INTERNATIONAL STANDARD

ISO 17943

First edition
2016-04-01

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)

Reference number
ISO 17943:2016(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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*.

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]).

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.

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.

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.

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.

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).

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.

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).

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.

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.

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 ±(0,1 × 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: ±(0,1 × 50 + 10) % = ±15 %, the relative intensity in the sample shall be between 35 % and 65 %;

— I_3: ±(0,1 × 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.

Table 2 — Examples of ions for identification and quantification in mass spectrometric detection

Name (compounds of Table 1)	Selected ions for identification and quantification[a] *m/z*
tert-amyl methyl ether (TAME)	73, 87
benzene	50, 77, 78
bromobenzene	77, (156, 158)
bromochloromethane	(128, 130, 132)
bromodichloromethane	47, (83, 85, 87), (127, 129)
n -butylbenzene	91, 92, 134
sec-butylbenzene	105, 134
tert-butylbenzene	91, 119, 134
chlorobenzene	77, 112
2-chlorotoluene	91, (126, 128)
4-chlorotoluene	91, (126, 128)
dibromochloromethane	(127, 129, 131)
1,2-dibromo-3-chloropropane (DBCP)	75, (155, 157, 159)
1,2-dibromoethane	(107, 109)
dibromomethane	(172, 174, 176)
1,2-dichlorobenzene	146, 148, 150
1,3-dichlorobenzene	146, 148, 150
1,4-dichlorobenzene	146, 148, 150
1,1-dichloroethane	(63, 65)
1,2-dichloroethane	(62, 64)
1,1-dichloroethene	(61, 63), (96, 98)
cis-1,2-dichloroethene	(61, 63), (96, 98)
trans-1,2-dichloroethene	(61, 63), (96, 98)
dichloromethane	(49, 51), (84, 86)
1,2-dichloropropane	63, 76
1,3-dichloropropane	63, (76, 78)
2,2-dichloropropane	(77, 79)
1,1-dichloropropene	(75, 77), (110, 112)
cis -1,3-dichloropropene	(75, 77), 110
trans-1,3-dichloropropene	(75, 77), 110
ethylbenzene	91, 106
ethyl *tert*-butyl ether (ETBE)	57, 59, 87
2-ethyl-4-methyl-1,3-dioxolane	59, 87
2-ethyl-5,5-dimethyl-1,3-dioxane	56, 115
geosmin	97, 111, 112, 125
hexachlorobutadiene	(223, 225, 227), (260, 262)
isopropylbenzene (cumene)	105, 120
4-isopropyltoluene (*p*-cymene)	91, 119, 134
2-methylisoborneol	95, 107
methyl *tert*-butyl ether (MTBE)	57, 73

[a] Other options may be possible. Base peaks often used for quantification are underlined. Groups of ions in brackets belong to the same cluster of a halogen isotope distribution.

Table 2 *(continued)*

Name (compounds of Table 1)	Selected ions for identification and quantification[a] *m/z*
naphthalene	127, 128, 129
n-propylbenzene	91, 120
styrene	78, 103, 104
1,1,1,2-tetrachloroethane	(131, 133, 135)
1,1,2,2-tetrachloroethane	(83, 85), (166, 168)
tetrachloroethene	(129, 131, 133), (164, 166, 168)
tetrachloromethane	(117, 119, 121)
toluene	65, 91, 92
tribromomethane (bromoform)	(79, 81), (171, 173, 175), (251, 253)
1,2,3-trichlorobenzene	(180, 182, 184)
1,2,4-trichlorobenzene	(180, 182, 184)
1,3,5-trichlorobenzene	(180, 182, 184)
1,1,1-trichloroethane	61, (97, 99), (117, 119)
1,1,2-trichloroethane	61, (97, 99)
trichloroethene	(95, 97), (130, 132, 134)
trichloromethane (chloroform)	47, (83, 85, 87)
1,2,3-trichloropropane	75, 110
1,2,4-trimethylbenzene (pseudocumene)	105, 120
1,3,5-trimethylbenzene (mesitylene)	105, 120
vinyl chloride	(62, 64)
m-xylene	91, 105, 106
o-xylene	91, 105, 106
p-xylene	91, 105, 106

[a] Other options may be possible. Base peaks often used for quantification are underlined. Groups of ions in brackets belong to the same cluster of a halogen isotope distribution.

8.4 Blank value measurements

Perform blank value measurements using water (5.2) as specified in 8.1. Use periodic blank value measurements (at least one measurement per sequence) to check the faultless condition of the instruments and chemicals. Blank value measurements shall comprise all steps of the analysis procedure. If blank values are abnormally high (over 50 % of the lowest reporting level), review every step in the procedure and determine the cause by systematic checks so as to be able to eliminate the contamination source. Try to reduce the blank values as much as possible by applying various measures such as avoiding contamination by ambient air and using suitable solvents (5.5), as well as checking the analytical instrumentation (e.g. GC-MS, autosampler).

9 Calibration

9.1 General

Correct calibration requires knowing the retention times of the analytes to be determined (see also Table 1). These shall be determined with aqueous reference solutions of individual reference substances at the specified chromatographic conditions. Furthermore, the fibre used shall be sensitivity sufficient for the substances to be analysed (4.2). The calibration function determined for a substance applies

only to the concentration range covered by it. Moreover, it depends on the operating condition of the gas chromatograph and on the type or age of the fibre and shall be checked at regular intervals.

— For each target compound, calibrate the determination procedure using aqueous individual or, more conveniently, multi-component reference solutions (5.8.4). Adjust the calibration range to the existing requirements.

— Design the total determination procedure such that a linear dependence of measurement signal to concentration is achieved for each compound to be determined (ISO 8466-1). Determine the linear working range using at least five concentration levels (which are distributed as evenly as possible over the working range).

— For routine operation, it is sufficient to recalibrate by measuring two concentration levels. Recalibrate at regular intervals within one sample sequence (e.g. after 10 to 12 samples).

Table 3 gives an explanation of the subscripts used in the formulae and in the following text.

Table 3 — Definition of subscripts

Subscript	Meaning
i	Substance
e	Calibration step
g	Total procedure
j	Consecutive figure for pairs of values
I	Internal standard

9.2 Calibration of the total procedure using the internal standard

The use of an internal standard helps to minimize unavoidable minor errors which may occur throughout the SPME procedure.

The determination of the concentrations will become, to a certain degree, independent of matrix effects in the water sample. It will become relatively independent of a potential deterioration of the fibre performance if recalibration of the reference function is done for routine operation at intervals of, for example, 10 to 12 samples (see 4.2).

NOTE Deterioration of the fibre is an unavoidable process. Under normal operating conditions, the sensitivity of the fibre gradually decreases throughout a longer sample sequence. The fibre may remain in use as long as it still shows the required sensitivity (4.2).

Suitable internal standards are substances having similar physico-chemical properties to those of the substances to be determined with regard to their extraction behaviours and their retention times.

The internal standard itself shall not be present in the water sample to be analysed. The selection of a suitable substance can be difficult and shall be done taking into account the aim of the analysis. Several deuterated and ^{13}C-labelled standards of the substances to be determined given in Table 1 are particularly suitable (5.8). More than one internal standard should be used.

Add a known mass of the internal standard, I, to the water sample prior to analysis (see 8.1).

The mass concentration, ρ_I, shall be the same for both calibration and the sample series. All aqueous multi-component reference solutions suitable for multipoint calibration should contain the same mass concentration of the internal standard (5.8.4).

For calibration of the total procedure, prepare aqueous multi-component reference solutions according to 5.8.4 and treat and analyse them as described in Clause 8 (e.g. in each case, 10 ml).

From the values obtained from the ratios of y_{ieg}/y_{Ieg} and ρ_{ieg}/ρ_{Ieg}, plot the reference function and determine the line of best fit by linear regression according to Formula (1) (ISO 8466-1).

$$\frac{y_{ieg}}{y_{Ieg}} = m_{iIg}\frac{\rho_{ieg}}{\rho_{Ieg}} + b_{iIg} \quad (1)$$

where

y_{ieg} is the measured value (dependent variable) of substance, *i*, during calibration as a function of ρ_{ie}, the unit depending on the evaluation, e.g. area unit;

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

ρ_{ieg} is the (independent variable) mass concentration of substance, *i*, in the aqueous reference solution, in micrograms per litre, µg/l;

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

m_{iIg} is the slope of the reference line of y_{ieg}/y_{Ieg} as a function of the ratio ρ_{ieg}/ρ_{Ieg} (response factor);

b_{iIg} is the ordinate intercept of the reference line, the unit depending on the evaluation.

10 Calculation of the results

For calibration over the total procedure using the internal standard, calculate the mass concentration, ρ_{ig}, of substance, *i*, in the water sample according to Formula (2), taking into account Formula (1).

$$\rho_{ig} = \frac{\frac{y_{ig}}{y_{Ig}} - b_{iIg}}{m_{iIg}} \cdot \rho_{Ig} \quad (2)$$

where

ρ_{ig} is the mass concentration of the target substance, *i*, in the water sample, in micrograms per litre, µg/l;

y_{ig} is the measured value of the target substance, *i*, in the water sample, e.g. in area units;

y_{Ig} is the measured value of internal standard, I, in the water sample, the unit depending on the evaluation, e.g. area unit;

ρ_{Ig} is the mass concentration of internal standard, I, in the water sample, in micrograms per litre, µg/l;

b_{iIg}, m_{iIg} see Formula (1).

