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Water quality — Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption

Qualité de l'eau — Dosage par chromatographie en phase gazeuse d'un certain nombre d'hydrocarbures aromatiques monocycliques, du naphtalène et de divers composés chlorés par dégazage, piégeage et désorption thermique

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Contents

Page

Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 15680 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Water quality — Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption

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.

1 Scope

This International Standard specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC). Annexes A, B and C provide examples of analytes that can be determined using this International Standard. They range from difluorodichloromethane (R-12) up to trichlorobenzene, including all non-polar organic compounds of intermediate volatility.

Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well.

The limit of detection largely depends on the detector in use and the operational parameters. Typically detection limits as low as 10 ng/l[1)] can be achieved. The working range typically is up to 100 µg/l.

This International Standard is applicable to drinking water, ground water, surface water, seawater and to (diluted) waste water.

2 Normative references

The following referenced documents are indispensable for the application 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 — Specifications and test methods*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

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*

1) The value given is an indication of the limit of detection. It is calculated as 3 times the standard deviation of a series of measurements of 10 replicate samples under conditions of repeatability.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
volatile organic compound
VOC
organic compound, generally non-polar, with boiling point between approximately −30 °C and 220 °C

3.2
target compound
selected component whose presence or absence is determined

NOTE This definition can also apply to a derivative of the original compound which is formed during an intentional derivatization procedure.

3.3
standard compound
target compound with the highest possible purity that can be used as a reference during the analysis and free of impurities having any influence on its mass spectrum

3.4
retention-time standard
compound that is added to the sample (or to the sample extract) and to the **external standard solution** (3.6) and whose retention time is used to calculate the relative retention times of the target compounds

NOTE The retention-time standard may be identical to the internal standard(s).

3.5
relative retention time
ratio between the retention time of the target compound and the retention time of the retention-time standard

3.6
external standard solution
solution of a known concentration of the target compounds

3.7
lowest concentration for identification
lowest concentration of the target compound which, if present in the sample, still can be identified using the identification criterion that the selected diagnostic ion with the lowest intensity is still present in the mass spectrum with a signal-to-noise ratio higher than 3:1

NOTE This concentration strongly depends on the sensitivity of the instrument and on the performance characteristics of the analytical method.

3.8
diagnostic ion
ion selected from the mass spectrum of the target compound with the highest possible specificity

NOTE For the selection of diagnostic ions, see D.5.

4 Principle

A fixed volume of sample is purged with a fixed volume of an inert gas to strip out the volatile components which are subsequently trapped. This trapping can be either:

a) on a packed adsorbent trap (preferably combined with or followed by a cryofocusing system), or

b) directly on a capillary cold-trap.

After completion of the purge process, the trap is heated to desorb the volatile components which are swept by the GC carrier gas on to a capillary GC column. This transfer to the GC column can be done in an on-line or in an off-line set-up. To achieve narrow injection bandwidths, the use of a cryofocusing system is recommended when the trapping is done on a packed adsorbent trap as in a) or the transfer is done through an injector-splitter set at approximately 20:1 if the sensitivity of the analytical system allows this.

The components are separated by GC utilizing temperature programming, and are detected by the use of a mass spectrometer. Data are acquired in the full-scan mode or at a sufficient number of specific fragments to enable matching against those of the standards. A compound is regarded to be present when the criteria of Annex D are met. Quantification is carried out using selected characteristic fragments for each determinand.

5 Interferences

5.1 General

In principle, any purgeable compound which elutes at the same chromatographic retention time and produces a mass spectrum identical, or very similar, to any determinand under investigation will interfere. In practice, this is unlikely as the spectra of most of the determinands are characteristic. With retention-time data and the availability of the spectrum over a wide range of masses, the possibility of misidentification is quite small. Co-eluting peaks with ions with non-specific m/z values might cause interference, but quantification ions can be chosen to preclude this.

Contamination introduced during the analytical procedure is monitored by the determination of blanks (9.4).

5.2 Interferences in the sampling process

VOCs are amenable to evaporation or degassing during the sampling process, transportation, storage and preparation of the samples. This can result in measured concentrations which are too low. VOCs can also diffuse into the samples from the ambient air of the laboratory or from air in the refrigerator where samples are stored. This results in concentrations which are too high.

5.3 Interferences due to the purge gas and the GC gas

Insufficient purity of the purge gas or the GC carrier gas can cause interferences.

5.4 Interferences in the purge-and-trap process

One of the main sources of contamination during sample transportation is contaminated laboratory air in the purge vessel or sample container. Therefore, the laboratory should be free of solvents and concentrated standard solutions.

Laboratory clothing is also a potential source of contamination, particularly of highly volatile halogenated hydrocarbons.

To avoid interferences, all materials (tubing, seals, valves, etc.) should be made from stainless steel or glass. The use of plastics material should be avoided. All glassware directly in contact with the sample or purged compounds should be cleaned thoroughly (see Annex E). There is an especially high risk of entrainment after the measurement of highly polluted samples.

Purge vessels incorporating a glass frit are liable to cause cross-contamination (see also 7.1).

Purging of water samples containing surfactants can result in formation of foam which might be in direct contact with the adsorbent. If this occurs, the purge procedure shall be stopped immediately.

5.5 Interferences in the thermal desorption process

During thermal desorption, substances can degrade.

The transfer lines between the adsorption trap and the gas chromatography injection system should not have any “cold” points which act as adsorbents, as this results in a loss of VOCs.

When using a cryofocusing system and if the adsorbents are not completely dried after the purge process, the capillaries can block with ice. This results in incomplete desorption, and evaluation of the analytical procedure will be impossible.

The adsorbents used in the purge-and-trap systems are subject to ageing (contamination, thermal stress) which can cause changes in the trapping capacity and in the blank values.

5.6 Interferences in automatic samplers

Samples in autosamplers intended for subsequent analysis shall be protected from light (e.g. by use of brown glass vials).

