INTERNATIONAL STANDARD

ISO 20595

First edition
2018-01

Water quality — Determination of selected highly volatile organic compounds in water — Method using gas chromatography and mass spectrometry by static headspace technique (HS-GC-MS)

Qualité de l'eau — Dosage de composés organiques hautement volatils sélectionnés dans l'eau — Méthode par chromatographie en phase gazeuse par la technique de l'espace de tête statique et spectrométrie de masse (HS-GC-MS)

Reference number
ISO 20595:2018(E)

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Published in Switzerland

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

Various methods are available for the determination of highly volatile organic compounds in water. This document specifies a gas chromatographic method with mass spectrometric detection (GC-MS) for the determination of volatile organic compounds using the static headspace technique (HS).

Water quality — Determination of selected highly volatile organic compounds in water — Method using gas chromatography and mass spectrometry by static headspace technique (HS-GC-MS)

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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.

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

1 Scope

This document specifies a method for the determination of selected volatile organic compounds in water (see Table 1). This comprises among others volatile halogenated hydrocarbons as well as gasoline components (BTXE, TAME, MTBE and ETBE).

The method is applicable to the determination of volatile organic compounds (see Table 1) in drinking water, groundwater, surface water and treated waste water in mass concentrations >0,1 µg/l. The lower application range depends on the individual compound, the amount of the blank value and the matrix.

The applicability of the method to further volatile organic compounds not indicated in Table 1 is not excluded, but this is checked in individual cases.

Table 1 — Volatile organic compounds determinable by this method

Name (other name)	Molecular formula	CAS-RN[a]	EC-Number[b]	Molar mass g/mol
allyl chloride[c] (3-chloropropene)	C_3H_5Cl	107-05-1	203-457-6	76,53
benzene	C_6H_6	71-43-2	200-753-7	78,11
biphenyl	$C_{12}H_{10}$	92-52-4	202-163-5	154,21
bromodichloromethane	$CHBrCl_2$	75-27-4	200-856-7	163,83
chlorobenzene	C_6H_5Cl	108-90-7	203-628-5	112,56
2-chloro-1,3-butadiene (chloroprene)	C_4H_5Cl	126-99-8	204-818-0	88,54
2-chlorotoluene	C_7H_7Cl	95-49-8	202-424-3	126,58
3-chlorotoluene	C_7H_7Cl	108-41-8	203-580-5	126,58
4-chlorotoluene	C_7H_7Cl	106-43-4	203-397-0	126,58
dibromochloromethane	$CHBr_2Cl$	124-48-1	204-704-0	208,28
1,2-dibromoethane	$C_2H_4Br_2$	106-93-4	203-444-5	187,86
1,2-dichlorobenzene	$C_6H_4Cl_2$	95-50-1	202-425-9	147,00
1,3-dichlorobenzene	$C_6H_4Cl_2$	541-73-1	208-792-1	147,00

[a] CAS-RN: Chemical Abstracts Service Registry Number.

[b] EC-Number: European Inventory of Existing Commercial Substances (EINECS) or European List of Notified Chemical Substances (ELINCS).

[c] Compounds do not have long-term stability.

[d] Compounds can coelute.

[e] Source: Hazardous Substance Data Base University Hamburg (Germany).

Table 1 *(continued)*

Name (other name)	Molecular formula	CAS-RN[a]	EC-Number[b]	Molar mass g/mol
1,4-dichlorobenzene	$C_6H_4Cl_2$	106-46-7	203-400-5	147,00
dichlorodiisopropyl ether	$C_6H_{12}Cl_2O$	108-60-1	203-598-3	171,06
1,1-dichloroethane	$C_2H_4Cl_2$	75-34-3	200-863-5	98,96
1,2-dichloroethane	$C_2H_4Cl_2$	107-06-2	203-458-1	98,96
1,1-dichloroethene	$C_2H_2Cl_2$	75-35-4	200-864-0	96,94
cis-1,2-dichloroethene	$C_2H_2Cl_2$	156-59-2	205-859-7	96,94
trans-1,2-dichloroethene	$C_2H_2Cl_2$	156-60-5	205-860-2	96,94
dichloromethane	CH_2Cl_2	75-09-2	200-838-9	84,93
1,2-dichloropropane	$C_3H_6Cl_2$	78-87-5	201-152-2	112,99
cis-1,3-dichloropropene	$C_3H_4Cl_2$	10061-01-5	233-195-8	110,97
trans-1,3-dichloropropene	$C_3H_4Cl_2$	10061-02-6	602-030-00-5[e]	110,97
2,3-dichloropropene	$C_3H_4Cl_2$	78-88-6	201-153-8	110,97
1,1-dimethylpropyl-methyl ether, *tert*-amyl methyl ether (TAME)	$C_6H_{14}O$	994-05-8	213-611-4	102,17
ethyl benzene	C_8H_{10}	100-41-4	202-849-4	106,17
ethyl *tert*-butyl ether (ETBE)	$C_6H_{14}O$	637-92-3	211-309-7	102,17
hexachlorobutadiene	C_4Cl_6	87-68-3	201-765-5	260,76
hexachloroethane	C_2Cl_6	67-72-1	200-666-4	236,74
isopropylbenzene (cumene)	C_9H_{12}	98-82-8	202-704-5	120,19
methyl *tert*-butyl ether (MTBE)	$C_5H_{12}O$	1634-04-4	216-653-1	88,15
naphthalene	$C_{10}H_8$	91-20-3	202-049-5	128,17
n-propylbenzene	C_9H_{12}	103-65-1	203-132-9	120,19
1,1,1,2-tetrachloroethane	$C_2H_2Cl_4$	630-20-6	211-135-1	167,85
tetrachloroethene	C_2Cl_4	127-18-4	204-825-9	165,84
tetrachloromethane (carbon tetrachloride)	CCl_4	56-23-5	200-262-8	153,82
toluene	C_7H_8	108-88-3	203-625-9	92,14
tribromomethane (bromoform)	$CHBr_3$	75-25-2	200-854-6	252,73
1,2,3-trichlorobenzene	$C_6H_3Cl_3$	87-61-6	201-757-1	181,45
1,2,4-trichlorobenzene	$C_6H_3Cl_3$	120-82-1	204-428-0	181,45
1,3,5-trichlorobenzene	$C_6H_3Cl_3$	108-70-3	203-608-6	181,45
1,1,1-trichloroethane	$C_2H_3Cl_3$	71-55-6	200-756-3	133,40
1,1,2-trichloroethane	$C_2H_3Cl_3$	79-00-5	201-166-9	133,40
trichloroethene	C_2HCl_3	79-01-6	201-167-4	131,39
trichloromethane (chloroform)	$CHCl_3$	67-66-3	200-663-8	119,38
1,1,2-trichlorotrifluoroethane	$C_2Cl_3F_3$	76-13-1	200-936-1	187,38
1,2,4-trimethylbenzene (pseudocumene)	C_9H_{12}	95-63-6	202-436-9	120,19

