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Method for the determination of trichloroethene and tetrachloroethene

Method tested and recommended by the Berufsgenossenschaften for the determination of trichloroethene (TCE) and tetrachloroethene (PCE) in working areas.
Both personal and stationary sampling can be conducted for the assessment of working areas.

Sampling with a pump and adsorption on activated carbon
Gas chromatography after desorption
Trichloroethene/Tetrachloroethene-1-GC
(Issue: March 2000)

	TCE	**PCE**
IUPAC name:	Trichloroethene (Trichloroethylene)	Tetrachloroethene (Tetrachloroethylene) (Perchloroethylene)
CAS No.:	79-01-6	127-18-4
Molecular formula:	C_2HCl_3	C_2Cl_4
Molar mass:	131.39 g/mol	165.82 g/mol

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Summary

This method permits the determination of TCE and PCE concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: A pump is used to draw a measured air volume through a tube filled with activated carbon. The adsorbed TCE and/or PCE is desorbed with carbon disulfide and determined by gas chromatography.

Technical data:

Limit of quantification: absolute: 8 ng TCE or PCE
relative: 4.2 mg/m^3 0.76 mL/m^3 (ppm) for TCE and 4.2 mg/m^3 0.60 mL/m^3 (ppm) for PCE, both determined for a 9.6-litre air sample, 5 mL desorption solution and 1µL injection volume

Selectivity: In the presence of interfering components, the values determined may be too high. Interference can generally be eliminated by choosing a column with different separation characteristics.

Advantages: Personal sampling and selective determinations possible

Disadvantages: No indication of peak concentrations

Apparatus: Pump
Gas meter or volumetric flow meter
Tubes filled 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, suitable for flow rates of 80 mL/min, e. g. PP1 from Gilian, suppliers in Germany: DEHA Haan + Wittmer GmbH, D-71292 Friolzheim
- Gas meter or volumetric flow meter
- Adsorption tubes filled with activated carbon (standardised, consisting of two sections filled with about 300 mg (sampling section) and 800 mg (backup section) of activated carbon and separated by a porous polymer material), type B, e. g. from Dräger, D-23560 Lübeck
- Caps for the opened activated carbon tubes

For sample preparation and analysis:
- Volumetric flasks, 10 mL, 25 mL, 50 mL
- Sample vials with PTFE[1]-coated septa and caps, approx. 10 mL
- Pipettes, 2 mL, 2.5 mL, 5 mL, 10 mL
- Mechanical shaker
- Syringes, 10 µL, 50 µL, 100 µL
- Gas chromatograph with FID
- Data system

1 Polytetrafluoroethylene.

1.2 Chemicals and Solutions

Trichloroethene, purity ≥ 99 %
Tetrachloroethene, purity ≥ 99 %
Carbon disulfide, purity ≥ 99.9 %, e. g. Uvasol, low-benzene, from Merck, D-64271 Darmstadt, Catalogue No. 102213.

Stock solution: Solution of approx. 64 mg/mL TCE and approx. 130 mg/mL PCE in carbon disulfide.
Approximately 6600 mg (approx. 4 mL) tetrachloroethene and then approx. 3200 mg trichloroethene (approx. 2.2 mL) are precisely weighed into a 50 mL volumetric flask. The flask is then filled to the mark with carbon disulfide and shaken.

Calibration solutions: Solutions of approx. 0.032, 0.16, 0.32 and 0.64 mg/mL TCE and approx. 0.065, 0.325, 0.65 and 1.3 mg/mL PCE in carbon disulfide.
Syringes are used to inject 5, 25, 50 and 100 µL of stock solution into four 10 mL volumetric flasks, each containing approx. 5 mL carbon disulfide. The flask is then filled to the mark. For a 9.6-litre air sample volume and 5 mL sample solution, these solutions cover respective TCE and PCE concentration ranges of approx. 17 to 330 mg/m^3 and approx. 34 to 690 mg/m^3 air.

Gases for gas chromatography: Helium, purity ≥ 99.999 %
Hydrogen, purity ≥ 99.995 %
Synthetic air, hydrocarbon-free
Nitrogen, purity ≥ 99.999 %

2 Sampling

An activated carbon tube is opened and connected to the pump such that the sampling section will be loaded first. The flow rate is set at 80 mL/min. A sampling time of 2 hours then corresponds to an air sample volume of 9.6 litres. The pump and tube are carried by a person during working hours or used in a stationary position. On completion of sampling, the tube is tightly sealed. The method was tested up to an air sample volume of 10 litres at a maximum flow rate of 80 mL/min.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded activated charcoal tube are transferred – sampling and backup sections separately – to 10 mL sample vials and 5 mL carbon disulfide is added to each vial. The vials are then immediately sealed and shaken for 30 minutes.
Aliquots of 1 µL of the desorption solutions are injected into the gas chromatograph.
When an autosampler is used, samples are first transferred to autosampler vials. The quantitative analysis of the chromatograms is performed by the external standard method.

