Solvent mixtures

Method number	1
Application	Air analysis
Analytical principle	Gas chromatography (activated charcoal/CS_2) (Double capillary technique)
Completed in	April 2013

Summary

This measurement method is suitable for monitoring the Occupational Exposure Limits (OELs) of solvent components at workplaces. Sampling is performed by drawing air through a tube filled with activated charcoal using a suitable sampling pump. The adsorbed substances are desorbed with carbon disulphide. The sample solution is analysed by means of gas chromatography fitted with flame ionisation detectors (FID) using two capillary columns of different polarity connected in parallel with the injector. Quantitative evaluation is based on calibration functions obtained by means of multiple-point calibrations using *n*-tetradecane as internal standard.

Characteristics of the method

Precision:	Standard deviation (rel.):	s = 0.9 to 3.3%
	Expanded uncertainty:	U = 15 to 17%
	in the concentration range of 0.1 up to twice the Occupational Exposure Limits and n = 6 determinations	
Limit of quantification:	0.02 to 1.3 mg/m^3 depending on the substance, for an air sample volume of 25 L, a desorption solution of 1.5 mL and an injection volume of 1 µL	
Recovery:	83 to 100%	
Sampling recommendations:	Air sample volume:	25 L
	Flow rate:	50 mL/min

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1 General principles

A defined air volume from the breathing zone is drawn through an activated charcoal tube (NIOSH type) by a suitable sampling pump. Solvent components occurring in the gaseous state in the workplace air are adsorbed onto the activated charcoal layer. The adsorbed substances are desorbed with carbon disulphide. The sample solution is analysed by means of gas chromatography fitted with flame ionisation detectors (FID) using two capillary columns of different polarity connected in parallel with the injector. Quantitative evaluation is based on calibration functions obtained by means of multiple-point calibrations using *n*-tetradecane as internal standard.

2 Equipment, chemicals and solutions

2.1 Equipment

- Activated charcoal tubes (NIOSH type) (standardised, consisting of two fillings of activated charcoal of approx. 100 mg and 50 mg separated by porous polymer material) (e.g. SKC, supplied by Analyt MTC, Müllheim, Germany)
- Tube holder
- Pump, suitable for a flow rate of 50 mL/min
- Flow meter
- Gas chromatograph with two flame ionisation detectors (FID), split/splitless injector and a column flow splitter after the precolumn
- Capillary columns of different polarity (DB1 and DB-WAX)
- Microlitre syringe, 10 µL
- Screw-capped vials with septum, 2 mL
- Autosampler vials, 1.5 mL, with screw caps and PTFE-coated butyl rubber septa
- Volumetric flasks, 10, 25 and 250 mL
- Ultrasonic bath
- Variable piston pipette

2.2 Chemicals

The substances to be determined should have the highest possible purity.

- Benzene, p.a., e.g. from Aldrich
- Toluene, p.a., e.g. from Aldrich
- *m*-Xylene, p.a., e.g. from Aldrich
- *n*-Tetradecane > 99% (internal standard), e.g. from Riedel-de-Haën
- Carbon disulphide, low benzene content, p.a., e.g. from Baker

Gases for operation of the gas chromatograph:

- Helium 4.6 (carrier gas)
- Synthetic air (free of hydrocarbons)
- Hydrogen 5.0
- Nitrogen 5.0 (make-up gas)

2.3 Solutions

The procedures for the determination of solvent mixtures consisting of benzene, toluene and *m*-xylene (BTX) are described below as an example. Furthermore, the preparation of the solutions necessary for calibration and sample preparation are also described.

n-Tetradecane stock solution (Internal standard)	Solution of 15.24 mg *n*-tetradecane/mL carbon disulphide

Approx. 9.5 mL of carbon disulphide are placed into a 10 mL volumetric flask and then a pipette is used to add 200 µL of *n*-tetradecane (density 0.762 g/mL). The volumetric flask is then filled to the mark with carbon disulphide and shaken.

Desorption solution:	Solution of 15.24 µg *n*-tetradecane/mL carbon disulphide

A pipette is used to add 250 µL of *n*-tetradecane to a 250 mL volumetric flask into which approx. 240 mL of carbon disulphide have already been placed. The flask is then filled to the mark with carbon disulphide and shaken.

The desorption solution is stable for two weeks at room temperature.

BTX stock solution:	Solution of 5.24 mg benzene, 5.17 mg toluene and 5.21 mg *m*-xylene/mL desorption solution

150 µL of *m*-xylene, toluene and benzene are each pipetted into a 25 mL volumetric flask in this order and weighed to the nearest 0.1 mg exactly. The volumetric flask is then filled to the mark with desorption solution and shaken.

