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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)

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)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

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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