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Phthalates – Method for the determination of nine phthalates in workplace air using gas chromatography-mass spectrometry (GC-MS)

Air Monitoring Method – Translation of the German version from 2014

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Keywords: phthalates; air analyses; analytical method; workplace measurement; hazardous substance; gas chromatography; mass spectrometry; GC-MS; glass fibre filter; PU foam

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Phthalates – Method for the determination of nine phthalates in workplace air using gas chromatography-mass spectrometry (GC-MS)

Air Monitoring Methods

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Abstract

This analytical method is a validated measurement procedure for the determination of several phthalates such as dimethyl phthalate, diethyl phthalate, diallyl phthalate, diisobutyl phthalate, dibutyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, bis(2-ethylhexyl) phthalate and bis(2-propylheptyl) phthalate in workplace air. With this method airborne phthalates in the gaseous state as well as bound to particles are collected simultaneously. Sampling is performed by drawing a defined volume of air through a sampling system consisting of a glass fibre filter located in a GSP sampling head and an adsorption tube filled with PU foam connected downstream using a suitable pump. The flow rate is set to 1 L/min with a recommended air sample volume of 60 to 120 litres. For sample preparation the collected phthalates are desorbed from the sample carriers (filter and PU foam) with 1,4-dioxane. The sample solution is analysed by means of gas chromatography-mass spectrometry (GC-MS). The quantitative determination is based on calibration functions obtained by means of multiple-point calibrations. The limit of quantification for an individual phthalate is between 0.015 and 0.096 mg/m^3.

Joint Publication of the Analytical Subcommittee of the Chemistry Board of Experts of the Expert Committee Raw Materials and Chemical Industry of the German Social Accident Insurance and the Working Group "Air Analyses" of the Permanent Senate Commission of the DFG for the Investigation of Health Hazards of Chemical Compounds in the Work Area.

Keywords

dimethyl phthalate; diethyl phthalate; diallyl phthalate; diisobutyl phthalate; dibutyl phthalate; benzyl butyl phthalate; dicyclohexyl phthalate; bis(2-ethylhexyl) phthalate; bis(2-propylheptyl) phthalate; air analysis; workplace measurement; hazardous substances; workplace monitoring; GGP sampling system; GSP sampling head; gas chromatography-mass spectrometry; GC-MS

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Phthalates – Method for the determination of nine phthalates in workplace air using gas chromatography-mass spectrometry (GC-MS)

Method number	3
Application	Air analysis
Analytical principle	Gas chromatography-mass spectrometry (GC-MS)
Completed in	June 2016

Summary

The analytical procedure described here permits the determination of nine relevant phthalates, such as dimethyl phthalate, diethyl phthalate, diallyl phthalate, diisobutyl phthalate, di-*n*-butyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, di-(2-ethylhexyl) phthalate and di-(2-propylheptyl) phthalate in workplace air. Phthalates in the gaseous state as well as bound to particles can be simultaneously determined with this method. A suitable flow-regulated pump is used for sampling by drawing ambient air through a combined sampling system consisting of a glass fibre filter and polyurethane foam (PU foam) connected downstream. Phthalates in the particulate state are thus deposited on the filter, whereas gaseous phthalates are adsorbed onto the PU foam. After sampling is complete, the loaded phthalates are desorbed from the filter and PU foam with 1,4-dioxane and analysed by means of GC-MS. The quantitative determination is based on calibration functions obtained by means of multiple-point calibrations.

Characteristics of the method

Precision:	Standard deviation (rel.):	s = 2.8 to 9.3%
	Expanded uncertainty:	U = 25.9 to 38.1%
	in the concentration range from 0.058 to 1.0 mg/m^3 and for n = 6 determinations	