11 Expression of results

The analytical results obtained using this International Standard are subject to an uncertainty which needs to be taken into account when interpreting the results. In this International Standard, water samples are spiked with various concentrations of volatile organic compounds for calculating the reproducibility as a percentage and expressed as reproducibility coefficient of variation, $C_{V,R}$. Examples of these values are given in Tables F.1, F.2, F.3, F.4, and F.5.

The mass concentration, in micrograms per litre, of the individual compounds listed in Table 1 shall be reported to two significant figures. When the mass concentration is <0,1 µg/l, only one significant figure shall be reported.

EXAMPLES

trichloromethane (chloroform)	11 µg/l
tetrachloroethene	4,1 µg/l
o-xylene	0,17 µg/l
vinyl chloride	0,09 µg/l
2-methylisoborneol	0,01 µg/l

12 Test report

This test report shall contain at least the following information:

a) the test method used, together with a reference to this International Standard, i.e. ISO 17943:2016;

b) all information necessary for the complete identification of the water sample;

c) relevant information about the sampling method used;

d) the test results obtained, expressed in accordance with Clause 11;

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

Annex A
(informative)

Examples of suitable SPME fibres

Table A.1 lists some examples of SPME-fibres which have been tested within standardization work and which have proved to be suitable for the purpose. The highest sensitivity for the majority of substances of Table 1 can be achieved using CAR/PDMS[a] fibres. Other fibres can be used as well if their suitability has been established in preliminary tests.

Table A.1 — Examples of suitable SPME fibres

Type of fibre (adsorbent)	Abbreviation	Film thickness	Fibre length
Carboxen® [a] Polydimethylsiloxane	CAR/PDMS[a]	75 µm or 85 µm	1 cm
Divinylbenzene Carboxen® [a] Polydimethylsiloxane	DVB/CAR/PDMS[a]	50/30 µm	1 cm

[a] Carboxen®, CAR/PDMS, and DVB/CAR/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.

Annex B
(informative)

Examples of GC columns

For the analysis of the volatile organic compounds given in Table 1 by means of gas chromatography, several capillary GC columns can be used. It is recommended to use columns with a length of more than 30 m and a film thickness of >1 µm. Special GC columns for analysing these compounds are available from different manufactures. Table B.1 lists some examples of capillary columns which have been tested as part of the standardization work and which have proved to be suitable for the purpose. Other columns can be used as well if their suitability has been established in preliminary tests.

Table B.1 — Examples of suitable GC capillary columns

Suitable phases and commercially available products	Dimension
Medium polar phase: 6 % cyanopropylphenyl, 94 % dimethylpolysiloxane	Length: 60 m, I.D.: 0,25 mm, film: 1,4 µm
Medium polar phase: 6 % cyanopropylphenyl, 94 % dimethylpolysiloxane	Length: 60 m, I.D.: 0,32 mm, film: 1,8 µm
Crossbond[a] Silarylene phase: 5 % phenyl arylene; 95 % dimethylpolysiloxane	Length: 30 m, I.D.: 0,25 mm, film: 0,25 µm
Specific VOC-type GC capillary column with a diphenyl-/dimethylpolysiloxane phase	Length: 60 m, I.D.: 0,32mm, film: 1,5 µm
Crossbond® [a] 6 % cyanopropylphenyl, 94 % dimethylpolysiloxane USP G43	Length: 60 m, I.D.: 0,25 mm, film: 1,4 µm Length: 60 m, I.D.: 0,32 mm, film:1,8 µm Length: 30 m, I.D.: 0,25 mm, film: 1,4 µm
Crossbond® [a] 5 % phenyl, 95 % dimethylpolysiloxane USP G27	Length: 30 m, I.D.: 0,25 mm, film: 0,25 µm Length: 60 m, I.D.: 0,32 mm, film: 1 µm
Medium polar VOCOL®-column [a]	Length: 60 m, I.D.: 0,25 mm, film: 1,5 µm
Rtx®-VMS (proprietary Crossbond® phase) [a]	Length: 60 m, I.D.: 0,32 mm, film: 1,8 µm
Rtx®-Volatiles (proprietary Crossbond® diphenyl/dimethyl polysiloxane phase) [a]	Length: 60 m, I.D.: 0,25 mm, film: 1,00 µm
[a] Crossbond®-columns: USP G43 and USP G27, Rtx®-VMS, Rtx®-Volatiles and VOCOL® 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	

Annex C
(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 C.1. The internal standard substances most frequently used by participants of the interlaboratory trial for validation carried out in June 2013 (see Tables F.1 and F.2) are indicated by their numbers according to Table C.2. Other substances can be used as well if their suitability has been established in preliminary tests.

Table C.1 — Internal standard substances

Name	Internal standard substances according to Table C.2				Name	Internal standard substances according to Table C.2			
tert-amyl methyl ether (TAME)	3	1	7	5	ethyl *tert*-butyl ether (ETBE)	3	1	7	5
benzene	7	1	5	4	2-ethyl-4-methyl-1,3-dioxolane	5	1	8	3
bromobenzene	5	4	1	7	2-ethyl-5,5-dimethyl-1,3-dioxane	5	4	16	3
bromochloromethane	1	5	8	7	geosmin	5	4	19	1
bromodichloromethane	1	5	8	7	hexachlorobutadiene	5	4	16	8
n-butylbenzene	5	4	16	1	isopropylbenzene (cumene)	5	16	4	1
sec-butylbenzene	5	4	16	1	4-isopropyltoluene (*p*-cymene)	5	4	1	16
tert-butylbenzene	5	4	16	1	2-methylisoborneol	5	4	19	1
chlorobenzene	5	1	4	14	methyl *tert*-butyl ether (MTBE)	3	1	7	8
2-chlorotoluene	5	4	1	16	naphthalene	5	4	19	1
4-chlorotoluene	5	4	1	16	*n*-propylbenzene	5	4	1	13
dibromochloromethane	5	1	8	22	styrene	5	16	1	4
1,2-dibromo-3-chloropropane (DBCP)	5	4	8	1	1,1,1,2-tetrachloroethane	5	1	16	7
1,2-dibromoethane	5	1	8	12	1,1,2,2-tetrachloroethane	5	8	4	16
dibromomethane	1	5	8	7	tetrachloroethene	5	1	8	16
1,2-dichlorobenzene	5	4	1	14	tetrachloromethane	7	1	8	5
1,3-dichlorobenzene	5	4	1	13	toluene	5	1	7	23
1,4-dichlorobenzene	5	4	1	13	tribromomethane (bromoform)	5	8	16	4
1,1-dichloroethane	1	8	5	7	1,2,3-trichlorobenzene	5	4	1	23
1,2-dichloroethane	8	1	5	7	1,2,4-trichlorobenzene	5	4	1	23
1,1-dichloroethene	1	8	7	5	1,1,1-trichloroethane	7	1	8	5
cis-1,2-dichloroethene	1	8	7	5	1,1,2-trichloroethane	5	1	8	3
trans-1,2-dichloroethene	1	8	7	5	trichloroethene	1	5	7	8
dichloromethane	1	7	8	5	trichloromethane (chloroform)	1	7	8	5
1,2-dichloropropane	1	5	8	7	1,2,3-trichloropropane	5	4	8	16
1,3-dichloropropane	5	1	8	22	1,2,4-trimethylbenzene (pseudocumene)	5	4	16	13

Table C.1 *(continued)*

Name	Internal standard substances according to Table C.2				Name	Internal standard substances according to Table C.2			
2,2-dichloropropane	1	5	7	8	1,3,5-trimethylbenzene (mesitylene)	5	4	16	13
1,1-dichloropropene	1	5	7	8	vinyl chloride	1	8	5	7
cis-1,3-dichloropropene	1	5	8	12	*o*-xylene	5	16	1	4
trans-1,3-dichloropropene	5	1	8	22	*p*-xylene	5	16	1	4
ethylbenzene	5	16	4	1					

Table C.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 C.2 — Examples of suitable internal standards