BTX calibration solution:	Six BTX solutions with concentrations from approx. 1 µg/mL to 20 µg/mL

Pipettes are used to add 5, 20, 40, 60, 80 and 100 µL of the BTX stock solution to six 25 mL volumetric flasks into which several millilitres of the desorption solution have already been placed. The volumetric flasks are then filled to the mark with desorption solution and shaken. The exact concentrations are listed in the Tables 1 and 2.

Table 1 Concentrations of the calibration solutions in mg/L

Stock solution volume [µL]	5	20	40	60	80	100
	c_1	c_2	c_3	c_4	c_5	c_6
Benzene	1.05	4.20	8.39	12.59	16.78	20.98
Toluene	1.03	4.14	8.28	12.41	16.55	20.69
m-Xylene	1.04	4.17	8.33	12.50	16.67	20.83

Table 2 Calculated concentrations of the calibration solutions in mg/m³*

	c_1	c_2	c_3	c_4	c_5	c_6
Benzene	0.063	0.252	0.503	0.755	1.007	1.259
Toluene	0.062	0.248	0.497	0.745	0.993	1.241
m-Xylene	0.062	0.250	0.500	0.750	1.000	1.250

* with respect to a desorption volume of 1.5 mL of carbon disulphide and an air sample volume of 25 L.

A solution that has been prepared independently from the calibration solutions described above must be used to check the calibration.

3 Sampling and sample preparation

3.1 Sampling

Sampling can be carried out as stationary or personal sampling. An activated charcoal tube is opened and connected to the pump. A flow rate of 50 mL/min is then set. At a sampling duration of 8 hours this is equivalent to an air sample volume of max. 25 L. After sampling, the flow rate must be checked for constancy. If the deviation from the set flow rate is greater than ± 5%, it is advisable to reject the measurements. The activated charcoal tube is then tightly sealed with the caps that are supplied with it and unambiguously labelled. The important parameters for the determination of the concentration in air (sample volume, temperature, air pressure and relative humidity) are documented in the sampling record. The method was checked with a flow rate of 200 mL/min and an air sample volume of up to 25 L.

3.2 Sample preparation

The contents of the loaded activated charcoal tube are transferred into a 2 mL sample vial for sample preparation. After addition of 1.5 mL of desorption solution, the sample vial is sealed and treated for five minutes in the ultrasonic bath. Then an aliquot of the supernatant solution (sample solution) is transferred into an autosampler vial and analysed.

4 Operating conditions for gas chromatography

Apparatus:	Agilent 7980A gas chromatograph with two FID, split/splitless-injector and a column flow splitter after the precolumn
Precolumn:	Deactivated fused silica capillary, length approx. 1 m, ID 0.32 mm with a column flow splitter (double capillary technique: both columns are connected in parallel with the precolumn by means of 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 DB1, cross-linked (methyl silicone), ID 25 mm, film thickness 1.0 µm, length 30 m
Temperatures:	Injector: 250 °C Detector: 250 °C
Column with temperature program:	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
Injector:	Split injection, split ratio 1:5
Injection volume:	1 µL
Carrier gas:	Helium 4.6
Detector gases:	Hydrogen 5.0 Synthetic air (free of hydrocarbons)
Make-up gas:	Nitrogen 5.0

5 Analytical determination

1 µL each of the sample solution is injected into the gas chromatograph, split between both columns and a chromatogram is recorded in each case. The quantitative evaluation is carried out according to the internal standard method using the peak areas of the relevant substance with respect to *n*-tetradecane as the internal

standard (IS). If the deviation of the results from both separation columns is less than 20%, the mean value is used for the evaluation. In the case of a greater deviation the lower value is used (on the assumption that the higher result was caused by overlapping with an interfering substance).

In order to ensure that the desorption solution and the activated charcoal used contain no interfering impurities, the filling of an activated charcoal tube that have not been used for sampling are extracted with 1.5 mL of the desorption solution (blank solution) at regular intervals or when the desorption solution is prepared anew. Thus the peak area of the internal standard is determined und the state of the analytical system checked at the same time. Blank values and the peak area of the internal standard are documented in a control chart. If the measured concentrations are above the calibration range, then a suitable dilution must be prepared and the analysis must be carried out again.