	Standard deviation (rel.):	s = 2.7 to 6.4%
	Expanded uncertainty:	U = 24.2 to 34.7%
	in the concentration range from 0.58 to 10 mg/m³ and for n = 6 determinations	
	Standard deviation (rel.):	s = 2.9 to 4.8%
	Expanded uncertainty:	U = 23.9 to 33.0%
	in the concentration range from 1.16 to 20 mg/m³ and for n = 6 determinations	
Limit of quantification:	Dimethyl phthalate (DMP)	0.025 mg/m³
	Diethyl phthalate (DEP)	0.029 mg/m³
	Diallyl phthalate (DAP)	0.077 mg/m³
	Diisobutyl phthalate (DiBP)	0.027 mg/m³
	Di-*n*-butyl phthalate (DBP)	0.015 mg/m³
	Benzyl butyl phthalate (BBP)	0.096 mg/m³
	Dicyclohexyl phthalate (DCHP)	0.021 mg/m³
	Di-(2-ethylhexyl) phthalate (DEHP)	0.037 mg/m³
	Di-(2-propylheptyl) phthalate (DPHP)	0.095 mg/m³
	at an air sample volume of 60 L, a sample solution of 20 mL and an injection volume of 1 µL	
Recovery:	Dimethyl phthalate (DMP)	83.1 to 94.3%
	Diethyl phthalate (DEP)	87.8 to 103.0%
	Diallyl phthalate (DAP)	81.8 to 103.1%
	Diisobutyl phthalate (DiBP)	89.8 to 101.4%
	Di-*n*-butyl phthalate (DBP)	92.6 to 97.0%
	Benzyl butyl phthalate (BBP)	84.3 to 100.3%
	Dicyclohexyl phthalate (DCHP)	86.3 to 102.3%
	Di-(2-ethylhexyl) phthalate (DEHP)	82.3 to 103.7%
	Di-(2-propylheptyl) phthalate (DPHP)	85.2 to 97.2%
Sampling recommendation:	Sampling time:	60 to 120 min
	Air sample volume:	60 to 120 L
	Flow rate:	1 L/min

Description of the substances

Phthalates

Phthalates are compounds of phthalic acid (1,2-benzenedicarboxylic acid) with various alcohols (phthalic acid esters). They are mainly water-insoluble, practically non-volatile liquids that are primarily used as plasticizers. Table D1 lists important substance-specific data for the phthalates under investigation.

Table D1 Substance-specific characteristics and physical parameters

Phthalate	CAS number	Boiling point [°C]	Melting point [°C]	Density [g/cm³]	Vapour pressure [hPa, 20 °C]
Dimethyl phthalate (DMP)	131-11-3	283	6	1.19	0.008
Diethyl phthalate (DEP)	84-66-2	302	–40	1.12	0.002
Diallyl phthalate (DAP)	131-17-9	290	–70	1.12	0.3 (100 °C)
Diisobutyl phthalate (DiBP)	84-69-5	320	–64	1.04	< –0.01
Di-*n*-butyl phthalate (DBP)	84-74-2	340	–35	1.05	9.7×10^{-5} (25 °C)
Benzyl butyl phthalate (BBP)	85-68-7	370	–35	1.12	>1 Pa (110 °C)
Dicyclohexyl phthalate (DCHP)	84-61-7	226 (5.3 hPa)	62–64	1.15	0.39 mPa (50 °C)
Di-(2-ethylhexyl) phthalate (DEHP)	117-81-7	390	–55	0.99	8.6×10^{-6}
Di-(2-propylheptyl) phthalate (DPHP)	53306-54-0	251–253 (7 hPa decomposition)	–48	0.96	3.7×10^{-8}

Phthalates are e.g. added to hard and brittle plastics such as polyvinyl chloride (PVC), thereby conferring elastic properties to PVC. More than 90% of the phthalates produced are used as plasticizers for soft PVC.

The greatest end-users of soft PVC are:

- the building industry (cables, tubes, flooring, foil, wallpaper)
- the electrical and cable industry (encasement of cables and electrical connections)
- the automobile industry (under body protection, interior cladding, seals)
- the manufacturers of sport and leisure items

Furthermore, phthalates are used as a carrier liquid in pesticides, cosmetics and perfumes and find use as intermediary products in duroplasts, synthetic fibres, foils and paint resins (phthalate resins, alkyd resins). Phthalates are almost ubiquitous. The main reason for this is, besides the large production quantities, the tendency of phthalates to accumulate on airborne particles (e.g. dust particles) and to be transported for long distances in this form.

Occupational limit values (OELs) for the phthalates listed in Table D1 currently only exist for DBP (0.58 mg/m³) and DEHP, whose OEL was lowered from 10 mg/m³ E to 2 mg/m³ E in 2014 [1, 2]. The minimum measuring range investigated as part

of the development of the method as stipulated in EN 482 [7] (a tenth to twice the limit value) is based on the OEL of 10 mg/m³ E for DEHP, valid until 2014. In the list of MAK and BAT values DEHP is also assigned to Carcinogen Category 4 [2]. Detailed information on the toxicity of the individual phthalates can be found in the toxicological-occupational health documentation of the MAK values [3, 4, 5, 6].