No.	Name	Molecular formula	CAS registry no.	Molar mass g/mol	Density kg/l
1	fluorobenzene	C_6H_5F	462–06–6	96,10	1,024
2	fluorobenzene-d5	C_6D_5F	1423–10–5	101,08	1,078
3	MTBE-d3	$C_5H_9D_3O$	29366–08–3	91,15	0,765
4	1,2-dichlorobenzene-d4	$C_6Cl_2D_4$	2199–69–1	151,03	1,341
5	toluene-d8	C_7D_8	2037–26–5	100,11	0,943
6	2-bromo-1-chloropropane	C_3H_6BrCl	127054–38–0	157,44	1,537
7	benzene-d6	C_6D_6	1076–43–3	84,15	0,948
8	1,2-dichloroethane-d4	$C_2Cl_2D_4$	17060–07–0	102,94	1,307
9	geosmin-d3	$C_{12}H_{19}D_3O$	135441–88–2	185,32	1,002
10	2-methylisoborneol-d3	$C_{11}H_{17}D_3O$	135441–89–3	171,29	0,986
11	acenaphthene-d10	$C_{12}D_{10}$	15067–26–2	164,17	—
12	bromoethane-d5	$C_2Br\ D_5$	3675–63–6	113,95	1,527
13	4-bromofluorobenzene	C_6H_4BrF	460–00–4	175,00	1,593
14	chlorobenzene-d5	C_6D_5Cl	3114–55–4	117,59	1,157
15	*n*-decane-d22	$C_{10}D_{22}$	16416–29–8	164,42	0,842
16	ethylbenzene-d10	C_8D_{10}	25837–05–2	116,23	0,949
17	hexane-d14	C_6D_{14}	21666–38–6	100,29	0,767
18	2-isopropyl-3-methoxypyrazine	$C_8H_{12}N_2O$	25773–40–4	152,19	0,996
19	naphthalene-d8	$C_{10}D_8$	1146–65–2	136,22	—
20	trichloroethene-d1	C_2Cl_3D	13291–68–4	132,39	1,474
21	trichloromethane-d1	CCl_3D	865–49–6	120,39	1,500
22	1,2,3-trichloropropane-d5	$C_3Cl_3D_5$	203578–27–2	152,46	0,790
23	trifluorotoluene	$C_7H_5F_3$	98–08–8	146,11	1,190
24	vinyl chloride-d3	C_2ClD_3	6745–35–3	65,52	0,911
25	*o*-xylene-d10	C_8D_{10}	56004–61–6	116,25	0,953
26	*p*-xylene-d10	C_8D_{10}	41051–88–1	116,25	0,948

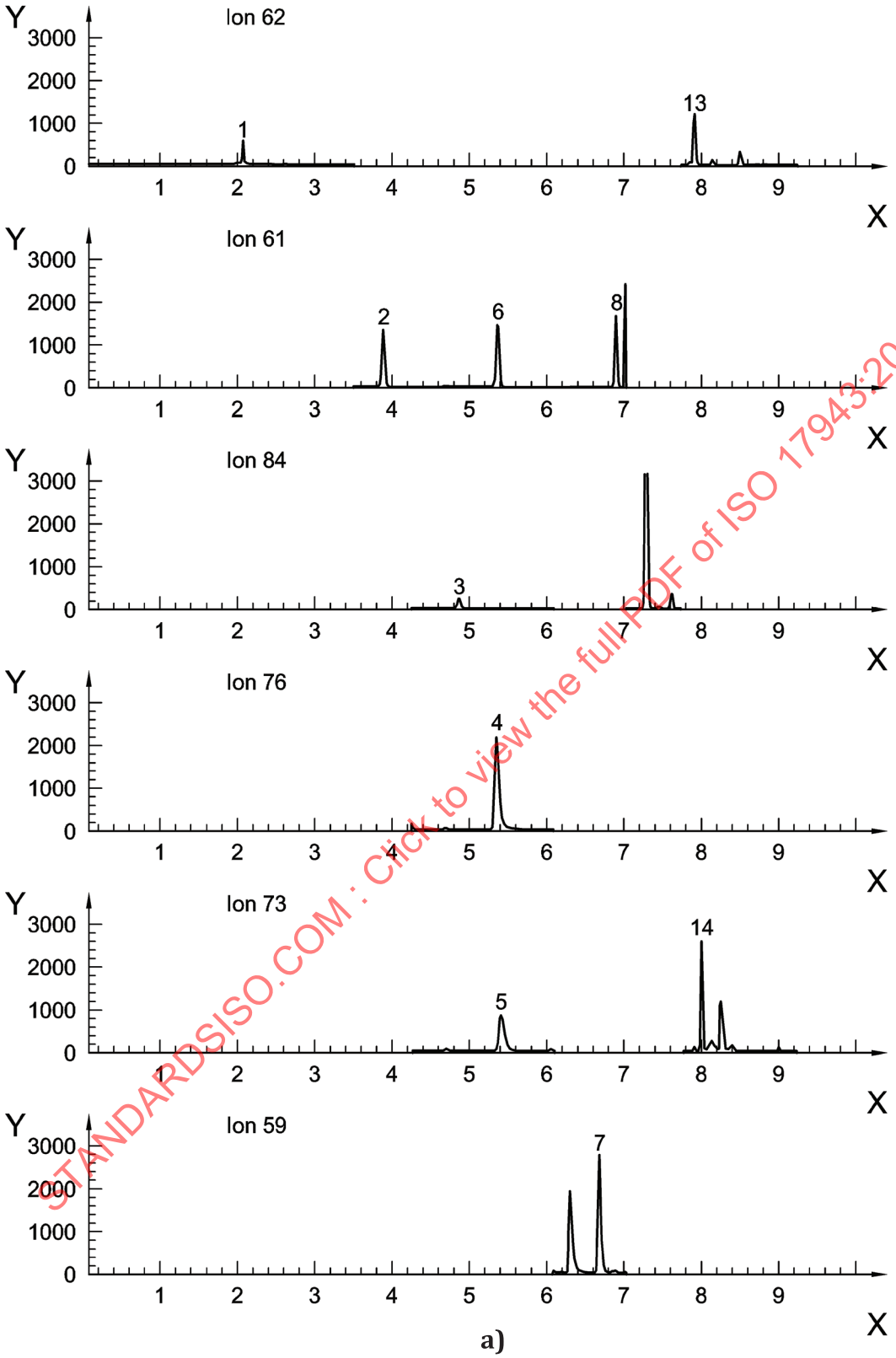
Annex D
(informative)

Suitable gas chromatographic conditions and example chromatograms for compounds of Table 1

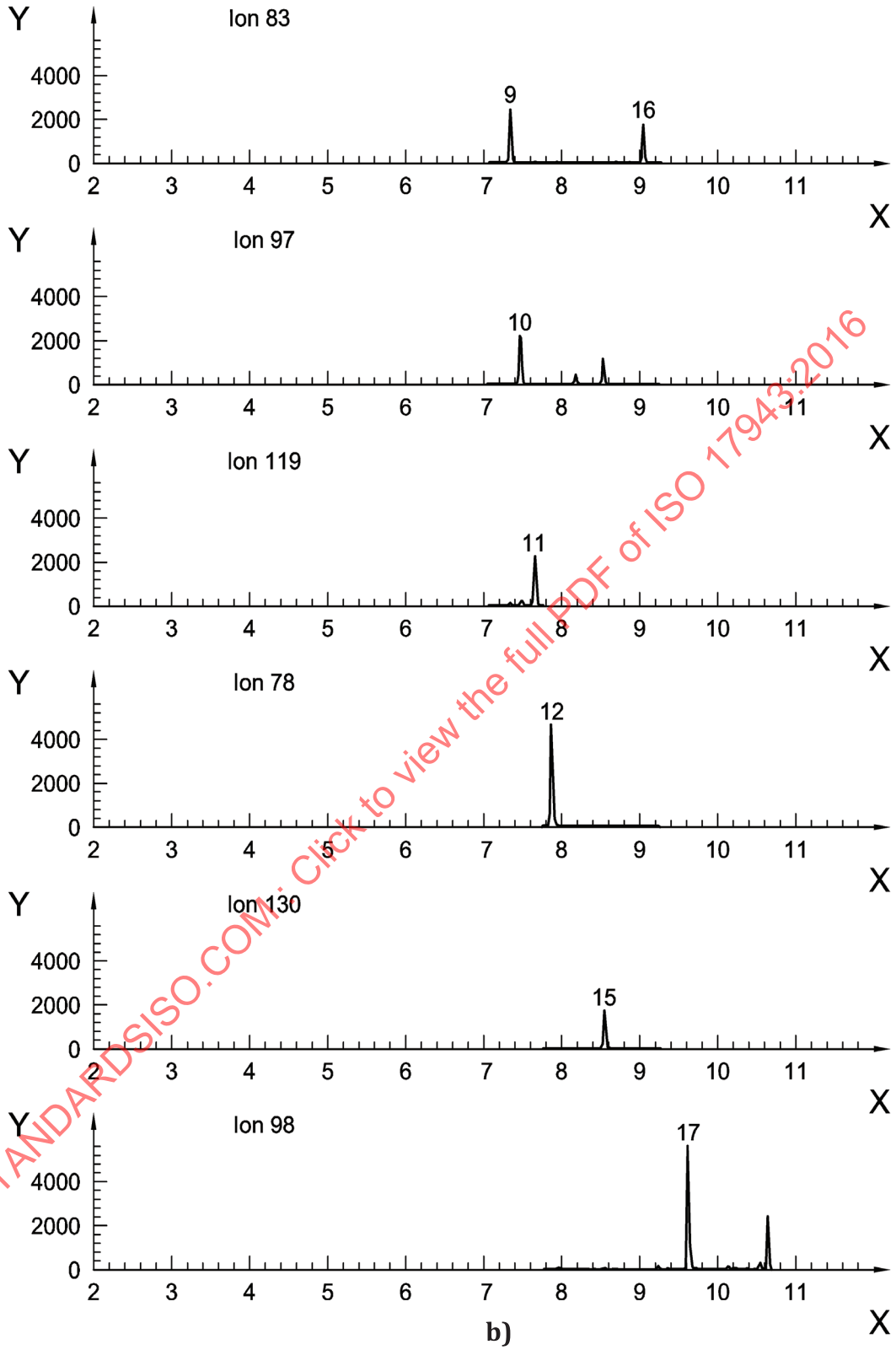
D.1 Gas chromatographic conditions for the chromatograms in Figure D.1

