

Benzene – Method for the determination of benzene in workplace air using gas chromatography after thermal desorption

Air Monitoring Method

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Abstract

This analytical method is a validated measurement procedure for the determination of benzene [71-43-2] in workplace air averaged over the sampling period after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a thermal desorption tube filled with Carboxen 1000/Carboxen 102 using a suitable flow-regulated pump. Before sampling a toluene-D8 standard solution is applied to the sieve of each sample carrier. For the following sampling the flow rate is set to 0.33 l/min whereby an air sample volume of 2 l must not be exceeded. The samples must be analysed within 28 days after loading with internal standard. After thermal desorption at 280 °C the sample is analysed by means of GC with a mass spectrometric detector (MSD). The relative limit of quantification (LOQ) is 4 µg/m³ benzene for an

air sample volume of 2 l. The mean recovery was 98% for an evaluation with MSD and the expanded uncertainty for benzene was approx. 25%.

This analytical method has been accredited by the accident insurance companies for the detection in workplace air of substances that are carcinogenic, mutagenic or toxic to reproduction.

This method has been tested and recommended for the determination of benzene at workplaces by the accident insurance companies.

Both personal and stationary sampling can be performed for measurements in order to evaluate work areas.

The method has been validated for the following substances:

Name	CAS No.	Molar mass [g/mol]
Benzene	71-43-2	78.11

1 Summary

The mean concentration of benzene at the workplace over the sampling period can be determined with this method using personal or stationary sampling.

Measurement Principle: A pump draws a defined volume of air through a thermal desorption tube packed with Carboxack B/Carboxack X. The adsorbed benzene is then thermally desorbed and determined using the mass-selective detector (MSD) after gas chromatographic separation.

Limit of quantification: Absolute: 8 ng
Relative: 4 µg/m³ of benzene based on an air sample volume of 2 l

Measurement range: Validated in the range of 4 µg/m³ to 190 µg/m³ of benzene for an air sample volume of 2 l.

Selectivity: Interference by other components is eliminated by mass-selective detection.

Advantages: Personal and selective measurements are possible.

Disadvantages: No indication of concentration peaks.

Apparatus: Pump, flow-regulated
Flow meter
Thermal desorption tube packed with Carboxack B/Carboxack X
Thermal desorber
Gas chromatograph with mass-selective detector (MSD)

2 Equipment and chemicals

2.1 Equipment

For sampling:

- Sampling pump, suitable for a flow rate of 0.3 l/min, e.g. Gilian LFS-113DC Low Flow Sampler, from GSM GmbH, 41469 Neuss, Germany
- Mass flow meter, ranging from 0 to 100 ml/min, e.g. from Analyt MTC, 79379 Müllheim, Germany

- Stainless steel thermal desorption tubes (length 8.9 cm, outer diameter 0.63 cm), layer 1: 200 mg of Carbopack B 40/60 mesh; layer 2: 270 mg of Carbopack X 40/60 mesh, e.g. from CAMSCO, USA
- Suitable tube material
- Sealing caps, e.g. Swagelok with PTFE seals, PTFE caps

For the analysis:

- Volumetric flasks with ground-glass stoppers, nominal volumes of 5 and 10 ml
- Glass volumetric pipette, nominal volumes of 5 and 10 ml
- Microlitre syringes, nominal volumes of 5, 10, 25, 50, 100 and 250 μl , e.g. from Hamilton Bonaduz AG, 7402 Bonaduz, Switzerland
- Screw-capped vials, nominal volumes of 10 ml (46 mm x 22.5 mm) and 20 ml (75.5 mm x 22.5 mm) for storing the standard solutions, e.g. from LABC Labortechnik, 53773 Hennef, Germany
- Thermal desorption system, e.g. Turbomatrix 650, from PerkinElmer, 63110 Rodgau, Germany
- Gas chromatograph, e.g. Autosystem XL, from PerkinElmer
- Mass spectrometer as a detector, e.g. Clarus 600T, from PerkinElmer
- Column: Rxi-5-Sil MS, 60 m, 0.25 mm ID and 1 μm film thickness, e.g. from Restek GmbH, 61348 Bad Homburg, Germany
- Instrumental software, e.g. TurboMass XL, from PerkinElmer

2.2 Chemicals

- Benzene, purity $\geq 99.9\%$, e.g. from AppliChem, 64291 Darmstadt, Germany
- Toluene-D8, purity 99.95%, e.g. from Acros, 2440 Geel, Belgium
- Methanol, purity $\geq 99.9\%$, e.g. from Merck, 64293 Darmstadt, Germany

Gases for operation of the gas chromatograph:

- Helium, purity 99.996%
- Synthetic compressed air, free of hydrocarbons, dew point $< -40\text{ }^{\circ}\text{C}$

2.3 Solutions

Internal standard solution (ISTD)

Toluene-D8 stock solution: Solution of 1.89 mg of toluene-D8 per ml of methanol
10 μl of toluene-D8 (density 0.943 g/ml) are dosed into a 5 ml volumetric flask, into which methanol has been previously placed. The flask is then filled to the mark with methanol and shaken.