6 Calibration

In each case 1 μL of the calibration solutions described in Section 2.3 as examples are injected into the gas chromatograph and analysed in the same manner as the sample solutions. Assignment of the retention times of the peaks in the chromatogram to the injected substances allows a calibration table to be compiled, which forms the basis for subsequent identification (see Table 6 in the Appendix). The calibration function is obtained with the help of regression analysis by correlating the ratios of the peak areas of the investigated substances to the peak areas of internal standard *n*-tetradecane with the mass ratios of the substances and *n*-tetradecane contained in each of the calibration solutions. The calibration must be performed anew if the analytical conditions change or the quality control results indicate that this is necessary.

7 Calculation of the analytical result

On the basis of the resulting peak areas the respective mass X in μg for a component can be obtained from the relevant calibration function. The corresponding mass concentration (ρ) is calculated according to Equation (1) below:

$$\rho = \frac{X}{V \times \eta} \qquad (1)$$

Equation (2) enables calculation of the value at 20 °C and 1013 hPa:

$$\rho_0 = \rho \times \frac{273 + t_a}{293} \times \frac{1013}{p_a} \qquad (2)$$

where:

ρ is the mass concentration of a solvent component in mg/m^3
ρ_0 is the mass concentration of the component in mg/m^3 at 20 °C and 1013 hPa
X is the mass of the component in the analytical sample in µg
V is the air sample volume (calculated from the flow rate and the sampling duration) in L
η is the recovery (in the case of calibration with a test gas and also complete desorption 1 can be entered here)
t_a is the temperature during sampling in °C
p_a is the air pressure during sampling in hPa

8 Reliability of the method

The characteristics of the method were calculated as stipulated in EN 482 [1] and EN 1076 [2] with activated charcoal tubes (NIOSH type, lot 2 000). Two solutions were prepared for validation. Validation solution 1 was prepared by weighing 17.4 mg of benzene and 956.8 mg of toluene into a 10 mL volumetric flask, the flask was then filled to the mark with carbon disulphide and shaken. 2 176.8 mg of *m*-xylene were weighed into a 10 mL volumetric flask for validation solution 2, the flask was then filled to the mark with carbon disulphide and shaken.

The method is suitable for the determination of numerous solvents. An overview of the solvents for which the validation data were determined according to EN 1076 [2] can be found in Table 5 (Appendix).

8.1 Precision

The precision was determined by connecting six activated charcoal tubes each to a pump and adjusting the flow rate to approx. 200 mL/min. A glass tube filled with a plug of quartz wool was fitted upstream of each tube by means of a short piece of Teflon tube (glass to glass connection). Three concentrations were tested for each validation solution with the arrangement described above, whereby 5, 50 and 100 µL of the validation solution were applied to the quartz wool with microlitre syringes. Subsequently, air with a relative humidity between 50 and 60% was drawn through the tube combination over a period of two hours. The investigated air concentrations and standard deviations at these concentrations are listed in Table 3.

Validation for further solvent components was carried out in an analogous manner at 0.1 of the Occupational Exposure Limits, at the Occupational Exposure Limits itself as well as at twice the Occupational Exposure Limits. The mean standard deviations are shown in Table 5 (Appendix).

8.2 Recovery

The recoveries were also determined from six parallel samples in the comparative experiments described in Section 8.1. The investigated concentrations as well as the resulting recoveries are listed in Table 3.

Table 3 Characteristics of the validation

Substance	Concentration [mg/m^3]	Standard deviation (rel.) [%]	Recovery	Expanded uncertainty *U* [%]
Benzene	0.35	2.4	0.91	16.2
	3.49	3.0	0.95	16.6
	6.97	3.1	0.99	16.7
Toluene	19.1	2.5	0.98	16.3
	191.4	2.6	0.98	16.4
	382.7	1.0	1.00	15.6
m-Xylene	43.5	1.3	0.97	15.7
	435.4	1.1	0.99	15.7
	870.7	0.8	0.98	15.6

8.3 Limit of quantification

The limits of detection (LODs) and limits of quantification (LOQs) were calculated from the measurement of the signal-to-noise ratio. A signal-to-noise ratio of 3 was used for the calculation of the LODs and the calculation of the LOQs was based on a ratio of 10. The absolute LOQ of a loaded charcoal tube is approx. 0.8 ng of enriched substance. This is equivalent to a relative LOQ of approx. 0.05 mg/m^3 at a sample volume of 25 L. The exact results are shown in Table 4.

Table 4 Limits of quantification for n = 6 determinations

Substance	Limit of quantification	
	[ng absolute]	[mg/m^3]*
Benzene	0.86	0.051
Toluene	0.83	0.050
m-Xylene	0.84	0.050

* with respect to a desorption volume of 1.5 mL of carbon disulphide and an air sample volume of 25 L.

The LOQs of other solvents that can be determined with this method are listed in Table 5 (Appendix).