GC equipment:	Agilent 7890A[a], Gerstel MPS 2[a], CTC Cycle Composer-software[a]
SPME-conditions:	According to Clause 8, sample volume: 10 ml, amount NaCl: 3,0 g, fibre: Supelco Carboxen®/PDMS[a] (75 µm), 1 cm, 23 gauge, agitation speed: 250 min^{-1}, incubation time: 10 min, extraction time: 10 min, extraction temperature: 40 °C
Injection:	Liner-I.D.: 1,0 mm, Gerstel CIS 4[a], 260 °C; 10 °C/s to 280 °C; 10 min; split: 1:5
Capillary column:	Phenomenex ZB 624[a], 30 m × 0,25 mm × 1,4 µm
Matrix and range of concentration:	Ground water spiked; 0,25 µg/l to 0,35 µg/l
Carrier gas:	Helium (5.0); 0,9 ml/min
Temperature Programme:	35 °C, 5 min; 20 °C/min to 250 °C; 5 min
MS detector:	Agilent 5975C MSD[a], quadrupole-MS, EI 70 eV, SIM

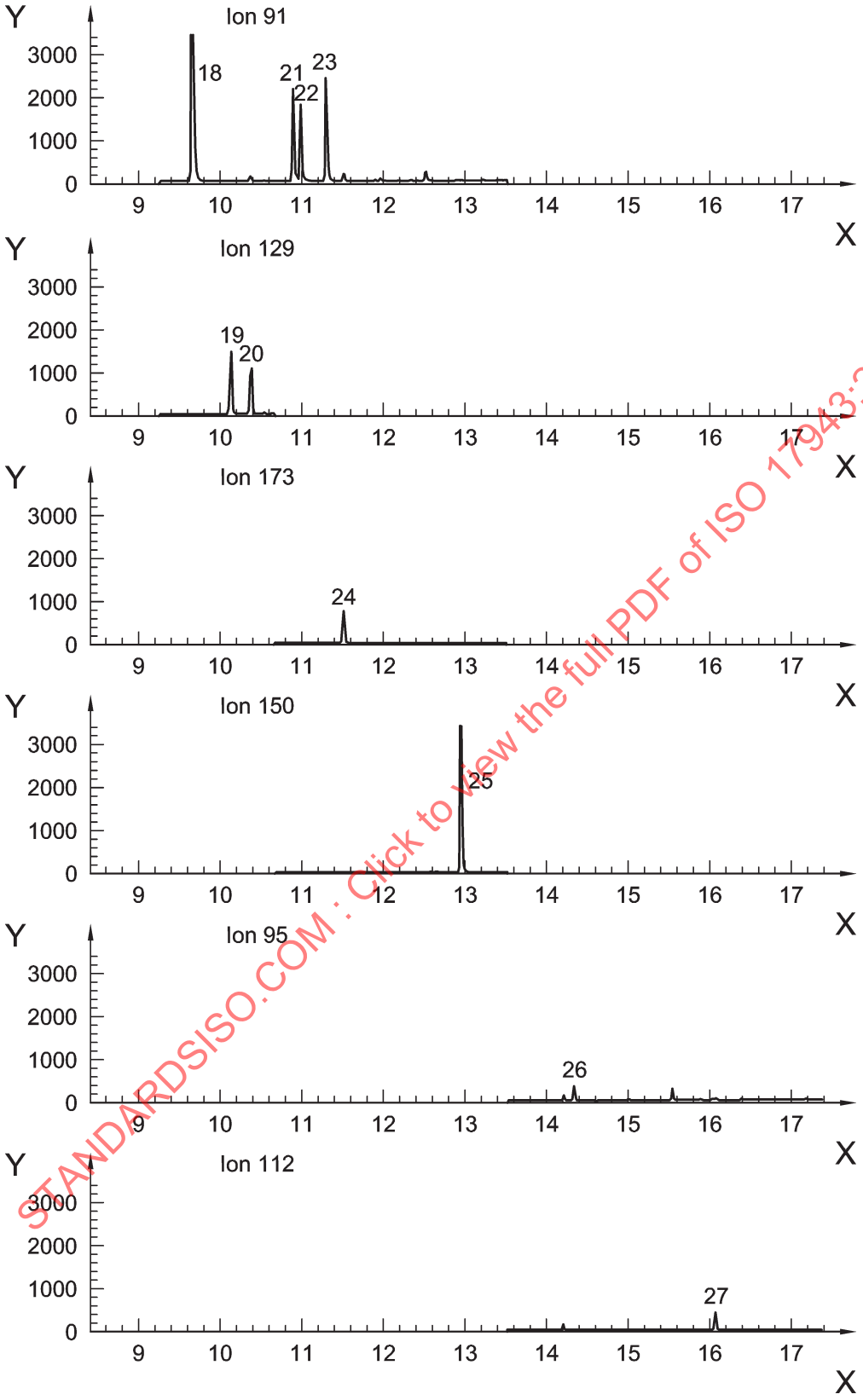
[a] Agilent 7890A, Agilent 5975C MSD, CTC Cycle Composer software, Gerstel MPS 2, Gerstel CIS 4, Supelco Carboxen®/PDMS, and Phenomenex ZB 624 are examples of suitable products which are commercially available. These examples are given only as information for the users of this International Standard and do not constitute an endorsement by ISO of these products.



a)



b)



c)

Figure D.1 — Example 1 of a gas chromatogram

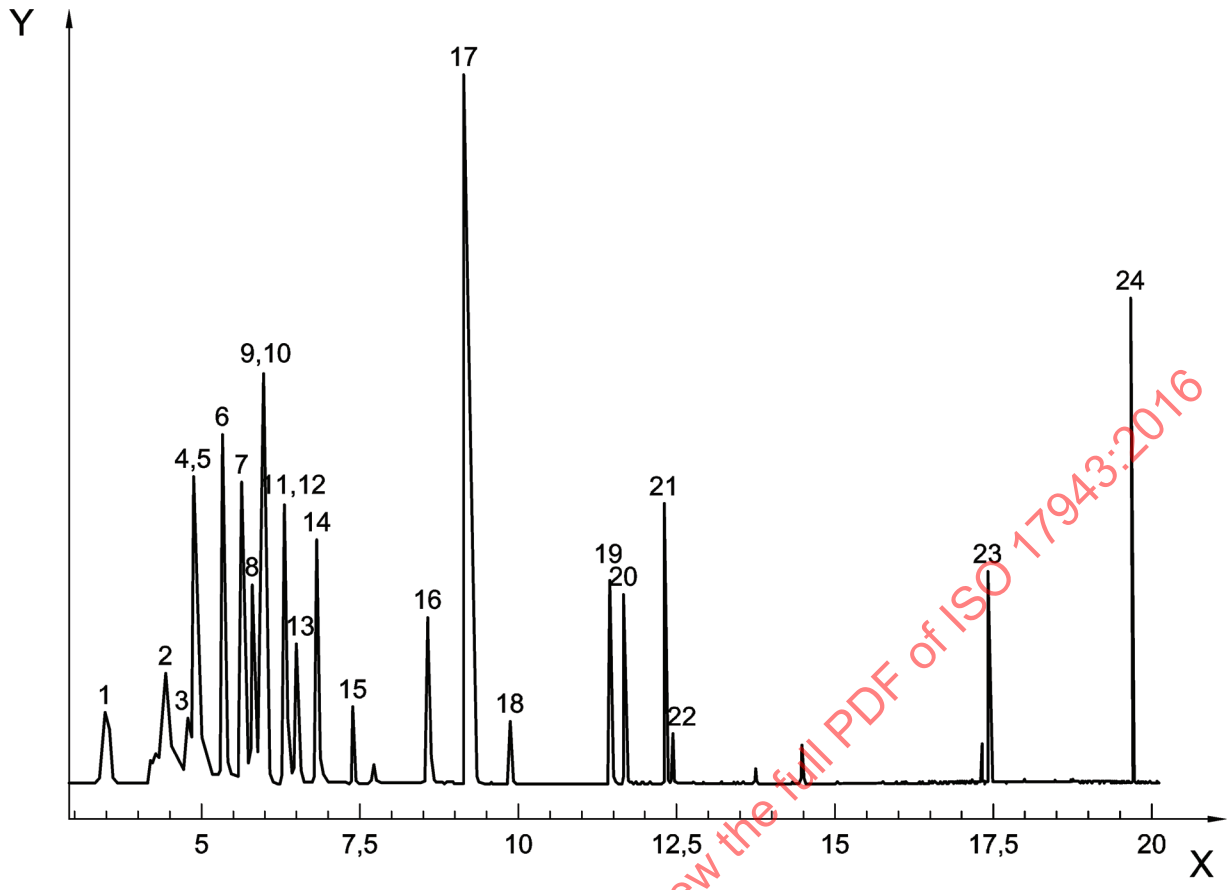
Key

X time, min
Y signal intensity
1 vinyl chloride
2 1,1-dichloroethene
3 dichloromethane
4 MTBE-d3
5 methyl *tert*-butyl ether (MTBE)
6 *trans*-1,2-dichloroethene
7 ethyl *tert*-butyl ether (ETBE)
8 *cis*-1,2-dichloroethene
9 trichloromethane (chloroform)
10 1,1,1-trichloroethane
11 tetrachloromethane
12 benzene
13 1,2-dichloroethane
14 *tert*-amyl methyl ether (TAME)
15 trichloroethene
16 bromodichloromethane
17 toluene-d8
18 toluene
19 tetrachloroethene
20 dibromochloromethane
21 ethylbenzene
22 *m*-/*p*-xylene
23 *o*-xylene
24 tribromomethane (bromoform)
25 1,2-dichlorobenzene-d4
26 2-methylisoborneol
27 geosmin

