The MAK Collection for Occupational Health and Safety

Diacetyl (Butanedione) – Method for the determination of diacetyl in workplace air using gas chromatography-mass spectrometry (GC-MS)

Air Monitoring Method – Translation of the German version from 2016

C. Schuh[1], M. Kirchner[2], R. Hebisch[3,*], T.H. Brock[4,*], A. Hartwig[5,*], MAK Commission[6,*]

[1] *Method development, German Social Accident Insurance Institution for the foodstuffs industry and the catering trade (BGN), Dynamostraße 7–11, 68165 Mannheim, Germany*

[2] *External verification, Institute for the Research on Hazardous Substances of the Insurance Institution for the raw materials and chemical industry (IGF), Institute at the Ruhr-University Bochum, Waldring 97, 44789 Bochum, 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] *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*

[5] *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*

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

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

Keywords: diacetyl; air analyses; analytical method; workplace measurement; hazardous substance; gas chromatography; mass spectrometry; GC-MS; silicagel; liquid desorption

Citation Note: Schuh C, Kirchner M, Hebisch R, Brock TH, Hartwig A, MAK Commission. Diacetyl (Butanedione) – Method for the determination of diacetyl in workplace air using gas chromatography-mass spectrometry (GC-MS). Air Monitoring Method – Translation of the German version from 2016. MAK Collect Occup Health Saf [Original edition. Weinheim: Wiley-VCH; 2017 Apr;2(2):1075-1090]. Corrected republication without content-related editing. Düsseldorf: German Medical Science; 2026. https://doi.org/10.34865/am43103e1917b_w

Originally published by Wiley-VCH Verlag GmbH & Co. KGaA; https://doi.org/10.1002/3527600418.am43103e1917b

Manuscript completed: 29 Oct 2015

Published (online): 28 Apr 2017

The commission established rules and measures to avoid conflicts of interest.

Diacetyl (Butanedione) – Method for the determination of diacetyl in workplace air using gas chromatography-mass spectrometry (GC-MS)

Air Monitoring Methods

C. Schuh[1], M. Kirchner[2], R. Hebisch[3, *], T.H. Brock[4, *], A. Hartwig[5, *], MAK Commission[6, *]

DOI: 10.1002/3527600418.am43103e1917b

Abstract

This analytical method is a validated measurement procedure for the determination of 2,3-butanedione (diacetyl) in workplace air in a concentration range of a tenth up to twice the currently valid Occupational Exposure Limit (OEL) or MAK value. Sampling is performed by drawing a defined volume of air through a silica gel tube using a suitable flow-regulated pump with a volumetric flow rate of 0.33 L/min. For sampling 1 hour or 15 min (checking the short-term value) can be used. The collected diacetyl is desorbed with acetone containing the internal standard cyclohexanone and then analysed by means of gas chromatography-mass spectrometry (GC-MS). Quantitative evaluation is based on a 10-point calibration using cyclohexanone as internal standard. The limit of quantification for diacetyl is 0.0034 mg/m^3 based on an air sample volume of approx. 20 L or 0.0137 mg/m^3 based on an air sample volume of approx. 5 L (for short-term value).

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 Monitoring Methods” of the Permanent Senate Commission of the DFG for the Investigation of Health Hazards of Chemical Compounds in the Work Area.

Keywords

2,3-butanedione; diacetyl; air analysis; workplace measurement; hazardous substances; air sampling; workplace monitoring; measurement method; measuring procedure; short-term measurement; silica gel tubes; gas chromatography; mass spectrometry; GC-MS

Author Information

[1] German Social Accident Insurance Institution for the foodstuffs industry and the catering trade, Dynamostr. 7 – 11, 68165 Mannheim, Germany
[2] Institute for the Research on Hazardous Substances of the Insurance Institution for the raw materials and chemical industry, Institute at the Ruhr-University Bochum, Waldring 97, 44789 Bochum, Germany
[3] Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1-25, 44149 Dortmund, Germany
[4] 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
[5] 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 for Applied Biosciences, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Geb. 50.41, 76131 Karlsruhe, Germany
[6] Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Kennedyallee 40, 53175 Bonn, Germany

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

1.54

Diacetyl (Butanedione) – Method for the determination of diacetyl in workplace air using gas chromatography-mass spectrometry (GC-MS)