[a] CAS-RN: Chemical Abstracts Service Registry Number.

[b] EC-Number: European Inventory of Existing Commercial Substances (EINECS) or European List of Notified Chemical Substances (ELINCS).

[c] Compounds do not have long-term stability.

[d] Compounds can coelute.

[e] Source: Hazardous Substance Data Base University Hamburg (Germany).

Table 1 *(continued)*

Name (other name)	Molecular formula	CAS-RN[a]	EC-Number[b]	Molar mass g/mol
1,3,5-trimethylbenzene (mesitylene)	C_9H_{12}	108-67-8	203-604-4	120,19
vinyl benzene (styrene)	C_8H_8	100-42-5	202-851-5	104,15
vinyl chloride (chloroethene)[c]	C_2H_3Cl	75-01-4	200-831-0	62,49
o-xylene	C_8H_{10}	95-47-6	202-422-2	106,17
m-xylene[d]	C_8H_{10}	108-38-3	203-576-3	106,17
p-xylene[d]	C_8H_{10}	106-42-3	203-396-5	106,17

[a] CAS-RN: Chemical Abstracts Service Registry Number.

[b] EC-Number: European Inventory of Existing Commercial Substances (EINECS) or European List of Notified Chemical Substances (ELINCS).

[c] Compounds do not have long-term stability.

[d] Compounds can coelute.

[e] Source: Hazardous Substance Data Base University Hamburg (Germany).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. 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 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 5667-4, *Water quality — Sampling — Part 4: Guidance on sampling from lakes, natural and man-made*

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

ISO 5667-6, *Water quality — Sampling — Part 6: Guidance on sampling of rivers and streams*

ISO 5667-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste waters*

ISO 5667-11, *Water quality — Sampling — Part 11: Guidance on sampling of groundwaters*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

An exact volume of an unfiltered water sample is sealed gastight in a headspace vial and heated. After an equilibrium has become established between the volatile organic compounds dissolved in the water and those located in the gas phase above the water level, an exact gas volume is taken from the gas phase and determined by gas chromatography with mass spectrometric detection.

5 Interferences

5.1 General

If a sample consists of several liquid phases, another method shall be applied.

5.2 Interferences in the laboratory

Some of the volatile organic compounds listed in Table 1 are frequently used as solvents in laboratories. Solvent vapours in the laboratory air can lead to overestimates during the analysis. Regular blank value examinations are therefore indispensable (see 9.3.1).

5.3 Interferences by the matrix

Matrix effects that lead to different recoveries and different response factors in samples in comparison to calibration standards can be reduced by adding specific amounts of salt. An increase in the sensitivity can also be attained by adding salt. The use of sodium sulfate or sodium chloride has proven effective. However, interferences can occur depending on the salt used.

5.4 Interferences in the headspace

Some compounds can decompose while the equilibrium forms at e.g. 80 °C. For example, 1,1,2,2-tetrachloroethane decomposes to trichloroethene. If 1,1,2,2-tetrachloroethane is present in the sample, overestimates of trichloroethene can result.

NOTE The decomposition of 1,1,2,2-tetrachoroethane can be eliminated by acidifying the water in the headspace vial with H_2SO_4 to pH <2 and using Na_2SO_4 as salt. But remember that the acid has an immense influence on the life span of the column and the injector.

5.5 Interferences during gas chromatography and mass spectrometry

To rectify interferences that are typically caused by the injection system or by inadequate separation, enlist experts and observe the manufacturer information in the apparatus manuals. The performance and stability of the analysis system shall be checked regularly (e.g. by measuring reference solutions of known composition).

Performance data from an interlaboratory trial held in 2013 are provided in Annex D.

6 Reagents

6.1 General

Unless otherwise indicated, reagents to be used are of purity grade “for analysis” or “for residue analysis”.

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

6.3 Operating gases for gas chromatograph and mass spectrometer, of high purity and according to the required specification of the manufacturer of the instrumentation, e.g. helium, minimum purity 99,996 %.

6.4 Salts, e.g. sodium sulfate, Na_2SO_4, sodium chloride, NaCl.

6.5 Solvents, for the preparation of stock solutions and as solubilizers in aqueous reference solutions, e.g. methanol, CH_3OH, or dimethylformamide (DMF), C_3H_7NO.

6.6 Reference compounds, every compound to be analysed shall be of defined purity.

6.7 Internal standard, for examples of suitable internal standards, see Annex B.

6.8 Examples of stock and standard solutions

6.8.1 Stock solution

The stock solution shall be produced by corresponding dilution of the individual compounds in e.g. methanol (6.5) or from certified standard mixtures. The concentration of every individual compound is e.g. 100 µg/ml in methanol (6.5).

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

They are stable for at least 12 months.