Toluene-D8 standard solution: Solution of 18.86 ng of toluene-D8 per μl of methanol
The toluene-D8 stock solution is diluted at a ratio of 1:100 with methanol, which has been previously placed into the volumetric flask.

Benzene stock solutions for the calibration

- Stock solution 1 (SL 1): Solution of 1.76 mg of benzene per ml of methanol
10 µl of benzene (density 0.8788 g/ml) are dosed into a 5 ml volumetric flask, into which methanol has been previously placed. The flask is then filled to the mark with methanol and shaken.
- Stock solution 2 (SL 2): Solution of 17.6 mg of benzene per ml of methanol
100 µl of benzene (density 0.8788 g/ml) are dosed into a 5 ml volumetric flask, into which methanol has been previously placed. The flask is then filled to the mark with methanol and shaken.

Benzene stock solutions for the validation solutions

- Stock solution 3 (SL 3): Solution of 4.4 mg of benzene per ml of methanol
25 µl of benzene (density 0.8788 g/ml) are dosed into a 5 ml volumetric flask, into which methanol has been previously placed. The volumetric flask is then filled to the mark with methanol and shaken.

Calibration solutions and control standards

The calibration standards solutions are prepared by dosing defined volumes of the benzene stock solutions SL 1 or SL 2 into 5 ml volumetric flasks, into which methanol has been previously placed. The respective volumes of the stock solutions SL 1 and SL 2 can be found in [Table 1](#). Dosing is carried out with appropriate microlitre syringes and the volumetric flasks are then filled to the mark and shaken.

For the purpose of calibration, the thermal desorption tubes are loaded with the calibration solutions. To this end the thermal desorption tubes are connected by short tube sections to a sampling pump and the flow rate of the pumps is set to 33 ml/min. First 2 µl of the internal standard solution are applied to the sieves on the suction side, as specified by the manufacturer, and air is drawn through the thermal desorption tubes for 15 minutes. Then 3 µl of the corresponding calibration standard is applied to the sieve using a 5 µl syringe. Three thermal desorption tubes are loaded per calibration concentration. The pumps remain active for a further 15 minutes after loading is complete. The exact concentrations can be found in [Table 1](#).

Tab. 1 Calibration solutions

Benzene stock solution	Addition of benzene stock solution [µl]	Concentration in the calibration solution [ng/µl]	Mass per tube [ng]	Concentration in the air sample ^{a)} [µg/m ³]
SL 1	3	1.1	3.2	1.6
SL 1	10	3.5	11	5.3
SL 2	6	21	64	32
SL 2	15	53	160	79
SL 2	36	130	380	190

^{a)} based on an air sample volume of 2 l

In order to test the calibration over the entire working range three control standards of different concentrations (lower, medium and higher concentration range) are prepared from a stock solution, which was prepared independently of the stock solution for the calibration. The control standards are prepared in the same manner as the calibration standards and 3 µl each of these control standards are dosed onto the tubes as described above.

3 Sampling

Before sampling commences, the sample carriers are loaded with 2 µl (37.72 ng) of toluene-D8 standard solution. For this purpose, the sample carriers are connected to the sampling pump via a tube. The flow rate of the pump is adjusted to 0.33 l/min. Then 2 µl of the internal standard solution are applied to the sieves on the suction side, as specified by the manufacturer. Air is drawn through the sample carrier for a further 15 minutes after loading is complete. The tubes loaded with internal standard must be analysed within 28 days at the latest.

For sampling, the Swagelok screw caps are removed from the adsorption tubes and the adsorption tubes are connected to the pump, which is set to a flow rate of 33 ml/min. This is checked using a gas flow meter and, if necessary, the flow rate is adjusted. The pump and tube are worn by a person during working hours or stationary sampling is carried out. The sampling period is no more than one hour. The air sample volume of 2 l must not be exceeded. After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, repeated sampling is recommended (see *DGUV Information 213-500 "General Part", Section 3 (DGUV 2015)*).

On completion of sampling, Swagelok fittings are used to seal both ends of the loaded adsorption tube.

The important parameters for determination of the concentration (sample volume, temperature, air pressure and relative humidity) are documented in a sampling record.