Method number	2
Application	Air analysis
Analytical principle	Gas chromatography/mass spectrometry (GC-MS)
Completed in	January 2016

Summary

Diacetyl (butanedione) can be determined in workplace air in a concentration range of a tenth up to twice the currently valid Occupational Exposure Limit (OEL) or MAK value of 0.071 mg/m^3 (0.02 ppm) using the analytical method described here [1, 2]. Ambient air is drawn through a silica gel tube using a suitable sampling pump, whereby diacetyl is adsorbed onto the silica gel. After sampling is complete, acetone is used to extract the diacetyl. The sample solution is analysed by gas chromatography with the aid of a mass spectrometer (MSD). The quantitative determination is based on a multiple-point calibration using cyclohexanone as an internal standard. The method is suitable for checking the shift average values and the short-term values.

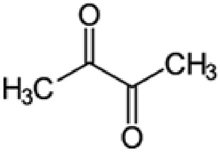
Characteristics of the method

Repeatability:	Standard deviation (rel.): at a concentration of 563 ng/mL	$s = 3.8\%$
Reproducibility:	Standard deviation (rel.): at a concentration of 493 ng/mL	$s = 4.6\%$ (60 L)
Recovery:	$\eta = 1$ (100%) at an air sample volume of 19.8 L	
Limit of quantification:	Absolute:	33.9 ng (for a sample solution of 1 mL)
	Relative:	3.4 µg/m^3 (0.0034 mg/m^3) for an air sample volume of 19.8 L

	Relative:	13.7 µg/m^3 (0.0137 mg/m^3) for an air sample volume of 4.95 L
Sampling recommendations:	Sampling time:	60 min
	Air sample volume:	19.8 L
	For short-term measurement:	15 min; 4.95 L

Description of the substance

Diacetyl (Butanedione) [431-03-8]



Synonyms: 2,3-Butanedione, dimethyl diketone, 2,3-diketobutane, butane-2,3-dione

Diacetyl (empirical formula $C_4H_6O_2$) is the simplest representative of the diketone substance class (molar mass 86.09 g/mol, melting point -2.4 °C, boiling point 88 °C, decomposition above 110 °C, density 0.99 g/cm^3, vapour pressure 65 hPa at 20 °C). It is a yellowish green liquid with a characteristic flavour and odour of butter and it is also a natural component of butter. It is readily soluble in water (250 g/L) and is also soluble in the commonly used organic solvents, such as ethanol and diethyl ether.

Due to its typical butter flavour, diacetyl is added to different foods during production e.g. margarines and various baked goods. Diacetyl occurs naturally in various fruit and vegetables such as apples, blueberries, raspberries, black currants, artichokes and beans. Furthermore, it is a natural by-product of fermentation and is contained in many dairy products such as butter, cream, dried milk and cheese, as well as in bread and coffee. In addition, it is formed during fermentation processes such as in the production of beer, wine and spirits; in this case, however, its presence is considered an undesirable flaw.

The Occupational Exposure Limit (OEL) or MAK value is 0.02 ppm (0.071 mg/m^3) [1, 2]. In the List of MAK and BAT Values diacetyl has been assigned to Peak Limit Category II with an excursion factor of 1 [2]. Detailed information on the toxicity of diacetyl can be found in the toxicological-occupational health documentation of the MAK values [3].

1 mL/m^3 (ppm) $\triangleq$ 3.52 mg/m^3

Diacetyl (Butanedione) – Method for the determination of diacetyl in workplace air using gas chromatography-mass spectrometry (GC-MS)

Method number	2
Application	Air analysis
Analytical principle	Gas chromatography/mass spectrometry (GC-MS)
Completed in	January 2016

Contents

1 General principles

The analytical method described here can be used to determine diacetyl (butanedione) in workplace air in a concentration range of one tenth up to twice the currently valid Occupational Exposure Limit (OEL) or MAK value of 0.071 mg/m^3 (0.02 ppm) [1, 2]. Sampling is performed by drawing ambient air through a silica gel tube using a suitable sampling pump, whereby airborne diacetyl is adsorbed onto the silica gel. After sampling is complete, acetone is used to desorb the loaded diacetyl from the silica gel. The sample solution is analysed by means of gas chromatography with the aid of a mass spectrometer (MSD). The quantitative determination is based on a multiple-point calibration using cyclohexanone as an internal standard. The method is suitable for checking the shift average value and the short-term value.