In addition to the experimental testing of the influence of temperature, relative humidity as well as the particle size, a plausibility check was carried out by the experts of the "Air Analyses" working group of the Permanent DFG Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (see "Preliminary Remarks", Vol. 11 Chapter „Evaluation of methods for air analysis without experimental examination" 2009*) as part of the measurement method described here.*

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Contents

1 General principles

The analytical procedure described here permits the determination of nine relevant phthalates, such as dimethyl phthalate, diethyl phthalate, diallyl phthalate, diisobutyl phthalate, di-*n*-butyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, di-(2-ethylhexyl) phthalate and di-(2-propylheptyl) phthalate in workplace air. Phthalates in the gaseous and particulate state can be simultaneously determined with this method. A suitable flow-regulated pump is used for sampling by drawing ambient air through a combined sampling system consisting of a glass fibre filter and polyurethane foam (PU foam) connected downstream. Phthalates occurring in particulate state or as aerosols are thus deposited on the filter, whereas gaseous phthalates are adsorbed onto the PU foam. After sampling is completed, the loaded sample carriers (glass fibre filter and PU foam) are immediately (on the spot!) transferred into a screw-capped vial and covered with solvent (1,4-dioxane). Analysis is carried out by means of gas chromatography with a mass selective detector (MSD), whereby the quantitative determination is based on calibration functions obtained by means of multiple-point calibrations.

2 Equipment, chemicals and solutions

2.1 Equipment

- Pump for personal sampling, suitable for a flow rate of 1 L/min
- Gas meter
- GGP sampling system and GSP sampling head with intake cones for flow rates of 0.5; 1.0 or 2.0 L/min for detection of the inhalable aerosol fraction (e.g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- Filter cassettes, ∅ 37 mm, with stainless steel support base and transport covers (e.g. from GSA Messgerätebau GmbH)
- Glass fibre filter, ∅ 37 mm (e.g. MN 85/90 BF from MACHEREY-NAGEL)
- Polyurethane foam (PU foam), length 76 mm, ∅ 22 mm (e.g. ORBO™–1000 Polyurethane Foam Replacement Plug, from Supelco, supplied by Sigma-Aldrich, 82024 Taufkirchen, Germany)
- Volumetric flasks, 10, 50 and 100 mL
- Piston pipettes, 10 µL to 5 mL
- Laboratory shaker
- Screw-capped vials, 40 mL, with PTFE-coated seals (e.g. from Supelco, Order No. 27182)
- Autosampler crimp-cap vials, 1.5 mL
- Aluminium sealing caps with PTFE-coated silicone septa
- Gas chromatograph with mass selective detector (e.g. SHIMADZU GCMS-QP2010, from Shimadzu Deutschland GmbH, 47269 Duisburg, Germany)
- Separation column: 30 m, ∅ 0.25 mm, 0.25 µm film thickness (e.g. ZB-5 ms, from Phenomenex Ltd, 63741 Aschaffenburg, Germany)

2.2 Chemicals

- Dimethyl phthalate (DMP), ≥ 99%, e.g. from Sigma-Aldrich, Order No. W508500
- Diethyl phthalate (DEP), ≥ 99%, e.g. from Sigma-Aldrich, Order No. 524972
- Diallyl phthalate (DAP), ≥ 98%, e.g. from Sigma-Aldrich, Order No. 36925
- Diisobutyl phthalate (DiBP), ≥ 99%, e.g. from Sigma-Aldrich, Order No. 152641
- Di-*n*-butyl phthalate (DBP), ≥ 99%, e.g. from Sigma-Aldrich, Order No. 524980
- Benzyl butyl phthalate (BBP), ≥ 99%, e.g. from Sigma-Aldrich, Order No. 36927
- Dicyclohexyl phthalate (DCHP), ≥ 99%, e.g. from Sigma-Aldrich, Order No. 306150
- Di-(2-ethylhexyl) phthalate (DEHP), ≥ 99%, e.g. from Sigma-Aldrich, Order No. 36735
- Di-(2-propylheptyl) phthalate (DPHP), ≥ 99%, e.g. from Sigma-Aldrich, Order No. 271494
- 1,4-Dioxane, ≥ 99.5%, stabilised, e.g. from Sigma-Aldrich CHROMASOLV® Plus, Order No. 34857
- Toluene, 99.9%, e.g. from Sigma-Aldrich CHROMASOLV®, Order No. 34866
- Helium, 5.0 for gas chromatography

2.3 Solutions

Stock solution:
150 mg each of dimethyl phthalate, diethyl phthalate, diallyl phthalate, diisobutyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, di-(2-propylheptyl) phthalate as well as 17.5 mg of di-*n*-butyl phthalate and 300 mg of di-(2-ethylhexyl) phthalate are weighed exactly to the nearest 0.1 mg into a 50 mL volumetric flask. Then the flask is filled to the mark with toluene and shaken. The exact concentrations in the stock solution can be calculated based on the weighed-in amounts.

