

Benzene – Method for the determination of benzene in workplace air using gas chromatography after solvent 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 an adsorption tube filled with carbon black using a suitable flow-regulated pump. For sampling the flow rate is set to 0.33 l/min with an air sample volume of 40 l (which corresponds to a sampling period of 2 h). For analysis the sample is treated with carbon disulfide and analysed by means of GC with a mass spectrometric detector (MSD). The quantitative evaluation is based on a calibration function obtained by means of a multiple-point calibration. The relative limit of quantification (LOQ) is 4 µg/m³ benzene for an air sample volume of 40 l. The mean recovery was 100% for an evaluation with MSD and the expanded uncertainty lays between 21 and 23%.

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 defined volume of air is drawn through a tube containing activated charcoal by a sampling pump. The adsorbed benzene is then desorbed using carbon disulfide and determined using the mass-selective detector (MSD) after gas chromatographic separation.

Limit of quantification: Absolute: 0.08 ng
per sample carrier: 0.16 µg
Relative: 0.004 mg/m³ of benzene for an air sample volume of 40 l, 2 ml of desorption solution and an injection volume of 1 µl

Measurement range: Validated in the range of 0.004 mg/m³ to 4.2 mg/m³ of benzene at an air sample volume of 40 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
Activated charcoal tubes
Gas chromatograph with mass-selective detector (MSD)

2 Equipment and chemicals

2.1 Equipment

For sampling:

- Sampling pump, suitable for a flow rate of approx. 0.3 l/min, e.g. GilAir PLUS, from Sensidyne, supplied by HM-Labortechnik, 41065 Mönchengladbach, Germany.
- Activated charcoal tube, BIA type (standardised, consisting of two sections of activated charcoal, a collection phase of 300 mg and a control phase of 600 mg, separated by porous polymer material), e.g. from Auer, 12059 Berlin or Dräger, 23560 Lübeck, Germany

- Flow meter, e.g. TSI 4100 Series, from DEHA Haan & Wittmer, 71296 Heimsheim, Germany

For sample preparation and analytical determination:

- Volumetric flasks 2 ml, 50 ml
- Microlitre syringes, nominal volumes of 5, 10, 25, 50, 100, 250 μl , e.g. from Hamilton Bonaduz, 7402 Bonaduz, Switzerland
- Pipette 2 ml, graduated
- Glass volumetric pipette, nominal volume 10 ml
- Autosampler vials, 2 ml, white and crimp caps made of aluminium with PTFE-coated butyl rubber septa
- Glass extraction vessels, 5 and 20 ml and crimp caps with PTFE-coated butyl rubber septa
- CERTAN capillary bottles, nominal volume 10 ml (30 mm x 71 mm), for storage of the stock solutions e.g. from Merck, 64293 Darmstadt, Germany
- Syringe filters made of polytetrafluoroethylene membrane, diameter 15 mm, pore size 0.45 μm , e.g. from Phenomenex, 63741 Aschaffenburg, Germany
- Disposable syringes with cannulas, 10 ml
- Flat bed shaker
- Gas chromatograph with mass-selective detector and split/splitless injector and autosampler

2.2 Chemicals

- Benzene, purity $\geq 99.9\%$, e.g. from Merck
- Toluene-D8, purity $\geq 99.5\%$ (internal standard (ISTD)), e.g. from Merck
- n-Decane, purity $\geq 99.9\%$, e.g. from Merck
- Carbon disulfide, purity $\geq 99.8\%$, e.g. from LGC Standards, 46485 Wesel, Germany

Gas to operate the gas chromatograph:

- Helium, purity 99.999%

2.3 Solutions

The stock solutions were prepared by weighing all the constituent components and then converting to the volume using the density of the solvent.

Toluene-D8 stock solution (ISTD): Solution of 1.885 mg of toluene-D8 per ml of n-decane
7.223 g of n-decane (approx. 10 ml; density 0.73 g/cm^3) were pipetted into a 20 ml glass extraction vessel and this was sealed with a crimp cap with septum. Approx. 20 μl of toluene-D8 were then added through the septum using a 20 μl syringe, weighed and the concentration was calculated via the density.