2 Equipment, chemicals and solutions

2.1 Equipment

- Pump for personal sampling, flow rate 20 L/h (e.g. SG 350, from GS Messtechnik, 40880 Ratingen, Germany)
- Gas chromatograph with mass-selective detector (e.g. Agilent GC 6890/MSD-N 5973, from Agilent, Waldbronn, Germany)
- CP-SIL 8 CB separation column: 8 CB 50 m, 0.32 mm ID, film thickness 5 µm (e.g. Agilent)
- Liner with quartz wool (e.g. from Gerstel, 45473 Mülheim, Germany, Order No. 007519-010-00)
- Adsorption tube filled with silica gel (1100 and 480 mg) (e.g. silica gel tubes B/G type from Dräger, 23560 Lübeck, Germany)
- Gas meter or volumetric flow meter (e.g. DryCal DC-1, from DEHA Haan & Wittmer, 71296 Heimsheim, Germany)
- Piston pipettes, 100 and 1000 µL (e.g. from Gilson)
- Screw-cap vials, sealable, nominal volume 4 mL (amber glass)
- Autosampler vials, amber glass and sealable, nominal volume 2 mL
- Microlitre syringe, 2 µL
- Syringes, 1 mL and 2.5 mL (e.g. from Hamilton)
- Magnetic stirrer

- Volumetric flasks, 5, 10 and 20 mL (amber glass)
- Headspace vials (HS vials), 10 mL, with PTFE-coated septa and aluminium sealing caps (amber glass)
- Syringe filter, Millex FH, PTFE, pore size 0.45 µm (e.g. from Millipore, Order No. SLFHX13 NL)
- Disposable syringes, 5 mL and disposable cannulae, 20G (Luer Lock connection)
- ATIS^{TM} Adsorbent Tube Injector System (e.g. from Sigma-Aldrich, 82024 Taufkirchen, Germany)
- Ultrasonic bath

2.2 Chemicals

- 2,3-Butanedione (diacetyl), pure substance (reference substance for GC) (e.g. from Sigma-Aldrich, Order No. 11038)
- Acetone, Uvasol (e.g. from Merck, 64293 Darmstadt, Germany, Order No. 1.00022.0250)
- Cyclohexanone (reference substance for GC) (e.g. from Merck, Order No. 8.22269)
- Helium, 5.0 for gas chromatography

2.3 Solutions

Internal standard solution (ISTD solution): (cyclohexanone in acetone: 0.947 mg/mL)

10 µL of cyclohexanone are dosed into a 10 mL volumetric flask, into which approx. 5 mL of acetone have been previously placed. The volumetric flask is then filled to the mark with acetone and shaken. The concentration of cyclohexanone is 0.947 mg/L.

Desorption agent: (cyclohexanone in acetone: 0.947 µg/mL)

20 µL of the ISTD solution are dosed into a 20 mL volumetric flask, into which approx. 5 mL of acetone have been previously placed. The volumetric flask is then filled to the mark with acetone and shaken. The concentration of cyclohexanone is 0.947 µg/mL.

The solutions must be freshly prepared before each sample series and calibration.

2.4 Calibration standards

Stock solution 1: (2561 µg of diacetyl/mL)

26 µL of diacetyl (density: 0.985 g/mL) are dosed into a 10 mL volumetric flask, into which approx. 5 mL of acetone have been previously placed. The volumetric flask is then filled to the mark with acetone and shaken. The concentration of diacetyl is 2561 µg/mL.

Stock solution 2: (12.805 µg of diacetyl/mL)

25 µL of stock solution 1 are dosed into a 5 mL volumetric flask, into which approx. 2 mL of acetone have been previously placed. The volumetric flask is then filled to the mark with acetone and shaken. The concentration of diacetyl is 12.805 µg/mL.

Stock solution 3: (985 µg of diacetyl/mL)

10 µL of diacetyl (density: 0.985 g/mL) are dosed into a 10 mL volumetric flask, into which approx. 4 mL of acetone have been previously placed. The volumetric flask is then filled to the mark with acetone and shaken. The concentration of diacetyl is 985 µg/mL.