4 Analytical determination

The screw caps made of brass are removed shortly before analysis and the thermal desorption tubes are sealed with Teflon caps. Then the thermal desorption tubes are placed into the autosampler of the thermal desorber. The tubes are thermally desorbed and analysed by means of gas chromatography-mass spectrometry.

4.1 Thermal desorption conditions

Apparatus:	Turbomatrix 650, from Perkin Elmer
Mode:	Two-stage desorption
Desorption temperature:	280 °C
Desorption period:	15 min
Valve temperature:	220 °C
Temperature of the transfer line:	220 °C
Cold trap (adsorption):	-30 °C
Cold trap (desorption):	280 °C
Desorption period (cold trap):	3 min
Cold trap filling:	Tenax TA
Heating rate:	99 °C/s
Carrier gas:	Helium
Carrier gas flow (column):	2 ml/min
Split (before the cold trap):	Splitless
Split (after the cold trap):	5 ml/min (outlet split)

4.2 Operating conditions for chromatography

GC conditions

Apparatus:	Autosystem XL gas chromatograph, from Perkin Elmer
Separation column:	Fused silica capillary, Rxi-5 Sil MS; length 60 m; inner diameter 0.25 mm; film thickness 1 µm
Rate of heating:	Initial temperature 50 °C, isothermal for 8 min Heating rate I: 3 °C / min up to 70 °C, isothermal for 3 min Heating rate II: 3 °C / min up to 120 °C, isothermal for 1 min Heating rate III: 10 °C / min up to 180 °C, isothermal for 20 min
Carrier gas:	Helium

MS conditions

Temperatures:	Ion source: 220 °C Transfer line: 220 °C	
Ionisation type:	Electron impact ionisation (70 eV)	
Measurement mode:	SIM	
Recorded masses (m/z in amu)	<u>Quantification</u> (target ion)	<u>Qualification</u> (qualifier ion)
Benzene:	<u>78</u>	51
Toluene-D8 (ISTD):	<u>98</u>	100

5 Evaluation

5.1 Calibration

The calibration standards prepared as specified in [Section 2.3](#) are analysed as described in [Section 4](#).

The calibration function is obtained from the measurement signals of the calibration solutions of known concentration. The signal ratio of analyte to the internal standard is used for calibration.

The calibration curve is linear in the investigated concentration range and should be checked regularly during routine analysis. For this purpose, a reference standard of known concentration must be analysed in each analytical series.

5.2 Calculation of the analytical result

The peak areas of benzene and of the internal standard are obtained from the chromatograms recorded, the quotient is calculated and the corresponding mass m in ng per sample is determined from the calibration function taking the mass of internal standard into account.

The mass concentration of benzene in the air sample in µg/m³ is calculated using the following [Equation 1](#).

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

where:

- c is the mass concentration of benzene in $\mu\text{g}/\text{m}^3$
- m is the mass of benzene in the analytical sample in ng
- V is the air sample volume in litres
- η is the recovery

6 Reliability of the method

The characteristics of the method were calculated as stipulated in DIN EN 482 (DIN 2021 a).

Validation solutions with the concentrations c_1 , c_2 and c_3 were prepared in order to determine the characteristics of the method.

For this purpose, volumes of the stock solution SL 3 (see Section 2.3) shown in Table 2 were dosed into three 5 ml volumetric flasks, into which methanol had been previously placed. The volumetric flasks were then filled to the mark.

Spiking occurred by initially applying 2 μl of internal standard solution (37.72 ng) to the sample carriers, air was then drawn through the thermal desorption tubes for 15 minutes and then 3 μl of each validation solution was applied to the tubes. Air was drawn through the sample carrier for a further 15 minutes after loading was complete.

Tab.2 Validation solutions (c_1 , c_2 and c_3)

Concentration	Addition of benzene stock solution SL 3 [μl]	Concentration in the validation solution [ng/ μl]	Mass per tube [ng]
c_1	5	4.4	13
c_2	10	8.8	26
c_3	100	88	260

Additional validation solutions at concentrations c_4 and c_5 were used for the storage stability experiments.

The solutions were prepared by dosing volumes of stock solution 1 (see Section 2.3) shown in Table 3 into two 5 ml volumetric flasks, into which methanol had been previously placed. The volumetric flasks is then filled to the mark and shaken.

Spiking of the sample carriers was carried out as described above.

Tab.3 Validation solutions (c_4 and c_5)

Concentration	Addition of benzene stock solution SL 1 [μl]	Concentration in the validation solution [ng/ μl]	Mass per tube [ng]
c_4	4	1.4	4.2
c_5	340	120	359

The capacity of the sample carrier was checked by loading the sample carrier with a benzene concentration of $180 \mu\text{g}/\text{m}^3$, at a relative humidity of approx. 80%. Air was drawn over the sample carrier for 2 hours at a flow rate of 0.033 l/min. No breakthrough was observed under these conditions.