Special care should be taken for autosamplers with respect to the remarks made under 5.4.

6 Reagents

Use reagents of sufficient purity that do not give rise to interfering peaks in the gas chromatographic analysis. Check freshly prepared standard solutions against previously prepared standard solutions to ensure for standard integrity. This should be checked with each batch of material by analysing procedural blank solutions with each batch of samples. Use solvents of high quality that do not contain interfering compounds and analytical reagent grade materials, as far as available. Reagents may contaminate by contact with air and/or other materials, particularly plastics, or by degradation caused by reaction with light. Reagents should be stored in all-glass containers or other vessels found to be suitable, and kept in the dark, if necessary.

6.1 Water, used for blank determination, dilution of samples and for the preparation of calibration solutions.

Water should be known to be free from contaminants (see Annex E). It should show negligible interferences in comparison with the smallest concentration to be determined, in accordance with ISO 3696.

A sufficient amount of water from the same batch should be available to complete each batch of analyses, including all preparations.

6.2 Methanol, CH_3OH, used as solvent, and for the preparation of standard stock solutions.

Other solvents that are readily soluble in water and do not interfere with the analytical process can be used as well. This includes *N,N*-dimethylformamide (DMF, C_3H_7NO), dimethyl sulfoxide (DMSO, C_2H_6SO) and acetone (C_3H_6O).

6.3 Sodium thiosulfate pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$.

If necessary, add sodium thiosulfate to samples to remove remaining oxidants like chlorine or ozone. Other non-interfering substances may be used for the same purpose (e.g. sodium sulfite).

NOTE Already formed intermediate oxidation products like halogenated acetic acids can still form trihalomethanes regardless of the preservation described in this clause.

6.4 Sodium hydrogensulfate, $NaHSO_4$.

Other suitable diluted acids or acid salts may be used as well.

6.5 Purge gas.

Use a high quality helium or nitrogen gas for purging, free of interfering substances. Impurities can be eliminated by a purification cartridge, if necessary.

6.6 Standard solutions.

Owing to the high volatility of the gases and the more volatile compounds to be analysed, great care is required in the preparation of standard solutions; losses may occur in the headspace of the vessel used to prepare standard solutions. For a detailed description of the preparation of standard stock solutions of volatile compounds see Annex F. It is advisable, and more appropriate, to use commercially available standard solutions. Store intermediate standard solutions at about 4 °C and allow them to reach room temperature before use.

Whilst the following procedures are given as examples, users may wish to prepare their own standard solutions by an alternative procedure or by diluting commercially available stock solutions (preferably certified), which are shown to produce equivalent results.

6.6.1 Stock calibration standard solution (2 mg/ml).

Dissolve defined quantities of approximately 200 mg of each VOC in a 100 ml volumetric flask partially filled with the same solvent (6.2), make up to the mark and mix well. See also Annex F.

6.6.2 Stock internal standard solutions (2 mg/ml).

Dissolve defined quantities of approximately 200 mg of each internal standard compound in a 100 ml volumetric flask partially filled with the same solvent (6.2), make up to the mark and mix well. See also Annex F.

At least one internal standard compound should be used for quantitation and additional internal standard compounds could be used as surrogate standards. Suitable compounds may be selected from Table 1. Use deuterated standards only for GC-MS. For the indicated internal standard compounds (*) of Table 1, the range of analytes covered by each of them is given in Annex A as an example (Table A.2).

6.6.3 Spiking solutions.

Prepare spiking solutions from solutions 6.6.1 and 6.6.2 by appropriate dilution in a volumetric flask containing the same solvent (6.2). As an example, Table 2 gives a dilution scheme in 100 ml of solvent and consecutive spiking of 5 µl of it to 100 ml water to give spiking solutions 6.6.3.1 to 6.6.3.6. In this example, analyte concentrations range from 0 µg/l to 5 µg/l in water.

If the desired measuring range differs from that of Table 2, different dilution ratios should be taken or the spiking volume should be adapted.

NOTE Solution 6.6.3.1 is used as the internal standard solution to be added to each sample (see 9.3).

6.6.4 Calibration solutions.

Add a small volume of the spiking solutions 6.6.3.2. to 6.6.3.6 from Table 2 to the water (6.1) in the purge vessel (7.1) [or in the sample container (7.3) when an autosampler is used]. Table 2 gives an example of a 5 µl addition to 100 ml of water (with concentrations as indicated in the fourth column). If larger sample volumes are analysed, add an equivalently larger volume of spiking solution.

Make sure that the content of the organic solvent in the final aqueous calibration standard solution does not exceed 2 % (volume fraction). If a high percentage of solvent is present, linearity should be checked.

6.6.5 Blank solution.

Reserve a portion of the unspiked water for use as a quality control blank.

Table 1 — Internal standard compounds

CAS-RN	Compound	Formula
462-06-6	* monofluorobenzene	C_6H_5F
3114-55-4	* monochlorobenzene-d_5	C_6ClD_5
3855-82-1	* 1,4-dichlorobenzene-d_4	$C_6Cl_2D_4$
540-36-3	* 1,4-difluorobenzene	$C_6H_4F_2$
460-00-4	1-bromo-4-fluorobenzene	C_6H_4BrF
2037-26-5	toluene-d_8	C_7D_8
1868-53-7	dibromofluoromethane	$CHBr_2F$
109-70-6	1-bromo-3-chloropropane	C_3H_6BrCl
107-04-0	1-bromo-2-chloroethane	C_2H_4BrCl
75-62-7	bromotrichloromethane	$CBrCl_3$
363-72-4	pentafluorobenzene	C_6HF_5
1076-43-3	benzene-d_6	C_6D_6
17060-07-0	1,2-dichloroethane-d_4	$C_2Cl_2D_4$
20302-26-5	ethylbenzene-ring-d_5	$C_8H_5D_5$
74-97-5	bromochloromethane	CH_2BrCl
3017-95-6	2-bromo-1-chloropropane	C_3H_6BrCl
110-56-5	1,4-dichlorobutane	$C_4H_8Cl_2$
56004-61-6	*o*-xylene-d_{10}	C_8D_{10}
* Range of analytes covered is given in Table A.2		

