The MAK Collection for Occupational Health and Safety

Method for the determination of 1,3-butadiene in workplace air using headspace GC

Air Monitoring Method

W. Krämer[1], T.H. Brock[2,*], R. Hebisch[3,*], A. Hartwig[4,*], MAK Commission[5,*]

[1] *Method development, BASF SE, ESE/MA – Z 570, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany*

[2] *Head of the working group “Analytics”, German Social Accident Insurance, Institution for the raw materials and chemical industry, Prevention - Department of Hazardous Substances, Biological Agents and Analytical Chemistry, Kurfürsten-Anlage 62, 69115 Heidelberg, Germany*

[3] *Head of the working group “Air Analyses” of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany*

[4] *Chair of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Institute of Applied Biosciences, Department of Food Chemistry and Toxicology, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Building 50.41, 76131 Karlsruhe, Germany*

[5] *Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Kennedyallee 40, 53175 Bonn, Germany*

* *email: T.H. Brock (analytik@bgrci.de), R. Hebisch (luftanalysen-dfg@baua.bund.de), A. Hartwig (andrea.hartwig@kit.edu), MAK Commission (arbeitsstoffkommission@dfg.de)*

Please direct correspondence to Berufsgenossenschaft RCI, Fachbereich Gefahrstoffe und biologische Arbeitsstoffe, P.O. Box 101480, 69004 Heidelberg, Germany; analytik@bgrci.de.

Keywords: 1,3-butadiene; air analysis; analytical method; workplace measurement; hazardous substance; headspace gas chromatography; mass spectrometry; headspace-GC-MS; activated charcoal

Citation Note: Krämer W, Brock TH, Hebisch R, Hartwig A, MAK Commission. Method for the determination of 1,3-butadiene in workplace air using headspace GC. Air Monitoring Method. MAK Collect Occup Health Saf [Original edition. Weinheim: Wiley-VCH; 2019 Nov;4(4):2353–2361]. Corrected republication without content-related editing. Düsseldorf: German Medical Science; 2025. https://doi.org/10.34865/am10699e2019_w

Republished (online): 30 Apr 2025

Originally published by Wiley-VCH Verlag GmbH & Co. KGaA; https://doi.org/10.1002/3527600418.am10699e2019

Manuscript completed: 01 Sep 2018

Published (online): 13 Nov 2019

Method for the determination of 1,3-butadiene in work-place air using headspace GC

Air monitoring methods

W. Krämer[1], T.H. Brock[2,*], R. Hebisch[3,*], A. Hartwig[4,*], MAK Commission[5,*]

DOI: 10.1002/3527600418.am10699e2019

Abstract

This analytical method is a validated measurement procedure for the determination of 1,3-butadiene [106-99-0] 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 charcoal tube using a suitable flow-regulated pump. The flow rate is set to 40 mL/min with a recommended air sample volume of 20 L. The collected 1,3-butadiene is desorbed with a mixture of benzyl alcohol/dimethyl sulfoxide/water (90+5+5 v:v) and then analysed by means of headspace-GC and a mass selective detector (MSD). The quantitative evaluation is based on a calibration function obtained by means of a multiple-point calibration using dichloromethane-D_2 as internal standard. Based on the resulting peak areas the respective mass of 1,3-butadiene can be obtained from the calibration function. The absolute limit of quantification (LOQ) is 0.5 µg for 1,3-butadiene deposited on a charcoal tube. The mean recovery was 84% and the expanded uncertainty for 1,3-butadiene was between 21 and 23%.

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 Deutsche Forschungsgemeinschaft for the Investigation of Health Hazards of Chemical Compounds in the Work Area.

Keywords

DGUV Information 213-526; 1,3-butadiene; air analysis; analytical method; workplace measurement; hazardous substances; headspace-GC

Author Information

[1] BASF SE, ESE/MA – Z 570, 67056 Ludwigshafen, Germany

[2] German Social Accident Insurance, Institution for the raw materials and chemical industry, Prevention – Department of Hazardous Substances, Biological Agents and Analytical Chemistry, Kurfürsten-Anlage 62, 69115 Heidelberg, Germany

[3] Head of the working group “Air Analysis” of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany

[4] Chair of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Department of Food Chemistry and Toxicology, Institute of Applied Biosciences, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Building 50.41, 76131 Karlsruhe, Germany

[5] Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Kennedyallee 40, 53175 Bonn, Germany

[*] Email: T.H. Brock (analytik@bgrci.de), R. Hebisch (luftanalysen-dfg@baua.bund.de), A. Hartwig (andrea.hartwig@kit.edu), MAK Commission (arbeitsstoffkommission@dfg.de)

2354

Method for the determination of 1,3-butadiene in workplace air using headspace GC

German Social Accident Insurance
Expert Committee Raw Materials and Chemical Industry
Subcommittee Hazardous Substances

Analytical Subcommittee of the Chemistry Board of Experts[1]

Recognised analytical procedures for the determination of carcinogens, mutagens or substances toxic to reproduction

Order number: DGUV Information 213-526 Method 02
Issued: September 2018

This method has been tested and recommended for the determination of 1,3-butadiene in workplaces by the German Social Accident Insurance.

