BS EN ISO 17943:2016

BSI Standards Publication

Water quality — Determination of volatile organic compounds in water — Method using headspace solid- phase micro-extraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS)

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National foreword

This British Standard is the UK implementation of EN ISO 17943:2016.

The UK participation in its preparation was entrusted to Technical Committee EH/3/2, Physical chemical and biochemical methods.

A list of organizations represented on this committee can be obtained on request to its secretary.

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EUROPEAN STANDARD

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English Version

Water quality - Determination of volatile organic compounds in water - Method using headspace solid-phase micro-extraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS) (ISO 17943:2016)

Qualité de l'eau - Détermination de composés organiques volatils dans l'eau - Méthode utilisant une micro-extraction en phase solide (MEPS) de l'espace de tête suivie d'une chromatographie en phase gazeuse-spectrométrie de masse (CG-SM) (ISO 17943:2016)

Wasserbeschaffenheit - Bestimmung flüchtiger organischer Verbindungen in Wasser - Verfahren mittels Headspace-Festphasenmikroextraktion (HS-SPME) gefolgt von der Gaschromatographie und Massenspektrometrie (GC-MS) (ISO 17943:2016)

This European Standard was approved by CEN on 13 February 2016.

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European foreword

This document (EN ISO 17943:2016) has been prepared by Technical Committee ISO/TC 147 "Water quality" in collaboration with Technical Committee CEN/TC 230 "Water analysis" the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2016, and conflicting national standards shall be withdrawn at the latest by October 2016.

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Endorsement notice

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Foreword

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The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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Introduction

Volatile organic compounds (VOCs) are often found in the manufacturing processes of paints, adhesives, petroleum products, pharmaceuticals, and refrigerants. Some are used as gasoline additives, solvents, hydraulic fluids, and dry-cleaning agents. This group of compounds belongs to the group of anthropogenic chemicals. VOC contamination of water resources is a human-health concern because many are toxic and are known or suspected human carcinogens.

For the determination of VOCs, several published procedures are available (see References [4],[5],[6],[7],[9],[12],[13], and [14]).

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Water quality — Determination of volatile organic compounds in water — Method using headspace solid-phase micro-extraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS)

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably qualified staff.

1 Scope

This International Standard specifies a method for the determination of volatile organic compounds (see Table 1). This comprises, for example, halogenated hydrocarbons, trihalogenated methanes, gasoline components (such as BTEX, MTBE, and ETBE), naphthalene, 2-ethyl-4-methyl-1,3-dioxolane, and highly odorous substances like geosmin and 2-methylisoborneol in drinking water, ground water, surface water, and treated waste water, by means of headspace solid-phase micro-extraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS). The limit of determination depends on the matrix, on the specific compound to be analysed, and on the sensitivity of the mass spectrometer. For most compounds to which this International Standard applies, it is at least 0,01 µg/l. Validation data related to a concentration range between 0,02 µg/l and 2,6 µg/l have been demonstrated in an interlaboratory trial. Additional validation data derived from standardization work show applicability of the method within a concentration range from 0,01 µg/l to 100 µg/l of individual substances. All determinations are performed on small sample amounts (e.g. sample volumes of 10 ml).

This method may be applicable to other compounds not explicitly covered by this International Standard or to other types of water. However, it is necessary to demonstrate the applicability for each case.

Table 1 — Volatile organic compounds determinable by this method

Name	Molecular formula	CAS registry no.[d]	Molar mass g/mol	Density kg/l
tert-amyl methyl ether (TAME)	$C_6H_{14}O$	994–05–8	102,17	0,76
benzene	C_6H_6	71–43–2	78,12	0,88
bromobenzene	C_6H_5Br	108–86–1	157,01	1,50
bromochloromethane	CH_2BrCl	74–97–5	129,38	1,99
bromodichloromethane	$CHBrCl_2$	75–27–4	163,83	1,98
n-butylbenzene	$C_{10}H_{14}$	104–51–8	134,22	0,86
sec-butylbenzene	$C_{10}H_{14}$	135–98–8	134,22	0,86
tert-butylbenzene	$C_{10}H_{14}$	98–06–6	134,22	0,87
chlorobenzene	C_6H_5Cl	108–90–7	112,56	1,11

[a] Signals of substances may overlap in chromatograms as they might co-elute.

[b] Density of liquid at boiling point (–13,4 °C)

[c] Refer to Tables F.1 and F.2 for validation data and additional information.

[d] CAS: Chemical Abstracts Service.