Stock solution 4: (3.94 µg of diacetyl/mL)

20 µL of stock solution 3 are dosed into a 5 mL volumetric flask, into which approx. 2 mL of acetone have been previously placed. The volumetric flask is then filled to the mark with acetone and shaken. The concentration of diacetyl is 3.94 µg/mL.

Calibration standards from stock solution 2

10 calibration solutions are prepared from stock solution 2 (12.805 µg diacetyl/mL) as follows: The volumes of stock solution 2 listed in Table 1 are dosed into

Table 1 Pipetting scheme for the preparation of the 10 diacetyl calibration standards from stock solution 2

Standard solution No.	Stock solution 2 [µL]	Concentration of the internal standard [ng/mL]	Concentration of diacetyl [ng/mL]
Calibration standard I	20	947	51.2
Calibration standard II	80	947	204.9
Calibration standard III	140	947	358.5
Calibration standard IV	200	947	512.2
Calibration standard V	260	947	665.9
Calibration standard VI	320	947	819.5
Calibration standard VII	380	947	973.2
Calibration standard VIII	440	947	1126.8
Calibration standard IX	500	947	1280.5
Calibration standard X	560	947	1434.2

5 mL volumetric flasks, into which approx. 2 mL of acetone have been previously placed. After addition of 5 µL of the internal standard solution, the volumetric flasks are filled to the mark with acetone and shaken.

Calibration standards from stock solution 4

10 calibration solutions are prepared from stock solution 4 (3.94 µg diacetyl/mL) as follows: The volumes of stock solution 4 listed in Table 2 are dosed into 5 mL volumetric flasks, into which approx. 2 mL of acetone have been previously placed. After addition of 5 µL of the internal standard solution, the volumetric flasks are filled to the mark with acetone and shaken.

The calibration standards must be freshly prepared before each calibration.

Table 2 Pipetting scheme for the preparation of the 10 diacetyl calibration standards from stock solution 4 (determination of the limit of quantification)

Standard solution No.	Stock solution 4 [µL]	Concentration of the internal standard [ng/mL]	Concentration of diacetyl [ng/mL]
Calibration standard I	20	947	15.8
Calibration standard II	40	947	31.5
Calibration standard III	60	947	47.3
Calibration standard IV	80	947	63.0
Calibration standard V	100	947	78.8
Calibration standard VI	120	947	94.6
Calibration standard VII	140	947	110.3
Calibration standard VIII	160	947	126.1
Calibration standard IX	180	947	141.8
Calibration standard X	200	947	157.6

3 Sampling and sample preparation

3.1 Sampling

Silica gel tubes of B/G type from Dräger are used for sampling, whereby the G phase is exclusively used as the collection phase.

Immediately before sampling, the fused glass ends of a silica gel tube are opened and connected to a flow-regulated pump. The flow rate is adjusted to 0.33 mL/min. Sampling times of 15 minutes (to check the short-term value) and one hour can be selected. A sampling time of 15 min is equivalent to an air sample volume of approx. 5 L and a sampling time of one hour corresponds to an air sample volume of approx. 20 L. Sampling can be carried out as stationary or personal sampling. After sampling, 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 [4]. After successful sampling, the silica gel tubes loaded with diacetyl are sealed with the caps provided and stored in a cool dark place until sample preparation.

One blank (field blank) per sample series must be prepared. For this purpose a silica gel tube – taken from the same batch as those used for air sampling - is opened and immediately sealed again and stored in the same manner as the analytical samples in a cool and dark place.

3.2 Sample preparation

The G phase (collection phase) of the silica gel tube together with the quartz wool plug (between the collection and control phases) are transferred into a 4 mL screw-cap vial and covered with 2 mL of the desorption agent for sample preparation. The sample vials are sealed and treated for 20 minutes in the ultrasonic bath. The sample solution is then filtered into a GC sample vial using a syringe filter (Millex FH 13).

The B phase (control phase) is prepared with 1 mL desorption agent in the same manner as the G phase (collection phase). The blank (field blank) must be prepared in the same manner as the analytical samples.

4 Operational parameters for gas chromatography

Apparatus:	Gas chromatograph Agilent 6890 with mass-selective detector MSD-N 5973 (e.g. from Agilent, Waldbronn, Germany)	
Separation column:	Material:	Fused silica
	Stationary phase:	CP-SIL 8 CB (95% dimethylpolysiloxane, 5% phenylpolydimethylsiloxane)
	Length:	50 m
	Inner diameter:	0.32 mm
	Film thickness:	5 µm
Carrier gas:	Helium 5.0:	60 kPa (1.7 mL/min)
Injection volume:	2 µL	
Injector:	Programmed Temperature Vaporiser (PTV), splitless Liner with quartz wool	

Column temperature:	35 °C $\xrightarrow{5\,^{\circ}\mathrm{C/min}}$ 140 °C (5 min) $\xrightarrow{16\,^{\circ}\mathrm{C/min}}$ 100 °C (10 min) $\xrightarrow{16\,^{\circ}\mathrm{C/min}}$ 270 °C (7 min)
PTV injector temperature:	35 °C for 0.5 min; rate: 300 °C/min final temperature 270 °C,
Transfer line:	270 °C
Ionisation mode:	Electron impact (EI)
Ionisation energy:	200 °C
Quadrupole temperature:	150 °C

The analysis is carried out in the SCAN mode and SIM mode, whereby the quantification is carried out in the SIM mode. Table 3 lists the ion traces used for the evaluation in the SIM mode.

Table 3 Ion traces used for the evaluation in the SIM mode with the recorded parameters

	Target/ion [m/z]	Qualifier 1 ion [m/z]	Qualifier 2 ion [m/z]
Diacetyl	43	86	–
Cyclohexanone (ISTD)	98	55	69

5 Analytical determination

2 µL are each injected into the GC for the analytical determination of the samples that have been processed as described in Section 3.2 and analysed under the working conditions stated in Section 4. Furthermore, a ‘lab blank’ (desorption solution used) must be measured in the same manner as the sample solutions.

It must be ensured that one blank (field blank) per sample series is prepared in the same manner as the sample solutions and analysed by means of GC and mass-selective detection. Moreover, for the purpose of checking the calibration curve one calibration standard of a mean concentration must be measured at the beginning and one at the end of an analytical series.

6 Calibration

The calibration standards prepared according to Section 2.4 are analysed as described in Sections 4 and 5. The calibration function is obtained by plotting the determined quotients of the peak areas of diacetyl and the internal standard versus the corresponding concentrations of diacetyl. There is a linear relationship, resulting in a calibration function of first degree. The concentration of diacetyl in the sample solution is calculated using this calibration function. The calibration function is calculated as follows according to Equation (1):

$$y_i = m \times x_i + b \tag{1}$$

where:

y_i	is the ratio of the peak areas of diacetyl to cyclohexanone (ISTD)
x_i	is the ratio of the concentrations of diacetyl to cyclohexanone (ISTD)
m	is the slope of the calibration graph
b	is the intercept of the calibration graph with the y axis

The calibration function should be checked regularly as part of routine analysis and calculated anew when changes to the analytical device have been made (e.g. tuning).

7 Calculation of the analytical result

The concentration of diacetyl in workplace air is calculated on the basis of the calibration function. If the value of the blank (field blank) does not equal zero, then this value must be subtracted from the results of the samples to be analysed in order to correct them. The correction is carried out by determining the difference between the concentrations of the sample and blank value.

The concentration of diacetyl is calculated according to Equation (2) as follows:

$$\rho = \frac{X \times 100 \times V_E}{V_A \times 1000 \times Rr} \tag{2}$$

Equation (3) enables calculation of the value at 20 °C and 1013 hPa (standard conditions):

$$\rho_0 = \rho \times \frac{273 + t_a}{293} \times \frac{1013}{p_a} \tag{3}$$

where:

ρ	is the mass concentration of diacetyl in mg/m^3
ρ_0	is the mass concentration of diacetyl in mg/m^3 at 20 °C and 1013 hPa
X	is the concentration of diacetyl in the sample solution minus the blank (field blank) in ng/mL
V_E	is the extraction volume (2 mL of acetone)
V_A	is the air sample volume (calculated from the flow rate and the sampling time) in litres
Rr	is the relative recovery rate in %

t_a is the temperature during sampling in °C
p_a is the air pressure at the sampling location during sampling in hPa

8 Reliability of the method

The characteristics of the method were calculated according to EN 482 [5] EN 1076 [6] and DIN 32645 [7].

8.1 Precision

A calibration standard with a concentration of 563.4 ng/mL was analysed on six separate days in order to determine the repeatability of the analytical method (see Section 2.4). The relative standard deviation was 3.8% in this case.

8.2 Recovery

The recovery was determined by spiking the G phases of 7 silica gel tubes with 50 µL of diacetyl solution each (approx. 60 ng/µL). After standing for two hours, air was drawn through the spiked silica gel tubes for one hour at a flow rate of 0.33 L/min. The silica gel tubes were then prepared and analysed by gas chromatography in the same manner as the analytical samples described in (Sections 3.2, 4 and 5). The results are listed in Table 4.

Table 4 Relative recovery of diacetyl after air is drawn through spiked silica gel tubes for one hour

	Theoretical concentration (determined experimentally) [ng/mL]	**Mean recovery [ng/mL]**	**Relative recovery [%]**
Diacetyl	1565	1516	97*

* The deviation from 97% is not statistically significant.

A reproducibility of 5.6% was determined in the course of the recovery experiments based on the relative standard deviation of the individual values. The determined recovery was subsequently checked by means of liquid spiking using an Adsorbent Tube Injector System (ATIS). For this purpose a diacetyl solution (6.16 µg absolute) was evaporated in the ATIS and then passed through a silica gel tube by means of a gas flow. The sample was processed and analysed in the same manner as the analytical samples. This test confirmed the recovery results.

As the determined relative recovery does not differ significantly from the reference value, a relative recovery of 100% is taken into account in the calculation of the results.

8.3 Expanded uncertainty of the entire procedure

The measurement uncertainty is obtained by estimation of all the relevant influencing factors (bottom-up-method) [5, 6]. The uncertainty of the entire procedure and thus also of the analytical result consists principally of the following uncertainty contributions:

- the air sample volume U_V,
- the extraction volume U_E,
- the recovery U_R,
- losses during storage U_S
- as well as the influences on the measurement values $U\rho$, in particular the scatter of the calibration function and of the calibration standards as well as the laboratory's own reproducibility (precision).

The uncertainties of the air sample volume and extraction volume are determined regardless of the analyte, diacetyl. Furthermore, the uncertainties for the recovery and the measurement value are ascertained. The total recovery U_{Rtot} consists of the contributions of the recovery experiments U_R, taking the uncertainty of the reference values as well as the uncertainty of the storage stability U_S into consideration. The combined uncertainty of the measurement value $U\rho$, which is concentration-dependent, is obtained from the uncertainties of the calibration curve, the calibration stock solutions as well as the calibration standards and the results of the precision. The combination of all uncertainty contributions results in the concentration-dependent combined uncertainty U_{comb}.

The corresponding expanded uncertainty U_{exp}, which simultaneously represents the substance-dependent and concentration-dependent uncertainties of the entire procedure, is obtained by multiplication with a probability factor (e.g. $k = 2$ for 95% certainty).

All individual values contributing to the expanded combined uncertainty are listed in Table 5 and 6, in the high, medium and low concentration range. Table 5 lists the values recorded for a 60-minute sampling time and Table 6 shows those for a 15-minute sampling time (to check the short-term value).

Table 5 Uncertainty contributions *U* as well as combined and expanded uncertainty contributions (bottom-up-method) for a 60-minute sampling time in %

U_E	U_V	U_R	U_S	U_{Rtot}	$U\rho_{\text{-h}}$	$U\rho_{\text{-m}}$	$U\rho_{\text{-l}}$
4.6	3.4	6.4	1.6	6.6	7.2	7.4	17.7
					$U_{comb.\,h}$	$U_{comb.\,m}$	$U_{comb.\,l}$
					11.3	11.5	19.7
					$U_{exp.\,h}$	$U_{exp.\,m}$	$U_{exp.\,l}$
					23	**23**	**39**
corresponding concentration range in mg/m^3					**0.144**	**0.067**	**0.009**