Table 2 — Dilution scheme in 100 ml solvent

Spiking solution (100 ml of solvent)	ml of 6.6.2 (added to 100 ml of solvent)[a]	ml of 6.6.1 (added to 100 ml of solvent)	Analyte concentration in spiking solution (in mg/l of solvent)	Concentration (in µg/l) in calibration solution (5 µl of spiking solution added to 100 ml of water)
6.6.3.1	5	0	0	0
6.6.3.2	5	1	20	1
6.6.3.3	5	2	40	2
6.6.3.4	5	3	60	3
6.6.3.5	5	4	80	4
6.6.3.6	5	5	100	5

[a] The concentration of the internal standard compound in each spiking solution is 100 mg/l.

7 Apparatus

Usual laboratory glassware and equipment is not specified, as the actual devices used depend on the specific application and circumstances. Make sure that all devices are free of interfering compounds. Clean all glassware, including sample bottles, thoroughly. A standard procedure for cleaning is included in Annex E.

7.1 Purge vessels

A variety of purge vessels are commercially available. The specific type is defined by the purge-and-trap apparatus in use. There are systems available which allow purging in the sampling vessels. Cleaning of the purge vessels should be carried out according to Annex E.

7.2 Sample containers

Various sample containers can be used, e.g. screw-cap containers fitted with PTFE-faced silicone discs. For purge-and-trap systems with an autosampler, use sample containers recommended by the autosampler manufacturer. Whenever septa are employed, do not re-use them.

7.3 Purge-and-trap apparatus

Purge-and-trap apparatus is commercially available or can be self-constructed. This includes fully automated, on-line purge-and-trap GC-equipment with an autosampler and the thermal desorption device incorporated in the instrument, as well as manually operated off-line equipment. All instruments may be used that meet the requirements and have proven to give reliable results. According to Annexes A, B and C, various instruments have been used. Other devices may be suitable but should be examined appropriately to ensure satisfactory performance.

The purge-and-trap apparatus should include:

a) autosampler;

b) purge vessel, heating mantle and temperature control, purge gas supply, flowrate control, timer;

c) condenser and coolant supply or dry-purge system;

d) adsorbent trap;

e) thermal desorption device, temperature control, timer;

f) cold trap, coolant supply, heater, temperature control;

g) GC-MS or a GC with suitable detector(s), GC-auxiliaries, data system.

Various combinations of components a), c), d), e) and f) are possible and don't all need to be included.

7.4 Adsorbent trap

7.4.1 For purge-and-trap apparatus using intermediate trapping on a packed adsorption column (see Clause 4), these traps are often home-made or can be obtained in various modifications. As an example, adsorption columns are made of glass or stainless steel with an internal diameter of 2 mm to 5 mm, appropriate for use in the apparatus for thermal desorption. Adsorbent traps are packed with a suitable adsorbent.

Generally a polymer, a carbonaceous or silica adsorbent is used[2]. Typical dimensions of the packing are diameter 2 mm to 5 mm, length 10 mm to 50 mm, corresponding to at least 90 mg of adsorbent. The adsorbent is kept in position by inert material such as glass wool plugs or glass screens. This description is an example; other adsorbent traps can be used as well, provided their performance meets the requirements of this International Standard.

Prior to their first use, adsorbent traps should be conditioned by heating them above their desorption temperature for approximately 30 min while passing a gentle stream of inert gas through them. A blank procedure shall be performed with the conditioned adsorbent trap before using it in routine.

7.4.2 Special requirements for use in off-line purge-and-trap equipment may apply.

In off-line purge-and-trap equipment, the adsorbent traps are not defined by the instrument in use, whereas most of the other parts under 7.3 a) to f) are. For off-line use, mark the traps on one side to allow desorption in a back-flush mode. In case of off-line purge-and-trap, for the adsorbent traps use caps of inert material, for example PTFE, or of metal with screw windings and a PTFE-washer, so that after purging they can be closed leakproof for storage or transfer to the apparatus for thermal desorption.

7.5 Gas chromatograph-mass spectrometer (GC-MS)

A variety of gas chromatographic columns can be used in purge-and-trap analysis. Examples of suitable columns are given in Annexes A, B and C.

The mass spectrometer should be capable of operating across the mass range of interest and incorporate a data system capable of quantifying ions using selected m/z values. See Annexes A, B and C for typical chromatograms.

Other GC detectors, such as flame ionization detector (FID), electron capture detector (ECD), photo-ionization detector (PID) or electrolytic conductivity detector (ELCD), can be used, depending on the substances to be analysed (see 9.7.2).

For operational aspects of the instruments, the manufacturer's instructions should be followed.

8 Sample collection, preservation and preparation

Collect samples in accordance with ISO 5667-3 in suitable containers, preferably directly into the sample containers (7.3). It is advisable to take two samples, one to be retained in the event of a repeat analysis being required. Fill sample containers, avoiding turbulence, until overflowing. Cap sample containers without leaving a headspace. For samples containing free chlorine or any other strong oxidant, solid sodium thiosulfate pentahydrate (6.3) or other reducing salt should be added to the container (approximately 100 mg/l). Additionally, for the preservation of aromatic compounds in surface waters, the pH should be lowered to 2 using sodium hydrogensulfate (6.4). Other appropriate acids are allowed.

Samples shall not be diluted if the concentration exceeds the working range established by the calibration function, as dilution can cause evaporative losses of the analytes. Preferably extend the calibration function or apply (static) headspace analysis, e.g. according to ISO 10301 [1] and/or ISO 11423-1[2]. Avoid contamination of the equipment by dirty samples.