6.8.2 Intermediate dilutions (spiking solutions)

Intermediate dilutions (spiking solutions) for the preparation of aqueous multi-component solutions for calibration over the total process (6.8.4) are produced by dilution of the stock solution (6.8.1) with a solvent (6.5). For example, use a microlitre syringe (7.7) to add between 5 µl and 500 µl of each of the required stock solution (6.8.1) in a 10 ml volumetric flask (7.9) filled about half-full with methanol and then fill up to the mark.

The concentrations in methanol are then between 0,05 µg/ml and 5 µg/ml.

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

They are stable for at least 6 months.

6.8.3 Solution of the internal standards

Prepare the solution by corresponding dilutions of the internal standards (6.7) with methanol (6.5), each component e.g. 1 µg/ml in methanol.

6.8.4 Aqueous multi-component solution for the calibration

The aqueous multi-component solutions (reference solutions) for the calibration can be produced as follows.

- Pour a defined volume of e.g. 10 ml water (6.2) in an e.g. 20 ml headspace vial (7.8) and add a defined volume of e.g. 10 µl of the relevant spiking solution (6.8.2) directly into the water.
- Then add a defined volume of e.g. 10 µl of the internal standard solution (6.8.3) directly into the water (6.2).
- Close the headspace vial (7.8) with the closing cap directly after the spiking and shake.

If salt is to be added, this is done before adding the water. The addition of salt (6.4) close to saturation (e.g. 3 g NaCl or 4 g Na_2SO_4 in 10 ml, respectively) is recommended to minimize matrix effects.

Alternatively, the spiking solution (6.8.2) and internal standard solution (6.8.3) can also be added via the septum. This will not result in losses; nevertheless, the quality of the septa used should be ensured by blank samples.

It is recommended that the spiking volume be kept constant.

The aqueous multi-component solutions for the calibration can also be prepared in volumetric flasks (7.9). Ensure that no losses result due to pipetting and homogenization. Stir the solution for at least 10 s. Take care of a thorough mixing but avoid the formation of a turbulence funnel.

6.9 **Sodium thiosulfate pentahydrate**, $Na_2S_2O_3 \cdot 5H_2O$.

NOTE Ascorbic acid can also be used for the neutralizing of the chlorine as far as validated.

7 Apparatus

7.1 General

Equipment or glass parts that come into contact with the water sample shall be free of the compounds to be analysed and free of residues that can cause interfering blank values. This can be attained by cleaning the glass equipment.

7.2 Sample bottles, e.g. narrow-necked flat-bottomed bottles with glass stoppers, preferably brown glass bottles, nominal volume e.g. 250 ml or less.

7.3 Dry cabinet.

7.4 Gas chromatograph (GC), with mass spectrometer (MS) and headspace (HS) sampler.

7.5 Capillary columns, with e.g. (medium-)polar stationary phase, e.g. inner diameter ≤ 0,32 mm, length about 30 m to 60 m, film thickness 1 µm to 3 µm (phase ratio > 300).

7.6 Magnetic stirring rod, polytetrafluorethylene (PTFE)-encased.

7.7 Microlitre syringes, various nominal volumes e.g. 10 µl, 100 µl, 250 µl, 1 000 µl.

7.8 Headspace vials (HS vial), e.g. 20 ml for automatic sampler.

7.9 Volumetric flasks, nominal volume e.g. 10 ml, 50 ml, 100 ml, e.g. volumetric flasks ISO 1042 - A10 - C.

7.10 Pipettes.

8 Sampling

Take and handle the samples, taking into account the specifications given in ISO 5667-3, ISO 5667-4, ISO 5667-5, ISO 5667-6, ISO 5667-10 and ISO 5667-11.

Completely fill the sample bottle (7.2) with the sample.

Ensure a laminar flow during the sampling. Turbulent flows can lead to losses of the substances to be analysed.

Add sodium thiosulfate pentahydrate (6.9) to water samples likely to contain chlorine, thus obtaining a concentration of approximately 80 mg/l to 100 mg/l.

Pre-rinsing of the sample bottle (7.2) with sample material is to be avoided, as this can possibly result in an increased concentration of suspended matter components and also the loss of stabilization reagents in the sample.

Glass equipment or equipment made from stainless steel or e.g. scoops made from glass shall be used. Plastic equipment is to be avoided as blank values and analyte losses due to adsorption effects can occur as a result of this.

It shall be ensured that no interfering compounds get into the sample and no losses occur in the compounds to be determined (see Clause 5).

The samples shall be treated and stored in accordance with ISO 5667-3.

If longer storage times are necessary and/or in case of presumed or validated instability, suitable measures shall be implemented (e.g. preservation with copper sulfate, sodium azide or the measurement-ready headspace vial shall be frozen horizontally).

9 Procedure

9.1 Sample preparation

The samples shall be handled as the multi-component solutions for the calibration (6.8.4).

In the case of a salt addition, add it to the vial prior to adding the sample.

The samples to be examined are transferred to headspace vials (7.8) while avoiding turbulences. Subsequently, the internal standard solution (6.8.3) is added. The headspace vials (7.8) shall be tightly sealed and the salt dissolved by shaking directly afterwards.

The correctness of the headspace analysis depends on maintaining constant phase-volume ratios, i.e. during the calibration and analysis, the same amounts of water and salt shall always be added to the headspace vials. Variations due to different batches of vials are compensated by the internal standard.

All samples of a sample sequence are thermostated in succession in the headspace-sampler for a constant time (e.g. 30 min) and at a constant temperature (e.g. 80 °C) and analysed by gas chromatography with mass spectrometric detection.

9.2 GC-MS operating conditions

The GC-MS apparatus (7.4) shall be optimized according to the manufacturer data. Capillary columns (7.5) shall be used for the separation (see Annex A).

9.3 Control measures

9.3.1 Blank value control

The flawless state of the reagents and equipment shall be checked daily if analyses are under acquisition by means of blank value examinations.