3.2 Operating conditions for gas chromatography

The method was characterised under the following experimental conditions:

Apparatus:	Hewlett-Packard Model 6890 gas chromatograph with FID, autosampler (6890 Series Injector) and CIS 3 cold injection system from Gerstel, D-45473 Mülheim.
Column:	Quartz capillary, stationary phase: Ultra 2 (5% diphenylpolysiloxane, 95% dimethylpolysiloxane), length: 25 m, internal diameter: 0.20 mm, film thickness: 0.33 µm.
Temperatures:	Cold injection system: From 20 °C to 180 °C at a rate of 12 °C/s, 0.5 min at 180 °C Furnace: Initial temperature: 35 °C, 3 minutes isothermal Heating rate 1: 5 °C/min up to 70 °C Heating rate 2: 40 °C up to 140 °C 140 °C, 1 minute isothermal Detector: 250 °C
Type of injection:	Cold injection
Carrier gas:	Helium, 1.0 mL/min
Split ratio:	20 : 1
Detector gases:	Hydrogen, 40 mL/min Synthetic air, 450 mL/min Nitrogen (make-up gas), 45 mL/min
Injection volume:	1 µL

4 Calculations

4.1 Calibration

Aliquots of 1 µL of each of the calibration solutions described in Section 1.2 are injected into the gas chromatograph. The peak areas determined are plotted against the corresponding TCE and PCE concentrations contained in the calibration solutions in order to construct the calibration curves. They are linear under the conditions described.

4.2 Calculation of the analytical result

The peak areas for TCE or PCE are determined, and the corresponding weight of analyte in the sample is read from the calibration curve in µg. If the weight of analyte adsorbed in the backup section exceeds by more than 30 % that adsorbed in the collection section, sampling must be repeated with a smaller air sample volume; if not possible, the two values are added.
The concentration by weight in the air sample in mg/m^3 is calculated according to Equation (1):

$$c_w = \frac{W}{V \cdot \eta} \tag{1}$$

The concentration by volume c_v in mL/m^3 at 20 °C and 1013 hPa is calculated from c_w as follows (Equation 2 and 3):

for TCE: $c_v = 0.183 \cdot c_w$ (2)
for PCE: $c_v = 0.145 \cdot c_w$ (3)

where:
c_w is the TCE or PCE concentration by weight in the air sample, given in mg/m^3
c_v is the TCE or PCE concentration by volume in the air sample, given in mL/m^3 (ppm)
w is the weight of TCE or PCE in the desorption solution(s) in µg as determined from the appropriate calibration curve
V is the air sample volume in litres
η is the recovery

5 Reliability of the method

5.1 Accuracy and recovery

The following spiking solutions were prepared in order to determine the relative standard deviation of the method:

Spiking solution 1: 7718 mg TCE (approx. 5 mL) and 16380 mg PCE (approx.10 mL) were weighed into a 25 mL volumetric flask, and methanol was added to the mark.

Spiking solution 2: 10 mL of Spiking solution 1 were placed in a 25 mL volumetric flask, and methanol was added to the mark.

Spiking solution 3: 2.5 mL of Spiking solution 1 were placed in a 25 mL volumetric flask, and methanol was added to the mark.

Four individual activated carbon tubes were spiked with separate aliquots of 10 µL Spiking solution 1 or 5 µL of Spiking solutions 1 to 3 using a syringe. Laboratory air (30–50% relative humidity) was subsequently drawn through each tube at a flow rate of 80 mL/min for two hours. This procedure covers the air concentrations given in Table 1. Six replicate determinations conducted according to the method described yielded the relative standard deviations and recoveries for TCE and PCE shown in Table 1.

Table 1.

Concentration mg/m^3		Relative standard deviation %		Recovery	
TCE	PCE	TCE	PCE	TCE	PCE
322	682	2.9	2.0	0.96	0.95
161	341	0.9	0.9	1.00	0.98
64.3	136	1.5	1.9	1.00	0.97
16.1	34.1	2.3	1.2	1.03	0.99

5.2 Limit of quantification

The absolute limit of quantification for TCE and PCE is 8 ng. This corresponds to 40 µg TCE or PCE per activated carbon tube or sample. The values were determined from the signal/noise ratio of the chromatogram.

The relative limit of quantification is
4.2 mg/m^3 ≙ 0.76 mL/m^3 (ppm) for TCE and
4.2 mg/m^3 ≙ 0.60 mL/m^3 (ppm) for PCE, both determined for a
9.6-litre air sample, 5 mL desorption solution and an injection volume of 1 µL.

5.3 Selectivity

The selectivity of the method depends above all on the type of column used. The column specified here has proved reliable in practice. In the presence of interfering components, it may be necessary to use a column with different separation characteristics.

6 Discussion

The loaded activated charcoal tubes can be stored in the dark for at least four weeks at room temperature without loss of adsorbed TCE or PCE.

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