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Table 1 *(continued)*

Name	Molecular formula	CAS registry no.[d]	Molar mass g/mol	Density kg/l
2-chlorotoluene	C_7H_7Cl	95–49–8	126,59	1,08
4-chlorotoluene	C_7H_7Cl	106–43–4	126,59	1,07
dibromochloromethane	$CHBr_2Cl$	124–48–1	208,34	2,45
1,2-dibromo-3-chloropropane (DBCP)	$C_3H_5Br_2Cl$	96–12–8	236,33	2,03
1,2-dibromoethane	$C_2H_4Br_2$	106–93–4	187,86	2,18
dibromomethane	CH_2Br_2	74–95–3	173,83	2,48
1,2-dichlorobenzene	$C_6H_4Cl_2$	95–50–1	147,00	1,30
1,3-dichlorobenzene	$C_6H_4Cl_2$	541–73–1	147,00	1,29
1,4-dichlorobenzene	$C_6H_4Cl_2$	106–46–7	147,00	1,25
1,1-dichloroethane	$C_2H_4Cl_2$	75–34–3	98,96	1,20
1,2-dichloroethane	$C_2H_4Cl_2$	107–06–2	98,96	1,25
1,1-dichloroethene	$C_2H_2Cl_2$	75–35–4	96,95	1,21
cis-1,2-dichloroethene	$C_2H_2Cl_2$	156–59–2	96,94	1,28
trans-1,2-dichloroethene	$C_2H_2Cl_2$	156–60–5	96,94	1,26
dichloromethane	CH_2Cl_2	75–09–2	84,93	1,33
1,2-dichloropropane	$C_3H_6Cl_2$	78–87–5	112,99	1,16
1,3-dichloropropane	$C_3H_6Cl_2$	142–28–9	112,99	1,19
2,2-dichloropropane[c]	$C_3H_6Cl_2$	594–20–7	112,99	1,08
1,1-dichloropropene	$C_3H_4Cl_2$	563–58–6	110,97	1,19
cis -1,3-dichloropropene[c]	$C_3H_4Cl_2$	10061–01–5	110,97	1,23
trans-1,3-dichloropropene[c]	$C_3H_4Cl_2$	10061–02–6	110,97	1,21
ethylbenzene	C_8H_{10}	100–41–4	106,17	0,86
ethyl *tert*-butyl ether (ETBE)	$C_6H_{14}O$	637–92–3	102,17	0,73
2-ethyl-4-methyl-1,3-dioxolane	$C_6H_{12}O_2$	4359–46–0	116,16	0,90
2-ethyl-5,5-dimethyl-1,3-dioxane	$C_8H_{16}O_2$	768–58–1	144,21	0,88
geosmin	$C_{12}H_{22}O$	16423–19–1	182,30	0,99
hexachlorobutadiene	C_4Cl_6	87–68–3	260,76	1,67
isopropylbenzene (cumene)	C_9H_{12}	98–82–8	120,19	0,86
4-isopropyltoluene (*p*-cymene)	$C_{10}H_{14}$	99–87–6	134,21	0,86
2-methylisoborneol	$C_{11}H_{20}O$	2371–42–8	168,28	0,97
methyl *tert*-butyl ether (MTBE)	$C_5H_{12}O$	1634–04–4	88,15	0,74
naphthalene	$C_{10}H_8$	91–20–3	128,17	1,14
n-propylbenzene	C_9H_{12}	103–65–1	120,19	0,86
styrene	C_8H_8	100–42–5	104,15	0,91
1,1,1,2-tetrachloroethane	$C_2H_2Cl_4$	630–20–6	167,85	1,55
1,1,2,2-tetrachloroethane	$C_2H_2Cl_4$	79–34–5	167,85	1,59
tetrachloroethene	C_2Cl_4	127–18–4	165,83	1,62
tetrachloromethane	CCl_4	56–23–5	153,82	1,59
toluene	C_7H_8	108–88–3	92,14	0,87

[a] Signals of substances may overlap in chromatograms as they might co-elute.

[b] Density of liquid at boiling point (–13,4 °C)

[c] Refer to Tables F.1 and F.2 for validation data and additional information.

[d] CAS: Chemical Abstracts Service.