D.2 Gas chromatographic conditions for the chromatogram in Figure D.2

GC equipment:	Varian CP 3800[a], CTC Combi-PAL[a] (agitator) with SPME-option
SPME-conditions:	According to Clause 8, sample volume: 10 ml, amount NaCl: 3,0 g, fibre: Supelco Carboxen®/PDMS[a] (75 µm), 1 cm, 23 gauge, agitation speed: 250 min^{-1}, incubation time: 10 min, extraction time: 10 min, extraction temperature: 40 °C
Injection:	Varian S/SL-Injector (280 °C, 12 min, splitless), Gerstel CIS 3[a], 60 °C; 10 °C/s to 280 °C
capillary column:	Restek Rtx®-VMS[a], 60 m × 0,32 mm × 1,8 µm
Matrix and range of concentration:	Drinking water spiked; 1,0 µg/l (benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene: 0,2 µg/l)
Carrier gas:	Helium (5.0); 1,6 ml/min (at 35 °C)
Temperature programme:	35 °C, 1 min; 25 °C/min to 100 °C; 7 min, 30 °C/min to 160 °C, 2 min, 40 °C/min to 240 °C, 8 min (runtime: 24,6 min)
MS detector:	Varian 1200 MS[a], EI 70 eV, SIM

[a] Varian CP 3800, CTC Combi-PAL, Supelco Carboxen®/PDMS, Gerstel CIS 3, Restek Rtx®-VMS, and Varian 1200 MS 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.



Key

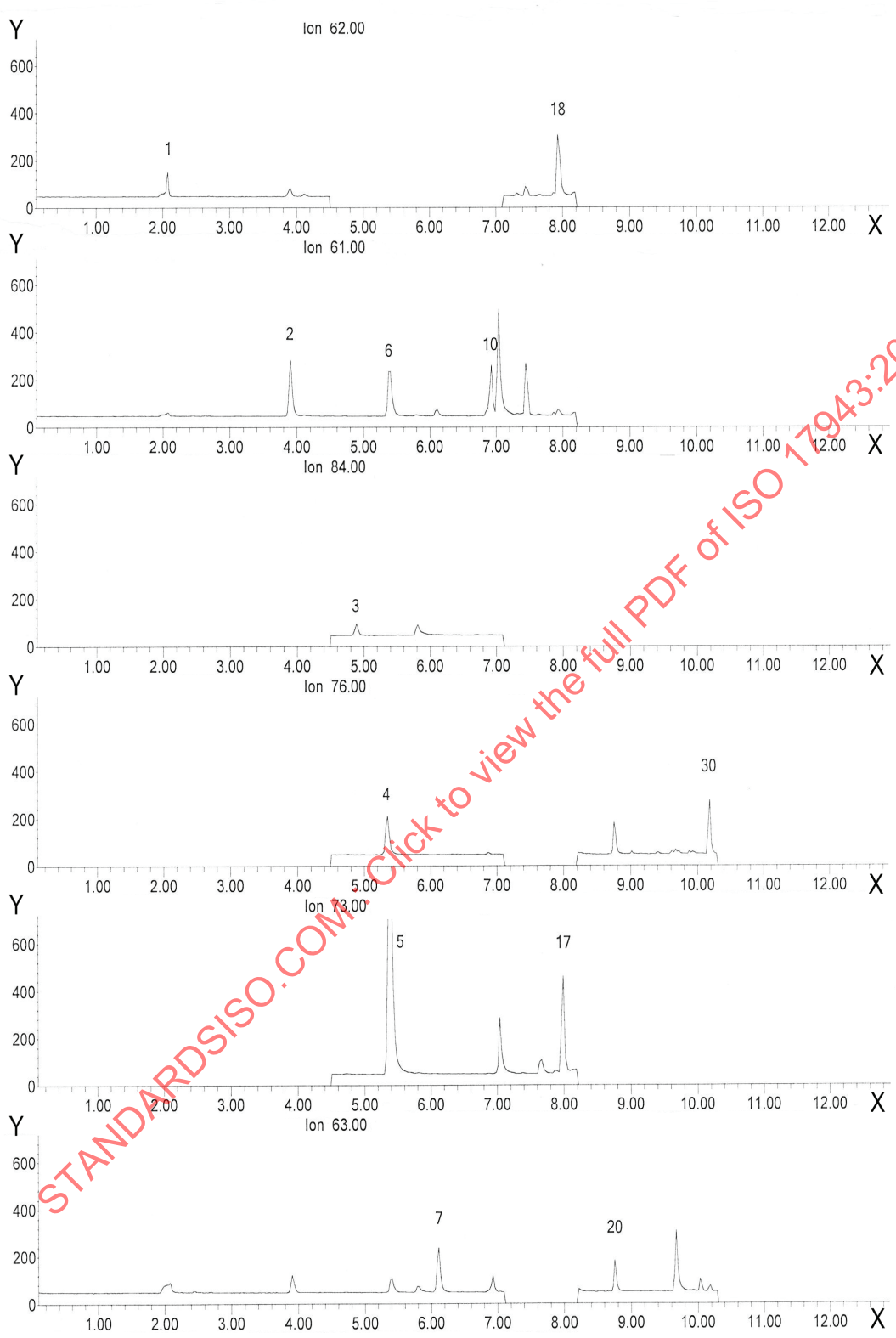
X	time, min	12	benzene
Y	signal intensity	13	1,2-dichloroethane
1	vinyl chloride	14	trichloroethene
2	1,1-dichloroethene	15	bromodichloromethane
3	dichloromethane	16	toluene
4	*trans*-1,2-dichloroethene	17	tetrachloroethene
5	methyl *tert*-butyl ether (MTBE)	18	dibromochloromethane
6	ethyl *tert*-butyl ether (ETBE)	19	ethylbenzene
7	*cis*-1,2-dichloroethene	20	*m*-/*p*-xylene
8	trichloromethane (chloroform)	21	*o*-xylene
9	tetrachloromethane	22	tribromomethane (bromoform)
10	1,1,1-trichloroethane	23	2-methylisoborneol
11	*tert*-amyl methyl ether(TAME)	24	geosmin