Both personal and stationary sampling can be employed for the assessment of workplaces.

Name	CAS No.	Molar mass
1,3-Butadiene	106-99-0	54.09

Summary

This analytical method describes the determination of the mean concentration of 1,3-butadiene in the workplace air averaged over the sampling period after personal or stationary sampling.

Principle:	A pump draws a defined volume of air from the breathing zone of the worker through an activated charcoal tube. The adsorbed 1,3-butadiene is desorbed with a mixture of benzyl alcohol/dimethyl sulphoxide/water (90+5+5 v/v). Analytical determination is performed by means of headspace gas chromatography (HSGC) and mass selective detection (MSD).

---

[1] Please direct correspondence to Berufsgenossenschaft Rohstoffe und chemische Industrie, Prävention, P.O. Box 101480, 69004 Heidelberg, Germany; analytik@bgrci.de

Limit of quantification:	Absolute: 0.5 µg of 1,3-butadiene per adsorption tube Relative: 0.025 mg/m^3 of 1,3-butadiene for an air sample volume of 20 L
Measurement range:	Validated in the range of 0.1 mg/m^3 to 2 mg/m^3 at an air sample volume of 20 L.
Selectivity:	Interference due to other components is eliminated by the gas chromatographic separation combined with mass selective detection.
Advantages:	Personal and selective measurements are possible.
Disadvantages:	No indication of concentration peaks.
Apparatus:	Pump Flow meter Activated charcoal tubes Headspace gas chromatograph (Headspace GC) with MSD

Detailed description of the method

Contents

1 Equipment and chemicals

1.1 Equipment

For sampling:

- Sampling pump, suitable for a flow rate of 40 mL/min (e.g. LFS 113, from Sensidyne, supplied by DEHA Haan & Wittmer, 71296 Heimsheim, Germany)
- Flow meter (e.g. Gilibrator-2, from Sensidyne, St. Petersburg, FL 33716, U.S.A.)
- Adsorption tubes packed with activated charcoal (standardised, comprising two fillings of activated charcoal of 400 mg and 200 mg, separated from each other by porous polymer material) (e.g. from SKC, supplied by Analyt, 79379 Müllheim, Germany)

For analysis:

- Volumetric flasks, 100 mL
- Microlitre syringes, airtight, 1 µL to 10 µL, 10 µL to 250 µl (e.g. from Hamilton, 7402 Bonaduz, Switzerland)
- Airtight syringes, 1 mL (for the MPS2 headspace autosampler), 10 mL (e.g. from Gerstel, 45473 Mülheim, Germany)
- Headspace vials, approx. volume of 10 mL
- Automatic piston pipette (e.g. Multipette pro, from Eppendorf, 22339 Hamburg, Germany)
- Headspace autosampler
- Gas chromatograph with a mass selective detector
- Liquid nitrogen supply

1.2 Chemicals

- 1,3-Butadiene, 99.3% (e.g. from GHC Gerling, Holz & Co, 22761 Hamburg, Germany)
- Benzyl alcohol, p.a. (e.g. from Merck, 64293 Darmstadt, Germany)
- Dimethyl sulphoxide, p.a. (e.g. from Merck, 64293 Darmstadt, Germany)
- Water, deionised
- Dichloromethane-D_2, 99.6% (e.g. from Merck, 64293 Darmstadt, Germany)

Gases for the operation of the gas chromatograph:
- Helium, purity 99.996%
- Nitrogen, purity 99.995%

Desorption solution: Solution of 0.135 mg of dichloromethane-D_2 in one litre of a benzyl alcohol/dimethyl sulphoxide/water mixture (90+5+5 v/v)

10 µL of dichloromethane-D_2 are added to a 100 mL volumetric flask into which several millilitres of the solvent mixture have been previously placed. The flask is filled to the mark with the solvent mixture.