The stability of certain determinands is known to be matrix-dependent. Therefore, if the matrix of the sample has not been evaluated, it is recommended that the sample be analysed preferably on the day of sampling and not later than 5 days from sampling. Until analysis, store samples at about 4 °C and protected from direct sunlight in air-tight closed containers.

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2) Tenax®, Porapak®, Carbopak® and Chromosorb® are examples of typical adsorbents available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

If the water samples were not originally taken in the sample containers for the autosampler, or if the sample is transferred manually into the purge vessel, pour a suitable volume of the sample gently into the respective container or vessel without turbulence or withdraw the sample using an all-glass syringe, avoiding the release of gas bubbles. Close the container immediately to avoid losses of the most volatile compounds.

Care should be taken if subsamples are taken with a syringe, as a partial vacuum can form, resulting in a change in the concentration of volatile components in the sample.

If severe foaming occurs, the application of antifoam agents shall be considered. Alternatively, the sample shall be analysed by static headspace or liquid extraction, if possible.

9 Analytical procedure

9.1 General

Depending on the instrumentation in use, deviations from the described procedure are allowed. This refers in particular to the working conditions of the purge-and-trap procedure. All conditions for the measurement of samples and for calibration should be identical.

9.2 Preparation

Set up the instrument(s) in accordance with the manufacturer's instructions. If an autosampler is used, load it with samples, calibration solutions (6.6.4) and blanks (6.6.5). If both clean and heavily contaminated samples are to be analysed in the same series, it is recommended to process the clean samples first because of the possible carry-over effects. To monitor carry-over, process blank samples directly after the contaminated ones.

Prepare fresh calibration solutions (6.6.4) in the respective concentration range.

9.3 Addition of internal standards

Add the internal standard to the samples and blanks by taking a proper aliquot of spiking solution (6.6.3) with a syringe and immerse it underneath the water level of the sample. Ensure that no headspace losses of the sample occur.

NOTE Some commercially available instruments automatically add the internal standard to the samples.

9.4 Blanks

Treat blanks (6.6.5) in the same way as the samples. At least one blank determination should be performed prior to analysing real samples, in order to judge the performance of the entire procedure with respect to contamination. The blank should not exceed 10 % of the lowest calibration solution or of the lowest level of interest.

9.5 Quality control samples

As there are no additional possibilities to control the total analytical procedure, the analysis of sufficient quality control samples is essential. This includes spiked samples.

Treat quality control samples as real samples, according to the laboratory's quality system. Evaluate the results, e.g. on the basis of control charts.

9.6 Purge-and-trap concentration of the sample

Optimum working conditions can differ for each substance. Method development and validation should provide appropriate values for the operational parameters in accordance with the specific application and

instrument. The data below show average practical values. Examples of actual working conditions are given in Annexes A, B and C.

The desired working range of the method, and more specifically the lowest detection limit, largely determines the required sample volume. To achieve a fairly constant recovery, the total volume of purge gas (purge time × flowrate) should be proportional to the sample volume. A ratio of approximately 10:1 (ml purge gas:ml sample) generally is most practical, i.e. a sample volume of 20 ml purged by a gas flowrate of 10 ml/min for 20 min. Prolonged purging can improve the recovery of less volatile or slightly polar compounds. The optimum purge time and gas flow rate for such compounds should be determined experimentally.

In general, a small sample volume is preferred to reduce analysis time and costs.

Purging at elevated temperatures is recommended for the analysis of less volatile or slightly polar compounds as this will considerably improve the recovery. To prevent blocking of the cold trap by ice, remove the entrained water vapour from the purge gas stream after it passes the purge vessel and prior to cryofocusing onto the cold trap. This can be done for instance by the application of a condenser (at e.g. −10 °C) placed between the purge vessel and the cold trap and/or by intermediate trapping onto an adsorption column filled with a hydrophobic sorbent and/or by a dry purge step of the adsorbent trap prior to desorption. This way purge temperatures as high as 95 °C can be used (see Annex C).

If an adsorbent trap (7.4) is incorporated in the purge-and-trap apparatus, the adsorption of purged compounds is, in general, carried out at room temperature. Thermal desorption is done at the maximum allowable temperature for the sorbent in use, generally between 200 °C and 250 °C for 5 min to 10 min.

When applying a cold trap, its temperature shall be low enough to condense the analytes quantitatively. The temperature shall be about 70 °C below the boiling point of the most volatile analyte. Cold traps using liquid carbon dioxide may be used down to −50 °C. Cold traps using liquid nitrogen may be used down to −120 °C. Inject the analytes by flash desorption at 200 °C to 250 °C.

9.7 GC-MS analysis

9.7.1 General

Optimize the instrumental parameters in accordance with the manufacturer's instructions.

Determine the appropriate GC oven temperature programme experimentally during method development and validation. The upper temperature should be higher than the desorption temperature of the adsorption column and the flash desorption temperature of the cold trap.

Record mass spectra in the full-scan mode for a relevant mass range within 35 u and 300 u, with the upper limit at least 10 u above the highest molecular mass of interest. Set the electron energy at approximately −70 eV. If for the sake of sensitivity, only selected ions are detected, register at least three diagnostic ions, preferably of the highest u-values. Additional MS operational aspects are given in Annex D.

Identify the compounds on the basis of their retention times and mass spectra. Criteria for GC-MS identification are given in Annex D.

9.7.2 Alternative detectors

Alternatively, use an electron capture detector (ECD) or an electrolytic conductivity detector (ELCD, Hall detector) to detect halogenated hydrocarbons. The sensitivity of an ECD varies with the nature of the analyte, and it can be more sensitive than MS for tri- or tetra-halogenated compounds. A flame ionization detector (FID) can be used as a universal detector for hydrocarbons (aliphatic, aromatic and halogenated) and a photo-ionization detector (PID) can be used for the detection of aromatic compounds. The atomic emission detector (AED) is an element-specific detector that can be used in this method. By the combination of the results from several element traces, a high reliability for the compound identification can be established.