Figure D.2 — Example 2 of a gas chromatogram

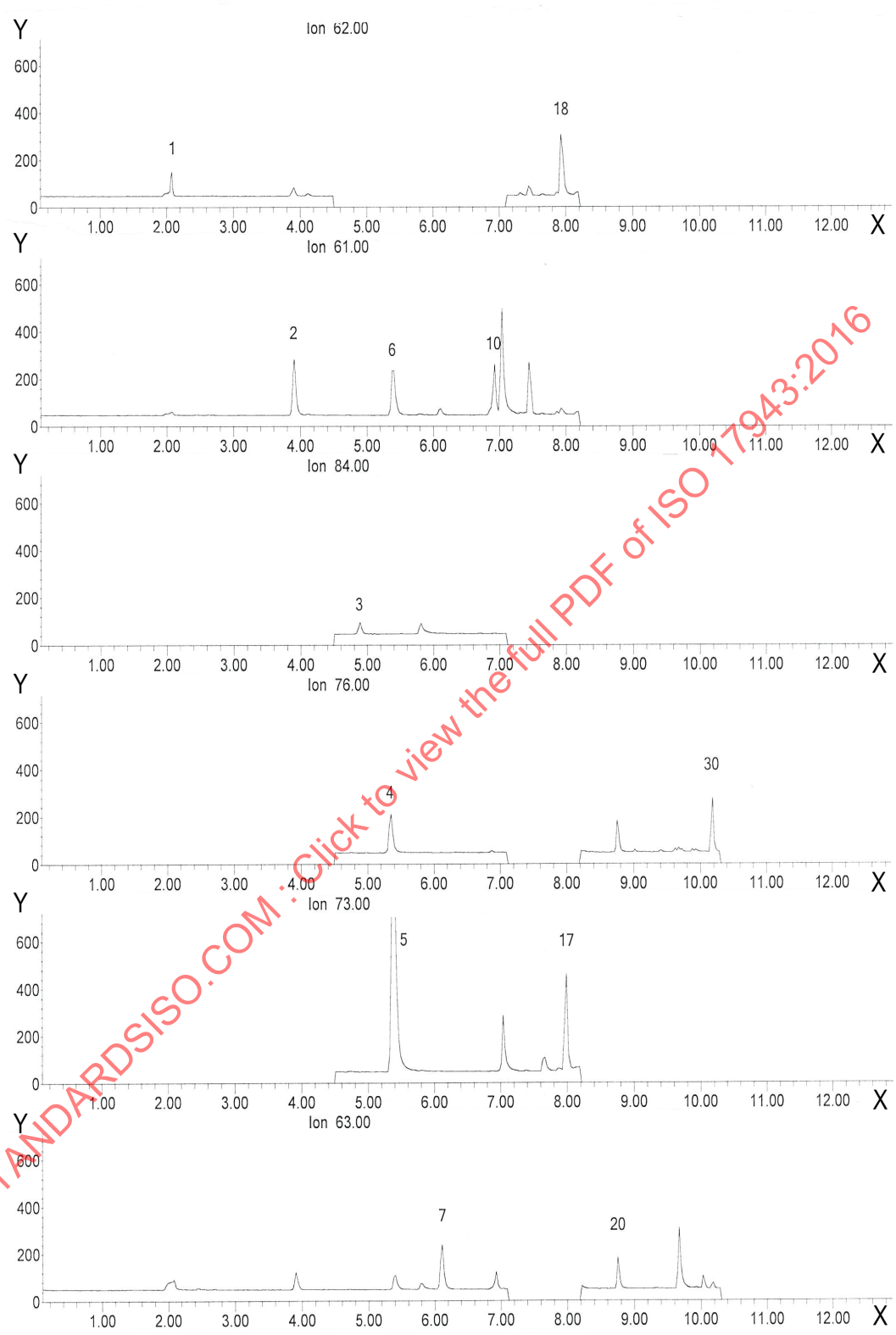
D.3 Gas chromatographic conditions for the chromatograms in Figure D.3

GC equipment:	Agilent 7890A[a], Gerstel MPS 2[a], CTC Cycle Composer-software[a]
SPME-conditions:	According to Clause 8, sample volume: 10 ml, amount NaCl: 3,0 g, fibre: Supelco Carboxen®/PDMS[a] (75 µm), 1 cm, 23 gauge, agitation speed: 250 min^{-1}, incubation time: 10 min, extraction time: 10 min, extraction temperature: 40 °C
Injection:	Liner-I.D.: 1,0 mm, Gerstel CIS 4[a], 260 °C; 10 °C/s to 280 °C; 10 min; split: 1:5
Capillary column:	Phenomenex ZB 624[a], 30 m × 0,25 mm × 1,4 µm
Matrix and range of concentration:	waste water spiked; 0,15 µg/l to 0,20 µg/l
Carrier gas:	Helium (5.0); 0,9 ml/min
Temperature programme:	35 °C, 5 min; 20 °C/min to 250 °C; 10 min
MS detector:	Agilent 5975C MSD[a], quadrupole-MS, EI 70 eV, SIM

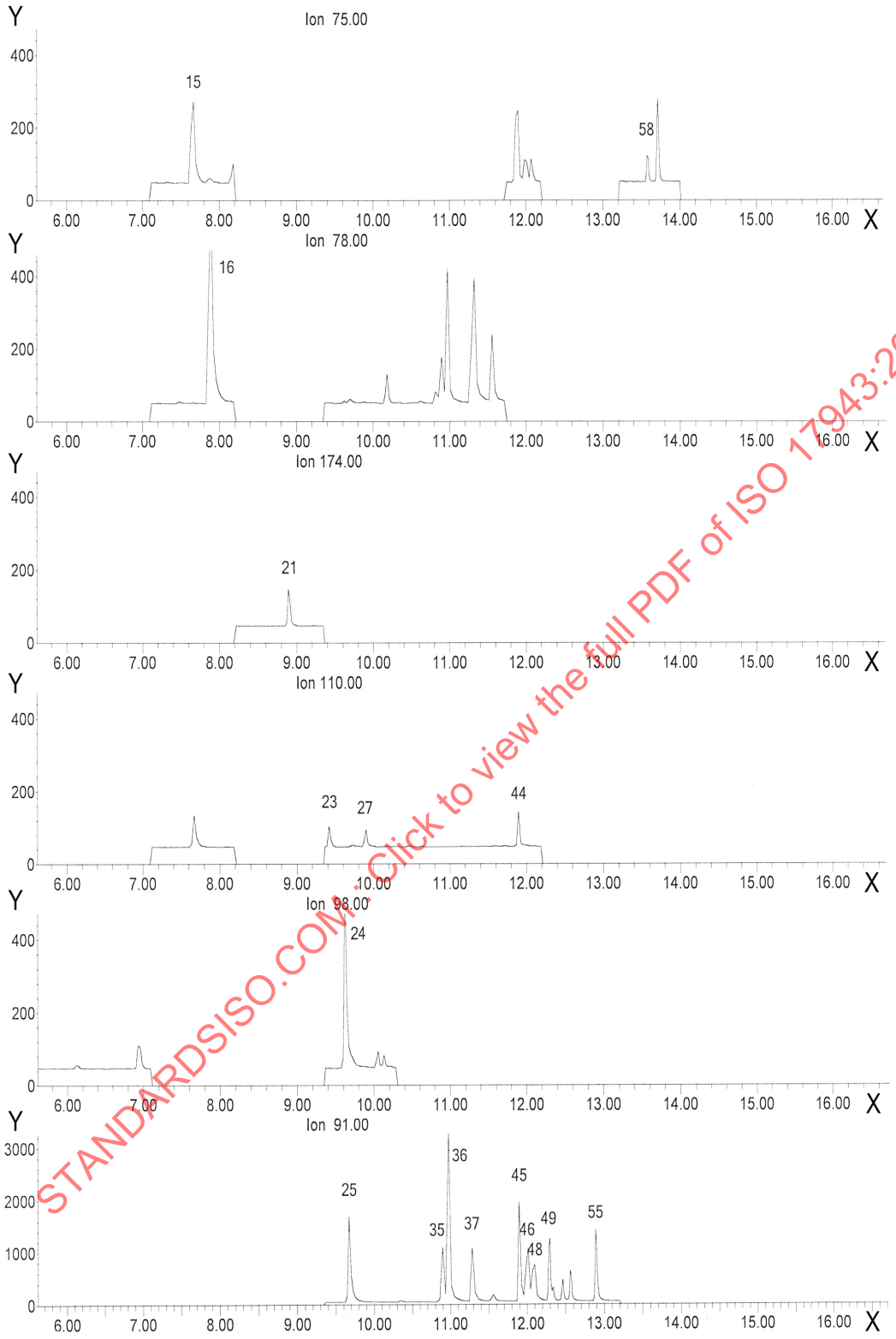
[a] Agilent 7890A, Agilent 5975C MSD, Gerstel MPS 2, Gerstel CIS 4, CTC Cycle Composer-software, Supelco Carboxen®/PDMS, and Phenomenex ZB 624 are examples of suitable products which are commercially available. These examples are given only as information for the users of this International Standard and do not constitute an endorsement by ISO of these products.