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Table 1 *(continued)*

Name	Molecular formula	CAS registry no.[d]	Molar mass g/mol	Density kg/l
tribromomethane (bromoform)	$CHBr_3$	75–25–2	252,75	2,89
1,2,3-trichlorobenzene	$C_6H_3Cl_3$	87–61–6	181,45	1,68
1,2,4-trichlorobenzene	$C_6H_3Cl_3$	120–82–1	181,45	1,45
1,3,5-trichlorobenzene	$C_6H_3Cl_3$	108–70–3	181,45	1,87
1,1,1-trichloroethane	$C_2H_3Cl_3$	71–55–6	133,40	1,34
1,1,2-trichloroethane	$C_2H_3Cl_3$	79–00–5	133,40	1,44
trichloroethene	C_2HCl_3	79–01–6	131,39	1,46
trichloromethane (chloroform)	$CHCl_3$	67–66–3	119,38	1,47
1,2,3-trichloropropane	$C_3H_5Cl_3$	96–18–4	147,43	1,38
1,2,4-trimethylbenzene (pseudocumene)	C_9H_{12}	95–63–6	120,19	0,88
1,3,5-trimethylbenzene (mesitylene)	C_9H_{12}	108–67–8	120,19	0,86
vinyl chloride	C_2H_3Cl	75–01–4	62,5	1,88[b]
m-xylene[a]	C_8H_{10}	108–38–3	106,17	0,86
o-xylene	C_8H_{10}	95–47–6	106,17	0,88
p-xylene[a]	C_8H_{10}	106–42–3	106,17	0,86

[a] Signals of substances may overlap in chromatograms as they might co-elute.

[b] Density of liquid at boiling point (–13,4 °C)

[c] Refer to Tables F.1 and F.2 for validation data and additional information.

[d] CAS: Chemical Abstracts Service.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 5667-5, *Water quality — Sampling — Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Principle

The analytes to be determined are extracted from the headspace above the water sample by means of solid-phase micro-extraction (SPME) according to their equilibrium of distribution. Extraction fibres are used whose surface is coated with suitable adsorbents. After the extraction, the SPME fibre is removed from the sample vial (headspace vial) and introduced into the injector of a gas chromatograph. The analytes are transferred to the capillary column by thermal desorption. The substances are separated and detected using GC-MS.

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4 Interferences

4.1 Sampling

To avoid interferences, collect samples as specified in Clause 7 observing the instructions specified in ISO 5667-1, ISO 5667-3, and ISO 5667-5.

4.2 Extraction

Commercially available SPME fibres often differ in quality. There may also be variations in the selectivity of the materials of the individual batches, thus, possibly causing significant deviations in extraction yield (see Annex E). However, apart from a higher detection limit of individual substances, which may be the result, this does not generally impair the suitability of such fibres.

Inadequately conditioned fibres often result in lower extraction yields (see Annex E) and poorly reproducible results, therefore, precondition new fibres by baking them out according to Clause 8. Used fibres shall also be conditioned before they are used again. For this purpose, use two sample vials containing only water (5.2) at the beginning of each sample sequence before starting with the first sample (see 8.1).

The performance of the fibres used may decrease slightly throughout a long sample sequence. Therefore, measure reference solutions (see 5.8.4) at regular intervals within the sample sequence. The fibre can be used as long as the method shows the sensitivity required for the substances under investigation. Depending on the matrix to be analysed, the durability of the fibre can be expected to be sufficient for the analysis of more than 500 samples.

Adding sodium chloride to the sample results in an improvement of the extraction yield for the majority of the substances listed in Table 1. It is recommended to add salt until the sample is nearly saturated (see 8.1). It is necessary to add exactly the same amount of salt to all samples of a calibration sequence and/or a sample sequence.

Salt deposits may accumulate in the metal syringe needle of the fibre holder after extended use. Heavier salt encrustations will always have to be expected if the metal syringe needle of the fibre holder is accidentally immersed in the water sample. This may damage the fibre and the injector liner. Therefore, precisely adjust the immersion depth of the metal syringe needle into the vial. If there are visible salt deposits, rinse the needle with water (5.2) to dissolve any salt deposits.

For automatic operation, sample, vials should be used with caps having thin septa (e.g. 0,9 mm to 1,3 mm) to avoid any mechanical problems when piercing the septum with the metal syringe needle (see 6.4).

Thin septa should always be used when using autosamplers that agitate the sample vials with a circular motion during the extraction process. Otherwise, the metal syringe needle (and the exposed fibre) may be damaged during extraction.

To ensure the precision and accuracy of the measurement results, maintain the extraction times constant during sample measurements or while measuring reference solutions (e.g. 10 min). For this purpose, preferably use automatic samplers which are suitable for SPME.