8.4 Expanded uncertainty

The expanded uncertainties were estimated as stipulated in EN 482 and EN 1076 [1, 2], 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 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 uncertainties are between 15 and 17%, depending on the substance and concentration (see also Tables 3 and 5).

8.5 Storage stability

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

Appendix

Characteristics of the investigated substances

Table 5 Characteristics of further investigated substances

Substance	CAS No.	Recovery	Standard deviation (rel.) [%]	LOQ* [mg/m^3]	Expanded uncertainty U [%]
Benzene	71-43-2	0.95	2.8	0.051	16.5
n-Butylbenzene	135-98-8	0.97	1.5	0.015	15.8
Chloroform	67-66-3	1.00	2.9	0.704	16.6
1,4-Dioxane	123-91-1	0.93	3.3	0.047	16.9
Isobutyl acetate	110-19-0	0.97	1.7	0.027	15.9
n-Butyl acetate	123-86-4	1.00	1.3	0.095	15.7
Isopropyl acetate	108-21-4	0.98	1.7	0.034	15.9
Propyl acetate	109-60-4	0.99	2.9	0.109	16.6
2-Ethyltoluene	611-14-3	0.97	2.1	0.051	16.1
3-Ethyltoluene	620-14-4	0.99	3.1	0.015	16.7
4-Ethyltoluene	622-96-8	0.99	2.7	0.056	16.4
n-Heptane	142-82-5	0.99	1.7	0.055	15.9
n-Hexane	110-54-3	0.99	1.4	0.060	15.8
Cumene	98-82-8	1.01	0.9	0.050	15.6
Methyl methacrylate	80-62-6	0.93	2.7	0.106	16.4
α-Methyl styrene	98-83-9	0.96	1.7	0.015	15.9

Table 5 (Continued)

Substance	CAS No.	Recovery	Standard deviation (rel.) [%]	LOQ* [mg/m^3]	Expanded uncertainty U [%]
n-Propylbenzene	103-65-1	0.99	1.5	0.046	15.8
Styrene	100-42-5	0.86	2.9	0.049	16.6
1,2,3,5-Tetramethylbenzene	527-53-7	0.97	2.1	0.051	16.1
Toluene	108-88-3	0.98	2	0.050	16.0
1,2,3-Trimethylbenzene	526-73-8	0.92	2.7	0.055	16.4
1,2,4-Trimethylbenzene	95-63-6	0.95	2.8	0.050	16.5
m-Xylene	108-38-3	0.98	1.1	0.050	15.7
p-Xylene	95-47-6	0.95	2.2	0.015	16.1
o-Xylene	106-42-3	0.99	1.6	0.051	15.8

* LOQ = Limit of quantification

Table 6 Retention times of the investigated substances on the separation columns specified in minutes

Substance [CAS No.]	DB1 [min]	DB Wax [min]
Benzene [71-43-2]	5.875	5.014
n-Butylbenzene [104-51-8]	23.654	19.541
Chloroform [67-66-3]	4.470	7.406
1,4-Dioxane [123-91-1]	7.180	9.000
Isobutyl acetate [110-19-0]	10.680	7.113
n-Butyl acetate [123-86-4]	12.989	9.500
Isopropyl acetate [108-21-4]	5.767	4.043
Propyl acetate [109-60-4]	7.636	5.900
2-Ethyltoluene [611-14-3]	20.900	17.719
3-Ethyltoluene [620-14-4]	20.248	16.408
4-Ethyltoluene [622-96-8]	20.328	16.300
n-Heptane [142-82-5]	7.769	–
n-Hexane [110-54-3]	4.432	1.730
Cumene [98-82-8]	18.798	14.269
Methyl methacrylate [80-62-6]	7.561	6.823
α-Methyl styrene [98-83-9]	20.879	19.983
n-Propylbenzene [103-65-1]	19.968	15.783
Styrene [100-42-5]	17.145	17.574
1,2,3,5-Tetramethylbenzene [527-53-7]	26.288	22.832
Toluene [108-88-3]	10.492	8.105

Table 6 (Continued)

Substance [CAS No.]	DB1 [min]	DB Wax [min]
1,2,3-Trimethylbenzene [526-73-8]	22.389	20.108
1,2,4-Trimethylbezene [95-63-6]	21.442	18.378
m-Xylene [108-38-3]	16.316	12.630
p-Xylene [95-47-6]	17.374	14.726
o-Xylene [106-42-3]	16.367	12.300

References

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

2 EN 1076 (2010) Workplace exposure – Procedures for measuring gases and vapours using pumped samplers – Requirements and test methods. Beuth Verlag, Berlin, Germany

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