Desorption solution:	Solution of 4.71 mg of toluene-D8 in one litre of carbon disulfide A 50 ml volumetric flask into which carbon disulfide had been previously placed, was spiked with 125 µl of the toluene-D8 stock solution and the flask was filled to the mark with carbon disulfide and shaken.
Stock solution 1 (SL 1):	Solution of 11.33 mg of benzene per ml of carbon disulfide 12.501 g of carbon disulfide (approx. 10 ml; density 1.26 g/cm ³) were dosed into a 20 ml glass extraction vessel and this was sealed with a crimp cap with septum. Approx. 130 µl of benzene were then added through the septum using a 250 µl syringe, weighed and the concentration was calculated using the density. The stock solution was shaken and transferred to a CERTAN bottle.
Stock solution 2 (SL 2):	Solution of 0.113 mg of benzene per ml of carbon disulfide 12.481 g of carbon disulfide were dosed into a 20 ml glass extraction vessel and this was sealed with a crimp cap with septum. Approx. 98 µl of SL1 were then added through the septum using a 100 µl syringe, weighed and the concentration was calculated using the density. The stock solution was shaken and transferred to a CERTAN bottle.
Calibration solutions:	15 solutions ranging from approx. 0.06 µg/ml to 5.7 µg/ml of benzene each with 4.7 µg/ml of toluene-D8 stock solution (ISTD) in carbon disulfide A suitable microlitre syringe was used to add the volumes of benzene stock solution SL 2 listed in Table 1 into one 2 ml volumetric flask each, into which several millilitres of carbon disulfide had been previously placed. 5 µl of the ISTD solution were also added using a 10 µl syringe. The volumetric flask was then filled to the mark with carbon disulfide and shaken. The calibration solutions were filled into autosampler vials and sealed with crimp caps. Based on an air sample volume of 40 l, a concentration range of approx. 0.003 to 0.28 mg/m ³ is covered by these solutions. The exact concentrations can be found in Table 1 .

Tab.1 Calibration solutions

Calibration solution	Addition of benzene stock solution SL 2 [µl]	Mass in the calibration solution [µg]	Concentration in the calibration solution [µg/ml]	Concentration in the air sample [mg/m ³]
1	1	0.11	0.057	0.0028
2	1.5	0.17	0.085	0.0043
3	3	0.34	0.170	0.0085
4	5	0.57	0.283	0.014
5	7	0.79	0.397	0.020
6	10	1.13	0.567	0.028
7	20	2.27	1.133	0.057
8	30	3.40	1.700	0.085
9	40	4.53	2.27	0.11
10	50	5.67	2.83	0.14
11	60	6.80	3.40	0.17

Tab.1 (continued)

Calibration solution	Addition of benzene stock solution SL 2 [μl]	Mass in the calibration solution [μg]	Concentration in the calibration solution [μg/ml]	Concentration in the air sample [mg/m ³]
12	70	7.93	3.97	0.20
13	80	9.06	4.53	0.23
14	90	10.2	5.10	0.26
15	100	11.3	5.67	0.28

For the purpose of checking the calibration, a control solution in the medium calibration range is used. This control solution has to be prepared independently from the calibration solutions described above.

3 Sampling

Sampling can be carried out as stationary or personal sampling. A tube containing activated charcoal is opened and connected to a pump. A flow rate of approx. 0.33 l/min is then set. This is equivalent to an air sample volume of approx. 40 l for a sampling period of 2 hours. After sampling, the flow rate must be checked for constancy. If the deviation from the adjusted flow rate is greater than $\pm 5\%$, it is advisable to discard the measurement (see *DGUV Information 213-500 "General Part", Section 3* (DGUV 2015)).

After sampling, the tube is sealed with the cap provided.

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

4 Analytical determination

4.1 Sample preparation and analysis

The entire contents of the loaded activated charcoal tube are transferred to a 5 ml glass extraction vessel and covered with 2 ml of the desorption solution using a 2 ml pipette. The vessel is sealed with a crimp cap, shaken for two hours and an aliquot of the extract is filtered into autosampler vials using a syringe filter and a disposable syringe.