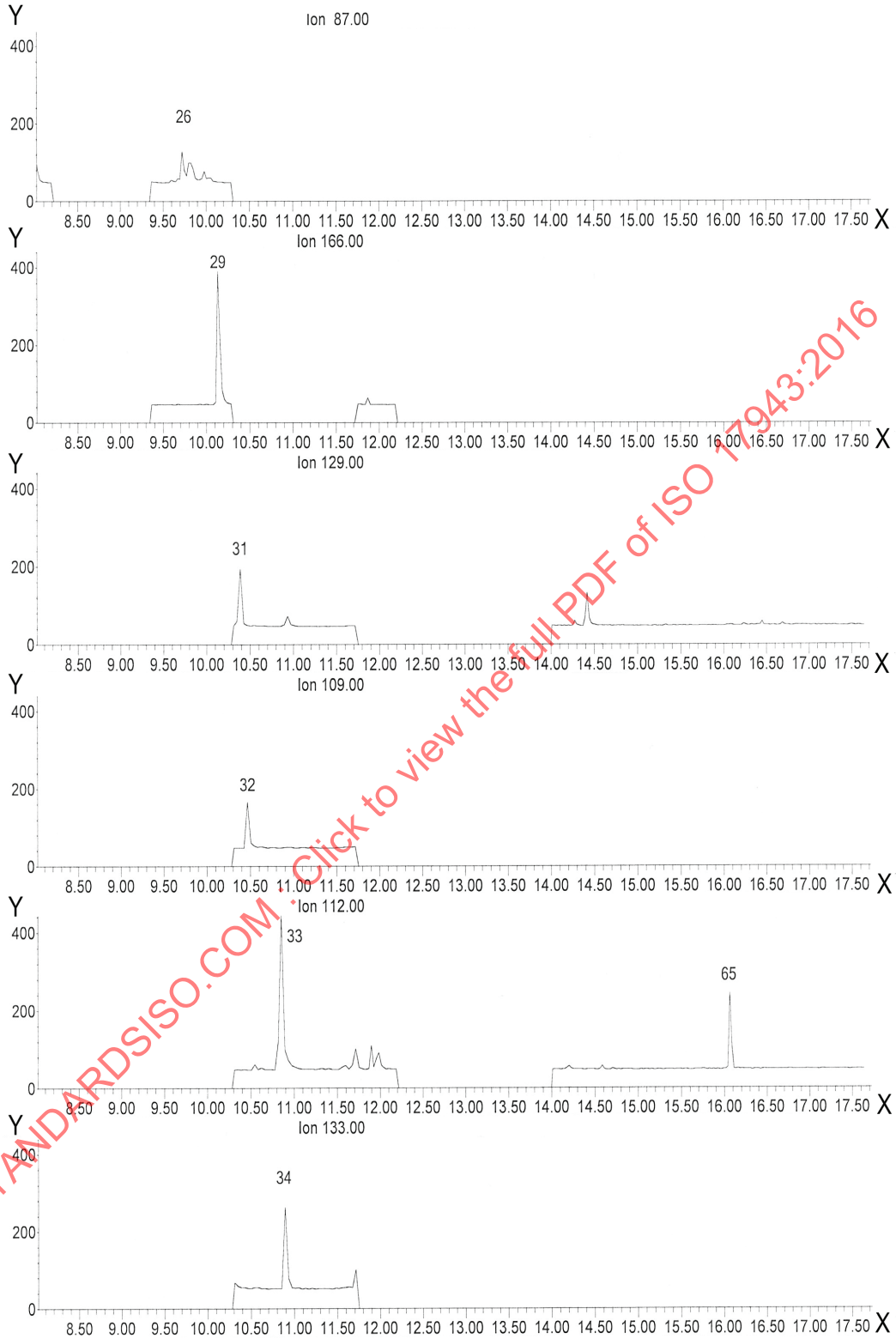
a)



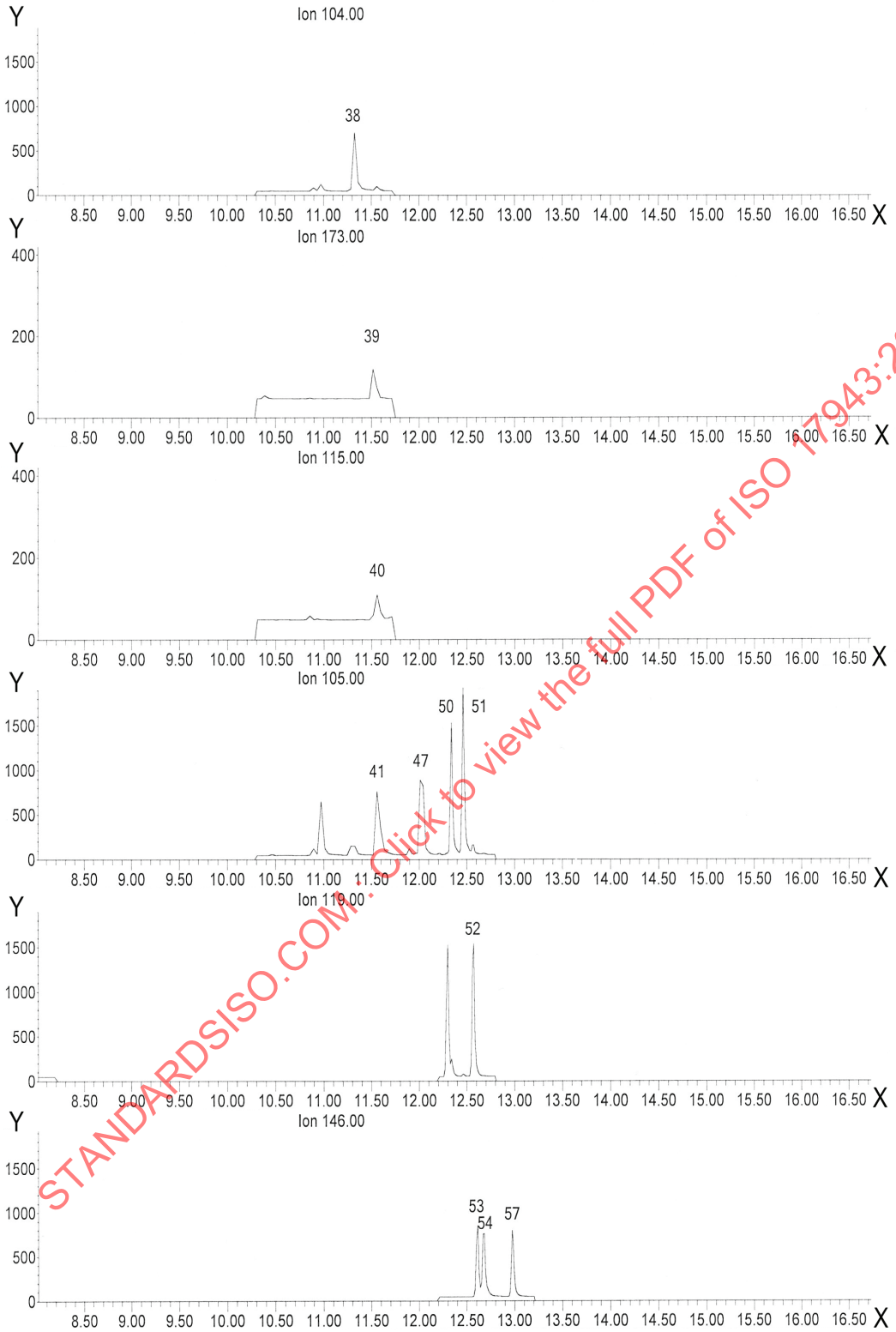
b)



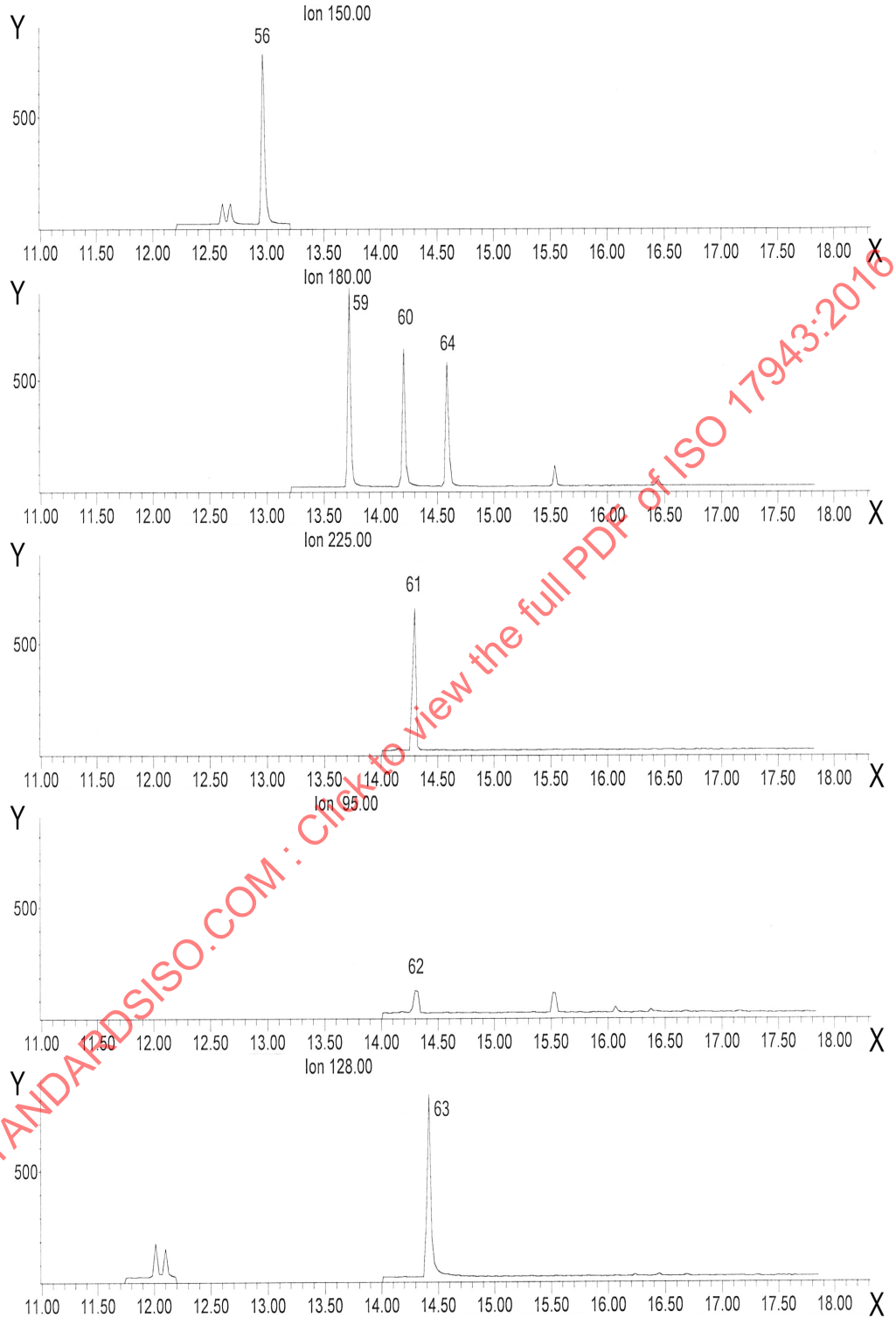
c)



d)



e)



f)