Calibration standards:
Nine calibration standards are prepared from the stock solution by means of suitable dilution with 1,4-dioxane. If the concentrations of di-*n*-butyl phthalate and di-(2-ethylhexyl) phthalate are equivalent to the corresponding OEL or MAK value, then the concentrations of these two phthalates at an assumed sampling time of one hour, a flow rate of 1 L/min and a sample solution of 20 mL, are equivalent to a dilution of the stock solution of 1 : 200.

Nine dilutions at a ratio of 1 : 2000 to 1 : 100 (see Table 1) are prepared from the stock solution, equivalent to the minimum measuring range (a tenth to twice the OEL or MAK value) according to EN 482 [7].

The calibration solutions are stable for at least 5 months when stored at –18 °C.

Spiking solution:
The stock solution can be used directly as spiking solution for the determination of the recovery. In this case the masses of di-*n*-butyl phthalate and di-(2-ethylhexyl) phthalate in 100 µL of the spiking solution are equivalent to the respective OEL of the two phthalates at an air sample volume of 60 litres. 100 µL of the solution are

Table 1 Dosing scheme for the preparation of the calibration standards

No.	Dilution of the stock solution	Volume of the stock solution [µL]	Final volume [mL]	Concentration of DBP [µg/mL]	Concentration of DEHP [µg/mL]	Concentration of other phthalates [µg/mL]
1	1 : 2000	5	10	0.175	3	1.5
2	1 : 1000	10	10	0.35	6	3
3	1 : 500	20	10	0.7	12	6
4	1 : 333	30	10	1.05	18	9
5	1 : 250	40	10	1.4	24	12
6	1 : 200	50	10	1.75	30	15
7	1 : 167	60	10	2.1	36	18
8	1 : 133	75	10	2.625	45	22.5
9	1 : 100	100	10	3.5	60	30

equivalent to a concentration of 5 mg/m^3 for all the other investigated phthalates under the same sampling conditions.

3 Sampling and sample preparation

3.1 Sampling

The GGP sampling system (*Gesamtstaub-Gas-Probenahmesystem* [total dust/gas sampling system]), consisting of a filter cassette with a glass fibre filter and PU foam downstream (Figure 1), is connected to a flow-regulated sampling pump before sampling begins. The GGP system is fitted with an intake cone, corresponding to a flow rate of 1 L/min. The definition of inhalable dust is fulfilled by this sampling system [8, 9]. Depending on the subject under investigation and the expected concentrations of phthalates, the sampling time can be set between 15 minutes (short-term value) up to 2 hours. This is equivalent to air sample volumes in the range of 15 to 120 litres. If other flow rates (e.g. 0.5 or 2 L/min) are selected, the sampling time must be adapted accordingly. The important parameters for the determination of the concentration of phthalates in air (sample volume, temperature, air pressure, relative humidity) are documented in the sampling record. After sampling is complete, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to discard the measurement [10].

Immediately after sampling (on the spot!) the sample carriers (glass fibre filter and PU foam) are carefully removed from the sampling system with tweezers and transferred together into a 40 mL screw-capped vial. Then the filter and PU foam are covered with 30 mL of 1,4-dioxane, the screw-capped vials are tightly sealed with the caps designated for this purpose and unambiguously labelled. It is absolutely

Figure 1 GGP sampling system (*Gesamtstaub-Gas-Probenahmesystem* [total dust/gas sampling system]) [11]

essential to ensure that the loaded sample carriers are transferred into a solvent immediately, as even a short storage period of the loaded sample carriers is associated with significant losses of the collected phthalates (see Section 8.5).

Note:
If screw-capped vials other than those stated in Section 2.1 are used, it must be ensured that the loaded sample carriers (glass fibre filter and PU foam) are completely immersed in 1,4-dioxane, meaning that if necessary larger volumes of extraction agent must be used. Depending on the subject of the analytical investigation, the filter and PU foam can also be transferred into separate screw-capped vials.

3.2 Sample preparation

The screw-capped vial, containing the loaded glass fibre filter and PU foam covered with 1,4-dioxane, is shaken for 15 minutes at room temperature on a laboratory shaker as part of the sample preparation. Then an aliquot of the sample solution is taken from the supernatant, transferred into an autosampler vial and analysed by means of gas chromatography-mass spectrometry.

4 Operational parameters for gas chromatography

Apparatus: Gas chromatograph with autosampler and mass selective detector (e.g. SHIMADZU GCMS-QP2010)

Operating conditions for gas chromatography

Column:	Material:	Fused silica
	Stationary phase:	e.g. ZB-5 ms, Phenomenex
	Length:	30 m
	Inner diameter:	0.25 mm
	Film thickness:	0.25 µm

Injector:	Split/splitless injector:	275 °C (isothermal)
	Split ratio:	1 : 20
	Injection volume:	1 µL
Carrier gas:	Helium 5.0:	1.25 mL/min
Temperature program:	50 °C (2 min) $\xrightarrow{15\ °C/min}$	150 °C $\xrightarrow{10\ °C/min}$ 285 °C (5 min)
Temperature:	Autosampler:	20 °C (at least 12 °C on account of the melting point of 1,4-dioxane)

Operating conditions for mass spectrometry

Temperatures:	Transfer line:	285 °C
	Ion source:	230 °C
Ionisation type:	Electron impact ionisation (EI)	
Ionisation energy:	70 eV	
Dwell time:	200 ms	
Data recording:	SIM mode (for selected masses see Table 2)	
Solvent suppression:	8 min; as well as from 11.33 to 11.65 min	

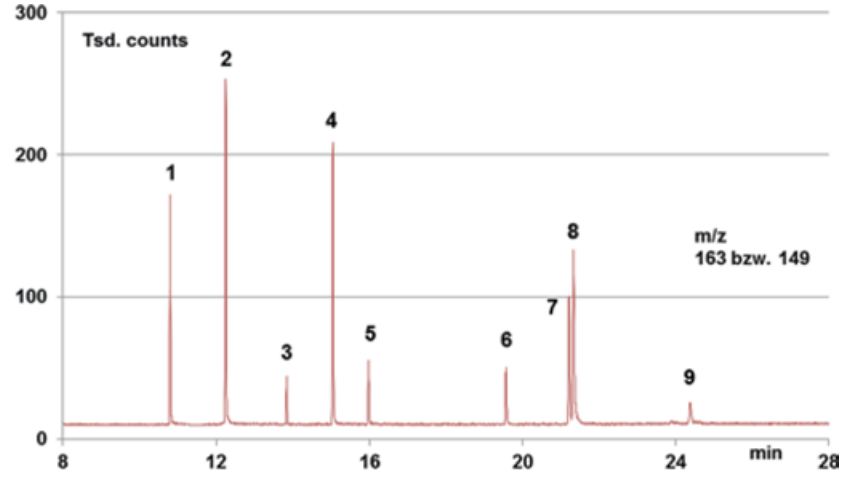
Figure 2 shows an example of the chromatogram of a standard solution with the nine phthalates under investigation recorded in the SIM (Selected Ion Monitoring) mode and Table 2 lists the corresponding retention times.

Table 2 Retention times and selected masses of the phthalates investigated

Phthalate	Retention time [min]	Quantifier [amu]	Qualifier [amu]
Dimethyl phthalate	10.77	163	133, 194
Diethyl phthalate	12.21	149	150, 177
Diallyl phthalate	13.80	149	132, 189
Diisobutyl phthalate	15.00	149	104, 223
Di-*n*-butyl phthalate	15.94	149	205, 223
Benzyl butyl phthalate	19.53	149	91, 206
Dicyclohexyl phthalate	21.16	149	167, 249
Di-(2-ethylhexyl) phthalate	21.27	149	167, 279
Di-(2-propylheptyl) phthalate	24.31	149	150, 167

5 Analytical determination

For analytical determination of the samples prepared as described in Section 3.2 1 µL of the sample solution is injected into the gas chromatograph in each case and



1 Dimethyl phthalate
2 Diethyl phthalate
3 Diallyl phthalate
4 Diisobutyl phthalate
5 Di-*n*-butyl phthalate
6 Benzyl butyl phthalate
7 Dicyclohexyl phthalate
8 Di(2-ethylhexyl) phthalate
9 Di-(2-propylheptyl) phthalate

Figure 2 Gas chromatogram in the SIM mode of a standard solution with the nine phthalates investigated

analysed under the conditions stated in Section 4. If the measured concentrations are above the calibration range, then a suitable dilution of the sample solution must be prepared and this must be analysed again.

6 Calibration

The calibration solutions described in Section 2.3 are used to obtain the calibration functions. 1 µL of these calibration solutions is injected into the gas chromatograph in each case and analysed in the same manner as the sample solutions. The resulting peak areas are plotted versus the corresponding concentrations. The calibration functions are usually linear in the investigated concentration range and should be checked each working day using a control sample. 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

The concentration of the phthalates investigated in workplace air is calculated from the concentrations of the available phthalates in the measurement solution by the data evaluation unit. For this purpose the data evaluation unit uses the calibration functions calculated as part of the calibration.

Based on the determined peak areas, the corresponding mass X in µg per sample is obtained from the calibration curve. The corresponding mass concentration (ρ) in mg/m³ is calculated according to Equation (1) as follows:

$$\rho = \frac{\mathrm{X}}{V} \tag{1}$$

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

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

The corresponding concentration by volume σ– independent of the pressure and temperature – is calculated using Equation (3) and Equation (4):

$$\sigma = \rho_0 \times \frac{V_\mathrm{m}}{M} \tag{3}$$

$$\sigma = \rho \times \frac{273 + t_\mathrm{a}}{p_\mathrm{a}} \times \frac{1013}{293} \times \frac{V_\mathrm{m}}{M} \tag{4}$$

where:

ρ is the mass concentration of a phthalate in mg/m³
ρ_0 is the mass concentration of the phthalate in mg/m³ at 20 °C and 1013 hPa
σ is the concentration by volume in mL/m³ (ppm)
M is the molar mass in g/mol
V_m is the molar volume in L/mol
V is the air sample volume (calculated from the flow rate and the sampling time) in L
X is the mass of the phthalate in the sample in µg
t_a is the temperature during sampling in °C
p_a is the atmospheric pressure during sampling in hPa

The concentration by volume σ in mL/m³ (ppm) at t_a = 20 °C and p_a = 1013 hPa for the phthalates investigated was calculated using the factors listed in Table 3.

Table 3 Factors for the calculation of the concentration by volume σ

Phthalate	Molar mass [g/mol]	Conversion factor $mg/m^3 \rightarrow mL/m^3$ (ppm)	Conversion factor mL/m^3 (ppm) $\rightarrow mg/m^3$
Dimethyl phthalate	194.19	0.124	8.07
Diethyl phthalate	222.24	0.108	9.24
Diallyl phthalate	246.26	0.098	10.24
Diisobutyl phthalate	278.35	0.086	11.57
Di-*n*-butyl phthalate	278.35	0.086	11.57
Benzyl butyl phthalate	312.37	0.077	12.98
Dicyclohexyl phthalate	330.42	0.073	13.73
Di-(2-ethylhexyl) phthalate	390.56	0.062	16.23
Di-(2-propylheptyl) phthalate	446.67	0.054	18.56

8 Reliability of the method

The characteristics of the method were calculated as stipulated in EN 482 [7], EN 1076 [12], DIN 32645 [13] and EN 13936 [8].

8.1 Precision and expanded uncertainty

In order to determine the precision and expanded uncertainty, six sampling systems (glass fibre filter and PU foam connected downstream) were spiked with defined masses of the selected phthalates in each case. Then purified laboratory air at a flow rate of 1 L/min was drawn through the sampling systems for one hour. The filter and PU foam were then prepared and analysed as described in Sections 3, 4 and 5. The results are listed in Table 4. Here the values shown in the table column headed "concentration" are calculated from the quotients of the phthalate masses (loaded glass fibre filters and PU foams) and the volume of air (in this case 60 L), that was drawn through the sample carriers. The concentrations of di-*n*-butyl phthalate and di-(2-ethylhexyl) phthalate are thus equivalent to a tenth of the reference value, the reference value and twice the reference value (OEL).

The expanded uncertainty was estimated taking all relevant influencing factors into consideration as stipulated in EN 482 [7] and was calculated with the aid of the software [14]. The expanded uncertainty for the individual phthalates can be found in Table 4.

Table 4 Relative standard deviations and expanded uncertainties for $n = 6$ determinations

Phthalate	Concentration [mg/m³]	Standard deviation (rel.) [%]	Expanded uncertainty U [%]
Dimethyl phthalate	0.5	6.4	30.5
	5	4.7	27.1
	10	3.2	25.8
Diethyl phthalate	0.5	4.9	30.3
	5	6.4	29.1
	10	3.0	27.7
Diallyl phthalate	0.5	8.9	38.1
	5	4.1	34.7
	10	3.0	33.0
Diisobutyl phthalate	0.5	3.7	26.9
	5	5.9	25.5
	10	4.4	25.0
Di-*n*-butyl phthalate	0.058	9.3	25.9
	0.58	5.4	24.2
	1.16	2.9	23.9
Benzyl butyl phthalate	0.5	5.9	32.8
	5	6.3	30.6
	10	3.8	28.5
Dicyclohexyl phthalate	0.5	3.1	33.7
	5	4.3	30.8
	10	4.8	29.7
Di(2-ethylhexyl) phthalate	1	2.8	35.8
	10	2.7	32.0
	20	4.4	31.4
Di-(2-propylheptyl) phthalate	0.5	6.4	29.7
	5	3.5	26.7
	10	3.3	25.5

8.2 Recovery

After the sample carriers were spiked and air was drawn through them, the recoveries of the phthalates were calculated from the data obtained from determining the precision. The results are documented in Table 5. Here the concentrations listed in the columns headed "lower" and "upper" concentration range are equivalent to one tenth and twice the reference value (OEL for di-*n*-butyl phthalate and di-(2-ethylhexyl) phthalate) respectively, for an assumed real air sample at a sampling time of one hour and a flow rate of 1 L/min.