When detectors other than MS are used, separation on two capillary columns of different polarity should be considered in order to reduce the risk of false positive results by overlapping peaks. When using two columns, the retention times on both columns should match with those of the standard. The lower concentration is then accepted as being the most accurate value.

10 Calibration

Perform the calibration using one or more internal standard compounds. If target compounds are spread over wide retention-time values, use different internal standards in accordance with D.2 in Annex D and Table A.2 in Annex A.

As a minimum, perform a five-point calibration by analysis of each of the calibration solutions (6.6.4), evenly distributed over the entire working range. Based on this, calculate the calibration function for each individual compound in accordance with ISO 8466-1.

The calibration function is only valid under the specified operating conditions and should be re-established if these conditions are altered.

The calibration function does not need to be recalculated for every batch of samples. For routine analysis it is sufficient to check the calibration function by means of a two-point calibration.

As the calibration is performed over the entire analytical procedure, no determination of the recoveries is needed. Nevertheless, it can be desirable to do so in the case of malfunctioning of the system or if the ruggedness is observed to be poor. A description of the determination of recoveries is presented in Annex G.

Establish a linear calibration function for analyte i using the pairs of values $y_{i\mathrm{ej}}/y_{l\mathrm{ej}}$ and $\rho_{i\mathrm{ej}}/\rho_{l\mathrm{ej}}$ of the measured calibration solutions in the following equation:

$$y_{i\mathrm{e}}/y_{\mathrm{se}} = [m_{i\mathrm{s}} \times (\rho_{i\mathrm{e}}/\rho_{\mathrm{se}})] + b_{i\mathrm{s}} \quad (1)$$

where

$y_{i\mathrm{e}}$ is the (dependent variable) measured response of analyte i in the calibration, depending on $\rho_{i\mathrm{e}}$ e.g. peak area;

y_{se} is the measured response of the internal standard compound s in the calibration, depending on ρ_{se} e.g. peak area;

$\rho_{i\mathrm{e}}$ is the (independent variable) mass concentration of the substance i in the calibration solution, in micrograms per litre;

ρ_{se} is the mass concentration of the internal standard compound s in the calibration solution, in micrograms per litre;

$m_{i\mathrm{s}}$ is the slope of the calibration curve from $y_{i\mathrm{e}}/y_{\mathrm{se}}$ as a function of the mass concentration ratio $\rho_{i\mathrm{e}}/\rho_{\mathrm{se}}$, often called the response factor;

$b_{i\mathrm{s}}$ is the axis intercept of the calibration curve on the ordinate;

i refers to analyte i;

s refers to the internal standard compound s;

e refers to values connected to the calibration function.

11 Calculation

Calculate the mass concentration of analyte i in the sample using Equation (2) after solving Equation (1):

$$\rho_i = \left\{[(y_i / y_s) - b_{is}] \times \rho_s\right\} / m_{is} \quad (2)$$

where

y_i is the measured response of analyte i in the water sample, e.g. peak area;

y_s is the measured response of the internal standard compound s in the water sample, e.g. peak area;

ρ_i is the mass concentration of analyte i in the water sample, in micrograms per litre;

ρ_s is the mass concentration of the internal standard compound s in the water sample, in micrograms per litre;

m_{is} is the slope of the calibration curve from y_{ie}/y_{se} as a function of the mass concentration ratio ρ_{ie}/ρ_{se}, often called the response factor, as determined in Clause 10;

b_{is} is the axis intercept of the calibration curve on the ordinate, as determined in Clause 10.

If detection is not by mass spectrometry but by an alternative detector in a dual column configuration (9.7.2), the lower concentration calculated is regarded as being the most accurate.

If mass spectrometry is used and the criteria for identification are met (see Annex D) there are no additional criteria for quantitation. The average value of the calculated concentrations based on more than one fragment is then regarded as being the best estimate of the true value.

NOTE For a compound, the maximum allowable difference in calculated concentrations based on two extracted ion current chromatograms has no fixed value, as it is determined by the relative intensity ("abundance") of the selected ions for quantitation (see Annex D).

12 Expression of results

Report mass concentrations of the purgeable analytes in the sample, in micrograms per litre or nanograms per litre; concentrations larger than the lowest point of calibration should be expressed to two significant figures.

13 Precision data

Precision data for specific applications of purge-and-trap analyses are included in Annexes A, B and C.

14 Test report

The report shall refer to this International Standard and contain the following information:

a) information necessary for identification of the analysed sample;

b) a short description of the applied purge-and-trap method, including sample preparation, sample volume, purge-and-trap concentration principle, automation, gas chromatography and detection;

c) conditions of storage (period) and preservation;

d) if and how confirmation of the data was done (e.g. dual column separation, dual detection or full-scan MS);

e) expression of results according to Clause 12;

f) all procedures and observations not described in this International Standard that can have affected the result.

Annex A
(informative)

Application of purge-and-trap concentration to the GC analysis of volatile compounds in water — Example 1: Validation study in the UK

A.1 Purge-and-trap conditions[3)]

Purge time:	11 min
Desorb pre-heat:	245 °C
Desorb:	5 min at 250 °C
Bake:	15 min at 260 °C
Trap stand-by temperature:	Less than 30 °C
Purge gas:	Helium
Column adsorbent material:	*Vocarb 3000*
Purge flowrate:	Helium, 40 ml/min

A.2 GC conditions

Column:	Fused silica WCOT, 60 m × 0,32 mm ID,
	1,8 µm film thickness, coated with DB624.
Carrier gas:	Helium, 1 ml/min.
Column temperature:	Programmed, 35 °C for 5 min, 6 °C/min to 125 °C, 15 °C/min to 240 °C. Hold for 7,5 min at 240 °C.