The extraction of some of the substances listed in Table 1 applying the procedure described in Clause 8 depends on the temperature. It is therefore necessary to maintain the extraction temperature constant for all samples of a sample sequence (e.g. at 40 °C). Somewhat higher extraction yields are often obtained at higher temperatures. However, the extraction temperature should not be significantly higher than 40 °C (see 8.1) so as to minimize desorption of the analytes resulting from higher temperatures and to avoid condensation on the fibre.

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4.3 Gas chromatography and mass spectrometry

Seek the help of experienced operators and refer to the information given in the user manual to eliminate interferences caused, for example, by the injection system or by insufficient separation. Check the performance and stability of the analytical system at regular intervals (e.g. by performing measurements with reference solutions of known composition).

Use an injector liner with an internal diameter which is as small as possible (e.g. 1 mm) to enable focusing of those substances on the column which elute particularly early (e.g. vinyl chloride).

The required immersion depth (position) of the fibre in the GC injector shall be determined for thermal desorption. It corresponds to the hottest point of the injector and shall be maintained constant over a sequence of measurements.

When using injectors with a septum, preferably, use SPME syringe needles with a diameter which is as small as possible (e.g. 24-gauge needles) so as to avoid damaging the septum. Before piercing a septum, the fibre should be drawn into the needle over a length of at least 1 mm to prevent the fibre from fracturing. Use pre-pierced septa where possible. When using septumless injectors, it is preferable to use SPME syringe needles with a larger diameter (e.g. 23-gauge needles) as they are more stable and easier to seal (see 6.14).

5 Reagents

5.1 General

The content of impurities present in the reagents and contributing to the blank value shall be negligibly small as compared to the analyte concentration which is to be determined. Check the blank value (8.4) at regular intervals and particularly, when using a new batch of SPME fibres. The reagents to be used are of highest quality or “analytical grade”, if available.

5.2 Water, complying with the requirements of ISO 3696, grade 1 or equivalent without any interfering blank values.

The water quality shall be tested.

5.3 Operating gases for gas chromatography and mass spectrometry, of high purity and in accordance with the specifications of the instrument manufacturer.

5.4 Sodium chloride, NaCl.

5.5 Solvents, for preparing stock solutions and as solutisers in aqueous reference solutions, e.g. methanol, CH_3OH or propylene carbonate, $C_4H_6O_3$.

5.6 Sodium thiosulfate pentahydrate, $Na_2S_2O_3{\cdot}5H_2O$.

5.7 Internal standard, examples for suitable internal standards are given below (see Annex C for further information).

Prepare stock solutions of individual internal standards in the same way as specified for the reference substances (5.8.2) or use commercially available certified solutions of individual substances (e.g. in methanol). Prepare spiking solutions for spiking the samples (8.1) by further diluting the stock solutions with the solvent (see 5.5).

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5.8 Preparation of reference solutions

5.8.1 Reference substances

Reference substances (as listed in Table 1) of defined concentration for the preparation of aqueous reference solutions used for calibration of the total procedure (see 9.2).

5.8.2 Stock solutions of reference substances

As an example, introduce solvent (5.5) into a 100 ml volumetric flask nearly up to the mark. Inject below the liquid surface 50 µl to 300 µl each of a reference substance using a microlitre syringe (6.9) and make up to the mark with solvent. Close the volumetric flask with a ground-glass stopper and agitate gently. Calculate the concentration of the added substance taking into account the density given in Table 1.

NOTE Alternatively, the concentration can also be calculated by weighing. For this purpose, determine the weight increase resulting from the addition of the reference substance with the microlitre syringe (e.g. for geosmin and 2-methylisoborneol and the internal standards).

Keep the stock solutions at a temperature not exceeding 6 °C and protect them from light.

They are stable for at least 12 months.

5.8.3 Multi-component stock solutions of reference substances

As an example, introduce methanol or propylene carbonate (5.5) into a 100 ml volumetric flask nearly up to the mark. Inject below the liquid surface 50 µl to 300 µl each of the required stock solutions of single reference substances (solutions in accordance with 5.8.2) using a microlitre syringe (6.9) and make up to the mark with solvent. Close the volumetric flask with a ground-glass stopper and agitate gently.

NOTE Alternatively, commercially available certified stock solutions of individual (or mixtures of several) reference substances, e.g. in methanol, can be used for preparing multi-component stock solutions.

Keep the multi-component stock solutions at a temperature not exceeding 6 °C and protect them from light.

They are stable for at least six months.