Table 6 Uncertainty contributions *U* as well as combined and expanded uncertainty contributions (bottom-up method) for a 15-minute sampling time in %

U_E	U_A	U_R	U_S	U_{Rtot}	$U\rho_{-h}$	$U\rho_{-m}$	$U\rho_{-l}$
4.6	3.9	6.4	1.6	6.6	8.1	10.0	17.7
					$U_{comb.\ h}$	$U_{comb.\ m}$	$U_{comb.\ l}$
					12.0	13.4	19.8
					$U_{exp.\ h}$	$U_{exp.\ m}$	$U_{exp.\ l}$
					24	**27**	**40**
corresponding concentration range in mg/m^3					**0.145**	**0.080**	**0.036**

where:

$U\rho_{-h}$	is the uncertainty of the measurement value at a **h**igh concentration (includes precision and scatter of the calibration curve)
$U\rho_{-m}$	is the uncertainty of the measurement value at a **m**edium concentration (includes precision and scatter of the calibration curve)
$U\rho_{-l}$	is the uncertainty of the measurement value at a **l**ow concentration (includes precision and scatter of the calibration curve)
$U_{comb.\ h}$	is the combined uncertainty at a **h**igh concentration
$U_{comb.\ m}$	is the combined uncertainty at a **m**edium concentration
$U_{comb.\ l}$	is the combined uncertainty at a **l**ow concentration
$U_{exp.\ h}$	is the expanded uncertainty at a **h**igh concentration
$U_{exp.\ m}$	is the expanded uncertainty at a **m**edium concentration
$U_{exp.\ l}$	is the expanded uncertainty at a **l**ow concentration

8.4 Limit of quantification

The limit of quantification of diacetyl was determined in the same manner as the calibration line method stipulated in DIN 32645 [7] with P = 95% and k = 3.33.

The absolute limit of quantification was determined using a separately generated calibration curve in the low concentration range close to the detection limit according to DIN 32645. The calibration standards prepared from stock solution 4 were used for this purpose (see Section 2.4 and Table 2). The absolute limit of quantification for diacetyl was 33.9 ng (for a sample solution of 1 mL), which is equivalent to a relative limit of quantification of 0.0034 mg/m^3 based on an air sample volume of 20 L and an injection volume of 2 µL.

8.5 Influence of the air humidity

The relative humidity does not influence the measurement results. This was tested and confirmed in experiments using an ATIS device at relative humidities of 9.3 and 93%.

8.6 Storage stability

The storage stability was tested by spiking the G phase of six silica gel tubes with 985 ng of diacetyl (40 µL of diacetyl solution with a concentration of 24.63 µg/mL) and storing them for up to two weeks in the refrigerator at 4 to 8 °C. Losses after a storage period of 14 days were less than 5%. The sample solutions are stable over a period of two weeks when stored in a refrigerator.

8.7 Interference

The analytical procedure by means of GC-MS is specific under the conditions stated here. Interference from accompanying substances was not observed in the investigated working range. Blank values are taken into account due to the parallel sample preparation of the field blanks.

9 Discussion

With the measurement method presented here, diacetyl vapours can be determined in workplace air in a concentration range of 0.0034 to 0.145 mg/m^3 at a sampling time of 60 minutes and 0.0137 to 0.579 mg/m^3 at a sampling time of 15 minutes.

References

1 TRGS 900 Arbeitsplatzgrenzwerte. Issue: January 2006. BArBl Heft 1/2006 pp. 41–55, recently revised and supplemented: GMBl 2015 pp. 1186-1189 dated 06/11/15 [No. 60], http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-900.html

2 DFG – Deutsche Forschungsgemeinschaft (2016) List of MAK and BAT Values 2016. Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Report No. 52. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/book/10.1002/9783527805983

3 Hartwig A (ed.) (2015) Diacetyl. Gesundheitsschädliche Arbeitsstoffe. Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb43103d0058/abstract

4 EN ISO 13137 (2014) Workplace atmospheres – Pumps for personal sampling of chemical and biological agents – Requirements and test methods. Beuth Verlag, Berlin, Germany

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

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

7 DIN 32645 (2008) Chemical analysis – Decision limit, detection limit and determination limit under repeatability conditions – Terms, methods, evaluation. Beuth Verlag, Berlin, Germany