A.3 MS conditions[4)]

Type of MS:	Ion trap
Mode:	Full scan
Mass range:	35 u to 265 u
Scan speed:	1,33 scans/s (3 µscans)

3) The purge-and-trap instrument used was from Tekmar. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

4) The purge-and-trap conditions are also applicable for GC analysis with detectors other than MS.

A.4 Performance

Performance data are given in Tables A.1 and A.2

Table A.1 —Performance data

No.	Compound	Deionized water		Sample	Sample spike (8,0 µg/l)		High standard (40 µg/l)		Low standard (0,8 µg/l)		
		s	LOD	s	s	η	s	Bias	s	Bias	LOD
4	dichlorodifluoromethane	0,008 9	0,041	0,011 5(21)	4,22	153	7,02(14)	−7,53	0,080 6(10)	2,32	0,227
5	monochloromethane	—	—	—	2,51	104	2,49(10)	−2,16	0,367(18)	16,94	0,178
6	vinyl chloride	—	—	0,001 3(21)	2,29	101	2,40(14)	−0,98	0,040(17)	2,03	0,114
9	trichlorofluoromethane	0,005 9	0,025	0,006 4(21)	0,553	104	1,88(11)	−0,17	0,044 7(21)	-0,70	0,074
10	1,1-dichloroethene	0,008 1	0,038	0,077 5(21)	1,84	100	1,84(15)	−1,30	0,032 6(19)	-1,18	0,101
11	dichloromethane	4,28	1,36	0,223(11)	3,89	83	10,41(16)	0,55	0,114(11)	54,52	0,358
12	*trans*-1,2-dichloroethene	0,009 0	0,042	0,009 8(21)	1,85	100	1,45(14)	−1,23	0,034 1(19)	0,24	0,093
13	1,1-dichloroethane	0,003 8	0,018	0,003 7(21)	1,85	100	1,67(14)	0,21	0,033 8(19)	0,48	0,091
14	2,2-dichloropropane	0,003 6	0,001	0,001 3(21)	2,55	77	12,93(10)	−17,6	0,210(21)	-23,30	0,115
15	*cis*-1,2-dichloroethene	0,008 6	0,040	0,005 6(21)	0,323	104	1,36(15)	−1,43	0,029 3(20)	0,11	0,088
16	bromochloromethane	0,004 2	0,020	0,016 5(21)	1,92	103	1,75(11)	−0,69	0,044 8(21)	-5,54	0,056
17	trichloromethane	0,015 6	0,39	0,099 9(10)	0,42	100	1,12(11)	−1,07	0,095 1(20)	10,76	0,103
18	1,1,1-trichloroethane	0,165	0,082	0,023 8(14)	1,84	97	1,26(11)	−0,29	0,074 9(20)	7,27	0,092
19	tetrachloromethane	0,002 4	—	—	0,322	106	1,69(13)	−2,19	0,027 7(18)	0,23	0,067
20	1,1-dichloropropene	0,006 6	0,031	0,007 8(21)	2,49	95	1,67(13)	−1,92	0,034 1(14)	1,33	0,085
21	benzene	0,012 6	0,058	0,009 4(21)	0,309	104	1,66(16)	−0,36	0,032 7(14)	3,57	0,104
22	1,2-dichloroethane	0,009 5	0,044	0,013(19)	1,9	98	1,65(11)	0,05	0,048 4(18)	5,00	0,075
23	trichloroethene	0,014 4	0,067	0,014 1(21)	0,318	102	2,15(11)	6,15	0,060 1(21)	12,88	0,100
24	1,2-dichloropropane	0,004 8	0,022	0,005 2(21)	0,362	106	1,18(11)	0,26	0,038 5(21)	2,59	0,065
25	1,2-dibromomethane	0,014 3	0,066	0,013 0(20)	0,419	104	1,66(11)	−0,90	0,065 3(14)	2,02	0,084
26	bromodichloromethane	0,008 2	0,038	0,006 3(19)	0,344	105	1,47(11)	−1,09	0,038 4(17)	2,93	0,059
27	*trans*-1,3-dichloropropene	0,011 9	0,055	0,010(19)	0,401	101	1,67(11)	1,09	0,053 1(15)	-3,96	0,077
28	toluene	0,077 1	0,063	0,022 7(11)	0,356	101	1,04(12)	−0,28	0,052 7(20)	11,82	0,103
29	*cis*-1,3-dichloropropene	0,016 5	0,077	0,014 5(20)	0,389	101	1,94(13)	−3,94	0,056 7(13)	1,11	0,131
30	1,1,2-trichloroethane	0,013 3	0,062	0,010 5(21)	0,396	105	1,46(11)	−0,28	0,049 3(20)	2,46	0,079
31	tetrachloroethene	0,018 5	0,068	0,013 5(21)	0,320	102	1,61(17)	−1,77	0,034 6(18)	2,47	0,117
32	1,3-dichloropropane	0,011 5	0,054	0,010 5(20)	0,498	105	2,30(12)	0,94	0,052 5(20)	4,23	0,093
33	dibromochloromethane	0,008 8	0,041	0,006 7(21)	0,398	105	1,47(11)	−0,94	0,045 8(15)	2,62	0,056
34	1,2-dibromoethane	0,014 7	0,068	0,015 2(20)	0,456	104	1,81(13)	−0,23	0,061 9(16)	5,52	0,137
35	monochlorobenzene	0,016 2	0,075	0,013 9(21)	0,330	105	1,13(13)	0,77	0,034 0(21)	4,09	0,084
36	1,1,1,2-tetrachloroethane	0,009 0	0,042	0,007 1(21)	0,327	106	1,32(11)	−0,16	0,035 9(17)	2,86	0,058
37	ethylbenzene	0,018 0	0,081	0,016 0(20)	0,516	101	2,63(19)	0,48	0,042 0(18)	3,44	0,169
38	*m*- and *p*-xylene	0,040 9	0,145	0,028 7(18)	0,722	105	2,21(15)	−0,54	0,072 2(18)	4,78	0,207
39	*o*-xylene	0,014 6	0,046	0,014 6(17)	0,375	105	1,05(16)	0,28	0,030 1(21)	3,88	0,094
40	styrene	0,034 6	0,091	0,016 1(20)	0,331	105	1,03(14)	−0,43	0,048 2(21)	6,36	0,132
41	tribromomethane	0,012 7	0,059	0,012 3(21)	0,502	106	1,82(11)	−1,17	0,060 6(15)	2,31	0,090
42	isopropylbenzene	0,014 4	0,067	0,013 1(21)	0,336	104	1,75(12)	1,84	0,042 2(20)	5,02	0,091