When applying the measurement procedure described here and if the relative recovery of a phthalate value is < 95% or > 105% (particularly in the lower concentration range), this must be included in the calculation.

Table 5 Recoveries of the phthalates

Phthalate	Rel. recovery in the "lower" concentration range [%]	Equivalent concentration in the air [mg/m³]	Rel. recovery in the "upper" concentration range [%]	Equivalent concentration in the air [mg/m³]
Dimethyl phthalate	83.1	0.5	94.3	10
Diethyl phthalate	87.8	0.5	103.0	10
Diallyl phthalate	81.8	0.5	103.1	10
Diisobutyl phthalate	89.8	0.5	101.4	10
Di-*n*-butyl phthalate	92.6	0.058	97.0	1.16
Benzyl butyl phthalate	84.3	0.5	100.3	10
Dicyclohexyl phthalate	83.6	0.5	102.3	10
Di(2-ethylhexyl) phthalate	82.3	1.0	103.7	20
Di-(2-propylheptyl) phthalate	85.2	0.5	97.2	10

8.3 Limit of quantification

The limits of quantification of the investigated phthalates are determined according to DIN 32645 [13] from 10-point calibrations corresponding to the concentration ranges documented in Table 6 with a statistical certainty of P = 95% and k = 3. The determination of the limits of quantification was based on an air sample volume of 60 litres for the individual phthalates listed in Table 6.

Table 6 Limits of quantification for the phthalates based on an air sample volume of 60 L

Phthalate	Concentration range [µg/mL]	Limit of quantification [mg/m³]
Dimethyl phthalate	0.04 – 0.4	0.025
Diethyl phthalate	0.04 – 0.4	0.029
Diallyl phthalate	0.1 – 1.0	0.077
Diisobutyl phthalate	0.04 – 0.4	0.027
Di-*n*-butyl phthalate	0.02 – 0.2	0.015
Benzyl butyl phthalate	0.1 – 1.0	0.096
Dicyclohexyl phthalate	0.04 – 0.4	0.021
Di-(2-ethylhexyl) phthalate	0.04 – 0.4	0.037
Di-(2-propylheptyl) phthalate	0.1 – 1.0	0.095

8.4 Influence of the humidity

The influence of humidity was investigated at two different humidity levels (20 and 80%) and a constant temperature of 25.0 ± 0.5 °C. For this purpose six sample carriers (filter and PU foam) were spiked with 10 µL and 200 µL of stock solution in each case (see Section 2.3). Then nitrogen with relative humidities of 20 and 80% was drawn through the sample carriers at a flow rate of 1 L/min for 30 minutes by means of a dynamic test gas facility. The filter and PU foam were then prepared and analysed as described in Sections 3, 4 and 5 immediately after sampling. The relative recoveries in relation to the relative humidity of the investigated phthalates are listed in Table 7. The investigations show that the relative humidity has no influence on the measurement results.

Table 7 Rel. recoveries of the phthalates at two different humidity levels (RH) and two different spiking volumes of stock solution (µL) respectively

Phthalate	Rel. recovery [%]			
	20% RH		80% RH	
	Spiked with 10 µL	Spiked with 200 µL	Spiked with 10 µL	Spiked with 200 µL
Dimethyl phthalate	117.2	92.9	106.0	89.7
Diethyl phthalate	104.8	97.7	104.3	95.4
Diallyl phthalate	112.2	99.9	105.2	98.0
Diisobutyl phthalate	113.1	99.7	107.0	98.7
Di-*n*-butyl phthalate	116.4	102.8	110.8	100.4
Benzyl butyl phthalate	113.2	102.6	106.7	101.4
Dicyclohexyl phthalate	111.6	103.4	105.7	100.7
Di(2-ethylhexyl) phthalate	118.7	102.0	106.9	101.6
Di-(2-propylheptyl) phthalate	126.0	102.8	123.7	102.3

8.5 Influence of the temperature

Tests to establish the influence of the temperature on the ratio between the particle and vapour contents during sampling were carried out at temperatures of 15 and 35 °C. Di-*n*-butyl phthalate (DBP) was used as test substance at a concentration of 1.2 mg/m^3, which was investigated in an aerosol generator at 15 and 35 °C with a flow rate of 1 L/min over a time period of 60 minutes at a relative humidity of 50%. The aerosol thus generated with a particle diameter of 0.75 µm was deposited onto the filter, whereas the gaseous proportion was adsorbed onto the PU foam. The results are listed in Table 8.