Figure D.3 — Example 3 of a gas chromatogram

Key

X	time, min	1) group (start time)			1) start of group, min
Y	signal intensity	2) selected ions, m/z			2) selected ions, m/z
1	vinyl chloride	group-1 (0,10 min)	31	dibromochloromethane	group-6 (10,30 min)
2	1,1-dichloroethene	61, 62, 63, 64, 96, 98	32	1,2-dibromoethane	56, 77, 78, 91, 103,
3	dichloromethane	group-2 (4,50 min)	33	chlorobenzene	104, 105, 106, 107,
4	MTBE-d3	57, 59, 61, 63, 65,	34	1,1,1,2-tetrachloroethane	109, 110, 112, 115,
5	methyl *tert*-butyl ether (MTBE)	73, 76, 77, 79, 84,	35	ethylbenzene	120, 127, 129, 131,
6	*trans*-1,2-dichloroethene	86, 87, 96, 97, 98,	36	*m*-/*p*-xylene	133, 135, 143, 171,
7	1,1-dichloroethane	99	37	*o*-xylene	173, 175
8	ethyl *tert*-butyl ether (ETBE)		38	styrene	
9	2,2-dichloropropane		39	tribromomethane (bromoform)	
10	*cis*-1,2-dichloroethene		40	2-ethyl-5,5-dimethyl-1,3-dioxane	
11	bromochloromethane	group-3 (7,10 min)	41	isopropylbenzene (cumene)	
12	trichloromethane (chloroform)	61, 62, 64, 73, 75,	42	1,1,2,2-tetrachloroethane	group-7 (11,70 min)
13	1,1,1-trichloroethane	77, 78, 79, 83, 85,	43	bromobenzene	75, 77, 83, 85, 91,
14	tetrachloromethane	87, 97, 110, 117,	44	1,2,3-trichloropropane	105, 110, 112, 120,
15	1,1-dichloropropene	119, 128, 130, 132	45	*n*-propylbenzene	126, 128, 147, 156,
16	benzene		46	2-chlorotoluene	158, 166, 168, 170
17	*tert*-amyl methyl ether (TAME)		47	1,3,5-trimethylbenzene	
18	1,2-dichloroethane		48	4-chlorotoluene	
19	trichloroethene	group-4 (8,20 min)	49	*tert*-butylbenzene	group-8 (12,20 min)
20	1,2-dichloropropane	63, 76, 83, 85, 93,	50	1,2,4-trimethylbenzene	91, 105, 119, 120,
21	dibromomethane	95, 130, 132, 134,	51	*sec*-butylbenzene	134, 146, 148, 150
22	bromodichloromethane	172, 174, 176	52	4-isopropyltoluene (*p*-cymene)	
23	*cis*-1,3-dichloropropene	group-5 (9,35 min)	53	1,3-dichlorobenzene	
24	toluene-d8	57, 59, 63, 75, 77,	54	1,4-dichlorobenzene	
25	toluene	87, 91, 92, 97, 98,	55	*n* -butylbenzene	group-9 (12,80 min)
26	2-ethyl-4-methyl-1,3-dioxolane	99, 110, 132, 164,	56	1,2-dichlorobenzene-d4	91, 92, 134, 146,
27	*trans*-1,3-dichloropropene	166	57	1,2-dichlorobenzene	148, 150
28	1,1,2-trichloroethane		58	1,2-dibromo-3-chloropropane	group-10 (13,20 min)
29	tetrachloroethene		59	1,3,5-trichlorobenzene	75, 155, 157, 159,
30	1,3-dichloropropane				180, 182, 184
			60	1,2,4-trichlorobenzene	group-11 (14,00 min)
			61	hexachlorobutadiene	95, 107, 112, 125,
			62	2-methylisoborneol	127, 128, 129, 180,
			63	naphthalene	182, 184, 223, 225,
			64	1,2,3-trichlorobenzene	260, 262
			65	geosmin	

Annex E
(informative)

General information on SPME

When using SPME, the analytes are not extracted completely from the water sample, rather, an equilibrium of distribution is established between the analyte molecules dissolved in the aqueous sample and those adsorbed to the stationary polymer phase. For most of the substances given in Table 1, this distribution equilibrium is established after 10 min. Depending on the selected conditions (e.g. extraction temperature), longer periods may be required. However, it is not necessary in practice to wait for the equilibrium to establish if the extraction times (e.g. 10 min) and the other influencing variables (e.g. incubation period, extraction temperature, phase material, amount of salt added) are kept precisely constant (see Clause 8). The diffusion-controlled transport of substances to the adsorbent is not primarily a function of the sample volume. The number of analyte molecules passing to the adsorbent (i.e. the extraction yield) is, however, directly proportional to the distribution coefficient, the volume of the stationary phase, and the concentration of the corresponding analyte in the water sample (see References [10],[11], and [15]).

The extraction yield is the percentage of the analytes adsorbed by the SPME fibre at given conditions (e.g. extraction time, extraction temperature, phase material, amount of salt added, stirring rate) in relation to the number of analytes in the sample volume used (e.g. 10 ml). Depending on the fibre batch used, the values for one substance can vary significantly. The extraction yield can also be determined by experiments. For this purpose, for each substance, the results (area units) from a liquid injection experiment are compared with those of an SPME experiment and the percentages by mass are established. Corresponding tests of the fibres used have been conducted within the working group of the standards committee. These tests are described in the validation document for DIN 38407-41. The results, which are for informative purposes only, only apply to the fibres used. It is not necessary in practice to determine the extraction yields. The fibres may be used as long as the procedure shows the sensitivity required for the substances to be analysed.

Annex F
(informative)

Performance data

The performance data given in Tables F.1 and F.2 were determined in an international interlaboratory trial carried out in June 2013 on surface water and treated waste water. Additional performance data given in Tables F.3 to F.5 were determined in an earlier interlaboratory trial carried out in May 2009 on drinking water, ground water, and surface water.

Table F.1 — Performance data for surface water, spiked

Compound	l	n	o	X	$\bar{\bar{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
			%	µg/l	µg/l	%	µg/l	%	µg/l	%
tert-amyl-methyl-ether (TAME)	24	96	2,0	0,089	0,088	98,9	0,015	17,3	0,005	5,9
benzene	25	100	3,8	0,100	0,099	99,0	0,020	19,7	0,006	6,2
bromobenzene	21	84	8,7	0,100	0,106	106,0	0,033	30,9	0,010	9,9
bromochloromethane	20	80	20,0	0,300	0,286	95,3	0,038	13,1	0,010	3,5
bromodichloromethane	24	96	11,1	0,298	0,294	98,7	0,044	15,0	0,012	4,0
n-butylbenzene	23	92	4,2	0,250	0,216	86,4	0,052	24,3	0,017	7,7
sec-butylbenzene	24	94	6,0	0,040	0,042	105,0	0,015	35,3	0,004	8,5
tert-butylbenzene	19	76	17,4	0,200	0,176	88,0	0,039	22,0	0,007	3,9
chlorobenzene	24	96	4,0	0,040	0,039	97,5	0,008	20,9	0,003	6,6
2-chlorotoluene	22	88	8,3	0,100	0,096	96,0	0,022	23,3	0,005	5,6
4-chlorotoluene	21	84	8,7	0,100	0,095	95,0	0,023	24,8	0,005	5,7
dibromochloromethane	25	100	7,4	0,300	0,287	95,7	0,058	20,2	0,016	5,4
1,2-dibromo-3-chloropropane	24	96	4,0	0,735	0,746	101,5	0,155	20,8	0,049	6,5
1,2-dibromoethane	25	100	7,4	0,500	0,501	100,2	0,072	14,3	0,025	5,0

l number of laboratories after outlier rejection

n number of individual test results after outlier rejection

o percentage of outliers

X assigned value

$\bar{\bar{x}}$ 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

[a] Results for 2,2-dichloropropane, *cis*-1,3-dichloropropene, and *trans*-1,3-dichloropropene show poor recovery and high coefficient of variation. These findings could not be confirmed in stability testing experiments carried out by the technical working group. However, it is recommended to carefully review recovery of these substances within the analytical procedure.

[b] The high value for the reproducibility coefficient of variation for dichloromethane can be traced back to blank values from the laboratory air. See Table F.3 and F.4 for blank value-free results.