Table A.1 (*continued*)

No.	Compound	Deionized water		Sample	Sample spike (8,0 µg/l)		High standard (40 µg/l)		Low standard (0,8 µg/l)		
		s	LOD	s	s	η	s	Bias	s	Bias	LOD
43	monobromobenzene	0,023 3	0,108	0,021 8(21)	0,347	106	1,22(15)	0,77	0,042 1(21)	5,92	0,128
44	1,1,2,2-tetrachloroethane	—	—	0,003 0(21)	0,548	109	2,75(11)	−9,47	0,098 6(13)	-10,40	0,120
45	1,2,3-trichloropropane	0,045 3	0,211	0,027 5(21)	0,637	107	2,02(13)	0,48	0,075 8(15)	-1,37	0,170
46	*n*-propylbenzene	0,011 1	0,050	0,005 9(19)	0,499	103	1,42(15)	−0,59	0,055 2(20)	3,77	0,160
47	2-chlorotoluene	0,013 0	0,060	0,008 8(21)	0,379	105	1,76(21)	1,38	0,050 8(20)	7,82	0,236
48	4-chlorotoluene	0,013 0	0,060	0,011 8(21)	0,641	104	3,30(17)	1,25	0,083 9(13)	13,20	0,291
49	1,3,5-trimethylbenzene	0,010 8	0,047	0,011 0(21)	0,347	105	1,29(21)	0,62	0,041 9(20)	6,80	0,195
50	*tert*-butylbenzene	0,011 8	0,055	0,013 8(21)	0,370	105	1,31(19)	0,43	0,042 1(20)	6,74	0,167
51	1,2,4-trimethylbenzene	0,026 4	0,123	0,015 7(20)	0,326	105	1,29(21)	0,37	0,047 0(21)	11,26	0,218
52	*sec*-butylbenzene	0,017 8	0,083	0,016 1(21)	0,352	101	1,66(16)	−1,33	0,039 4(17)	7,14	0,127
53	1,3-dichlorobenzene	0,032 2	0,15	0,025 1(21)	0,357	105	1,24(17)	0,36	0,153(21)	5,54	0,533
54	1,4-dichlorobenzene	0,032 1	0,15	0,026 4(21)	0,405	103	1,85(18)	−0,20	0,147(20)	4,81	0,557
55	4-isopropyltoluene	0,029 3	0,14	0,017 0(21)	0,404	104	1,83(16)	0,75	0,192(20)	2,98	0,623
56	1,2-dichlorobenzene	0,053 7	0,25	0,047 7(19)	0,382	104	2,24(18)	−0,66	0,192(21)	4,11	0,700
57	*n*-butylbenzene	0,466	0,22	0,042 5(19)	0,565	100	3,21(19)	−3,91	0,238(18)	0,75	0,943
58	1,2-dibromo-3-chloropropane	0,083 6	0,388	0,080 1(21)	0,781	103	3,75(18)	−0,70	0,379(20)	3,11	1,39
59	1,2,4-trichlorobenzene	0,239	1,11	0,200(19)	0,513	100	1,33(20)	−0,70	0,218(19)	8,92	0,897
60	hexachlorobutadiene	0,134	0,62	0,118(20)	0,416	102	1,65(17)	−0,92	0,178(21)	4,67	0,604
61	naphthalene	0,381	1,77	0,308(21)	0,778	98	2,40(18)	−0,50	0,379(11)	10,76	1,40
62	1,2,3-trichlorobenzene	0,310	1,44	0,264(21)	0,598	102	1,61(18)	−0,56	0,291(18)	10,17	1,07
63	1,3,5-trichlorobenzene	0,195	0,81	0,167(18)	0,647	99	0,765(12)	0,50	0,207(6)	7,57	0,762

NOTE 1 s = standard deviation, LOD = limit of detection, η = recovery. Figures in brackets represent degrees of freedom.

NOTE 2 Units expressed in µg/l except for recovery and bias which are expressed as a %.

NOTE 3 LOD calculated as $4{,}65 \times s_w$ (i.e. the within-batch standard deviation).

NOTE 4 Sample consisted of a borehole water.