6.1 Precision and recovery

The precision in the lowest measurement range as well as the recovery for three concentrations (see Table 4) were determined.

The recoveries and relative standard deviations shown in [Table 4](#) were obtained for the individual concentrations. The procedure described above was carried out six times in each case.

The recovery was found to be independent of the concentration.

Tab.4 Characteristics of the validation

Mass [ng]	Mass concentration ^{a)} [µg/m ³]	Recovery	Relative standard deviation [%]
13	6.6	0.98	8.7
26	13	1.01	8.4
260	130	0.97	4.6

^{a)} based on an air sample volume of 2 l

6.2 Limit of quantification

The absolute limit of quantification was determined according to DIN 32645 (DIN 2008) based on the blank value method.

For this purpose, ten thermal desorption tubes were first loaded with 2 µl of the internal standard solution (37.72 ng) and air was drawn through the thermal desorption tubes for 15 minutes. Then a mass of 4 ng of benzene was applied onto the tubes. Air was drawn through the sample carrier for a further 15 minutes after loading.

The thermal desorption tubes were then thermally desorbed and analysed by means of gas chromatography-mass spectrometry.

The limit of quantification obtained is shown in [Table 5](#).

Tab.5 Limit of quantification according to the blank value method (P = 95% and k = 3)

Spiked mass [ng]	Limit of quantification	
	absolute [ng]	relative ^{a)} [µg/m ³]
4.0	8.0	4.0

^{a)} based on an air sample volume of 2 l

6.3 Storage stability

Storage stability was determined using sample carriers loaded with two test concentrations at a relative humidity of approx. 50% (see [Table 6](#)). The thermal desorption tubes were stored at room temperature and sealed with Swagelok caps. The investigations were carried out over time periods of 1, 9, 17 (or 19) and 28 days. The results are shown in [Table 6](#). The loaded sample carriers can be stored without losses for 28 days.

Tab.6 Storage stability

Storage period [days]	Mass concentration [µg/m ³]	Recovery η (n = 3)	Mean recovery
1	2.1	1.04	1.04
9		1.05	
17		0.99	
28		1.07	

Tab. 6 (continued)

Storage period [days]	Mass concentration [$\mu\text{g}/\text{m}^3$]	Recovery η (n = 3)	Mean recovery
1	190	1.09	1.08
9		1.09	
19		1.05	
28		1.11	

6.4 Selectivity

Selectivity of the method is ensured by the use of a mass-selective detector.

Remark

An overlap of the signal of a C_7 -alkane with the signal of the internal standard, toluene-D8 (mass m/z 98), can occur in some analyses. In this case benzene-D6 can be introduced as a second internal standard and used in the evaluation.

Experiments on the recovery of benzene were carried out for a lower and higher concentration. Evaluation was carried out with both internal standards (toluene-D8 and benzene-D6). The results were comparable.

Furthermore, the storage stability experiment over 28 days was repeated using benzene-D6 as an internal standard. A reduction in the concentration of benzene-D6 could not be detected.

6.5 Uncertainty

The expanded uncertainty was determined as stipulated in DIN EN 482 (DIN 2021 a) and DIN EN ISO 22065 (DIN 2021 b) taking all relevant influencing factors into consideration. 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 uncertainty for the method is 25% (see Table 7).

Tab. 7 Uncertainty of the method

Mass [ng]	Expanded uncertainty [%]
13	25.2
26	25.0
260	24.3

6.6 Remarks

Cold trap

Initially an Air Toxics cold trap was used for the implementation of the method. In practice, due to the constant change between a minimum operating temperature of $-30\text{ }^\circ\text{C}$ and a maximum temperature of $280\text{ }^\circ\text{C}$, the material was found to be stressed, leading to possible decomposition. This led to benzene blank values and a short period of use of the cold trap.

According to the manufacturer's specification the Air Toxics cold trap is not suitable for an operating temperature of $-30\text{ }^\circ\text{C}$.

Therefore, further experiments using this cold trap were carried out at operating temperatures of $4\text{ }^\circ\text{C}$ and $20\text{ }^\circ\text{C}$. The recovery of benzene was insufficient and not reproducible under these conditions.

Subsequently, the Air Toxics cold trap was replaced by the Tenax TA cold trap in the course of the development of the method.

The characteristics of the method were determined from results obtained using the Tenax TA cold trap, which is also used for the routine analysis of the benzene samples.

Notes

Competing interests

The established rules and measures of the Commission to avoid conflicts of interest (https://www.dfg.de/en/dfg_profile/statutory_bodies/senate/health_hazards/conflicts_interest/index.html) ensure that the content and conclusions of the publication are strictly science-based.

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