Calibration stock solution: Solution of approx. 0.45 mg of 1,3-butadiene/mL of benzyl alcohol

10 mL of benzyl alcohol are placed into a 10 mL headspace vial and the vial is sealed with a crimp cap. The vial is then weighed exactly to the nearest 0.1 mg. Subsequently an empty cannula is pierced through the septum to adjust the pressure during the subsequent filling. Approx. 2.5 mL of 1,3-butadiene (density 2.26 g/L) are removed from the pressurised gas bottle using an airtight syringe and directly injected into the liquid in the headspace vial at a flow rate of approx. 10 mL/min. Before the last millilitre of the gas is ejected from the syringe into the solvent, the cannula is withdrawn to the headspace of the vial, so that this is flushed during the continued transfer of the remaining gas and thus any solvent that may have permeated into the headspace is expelled. The vial is gently shaken after the removal of both cannulae and is again weighed exactly to the nearest 0.1 mg to determine the added amount of 1,3-butadiene.

Calibration solutions: Solutions of approx. 0.1 mg to approx. 4.5 mg of 1,3-butadiene/L of desorption solution

The contents of non-loaded activated charcoal tubes are each placed into eight 10 mL headspace vials. The volumes of calibration stock solution listed in Table 1 as well as 5 mL of desorption solution are added to the charcoal in each case and the vials are sealed with crimp caps.
The concentrations of the 1,3-butadiene in the calibration solutions are shown in Table 1. The concentrations in air, equivalent to an air sample volume of 20 L, are in the range of 0.02 mg/m^3 up to 1.1 mg/m^3 for 1,3-butadiene.

Table 1 Concentrations of 1,3-butadiene in the calibration solutions

Calibration solution	1	2	3	4	5	6	7	8
Addition [µL]	1	2.5	5	10	20	30	40	50
[mg/L]	0.09	0.23	0.45	0.90	1.80	2.70	3.60	4.50
[mg/m^3]*	0.02	0.06	0.11	0.23	0.45	0.68	0.90	1.13

* based on a desorption volume of 5 mL and an air sample volume of 20 L

2 Sampling

A tube packed with activated charcoal is opened, connected to the pump and the flow rate is adjusted to 40 mL/min. The pump and tube are worn by a person during working hours or stationary sampling is carried out. A sampling period of eight hours at the stated flow rate is possible with this method. After sampling, the adsorption tubes are sealed with the plastic caps.

Before and after sampling, the flow rate must be checked for constancy using a comparable sample carrier. If the deviation from the adjusted flow rate is greater than 5%, it is advisable to discard the sample (see DGUV Information 213-500 “General Part”, Section 3 [1]).

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded activated charcoal tube are transferred into a 10 mL headspace vial and 5 mL of desorption solution are added. Then the headspace vial is sealed tightly using a septum and crimp cap and conditioned in the sample thermostat at 90 °C and 750 rpm for 10 minutes. 500 µL taken from the headspace of the sample are injected into the gas chromatograph.

In order to ensure that the desorption solution and the activated charcoal do not contain any interfering impurities the entire contents of an activated charcoal tube that has not been used for sampling is treated at regular intervals (see SOP-I 005) as described above (blank solution).

500 µL each taken from the headspace above the sample solution, the calibration solution and the blank solution are injected into the gas chromatograph and a gas chromatogram is recorded as described in Section 3.2. The quantitative evaluation is carried out according to the internal standard method using the peak areas of the relevant masses of 1,3-butadiene and the deuterated dichloromethane.

3.2 Operational parameters for gas chromatography

The characteristics of the method stated in Section 5 were obtained under the following operating conditions:

Apparatus:	HP6890 gas chromatograph with MSD, from Agilent, 76447 Waldbronn, Germany and MPS2 headspace autosampler, from Gerstel, 45473 Mülheim, Germany
Separation column:	Fused silica capillaries; stationary phase: 6% cyanopropylphenyl/94% polydimethylsiloxane, e.g. DB-624, e.g. from Agilent, inner diameter 0.25 mm, length 30 m, film thickness 1.4 µm
Temperatures:	Injector: 250 °C Column with temperature program: Initial temperature 20 °C, isothermal for 3 min Heating rate 40 °C/min up to 220 °C, isothermal for 1.5 min

HS autosampler: Oven temperature 90 °C, syringe temperature 100 °C, conditioning period 10 min, stirring velocity 750 min^{-1}, injection volume 500 µL
Split: Split ratio 1:100
MSD parameters: Ionisation type: Electron impact ionisation (70 eV)
Measurement mode: Scan
Mass range: 29 to 100 amu
Recorded masses (m/z) Quantification/Qualification:
1,3-Butadiene: 54, 39 amu
Dichloromethane-D_2: 86, 88 amu
Gases: Helium, 40 cm/s, constant flow rate 1.3 mL/min
Nitrogen (for purging the syringe)