5.8.4 Aqueous multi-component reference solutions used for calibration of the total procedure

Prepare the aqueous reference solution for calibration of the total procedure, for example, as follows:

Measure 100 ml of water (e.g. into a volumetric flask) and add a magnetic stir bar.

Place the flask on a magnetic stirrer (6.10) and switch on.

Using a microlitre syringe (6.9), measure out, for example, 10 µl of the multi-component stock solution (5.8.3), inject it below the water surface of the stirred water, and stir for about 5 min with the flask closed.

Adjust the stirring rate such that no turbulence vortex will form.

Prepare reference solutions of higher and lower concentrations in the same way using correspondingly prepared multi-component stock solutions (5.8.3). All aqueous multi-component reference solutions used for multipoint calibration shall contain equal spiking volume of the respective multi-component stock solution required.

Do not dilute the spiked aqueous solutions.

A small spiking volume (e.g. 10 µl in 100 ml of water) is recommended to minimize interferences of the solutizer with the adsorption process of the substances of Table 1.

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Keep the aqueous reference solutions at temperatures between 1 °C and 6 °C and protected from light until their use.

The solutions may be stable for a very short time only and thus, shall be prepared each working day.

6 Apparatus

6.1 General

Equipment or parts of equipment which will come into contact with the water sample or the extract shall be free from residues which might cause interfering blank values. Preferably, use equipment made of glass, stainless steel, or polytetrafluoroethylene (PTFE).

6.2 Sample flask, glass bottle, e.g. flat-bottomed of amber glass, with glass or PTFE coated stopper, nominal capacity 100 ml or 250 ml, e.g. an ISO 4796-2 — 250 NJ laboratory bottle.

6.3 Headspace vials, e.g. crimp neck vials or threaded bottles, nominal capacity 20 ml.

6.4 Magnetic crimp or screw caps, with PTFE-coated septa (e.g. butyl/PTFE septum with a thickness of 0,9 mm to 1,5 mm).

6.5 Crimper and decapper, e.g. manual crimper and manual decapper, 20 mm.

6.6 Volumetric flask, nominal capacities of 10 ml, 25 ml, 50 ml, and 100 ml, e.g. an ISO 1042 — A10 — C volumetric flask.

6.7 Volumetric pipette, of different nominal capacities from 1 ml to 50 ml, e.g. pipette according to ISO 648.

6.8 Glass piston-type pipette, with ground-glass piston, e.g. 10 ml.

6.9 Microlitre syringes, of different nominal capacities from 5 µl to 500 µl.

6.10 Magnetic stirrer, with magnetic stir bar.

6.11 Capillary gas chromatograph with mass spectrometric detector (GC-MS), gas supply in accordance with manufacturer's instructions.

6.12 Injector, with e.g. split/splitless or programmable temperature vaporising (PTV) injector.

6.13 Automatic sampler, equipped for SPME including the required driver software.

6.14 SPME fibres, e.g. Carboxen®/PDMS[1)] (85 µm), DVB/Carboxen®/PDMS[1)] (50/30 µm). Examples are given in Annex A.

Preferably, use fibres with 23-gauge needles in combination with septumless injectors. If using a septum-type injection system, 24-gauge needles should be used (see 4.3) to avoid damaging the septa.

6.15 Capillary columns, for gas chromatography, e.g. columns recommended for the analysis of volatile compounds preferably with a coating thickness of >1 µm (see Annex B for examples).

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1) Carboxen®/PDMS and DVB/Carboxen®/PDMS are examples of suitable products which are commercially available. These examples are given only as information for the users of this International Standard and do not constitute an endorsement by ISO of these products.

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7 Sampling and sample pretreatment

For sampling, use thoroughly cleaned, sample flasks (6.2). Before use, rinse bottles and ground-glass stoppers with the water to be sampled.

Fill the bottles completely with the water to be analysed and close them carefully avoiding any entrapment of air.

To fill the bottles, preferably use a metal tube connected to the tap and inserted down to the bottom of the bottle. Adjust the water flow such that the bottle can be filled avoiding any turbulences.

Add sodium thiosulfate pentahydrate (5.6) to water samples containing chlorine, thus, obtaining a concentration of approximately 80 mg/l to 100 mg/l.

Sodium thiosulfate can, for example, be added by means of a spatula spoon prior to inserting the stopper. The mass of sodium thiosulfate added to the sample is non-critical. It shall be sufficient, however, to dechlorinate the water sample.

Treat and analyse the water samples as soon as possible after their collection. Keep the water sample in a dark place at temperatures between 1 °C and 5 °C. Storage shall not exceed 5 days.