For the blank value examination, examine e.g. water (6.2) in the same way as a sample.

Blank values are location specific. The contamination source shall be localized and, if necessary, eliminated if blank values occur.

Depending on the blank fluctuation, the blank values should not exceed 30 % to 50 % of the lower application limit of the method.

9.3.2 Control over the total procedure

The quality of the procedure shall be checked daily by means of control examinations.

For this control examination, for example, water (6.2) shall be spiked with the compounds to be examined (6.8.4) and examined in the same way as a sample (see 9.1). If deviations are determined (e.g. out-of-control situations from a control chart), the individual process steps shall be monitored.

9.4 Identification of individual compounds

9.4.1 General

A compound is identified in the sample by comparing the retention times measured under the same conditions and associated relative intensities of selected identification masses (see Table 2) with those of the reference compounds in the aqueous multi-component solution for the calibration (6.8.4).

9.4.2 Identification of individual compounds with mass spectrometric detector

Individual compounds are regarded as identified in the sample if:

- the retention time (t_R) of the corresponding peak in the total ion current chromatogram or in the single ion chromatogram (SIM) is within t_R ± 0,5 % or a maximum of ±5 s, compared with the retention times of the relevant compound measured under the same conditions in the total ion current chromatogram or the individual mass chromatogram of a reference solution;
- the complete mass spectra of the background corrected reference compounds match the spectra present at the relevant retention time in the chromatogram of the water sample, which is also background corrected;
- at least the diagnostic ions of the reference compounds (see Table 2) deviate from those of the compounds to be identified in their relative peak intensities by less than 30 %;
- for some compounds, only two diagnostic ions are available (see Table 2).

Table 2 — Examples of diagnostic ions of reference compounds to be used for identification and quantification in mass spectrometric detection

Name (compounds of Table 1)	Retention time[a] min	Target ion m/z	Qualifier ion 1 m/z	Qualifier ion 2 m/z
vinyl chloride (chloroethene)	2,900	62	64	56
1,1-dichloroethene	5,005	61	96	63/98
1,1,2-trichlorotrifluoroethane	5,008	101	151	103
allyl chloride (3-chloropropene)	5,622	41	39	76
dichloromethane	5,832	84	86	49/51
trans-1,2-dichloroethene	6,335	96	61	63/96/98
methyl *tert*-butyl ether (MTBE)	6,320	73	57	61
1,1-dichloroethane	7,082	63	83	65
2-chloro-1,3-butadiene (chloroprene)	7,258	88	53	
ethyl *tert*-butyl ether (ETBE)	7,899	59	87	57
cis-1,2-dichloroethene	8,203	96	61	98
trichloromethane (chloroform)	8,852	83	85	47
1,1,1-trichloroethane	9,234	97	99	117
tetrachloromethane (carbon tetrachloride)	9,580	117	119	121
benzene	10,020	78	77	50
1,2-dichloroethane	10,060	62	64	98
1,1-dimethylpropyl-methyl ether, *tert*-amyl methyl ether (TAME)	10,282	55	73	
trichloroethene	11,490	130	95	132

[a] The gas chromatographic conditions are listed in Annex C.

Table 2 *(continued)*

Name (compounds of Table 1)	Retention time[a] min	Target ion m/z	Qualifier ion 1 m/z	Qualifier ion 2 m/z
1,2-dichloropropane	12,020	63	62	76
2,3-dichloropropene	12,145	75	110	77
bromodichloromethane	12,710	83	85	129
cis-1,3-dichloropropene	13,867	75	110	77
toluene	14,764	91	65	92
trans-1,3-dichloropropene	15,398	75	110	77
1,1,2-trichloroethane	15,805	97	83	99
tetrachloroethene	16,289	166	129	164
dibromochloromethane	17,018	129	127	131
1,2-dibromoethane	17,318	107	109	
chlorobenzene	18,834	112	77	114
1,1,1,2-tetrachloroethane	19,115	131	117	133
ethyl benzene	19,214	91	106	
m-/*p*-xylene	19,602	91	106	
o-xylene	20,805	91	106	
vinyl benzene (styrene)	20,906	104	78	
tribromomethane (bromoform)	21,439	173	175	171
isopropylbenzene (cumene)	22,092	105	120	
n-propylbenzene	23,474	91	120	
2-chlorotoluene	23,686	91	126	
3-chlorotoluene	23,908	91	126	
4-chlorotoluene	24,067	91	126	
1,3,5-trimethylbenzene (mesitylene)	24,107	105	120	
1,2,4-trimethylbenzene (pseudocumene)	25,368	105	120	
1,3-dichlorobenzene	26,236	146	111	148
1,4-dichlorobenzene	26,550	146	111	148
1,2-dichlorobenzene	27,836	146	111	148
dichlorodiisopropyl ether	28,963	45	121	
hexachloroethane	28,783	117	201	
1,3,5-trichlorobenzene	32,260	180	145	182
1,2,4-trichlorobenzene	35,969	180	145	182
hexachlorobutadiene	37,969	225	260	227
naphthalene	37,606	128	102	127
1,2,3-trichlorobenzene	39,589	180	145	182
biphenyl	61,678	154	153	
benzene-d6	9,928	84	52	
toluene-d8	14,576	98	100	
1,2-dichlorobenzene-d4	27,782	152	150	

[a] The gas chromatographic conditions are listed in Annex C.

The masses listed for the target ions as well as the qualifier ions in Table 2 serve as an orientation example. The selection of internal standards should be adapted correspondingly to the compound group to be analysed. This applies, in particular, to analysis in respect to the recovery rates as well as to the gas chromatographic step. The internal standards listed are examples. Further internal standards can be used (see Annex B).

10 Calibration

10.1 General

- A calibration function shall be determined for each compound to be determined. Multi-component solutions (6.8.4) can be used for this.
- The linear working range shall be determined by measuring at least five points (basic calibration) for five different concentrations.
- The calibration function of an individual compound only applies to the relevant concentration range. It depends on the operating conditions of the gas chromatograph and shall be checked regularly.

At least six measuring points shall be determined when selecting a quadratic function.

In routine operation, a two-point calibration can be adequate for a linear function, but shall be checked in individual cases (e.g. working range, matrix influences). This shall correspond to the basic calibration.

For setting up a calibration function, the reference solutions shall be adapted to the working range to set up a basic function (for the preparation of reference solutions, see 6.8.4).

See Table 3 for the meaning of the indices in the following text.

Table 3 — Meaning of the indices

Index	Meaning
i	Compound
e	Measuring variables for the calibration
g	Total procedure
j	Consecutive figure for pairs of values
I	Internal standard

10.2 Calibration with internal standard

The use of an internal standard renders the concentration determination independent of potential dosing errors during the injection and of various matrix effects.

Errors that can occur due to sample losses during individual steps of the sample preparation are also partially compensated.

The mass concentration $\rho_{i\mathrm{I}}$ shall be equal for the calibration and for the sample to be analysed.

— The values for $y_{i\mathrm{eg}}/y_{\mathrm{Ieg}}$ (peak area, peak height or integration units) shall be applied for every compound *i* on the ordinate as a function of the associated mass concentration $\rho_{i\mathrm{eg}}/\rho_{\mathrm{Ieg}}$.

— The value pairs $y_{i\mathrm{eg}}/y_{\mathrm{Ieg}}$ and $\rho_{i\mathrm{eg}}/\rho_{\mathrm{Ieg}}$ are used to determine a linear regression line according to Formula (1):

$$\frac{y_{i\mathrm{eg}}}{y_{\mathrm{Ieg}}} = m_{i\mathrm{Ig}} \frac{\rho_{i\mathrm{eg}}}{\rho_{\mathrm{Ieg}}} + b_{i\mathrm{Ig}} \tag{1}$$

where

$y_{i\mathrm{eg}}$ is the measured value of compound *i* during calibration as a function of $\rho_{i\mathrm{e}}$, the unit depending on the evaluation, e.g. area unit;

y_{Ieg} is the measured value of internal standard I during calibration as a function of ρ_{Ieg}, the unit depending on the evaluation, e.g. area unit; all reference solutions contain equal concentrations of the internal standard;

$\rho_{i\mathrm{eg}}$ is the (independent variable) mass concentration of compound *i* in the reference solution, in micrograms per litre (µg/l);

ρ_{Ieg} is the (independent variable) mass concentration of internal standard I in the reference solution, in micrograms per litre (µg/l);

$m_{i\mathrm{Ig}}$ is the slope of the reference line of $y_{i\mathrm{eg}}/y_{\mathrm{Ieg}}$ as a function of the mass concentration $y_{i\mathrm{eg}}/y_{\mathrm{Ieg}}$ (response factor);

$b_{i\mathrm{Ig}}$ is the ordinate intercept of the reference line, the unit depending on the evaluation.

11 Evaluation

The mass concentrations ρ_{ig} of the individual compound shall be calculated according to Formula (2):

$$\rho_{ig} = \frac{\dfrac{y_{ig}}{y_{\text{I}g}} - b_{i\text{I}g}}{m_{i\text{I}g}} \cdot \rho_{\text{I}g} \tag{2}$$

where

ρ_{ig}	is the mass concentration of the analysed compound *i* in the water sample, in micrograms per litre (µg/l);
y_{ig}	is the measured value of the analysed compound *i* in the water sample, e.g. area unit;
$y_{\text{I}g}$	is the measured value of the internal standard I in the water sample, e.g. area unit;
$\rho_{\text{I}g}$	is the mass concentration of the internal standard I in the water sample, in micrograms per litre (µg/l);
$b_{i\text{I}g}$, $m_{i\text{I}g}$	see Formula (1).

12 Expression of results

The analysis results obtained when applying this document are subject to a measurement uncertainty that is to be considered in the interpretation of the results.

NOTE The relative measurement uncertainty depends on the concentration and the matrix and is greatest in the lower application range of the method.

The mass concentration of the substances according to Table 1 is indicated in micrograms per litre at two significant figures.

EXAMPLES

trichloromethane (chloroform)	11 µg/l
tetrachloroethene	4,1 µg/l
o-xylene	0,17 µg/l

13 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this document, i.e. ISO 20595;

b) the identity of the sample;

c) sampling, sample transport and preparation (if applicable);

d) expression of the results according to Clause 12;

e) any deviation from this method and report of all circumstances that may have affected the results.

Annex A
(informative)

Example of GC column, headspace vial and septum

Capillary column:	DB-624 polyphenylmethyl siloxane (see NOTE), length: 60 m, film thickness: 1,8 µm, diameter: 0,32 mm Restek Rxi-624Sil MS (see NOTE) (60 m × 0,25 mm × 1,4 µm)
HS vial:	20 ml headspace vial, crimp neck vials
Septum:	Magnetic crimp cap, gold painted, with 8 mm hole, butyl/PTFE

NOTE DB-624 polyphenylmethyl siloxane and Restek Rxi-624Sil MS are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

Annex B
(informative)

Examples of internal standards

Recommendations for an appropriate choice of internal standard substances to be used within the analysis of individual substances of Table 1 are listed in Table B.1. The internal standard substances most frequently used by participants of the interlaboratory trial for validation, carried out in March 2013 (see Tables D.1, D.3 and D.5), are indicated by their numbers according to Table B.2. Other substances can be used as well if their suitability has been established in preliminary tests.

Table B.1 — Internal standard substances

Name	Internal standard substances according to Table B.2				Name	Internal standard substances according to Table B.2			
allyl chloride (3-chloropropene)	4	1	2	20	ethyl *tert*-butyl ether (ETBE)	4	1	2	10
benzene	4	1	2	21	hexachlorobutadiene	4	3	2	10
biphenyl	4	3	21	2	hexachloroethane	4	3	2	10
bromodichloromethane	4	1	2	9	isopropylbenzene (cumene)	4	2	3	13
chlorobenzene	4	2	10	21	methyl *tert*-butyl ether (MTBE)	4	1	2	10
2-chloro-1,3-butadiene (chloroprene)	4	1	2	10	naphthalene	4	3	2	21
2-chlorotoluene	4	3	2	21	*n*-propylbenzene	4	2	3	13
3-chlorotoluene	4	3	2	21	1,1,1,2-tetrachloroethane	4	2	10	20
4-chlorotoluene	4	3	2	21	tetrachloroethene	4	2	10	9
dibromochloromethane	4	2	9	10	tetrachloromethane (carbon tetrachloride)	4	1	2	10
1,2-dibromoethane	4	2	9	10	toluene	4	2	21	10
1,2-dichlorobenzene	4	3	2	21	tribromomethane (bromoform)	4	2	10	21
1,3-dichlorobenzene	4	3	2	21	1,2,3-trichlorobenzene	4	3	2	21
1,4-dichlorobenzene	4	3	2	21	1,2,4-trichlorobenzene	4	3	2	21
dichlorodiisopropyl ether	4	3	11	21	1,3,5-trichlorobenzene	4	21	2	3
1,1-dichloroethane	4	1	2	10	1,1,1-trichloroethane	4	1	2	10
1,2-dichloroethane	4	1	2	10	1,1,2-trichloroethane	4	2	9	20
1,1-dichloroethene	4	1	2	10	trichloroethene	4	1	2	10
cis-1,2-dichloroethene	4	1	2	10	trichloromethane (chloroform)	4	1	2	10
trans-1,2-dichloroethene	4	1	2	10	1,1,2-trichlorotrifluoroethane	4	1	2	10
dichloromethane	4	1	2	10	1,2,4-trimethylbenzene (pseudocumene)	4	2	3	13
1,2-dichloropropane	4	1	2	10	1,3,5-trimethylbenzene (mesitylene)	4	2	3	13
cis-1,3-dichloropropene	4	2	9	10	vinyl benzene (styrene)	4	2	13	21
trans-1,3-dichloropropene	4	2	9	10	vinyl chloride (chloroethene)	4	1	2	10

Table B.1 *(continued)*

Name	Internal standard substances according to Table B.2				Name	Internal standard substances according to Table B.2			
2,3-dichloropropene	4	1	2	10	*o*-xylene	4	2	13	21
1,1-dimethylpropyl-methyl ether, *tert*-amyl methyl ether (TAME)	4	1	2	10	*m*-/*p*-xylene	4	2	13	21
ethyl benzene	4	2	13	21					

Table B.2 lists examples of internal standards which have been tested as part of the standardization work and which have proved to be suitable for the purpose.

Table B.2 — Examples of suitable internal standards

No.	Name	Molecular formula	CAS-RN	EC-Number	Molar mass g/mol	Target ion *m*/*z*	Qualifier ion 1 *m*/*z*
1	benzene-d6	C_6D_6	1076-43-3	214-061-8	84,15	84,1	56,1
2	fluorobenzene	C_6H_5F	462-06-6	207-321-7	96,10	96,0	70,0
3	1,2-dichlorobenzene-d4	$C_6Cl_2D_4$	2199-69-1	218-606-0	151,03	151,9	149,9
4	toluene-d8	C_7D_8	2037-26-5	218-009-5	100,11	98,0	100,1
5	methyl *tert-butyl* ether-d3 (MTBE-d3)	$C_5H_9D_3O$	29366-08-3		91,15	73,0	73,0
6	methyl tert-butyl ether-d9 (MTBE-d9)	$C_5H_3D_9O$	1219795-06-8		97,20	79,0	80,0
7	1,4-difluorobenzene	$C_6H_4F_2$	540-36-3	208-742-9	114,09		
8	1,3,5-trichlorobenzene-d3	$C_6Cl_3D_3$	1198-60-3		184,47	183,0	148,0
9	2-bromo-1-chloropropane	C_3H_6BrCl	3017-95-6	221-157-3	157,44	41,0	77,0
10	1,2-dichloroethane-d4	$C_2Cl_2D_4$	17060-07-0	17060-07-0	102,98	65,0	67,0
11	1-bromo-2-chloroethane	C_2H_4BrCl	107-04-0	203-456-0	143,41	63,0	
12	chlorobenzene-d5	C_6D_5Cl	3114-55-4	221-482-0	117,59	117	119
13	*o*-xylene-d10	C_8D_{10}	56004-61-6	259-942-8	116,25	98,0	116,0
14	bromobenzene-d5	C_6D_5Br	4165-57-5	224-013-8	162,05	161,0	163,0
15	naphthalene-d8	$C_{10}D_8$	1146-65-2	214-552-7	136,22	136,0	
16	2-hexanone	$C_6H_{12}O$	591-78-6	209-731-1	100,16	58,0	85
17	1,1,1-trichloroethane-d3	$C_2D_3Cl_3$	2747-58-2		136,42		
18	α,α,α-trifluorotoluene	$C_7H_5F_3$	98-08-8	202-635-0	146,11		
19	4-bromofluorobenzene	C_6H_4BrF	460-00-4	207-300-2	175,00	95,0	174,0
20	bromoethane-d5	C_2H_5Br	74-96-4	200-825-8	108,97	113,0	115,0
21	2,3,4-trifluorotoluene	$C_7H_5F_3$	193533-92-5		146,11	145,0	146,0

Annex C
(informative)

Example of headspace and gas chromatographic conditions

C.1 Headspace conditions

Headspace injection volume:	2,5 ml
Injection volume:	1 ml
Syringe temperature:	80 °C
Incubation temperature:	80 °C
Incubation time:	30 min
Agitator time:	5 s
Agitator time (off):	2 s

C.2 GC conditions

Detector:	MS-quadrupole
Detector temperature:	300 °C
Temperature of the transfer line:	300 °C
Injector temperature:	90 °C/1 min/10 °C s^{-1}/280 °C/5 min isothermal
Ionization energy:	70 eV
Capillary column:	DB-624 polyphenylmethyl siloxane (see NOTE), length: 60 m, film thickness: 1,8 µm, diameter: 0,32 mm
Temperature program:	35 °C/1 min isothermal → 4 °C min^{-1} → 120 °C → 4 °C min^{-1} → 140 °C → 15 min isothermal → 25 °C min^{-1} → 255 °C → 1,5 min isothermal
Sample introduction:	Headspace autosampler
Injection:	Split ratio 1:1
Column flow:	1,2 ml/min
Carrier gas:	Helium

NOTE DB-624 polyphenylmethyl siloxane is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Annex D
(informative)

Performance data

An interlaboratory trial for validation was conducted in March 2013 with the participation of 21 laboratories. Labs from three different countries, Germany, Switzerland and Austria, participated in the interlaboratorial trial. Drinking water, surface water and treated waste water samples were taken respectively. A fourfold-examination was conducted for each sample.

A sample volume of 10 ml was used by 85 % of the participants in the interlaboratory trial.

A sample volume <10 ml (5 ml) was used for 7,5 % of the participants and a sample volume >10 ml (12,5 ml or 15 ml) was used for 7,5 % of the participants.

40 % of the laboratories did not use a salt addition for the sample preparation. Na_2SO_4 was added to the sample water between 3 g and 5 g by 40 % of the laboratories and NaCl between 2 g and 3 g by 20 % of the laboratories.

A 60 m capillary column was used by 64 % of the laboratories and by 36 % a column of ≤25 m length.

The parameters *cis*-1,3-dichloropropene, *trans*-1,3-dichloropropene, allyl chloride and 1,3,5-trichlorobenzene could not be validated in the interlaboratory trial for validation.

To be able to nevertheless make statements concerning these parameters, the results from the comparative study within the study group are listed in Tables D.2, D.4 and D.6. In case of *cis*-1,3-dichloropropene and *trans*-1,3-dichloropropene, the number of participating laboratories is 7 and higher, but the concentrations specified in the comparative study are higher than in the interlaboratory trial for validation.

In case of allyl chloride, only values from four laboratories are present, with the result that this parameter is not to be regarded as validated.

In case of 1,3,5-trichlorobenzene, only data from two laboratories are available. This parameter is also to be regarded as not validated. As, however, 1,3,5-trichlorobenzene exhibits a similar behaviour to 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene, these two parameters also allow conclusions concerning 1,3,5-trichlorobenzene.

The performance data from this interlaboratory trial for validation were determined according to ISO 5725-2. The results are given in Tables D.1, D.3 and D.5. The validation document contains further data on the interlaboratory trial.

Table D.1 — Performance data according to ISO 5725-2 for volatile organic compounds, sample 1 drinking water

Compound	l	n	o %	X µg/l	$\bar{\bar{x}}$ µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
benzene	20	80	4,8	0,150	0,144 1	96,1	0,030 5	21,2	0,009 4	6,5
biphenyl	14	56	6,7	1,142	0,934 3	81,8	0,280 3	30,0	0,093 4	10,0
bromodichloromethane	17	68	0,0	0,158	0,148 7	94,1	0,032 6	21,9	0,009 9	6,7
chlorobenzene	17	68	5,6	0,132	0,120 1	91,0	0,023 8	19,9	0,007 7	6,4
2-chloro-1,3-butadiene (chloroprene)	14	55	12,7	0,193	0,136 9	70,9	0,048 3	35,3	0,007 2	5,3
2-chlorotoluene	14	56	17,6	0,131 0	0,119 1	90,9	0,031 2	26,2	0,008 7	7,3
3-chlorotoluene	16	64	5,9	0,211 0	0,181 8	86,2	0,033 6	18,5	0,014	7,7
4-chlorotoluene	16	64	5,9	0,263 0	0,204 1	77,6	0,056 9	27,9	0,011 7	5,8
dibromochloromethane	18	72	0,0	0,263 0	0,284 5	108,2	0,058 7	20,7	0,016 1	5,7
1,2-dibromoethane	16	64	0,0	0,167 0	0,184 9	110,7	0,061 2	33,1	0,017 2	9,3
1,2-dichlorobenzene	17	68	5,6	0,159 0	0,146 4	92,1	0,022 6	15,5	0,012 2	8,3
1,3-dichlorobenzene	18	72	5,3	0,194 0	0,176 2	90,8	0,025 9	14,7	0,013 3	7,6
1,4-dichlorobenzene	16	62	6,1	0,176 0	0,164 0	93,2	0,020 3	12,4	0,011 6	7,1
dichlorodiisopropyl ether	13	51	19,0	1,142 0	1,049 5	91,9	0,098 3	9,4	0,061 8	5,9
1,1-dichloroethane	17	66	5,7	0,134 0	0,138 9	103,7	0,045 0	32,4	0,008 6	6,2
1,2-dichloroethane	15	60	16,7	0,140 0	0,153 1	109,4	0,037 9	24,8	0,011 6	7,6
1,1-dichloroethene	16	64	8,6	0,167 0	0,181 3	108,6	0,052 5	28,9	0,010 2	5,6
cis-1,2-dichloroethene	16	64	15,8	0,228 0	0,259 9	114,0	0,069 5	26,7	0,013 1	5,0
trans-1,2-dichloroethene	18	71	10,1	0,440 0	0,417 1	94,8	0,070 9	17,0	0,018 4	4,4
dichloromethane	19	76	0,0	1,055 0	0,944 7	89,5	0,194 3	20,6	0,054 0	5,7
1,2-dichloropropane	17	68	0,0	0,351 0	0,326 6	93,0	0,069 1	21,2	0,017 1	5,2
2,3-dichloropropene	10	40	9,1	0,193 0	0,092 3	47,8	0,056 6	61,4	0,007 5	8,2
1,1-dimethylpropyl-methyl ether, *tert*-amyl methyl ether (TAME)	17	67	0,0	0,351 0	0,318 9	90,9	0,064 8	20,3	0,018 0	5,7
ethyl benzene	19	76	0,0	0,158 0	0,143 0	90,5	0,028 8	20,1	0,008 1	5,7
ethyl *tert*-butyl ether (ETBE)	18	72	5,3	0,351 0	0,327 1	93,2	0,057 1	17,5	0,012 9	3,9
hexachlorobutadiene	19	76	0,0	0,211 0	0,197 2	93,5	0,040 4	20,5	0,017 0	8,6
hexachloroethane	15	60	3,2	0,176 0	0,165 5	94,0	0,042 9	25,9	0,013 0	7,9
isopropylbenzene (cumene)	20	79	1,3	0,149 0	0,132 6	89,0	0,027 1	20,4	0,008 6	6,5
methyl *tert*-butyl ether (MTBE)	17	68	10,5	0,211 0	0,209 5	99,3	0,034 1	16,3	0,013 2	6,3

