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# Method for the determination of α-chlorotoluene

Method tested and recommended by the Berufsgenossenschaften for the determination of α-chlorotoluene (benzyl chloride) 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 Tenax, gas chromatography after desorption.
“α-Chlorotoluene-1-GC”
(Issue: December 1996)

| **IUPAC name:** | **CAS No:** |
|---|---|
| α-chlorotoluene | 100-44-7 |

# 1 Sampling with a pump and adsorption on Tenax, gas chromatography after desorption

This method permits the determination of α-chlorotoluene 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 Tenax tube. The adsorbed α-chlorotoluene is then desorbed with *n*-hexane and determined by gas chromatography.

**Technical data:**

Quantification limit: absolute: 0.5 ng α-chlorotoluene,
relative: 0.01 mg/m$^3$ α-chlorotoluene for 48 L air sample, 1 mL desorption solution and 1 μL injection volume.

Selectivity: Interfering components may cause too high values. In general, interferences can be eliminated by selecting a column with different separating characteristics.

**Advantages:** Both personal and selective sampling are possible.

**Disadvantages:** No indication of concentration peaks.

**Apparatus:** Pump,
gas meter or flow meter,
Tenax tubes,
gas chromatograph (GC) with flame ionisation detector (FID).

## Detailed description of the method

### Contents

## 1 Equipment, chemicals and solutions

### 1.1 Equipment

For sampling:
Pump, suitable for a flow rate of 100 mL/min (e.g. PP1 from Gilian, supplier in Germany: DEHA-Haan & Wittmer GmbH, 71288 Friolzheim)
Gas meter or flow meter
Adsorption tubes with Tenax, standardised, consisting of two Tenax fillings of about 50 mg and 100 mg separated with glass wool (e.g. Catalogue No 226-35-03 from SKC, supplier in Germany: MTC-GmbH, Müllheim)
Caps for the opened Tenax tubes

For sample preparation and analysis:
2 mL Beaded rim vials with polytetrafluoroethylene (PTFE)-coated septa and crimp caps
Crimper
Shaking machine
50 mL Volumetric flask
0.2, 0.5, 1, 2 and 5 mL Pipettes
10 and 50 µL Injection syringes

Gas chromatograph with FID
Data analysis device

### 1.2 Chemicals

*n*-Hexane, purity at least 99%, water-free
α-Chlorotoluene, purity at least 99%
Gases for operating the gas chromatograph: Helium, purity 99.995%
Hydrogen, purity 99.995%
Synthetic air, free from hydrocarbons

### 1.3 Solutions

α-Chlorotoluene stock solution:
Solution of 10 mg/mL α-chlorotoluene in *n*-hexane.
Approx. 500 mg of α-chlorotoluene is weighed into a 50 mL volumetric flask to the nearest 0.1 mg. The volumetric flask is filled to the mark with *n*-hexane.

Calibration solutions:
Solutions of 1.0 µg/mL, 4 µg/mL, 10 µg/mL, 40 µg/mL, 0.1 mg/mL, 0.4 mg/mL and 1 mg/mL of α-chlorotoluene in *n*-hexane.
5 µL, 20 µL, 50µL, 0.2 mL, 0.5 mL, 2 mL and 5 mL of the α-chlorotoluene stock solution are each transferred to 50 mL volumetric flasks already containing about 10 mL of *n*-hexane. The volumetric flasks are filled to the mark with *n*-hexane.
With these solutions and an air sample volume of 48 L and 1 mL of desorption solution a concentration range of 21 µg/m$^3$ to 21 mg/m$^3$ α-chlorotoluene in air is covered.

## 2 Sampling

The flow rate of the pump is set to a maximum of 100 mL/min. With sampling for 8 hours this corresponds to a maximum air sample volume of 48 L. A Tenax tube is opened and connected to the pump. During working hours the pump and tube are worn by a person or used in a stationary position. After sampling, the tube is closed with caps.

# 3 Analytical determination

## 3.1 Sample preparation and analysis

The contents of the loaded Tenax tube are transferred to a 2 mL beaded rim vial and 1 mL of *n*–hexane is added. The beaded rim vial is closed and shaken for 30 minutes. 1 µL of the supernatant solution (desorption solution) is injected into the gas chromatograph.
To ensure that the desorption solvent and the Tenax tube do not contain any impurities, the filling of an unloaded Tenax tube is treated with 1 mL of *n*-hexane (blank solution). 1 µL of the blank solution is injected into the gas chromatograph.

## 3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

| | | |
|---|---|---|
| Apparatus: | Gas chromatograph, Hewlett-Packard 5890 with FID | |
| Column: | Material: | Quartz capillary |
| | Length: | 50 m |
| | Internal diameter: | 0.32 mm |
| | Stationary phase: | SE 54 |
| | Film thickness: | 0.5 µm |
| Temperatures: | Injector: | 200 °C |
| | Detector: | 300 °C |
| | Furnace temperature programme: | |
| | Starting temperature: | 60 °C, 2 min isothermal |
| | Heating rate: | 10 °C/min |
| | Final temperature: | 280 °C |
| Injection mode: | Splitless, 0.5 min | |
| Carrier gas: | Helium, approx. 2.5 mL/min | |
| Detector gases: | Hydrogen, 35 mL/min | |
| | Air, 400 mL/min | |
| Make-up gas: | Helium, 15 mL/min | |
| Injection volume: | 1 µL | |

# 4 Evaluation

## 4.1 Calibration

1 mL of each of the calibration solutions described in Sect. 1.3 are added to the contents of an unloaded Tenax tube in beaded rim vials and analysed as described in Sect. 3.1.

The calibration curve is obtained by plotting the measured peak areas or peak heights against the α-chlorotoluene weights contained in the various calibration solutions. The calibration curve is linear in the given concentration range.

### 4.2 Calculation of the analytical result

Quantitative evaluation of the chromatogrammes is carried out according to the external standard method. The concentration by weight $c_w$ 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$^3$ calculated from $c_w$ for 20 °C and 1013 hPa is:

$$c_v = 0.19 \cdot c_w \tag{2}$$

Legend:

$c_w$ Concentration by weight of α-chlorotoluene in the air sample in mg/m$^3$
$c_v$ Concentration by volume of α-chlorotoluene in the air sample in mL/m$^3$
$w$ Weight of α-chlorotoluene in the desorption solution in µg
$V$ Air sample volume in L
$\eta$ Recovery rate

## 5 Reliability of the method

### 5.1 Accuracy and recovery

To determine the relative standard deviation of the method, different weights of α-chlorotoluene were each loaded onto six Tenax tubes by means of a syringe. Six tubes were prepared with 0.5 µL of the calibration solution with the highest concentration, 0.5 µL stock solution and 1 µL stock solution. Under the sampling conditions described in Sect. 2, 48 L of air were drawn through each of the tubes. The tubes were then analysed. This loading corresponded to air sample concentrations of 0.01, 0.1 and 0.2 mg/m$^3$ α-chlorotoluene.

Under the given conditions the 6 independent measurements yielded the relative standard deviations and recoveries listed in Table 1.

**Table 1.** Standard deviation (rel.) *s* and recovery rate.

| Concentration mg/m$^3$ | Standard deviation (rel.) *s* % | Recovery rate |
|---|---|---|
| 0.01 | 6.9 | 0.91 |
| 0.1 | 2.3 | 0.85 |
| 0.2 | 7.5 | 0.87 |

### 5.2 Quantification limit

The absolute quantification limit is 0.5 ng of α-chlorotoluene. It was determined from the signal noise ratio of the chromatogrammes.
The relative quantification limit is 0.01 mg/m$^3$ α-chlorotoluene for a 48 L air sample, 1 mL desorption solution and a 1 µL injection volume.

### 5.3 Selectivity

The selectivity of the method depends on the type of column used. In practice the given column has proved reliable. In case of interfering components, a column with other separation characteristics should be used.

## 6 Discussion

As the quality of the Tenax tubes varies greatly, the blank value of each Tenax tube used should always be checked.
The loaded tubes can be stored at 5–7 °C for at least 7 days without any loss of adsorbed α–chlorotoluene.
The stock solution and calibration solutions must be freshly prepared each day due to the sensitivity of α-chlorotoluene to hydrolysis.