Keep the samples from heating up during transport.

8 Procedure

8.1 Sample preparation and extraction

As an example, introduce 3,0 g sodium chloride (5.4) to a 20 ml headspace vial (6.3). Keep the added amount of NaCl constant for all samples of a sample sequence.

The amount of NaCl added should lead to nearly saturation, i.e. 0,3 g per millilitre of the sample volume (e.g. 3,0 g NaCl in 10 ml of water).

Measure 10 ml of the water sample to be analysed, e.g. using a piston-type pipette (6.8), and add to the headspace vial (6.3). The measured-out volume shall be the same for both sample measurements and the reference solutions used for calibration.

Add the internal standard (5.7), dissolved in solvent (5.5) to the sample, and the reference solutions for calibration, e.g. by injecting 10 µl below the water surface using a microlitre syringe (6.9). The total volume of solvent (5.5) added per headspace vial shall not exceed 20 µl.

Close the headspace vial (6.3) tightly and dissolve the salt.

Place, for example, the headspace vials on the automatic sampler equipped for SPME (6.13) according to their sample sequence and select a sample incubation time of, e.g. 10 min.

The incubation time selected for all samples should be between 10 min and 15 min so as to reach the extraction temperature. Always maintain the incubation time constant for all samples over one sequence.

Preferably use SPME fibres as specified in 6.14.

Condition new fibres by heating them in the “bake-out” station of the SPME autosampler or in the GC injector. Select the duration and temperature of the fibre bake-out according to the manufacturer’s instructions. Prior to starting with the first sample of a sequence, process at least two headspace vials containing only water (5.2). Recalibration is required whenever a new fibre has been installed.

Adjust the extraction temperature to, for example, 40 °C (recommended) and always maintain this temperature constant over one sample sequence.

Extraction temperatures below 30 °C and above 45 °C should be avoided.

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Always maintain the stirring rate constant over one sample sequence (e.g. adjust to 250 min^{-1}). In systems using a magnetic stirrer, insert the SPME needle approximately 3 mm from the middle.

The extraction time should be set to approximately 10 min and shall be maintained constant over one sample sequence.

NOTE The extraction time can be adjusted (e.g. to 20 min or 30 min) for increasing sensitivity of medium volatile substances (e.g. geosmin or 2-methylisoborneol).

Desorb in the injector (e.g. for 10 min at 280 °C). If the maximum operating temperature specified by the manufacturer is below 280 °C, this temperature shall be selected.

8.2 Gas chromatography

Optimize the instrument parameters in accordance with the manufacturer's operating instructions.

For separation, use capillary columns as specified in 6.15 (see Annex B for examples).

Select splitless injection to achieve the highest sensitivity.

A reduced split ratio (e.g. 5:1) may also be used if the required sensitivity is ensured. This can give an improved signal symmetry for early-eluting substances.

8.3 Identification of individual compounds by means of mass spectrometry (GC-MS)

Identify a compound in the sample by comparing the measured retention times and the corresponding relative intensities of selected identification masses (Table 2) with those of the references substances in the multi-component reference solution (5.8.4).

The target compound in the sample is to be regarded as identified if

— the relative or absolute retention time (RT) of the substance in the SIM chromatogram matches the relative or absolute retention time of the corresponding reference substance in the chromatogram of the most recently measured multi-component reference solution (5.8.4) with a limit deviation of no more than ±0,2 %,

— at least two to three selected identification masses (Table 2) are present at the substance-specific retention time, and

— the relative intensities of all selected identification masses of individual substances measured in the sample do not deviate by more than $\pm(0{,}1 \times I + 10)$ % from those of the corresponding substances in the reference solution (where I is the relative intensity of the identification mass of the individual reference substance).

EXAMPLE Three selected identification masses have the following relative intensities: 100 %, 50 %, and 15 %. The maximum acceptable deviation for I_2 and I_3 in the sample is (I_1 is by definition 100 % in both the sample and reference standard):

— I_2: $\pm(0{,}1 \times 50 + 10)$ % = ±15 %, the relative intensity in the sample shall be between 35 % and 65 %;

— I_3: $\pm(0{,}1 \times 15 + 10)$ % = ±11,5 %, the relative intensity in the sample shall be between 3,5 % and 26,5 %.

In general, the following condition applies. After background subtraction, no ion of significant intensity should be present in the mass spectrum which has a mass larger than the maximum possible mass of a compound to be identified.

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