l number of laboratories after outlier rejection.

n number of test results after outlier rejection.

o percentage of outliers.

X conventionally correct value of the test sample.

$\bar{\bar{x}}$ overall mean of results (without outliers).

η recovery rate.

s_R reproducibility standard deviation.

$C_{V,R}$ coefficient of variation of reproducibility.

s_r repeatability standard deviation.

$C_{V,r}$ coefficient of variation of repeatability.

Table D.1 *(continued)*

Compound	*l*	*n*	*o* %	*X* µg/l	$\overline{\overline{x}}$ µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
naphthalene	18	72	5,3	0,545 0	0,515 0	94,5	0,074 1	14,4	0,038 3	7,5
n-propylbenzene	19	76	5,0	0,167	0,146 6	87,8	0,023 3	15,9	0,007 9	5,4
1,1,1,2-tetrachloroethane	16	64	11,1	0,149 0	0,140 9	94,6	0,024 1	17,1	0,015 3	10,9
tetrachloroethene	18	72	14,3	0,167 0	0,149 3	89,4	0,032 1	21,5	0,009 5	6,4
tetrachloromethane	21	83	0,0	0,159 0	0,146 1	91,9	0,026 5	18,1	0,012 5	8,6
toluene	18	72	10,0	0,263 0	0,247 2	94,0	0,056 4	22,8	0,010 9	4,4
tribromomethane (bromoform)	17	68	15,0	0,439 0	0,438 0	99,8	0,075 5	17,2	0,024 7	5,6
1,2,3-trichlorobenzene	17	68	0,0	0,158 0	0,154 5	97,8	0,032 7	21,2	0,019 0	12,3
1,2,4-trichlorobenzene	14	55	17,9	0,211 0	0,195 8	92,8	0,020 5	10,5	0,011 6	5,9
1,1,1-trichloroethane	17	66	19,5	0,167 0	0,154 6	92,6	0,031 5	20,4	0,007 3	4,7
1,1,2-trichloroethane	17	65	0,0	0,263 0	0,269 4	102,4	0,048 2	17,9	0,022 8	8,5
trichloroethene	21	83	1,2	0,141 0	0,128 7	91,3	0,022 2	17,2	0,008 9	7,0
trichloromethane (chloroform)	19	74	9,8	0,141 0	0,140 2	99,4	0,029 2	20,8	0,010 3	7,4
1,1,2-trichlorotrifluoroethane	19	76	0,0	0,167 0	0,174 5	104,5	0,066 0	37,9	0,013 8	7,9
1,2,4-trimethylbenzene	18	72	5,3	0,141 0	0,123 4	87,5	0,023 3	18,9	0,008 3	6,7
1,3,5-trimethylbenzene	18	72	5,3	0,194 0	0,169 4	87,3	0,029 4	17,4	0,009 1	5,4
vinyl benzene (styrene)	18	72	10,0	0,633 0	0,398 7	63,0	0,105 1	26,4	0,020 9	5,2
vinyl chloride (chloroethene)	20	79	4,8	1,757 0	1,700 4	96,8	0,465 2	27,4	0,096 1	5,7
o-xylene	20	79	1,3	0,167 0	0,151 4	90,7	0,030 3	20,0	0,007 3	4,8
m-/*p*-xylene	18	72	5,3	0,281 0	0,245 9	87,5	0,043 1	17,5	0,013 5	5,5

l	number of laboratories after outlier rejection.
n	number of test results after outlier rejection.
o	percentage of outliers.
X	conventionally correct value of the test sample.
$\overline{\overline{x}}$	overall mean of results (without outliers).
η	recovery rate.
s_R	reproducibility standard deviation.
$C_{V,R}$	coefficient of variation of reproducibility.
s_r	repeatability standard deviation.
$C_{V,r}$	coefficient of variation of repeatability.

The results listed in Table D.2 were determined in a comparative study within the study group.

Table D.2 — Performance data according to ISO 5725-2 for volatile organic compounds, sample 1 drinking water, not validated (from the comparative study)

Compound	*l*	n	*o* %	*X* µg/l	$\overline{\overline{x}}$ µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
allyl chloride	4	16	0	4,500	3,220	71,6	0,843 0	26,2	0,244 8	7,6
cis-1,3-dichloropropene	7	28	12,5	2,250	1,716	76,3	0,698 7	40,7	0,106 9	6,23
trans-1,3-dichloropropene	8	32	0	4,500	3,640	80,9	1,264	35,3	0,225 8	6,2
1,3,5-trichlorobenzene	2	8	0	0,450 0	0,348 6	77,5	0,186 1	53,4	0,011 8	3,38

For explanation of symbols, see Table D.1.