Table 8 Distribution of the collected DBP between filter and PU foam in relation to the temperature

Temperature	Filter [%]	PU foam [%]
15 °C	97.9–99.6	0.4–2.1
35 °C	54–60	40–46

The results show that the temperature has a significant influence on the composition ratio of the particle/vapour mixture of phthalates with regard to its distribution between the particle and vapour phases. However, as the determined measurement result is the total concentration (sum of the concentrations found on the filter and PU foam), the influence of the temperature can be disregarded.

8.6 Storage stability

Tests on storage stability were carried out using the same sample solutions (1,4-dioxane extract of filter and PU foam) as those used to investigate the influence of the humidity (see Section 8.4). For this purpose the sample solutions were stored in a refrigerator over a period of four weeks at approx. 4 °C and then analysed according to Sections 4 and 5. The results on storage stability are shown in Table 9 in the form of relative recoveries. Here the concentrations listed in the columns headed "lower" and "upper" concentration range are equivalent to one tenth and twice the reference value (OEL for di-*n*-butyl phthalate and di-(2-ethylhexyl) phthalate) respectively, for an assumed real air sample at a sampling time of one hour and a flow rate of 1 L/min.

Table 9 Recoveries of the phthalates after storage in a refrigerator for four weeks

Phthalate	Rel. recovery in the "lower" concentration range [%]	Equivalent concentration in the air [mg/m³]	Rel. recovery in the "upper" concentration range [%]	Equivalent concentration in the air [mg/m³]
Dimethyl phthalate	96.3	0.5	99.5	10
Diethyl phthalate	96.0	0.5	97.7	10
Diallyl phthalate	90.0	0.5	92.7	10
Diisobutyl phthalate	92.9	0.5	95.4	10
Di-*n*-butyl phthalate	92.4	0.058	98.5	1.16
Benzyl butyl phthalate	91.8	0.5	96.5	10
Dicyclohexyl phthalate	95.3	0.5	93.6	10
Di-(2-ethylhexyl) phthalate	92.2	1.0	93.5	20
Di-(2-propylheptyl) phthalate	85.3	0.5	93.9	10

8.7 Blank values

The glass fibre filters and PU foams used may possibly exhibit phthalate blank values. For the determination of blank values at least one unused filter and PU foam from each new batch of glass fibre filters and PU foams are placed into a screw-capped vial with cap (also on the spot), covered with extraction agent and prepared and analysed in the same manner as the samples described in Sections 3, 4 and 5.

8.8 Interference

The analytical procedure by means of GC-MS is specific and robust under the conditions stated here. No interferences could be detected.

9 Discussion

The concentrations of selected phthalates, such as dimethyl phthalate, diethyl phthalate, diallyl phthalate, diisobutyl phthalate, di-*n*-butyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, di-(2-ethylhexyl) phthalate and di-(2-propylheptyl) phthalate in workplace air with limits of quantification in the range of 0.015 to 0.096 mg/m^3 can be selectively and sufficiently sensitively determined using the method described here. The combination of glass fibre filter with PU foam connected downstream is suitable as a sampling system. It should be taken into account that phthalates which are semi-volatile organic compounds (SVOC) have a tendency to deposit on particles (e.g. dust particles). This ultimately means that airborne phthalates are deposited on the filter together with 'dust particles' during sampling.

The experiments to determine the characteristics of the method were carried out using spiking solutions of the standard. In this context it was shown that individual phthalates, after evaporation of the solvent, can also be evaporated from the filter – despite high boiling temperatures – and can thus be further transported by the stream of air to be ultimately adsorbed onto the PU foam. It was also found that phthalates can evaporate relatively rapidly, as exhibited by the significant losses of phthalates from the loaded glass fibre filters, even after short storage periods. For this reason it is of critical importance that the loaded sample carriers (glass fibre filter and PU foam) should be immediately transferred into a solvent after sampling.

The loaded glass fibre filter and PU foam can also be analysed separately, if necessary, in order to ascertain in which physical state (particle-bound or gaseous) the phthalates to be determined occur in workplace air. In this case the filter should be transferred into a 22 mL screw-capped vial (e.g. Supelco Order No. 27004) and covered with 20 mL of 1,4-dioxane, separately from the PU foam. Other phthalates may be determined with the measurement method presented here. In this case the analytical performance characteristics as well as the chromatographic conditions must be checked and adapted accordingly.

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