Table A.2 — Calibration compounds, retention times and quantification ions

No.	Compound	Retention time min/s	Int. std[a]	Selected ions	
				primary	secondary
Internal and surrogate standard compounds					
S1	fluorobenzene	7:53		96	
S2	1,4-difluorobenzene	11:45		114	63, 88
S3	monochlorobenzene-d_5	17:15		117	
S4	1,2-dichlorobenzene-d_4	21:06		132	115, 150
Target compounds					
4	dichlorodifluoromethane	1:21	S1	85	87
5	monochloromethane	1:30	S1	50	52
6	vinyl chloride	1:36	S1	62	64
7	monobromomethane	2:08	S1	94	96
8	monochloroethane	2:00	S1	49	—
9	trichlorofluoromethane	2:14	S1	101	103
10	1,1-dichloroethene	2:46	S1	96	61, 63
11	dichloromethane	3:22	S1	84	86, 49
12	*trans*-1,2-dichloroethene	3:45	S1	96	61, 98
13	1,1-dichloroethane	4:25	S1	63	65, 83
14	2,2-dichloropropane	5:29	S1	77	97
15	*cis*-1,2-dichloroethene	5:31	S1	96	61, 98
16	bromochloromethane	5:58	S1	128	49, 130
17	trichloromethane	6:12	S1	83	85
18	1,1,1-trichloroethane	6:30	S1	97	99, 61
19	tetrachloromethane	6:50	S2	117	119
20	1,1-dichloropropene	6:52	S2	75	110, 77
21	benzene	7:15	S2	78	—
22	1,2-dichloroethane	7:18	S2	62	98
23	trichloroethene	8:40	S2	95	130, 132
24	1,2-dichloropropane	9:06	S2	63	112
25	dibromomethane	9:20	S2	93	95, 174
26	bromodichloromethane	9:47	S2	83	85, 127
27	*trans*-1,3-dichloropropene	10:47	S2	75	110
28	toluene	11:30	S2	92	91
29	*cis*-1,3-dichloropropene	12:04	S2	75	110
30	1,1,2-trichloroethane	12:27	S2	83	97, 85
31	tetrachloroethene	12:43	S3	166	168, 129
32	1,3-dichloropropane	12:48	S3	76	78
33	dibromochloromethane	13:17	S3	129	127
34	1,2-dibromoethane	13:28	S2	107	109, 188

Table A.2 (*continued*)

No.	Compound	Retention time min/s	Int. std[a]	Selected ions	
				primary	secondary
35	monochlorobenzene	14:41	S3	112	77, 114
36	1,1,1,2-tetrachloroethane	14:56	S3	83	131, 85
37	ethylbenzene	15:02	S3	91	106
38	*m*- and *p*-xylene	15:20	S3	106	91
39	*o*-xylene	16:16	S3	106	91
40	styrene	16:18	S3	104	78
41	tribromomethane	16:37	S3	173	175, 254
42	isopropylbenzene	17:12	S4	105	120
43	monobromobenzene	17:46	S4	156	77, 158
44	1,1,2,2-tetrachloroethane	17:58	S4	86	131, 85
45	1,2,3-trichloropropane	17:59	S4	75	77
46	*n*-propylbenzene	18:13	S4	91	120
47	2-chlorotoluene	18:19	S4	91	126
48	4-chlorotoluene	18:36	S4	91	126
49	1,3,5-trimethylbenzene	18:42	S4	105	120
50	*tert*-butylbenzene	19:28	S4	119	91, 134
51	1,2,4-trimethylbenzene	19:35	S4	105	120
52	*sec*-butylbenzene	20:01	S4	105	134
53	1,3-dichlorobenzene	20:09	S4	146	111, 148
54	1,4-dichlorobenzene	20:22	S4	146	111, 148
55	4-isopropyltoluene	20:25	S4	119	134, 91
56	1,2-dichlorobenzene	21:08	S4	146	111, 148
57	*n*-butylbenzene	21:16	S4	91	92, 134
58	1,2-dibromo-3-chloropropane	22:35	S4	75	155, 157
59	1,2,4-trichlorobenzene	23:55	S4	180	182, 145
60	hexachlorobutadiene	24:13	S4	225	223, 227
61	naphthalene	24:15	S4	128	—
62	1,2,3-trichlorobenzene	24:37	S4	180	182, 145
63	1,3,5-trichlorobenzene	22.58	S4	180	182, 145

NOTE 1 The ions given in this table only refer to the mass spectrometric conditions applied in (Annex A). Different instruments and settings may result in a different selection of diagnostic ions.

NOTE 2 Scan and retention times will vary with column age and after replacement of columns.

[a] Under “Int. std” the internal or surrogate standard compound is mentioned (S1 through S4, indicated by number) by which the analyte is covered (see also 6.6.2).

Annex B
(informative)

Application of purge-and-trap concentration to the GC analysis of volatile compounds in water — Example 2: Data provided by DIN

B.1 Purge-and-trap conditions

Parameter	System A[5)]	System B[6)]
Sample volume		5 ml
Trap	cryofocusing	sorbent (Tenax TA)
Temperature (purge-container)	room temperature	room temperature
Temperature (pre-cooler)	−10 °C	—
Temperature (trap)	−110 °C	< 30 °C
Pre-cooling time	2 min	—
Purge gas	He	He
Volume flowrate	10 ml/min	40 ml/min
Purge time	20 min	10 min
Drying time	—	5 min

B.2 Desorption and transfer to the capillary columns

Parameter	System A[5)]	System B[6)]
Temperature (cold trap and moisture trap)	—	−10 °C
Temperature (cryofocusing)	—	−120 °C
Temperature (trap)	200 °C	200 °C
Desorption time	3 min	3 min
Volume flowrate	carrier gas flow	1 ml/min
Heating and conditioning time	—	225 °C, 7 min

5) The purge-and-trap instrument was from Chrompack. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

6) The purge-and-trap instrument was from Tekmar. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

B.3 GC conditions

Typical GC conditions are (applied for system B):

Column: 30 m × 0,53 mm ID, DB624 stationary phase

Carrier gas: Helium

Temperature programme: 40 °C for 15 min, 5 °C/min to 120 °C, 20 °C/min to 220 °C, 2 min at 220 °C

B.4 MS conditions[7)]

Typical MS conditions are (applied for system B):

Type: Ion trap

Ionization: EI 70eV

Mode: Full scan

Mass range: 25 u to 300 u

Scan speed: 1 scan/s (5-μ scans)

For the compounds analysed by this method and the selected ions for identification and quantitation, see Table B.1.

7) The purge-and-trap conditions are also applicable for GC analysis with detectors other than MS.

Table B.1 — