air sample volume of 25 L, a concentration range of approx. 0.2 to 10 mg/m^3 is covered by these solutions. The exact concentrations can be found in Tables 1, 2, 3 and 4.

For the purpose of checking the calibration a solution, which has been prepared independently from the calibration solutions described above, must be used.

Table 1 Concentrations of series I of the calibration solution in mg/L

Addition of S I [µL]	**2** c_1	**5** c_2	**10** c_3	**20** c_4	**40** c_5	**60** c_6	**80** c_7	**100** c_8
Carbon tetrachloride	3.22	8.06	16.1	32.3	64.5	96.8	129	161
1,1,2-Trichloroethane	2.80	7.01	14.0	28.0	56.1	84.1	112	140
Trichloromethane	3.03	7.57	15.1	30.3	60.6	90.8	121	151

Table 2 Concentrations of series I of the calibration solution converted to mg/m^3

Addition of S I [µL]	**2** c_1	**5** c_2	**10** c_3	**20** c_4	**40** c_5	**60** c_6	**80** c_7	**100** c_8
Carbon tetrachloride	0.19	0.48	0.97	1.93	3.87	5.80	7.74	9.67
1,1,2-Trichloroethane	0.17	0.42	0.84	1.68	3.36	5.05	6.73	8.41
Trichloromethane	0.18	0.45	0.91	1.82	3.63	5.45	7.27	9.08

Table 3 Concentrations of series II of the calibration solution in mg/L

Addition of S I [µL]	**2**	**5**	**10**	**20**	**40**	**60**	**80**	**100**
	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8
Tetrachloroethylene	3.21	8.02	16.0	32.1	64.2	96.2	128	160
1,1,1-Trichloroethane	2.65	6.62	13.2	26.5	52.9	79.4	106	132
Trichloroethylene	2.92	7.30	14.6	29.2	58.4	87.6	117	146

Table 4 Concentrations of series II of the calibration solution in mg/L converted to mg/m^3

Addition of S I [µL]	**2**	**5**	**10**	**20**	**40**	**60**	**80**	**100**
	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8
Tetrachloroethylene	0.19	0.48	0.96	1.92	3.85	5.77	7.70	9.62
1,1,1-Trichloroethane	0.16	0.40	0.79	1.59	3.18	4.76	6.35	7.94
Trichloroethylene	0.18	0.44	0.88	1.75	3.50	5.25	7.00	8.76

2 Sampling

Sampling can be carried out as stationary or personal sampling. An activated charcoal tube is opened and connected to a pump. A flow rate of 50 L/min is then set. This is equivalent to an air sample volume of approx. 24 L at a sampling time of 8 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 (see DGUV Information 213-500 “Allgemeiner Teil”, Section 3 [2]). After sampling, the tube is sealed with the caps provided.

The important parameters for the determination of the concentration in air (sample volume, temperature, air pressure, relative humidity) are documented in the sampling record. The method was checked with a flow rate of 200 mL/min up to an air sample volume of 25 L.

3 Analytical determination

3.1 Sample preparation and analysis

The content of the loaded charcoal tube is transferred into a 2 mL sample vial. After addition of 1.5 mL of the desorption solution, the vial is sealed and treated for five minutes in the ultrasonic bath. Then the supernatant solution is separated from the activated charcoal by means of a pipette.

In order to ensure that the desorption solution and the charcoal tubes used do not contain any interfering impurities, the charcoal of an adsorption tube per sample series is desorbed, as described above, with 1.5 mL of the desorption solution (blank solution).

1 µL each of the sample solution and the blank solution are injected into the gas chromatograph and a chromatogram is recorded as described below. The quantitative evaluation is carried out according to the internal standard method using the peak areas of the respective substance and of *n*-tetradecane as the internal standard.

3.2 Operating conditions for gas chromatography

The characteristics of the method stated in Section 5 were obtained under the following operating conditions:

Apparatus:	Agilent 7980A gas chromatograph with autosampler, split/splitless injector, column flow splitter and two flame ionisation detectors. Double capillary technique; both the capillary columns are connected in parallel with the precolumn by means of a column flow splitter.
Precolumn:	Blank, deactivated fused silica capillary, length approx. 1 m, ID 0.32 mm with a column flow splitter.
Separation columns:	Fused silica capillaries: 1st column: Stationary phase DB-WAX cross-linked (polyethylene glycol 20 000), ID 0.25 mm, film thickness 0.5 µm, length 30 m. 2nd column: Stationary phase DB-1, cross-linked (methyl silicone), ID 0.25 mm, film thickness 1.0 µm, length 30 m.
Temperatures:	Injector: 250 °C Detector: 250 °C Oven with temperature programme: Initial temperature 45 °C, isothermal for 3 min Heating rate I: 3 °C/min up to 65 °C Heating rate II: 6 °C/min up to 120 °C, 3 min isothermal Heating rate III: 10 °C/min up to the final temperature Final temperature: 220 °C, 8 min isothermal
Injection:	Split ratio of 1 : 5
Injection volume:	1 µL
Carrier gas:	Helium 5.0
Detector gases:	Hydrogen 5.0 Synthetic air
Make-up gas:	Nitrogen 5.0

4 Evaluation

4.1 Calibration

1 µL of the calibration solutions described in Section 1.3 as examples is injected into the gas chromatograph in each case. Assignment of the retention times of the peaks in the chromatogram to the injected substances allows a calibration table to be compiled, that forms the basis for subsequent identification.

The calibration function is obtained with the help of linear regression by plotting the ratios of the peak areas of the substances to the peak areas of *n*-tetradecane as the internal standard (ISTD) versus the mass ratios of the substances and *n*-tetradecane contained in the respective calibration solutions.

4.2 Calculation of the analytical result

The peak areas of the CHCs and of *n*-tetradecane (ISTD) are obtained from the recorded chromatograms, the respective quotients are calculated and the corresponding value for the mass in the sample solution in µg is determined from the respective calibration function.

The mass concentration of the respective individual CHC in the air sample in mg/m^3 is calculated using Equation (1) as follows:

$$c = \frac{m}{V \cdot \eta} \tag{1}$$

where:

c is the mass concentration of a component in mg/m^3
m is the mass of the component in the analytical sample in µg
V is the air sample volume in litres
η is the recovery

If the calculated concentrations of the individual CHC are outside the calibration range, then the sample solution must be appropriately diluted with desorption solution and the quantification for these CHCs must be repeated using the diluted sample solution.

5 Reliability of the method

The characteristics of the method were calculated as stipulated in DIN EN 482 [1]. For the purpose of validation, undiluted 1,1,1-trichloroethane was used for spiking and two validation solutions were prepared for the remaining CHCs. Validation solution 1 was prepared by weighing 65.6 mg of 1,1,2-trichloroethane, 339.4 mg of trichloroethylene, 78.2 mg of carbon tetrachloride and 63.8 mg of trichloromethane into a 10 mL volumetric flask. The flask is then filled to the mark with methanol. 4399 mg of tetrachloroethylene were weighed into a 10 mL volumetric flask for validation solution 2. The flask was then filled to the mark with methanol.

5.1 Precision and recovery

The precision and recovery were determined by connecting six activated charcoal tubes with the pump and setting a flow rate of 200 mL/min. A glass tube filled with a plug of quartz wool was fitted in front of each charcoal tube by means of a short piece of Teflon tube (glass to glass connection). Three concentrations were checked in each case for 1,1,1-trichloroethane and the CHCs in the validation solutions in the set-up described above, whereby 2, 20 and 40 µL of 1,1,1-trichloroethane or the corresponding validation solution are applied onto the quartz wool plug using microlitre syringes. Subsequently, laboratory air was drawn through the tube combination over a time period of two hours at a temperature of 23 °C and a relative humidity of between 50 and 60%. The adjusted concentrations in air as well as the relative standard deviations from each of six measurements in each case at these

Table 5 Characteristics of the validation

Substance	Concentration [mg/m^3]	Standard deviation (rel.) [%]	Recovery	Expanded uncertainty [%]
Tetrachloroethylene	36.0	2.3	0.98	16
	348	2.7	0.98	16
	697	1.6	0.99	16
Carbon tetrachloride	6.3	2.0	1.00	16
	62.5	1.0	1.01	16
	125	0.8	1.04	15
1,1,1-Trichloroethane	106	1.0	1.02	16
	1056	1.1	0.98	16
	2112	1.7	1.03	16
1,1,2-Trichloroethane	5.3	2.3	1.02	16
	52.5	2.8	0.98	16
	105	1.6	1.03	16
Trichloroethylene	27.1	1.6	1.02	16
	271	0.5	0.99	15
	543	0.7	1.01	15
Trichloromethane	5.1	2.8	0.99	16
	51.0	2.4	1.02	16
	102	3.6	1.00	17

concentrations are listed in Table 5. The relative standard deviations were between 0.5% and 3.6%. The recoveries for the CHCs were determined using reference solutions and were between 0.98 and 1.04. The exact results can be found in Table 5.

5.2 Limit of quantification

The limits of detection (LODs) and limits of quantification (LOQs) were calculated from the signal-to-noise ratio of the baseline. A signal-to-noise ratio of 3 was used for the calculation of the LOD and the calculation of the LOQ was based on a ratio of 10.

The absolute LOQ per tube are between 0.6 and 3.9 ng of enriched CHCs. This is equivalent to relative LOQ of 0.04 to 0.24 mg/m^3 at a sample volume of 25 L. The exact results are shown in Table 6.

Table 6 Limits of quantification (LOQs) of the chlorinated hydrocarbons

Substance	**Limits of quantification**	
	absolute [ng]	**relative [µg/m^3]**
Tetrachloroethylene	0,7	0,04
Carbon tetrachloride	3,9	0,24
1,1,1-Trichloroethane	0,6	0,04
1,1,2-Trichloroethane	0,6	0,04
Trichloroethylene	0,6	0,04
Trichloromethane	1,5	0,09

5.3 Uncertainty

The expanded uncertainty was estimated taking all relevant influencing into consideration factors as stipulated in DIN EN 482 [1]. The uncertainty of the entire method and thus also of the analytical result consists principally of the uncertainty contributions of the air sampling (e.g. air sample volume, deviation from the sampling convention) and the analytical preparation (extraction agent volume, scatter of the calibration function, fluctuations in the recovery and the reproducibility). The expanded uncertainty is between 15% and 17% depending on the investigated chlorinated hydrocarbon and concentration (see Table 5).

5.4 Storage stability

The adsorbed components can be stored at room temperature without losses for at least 14 days.

5.5 Comments

All investigated chlorinated hydrocarbons can be separated on the non-polar capillary column DB 1 by means of gas chromatography. Tetrachloroethylene and trichloromethane as well as carbon tetrachloride and 1,1,1-trichloroethane cannot be separated on the polar capillary column DB-WAX.

References

1 DIN EN 482 (2012) Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents. Beuth Verlag, Berlin, Germany

2 DGUV Information 213-500 (2015) Allgemeiner Teil. Von den Unfallversicherungsträgern anerkannte Analysenverfahren zur Feststellung der Konzentration krebserzeugender, erbgutverändernder oder fortpflanzungsgefährdender Stoffe in der Luft in Arbeitsbereichen. Deutsche Gesetzliche Unfallversicherung (DGUV), Berlin, Germany, http://publikationen.dguv.de/dguv/pdf/10002/213-500.pdf

Authors: W. Krämer, T.H. Brock for the Analytical Subcommittee of the Chemistry Board of Experts of the Expert Committee Raw Materials and Chemical Industry of the German Social Accident Insurance