4 Evaluation

4.1 Calibration

The calibration solutions described in Section 1.2 are conditioned as specified in Section 3.1 and analysed as described in Section 3.2. The calibration curve is obtained by plotting the resulting peak area ratios of the relevant masses of the 1,3-butadiene and those of deuterated dichloromethane as an internal standard versus the concentration ratios of the 1,3-butadiene and the dichloromethane-D_2 in the relevant calibration solutions.

4.2 Calculation of the analytical result

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) is calculated according to the following equation:

$$\rho = \frac{X}{V \cdot \eta}$$

where:

ρ is the mass concentration of 1,3-butadiene in the ambient air in mg/m^3
X is the mass of 1,3-butadiene in the analytical sample in µg
V is the air sample volume in litres
η is the recovery (see Section 5.1)

5 Reliability of the method

5.1 Precision and recovery

The precision in the lowest measurement range according to DIN EN 482 [2] as well as the recovery rates for three concentrations (see Table 2) were determined. The sample carriers were spiked with the solutions described below:

Validation solution: Solution of approx. 0.52 mg of 1,3-butadiene/mL of benzyl alcohol

10 mL of benzyl alcohol are placed into a 10 mL headspace vial and the vial is sealed with a crimp cap. The vial is then weighed exactly to the nearest 0.1 mg. Approximately 2.5 mL of 1,3-butadiene were added with an airtight syringe in the same manner as the calibration stock solution was prepared as described in Section 1.2. In order to determine the added mass of 1,3-butadiene the vial was weighed exactly to the nearest 0.1 mg.

While the pump was in operation, the activated charcoal tubes were directly spiked with 4 µL, 40 µL and 80 µL of the validation solution in each case, and then air was drawn through the tubes at a flow rate of 2.4 L/h for 8 hours. The experiment was conducted six times for each amount applied. The spiked quantities of the 1,3-butadiene were equivalent to the concentrations in air listed in Table 2 at an air sample volume of 20 L.

The samples were prepared and analysed as described in Section 3.

The standard deviations and recoveries determined are shown in Table 2.

Table 2 Characteristics of the validation

Spiked volumes	Spiked mass	Concentration in the air sample	Recovery	Relative standard deviation
[µL]	[µg]	[mg/m^3]*		[%]
4.0	2.1	0.103	0.83	4.7
40	20.8	1.032	0.82	2.8
80	41.6	2.064	0.87	4.2

* based on a desorption volume of 5 mL and an air sample volume of 20 L

The method was tested up to an air sample volume of 20 L. No breakthrough of the 1,3-butadiene to a second tube connected in series downstream could be detected.

5.2 Limit of quantification

The limit of quantification was calculated from the ratio of the measurement signal to the noise level at the baseline. In this case a signal/background noise ratio of 10 was used as a basis.

The absolute limit of quantification per tube is 0.5 µg for 1,3-butadiene. This is equivalent to a relative limit of quantification of 0.025 mg/m^3 at an air sample volume of 20 L and a desorption agent volume of 5 mL.

5.3 Storage stability

In the adsorbed state the substances can be stored at room temperature without losses for at least 14 days.

5.4 Selectivity

Interference from other compounds is eliminated to a large extent by the gas chromatographic separation combined with mass-selective detection.

5.5 Uncertainty

The expanded uncertainty was determined taking all the relevant influencing factors into consideration as stipulated in DIN EN 482 [2]. 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) and the analytical preparation (complete desorption, scatter of the calibration function, fluctuations in the recovery and the reproducibility). The expanded uncertainty is between 21% and 23% for the three validation concentrations.

References

[1] DGUV Information 213-500 (2015) Allgemeiner Teil. Von den Unfallversicherungsträgern anerkannte Analysenverfahren zur Feststellung der Konzentration krebserzeugender, erbgutverändernder oder fortpflanzungsgefährdender Stoffe in der Luft in Arbeitsbereichen. Deutsche Gesetzliche Unfallversicherung (DGUV), Berlin, Germany, http://publikationen.dguv.de/dguv/pdf/10002/213-500.pdf

[2] DIN EN 482:2015-12 (2015) Workplace exposure – General requirements for the performance of procedures for the measurement of chemical agents, Beuth Verlag GmbH, Berlin, Germany