In order to ensure that the solvent, the ISTD solution and the adsorption tubes used do not contain any interfering impurities, an adsorption tube per sample series is prepared as described above (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. Quantitative evaluation is performed using the internal standard method taking the peak areas of benzene and toluene-D8 into account.

4.2 Operating conditions for chromatography

The characteristics of the method given in [Section 6](#) were obtained under the following instrumental operating conditions:

GC conditions

Apparatus: 6890N Gas chromatograph with split/splitless injector and 5973N mass-selective detector from Agilent and Combi PAL autosampler from CTC Analytics

Separation column:	Fused silica capillaries; stationary phase: 6% of cyanopropylphenyl/94% of dimethylsiloxane (Zebron ZB-624, from Phenomenex, 63741 Aschaffenburg, Germany), length 60 m, inner diameter 0.32 mm; film thickness 1.8 µm
Rate of heating:	Initial temperature 50 °C, isothermal for 8 min Heating rate I: 5 °C / min up to 100 °C, isothermal for 5 min Heating rate II: 10 °C/min until the final temperature Final temperature: 180 °C, 5 min isothermal
Carrier gas:	Helium, 0.9 ml/min, constant flow

MS conditions

Temperatures:	Ion source: 230 °C Transfer line: 230 °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

1 µl of the calibration solutions described in [Section 2.3](#) is injected into the gas chromatograph in each case and analysed.

The calibration function is obtained by plotting the resulting peak area ratios of the benzene to the toluene-D8 as internal standard versus the concentration ratios of the benzene to the internal standard in the respective calibration solutions.

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.

5.2 Calculation of the analytical result

The peak areas of the benzene and of the internal standard are obtained from the chromatograms recorded, the quotient is calculated and the corresponding value for the mass in the sample solution in µg is determined from the calibration function.

The mass concentration m of benzene in the air sample in mg/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).

6.1 Precision and recovery

The precision and recovery were determined by loading six adsorption tubes in each case with the different volumes of the stock solutions SL1 and SL2 listed in Table 2.

After a waiting time of 2 hours, air at a flow rate of 0.33 l/min was drawn through the sample carriers for 2 hours and the sample carriers were then prepared and analysed as described in Section 4.1.

The extracts of the two highest validation masses were diluted with desorption solution by a factor of 10 or 100.

The spiked amounts of benzene were equivalent to the concentrations in the air sample listed in Table 2 for an air sample volume of 40 l. The determined relative standard deviations from the six measurements in each case were between 1% and 4.3% and the mean recovery was 1.0.

Tab.2 Characteristics of the validation

Spiked volumes	Spiked mass [μg]	Concentration in the air sample [mg/m^3]	Recovery	Relative standard deviation [%]
1.5 μl of SL 2	0.170	0.004	1.02	3.9
7 μl of SL 2	0.791	0.020	0.98	4.3
15 μl of SL 2	1.70	0.04	1.05	1.6
150 μl of SL 2	17.0	0.42	0.99	1.0
15 μl of SL 1	170	4.2	0.98	2.3

6.2 Limit of quantification

The absolute limit of quantification derived from a low calibration concentration was estimated according to DIN 32645 (DIN 2008) based on the blank value method. This value is 0.08 ng for a statistical certainty of 95% and a relative uncertainty of the result of 33% or $k = 3$.

A relative limit of quantification of 0.004 mg/m^3 or limit of quantification of 0.16 μg per sample carrier is obtained for an air sample volume of 40 l and injection volume of 1 μl .

6.3 Storage stability

The storage stability without losses of benzene in an adsorbed state is at least 7 days at room temperature.

6.4 Selectivity

Interference caused by other components is eliminated to a large extent by gas chromatographic separation combined with mass-selective detection.

6.5 Uncertainty

The expanded uncertainty was estimated taking all relevant influencing factors as stipulated in DIN EN 482 (DIN 2021) into account. 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 (extraction volume, complete desorption, scatter of the calibration function, fluctuations in the recovery and the reproducibility).

The expanded uncertainty is between 21% and 23% for the method.

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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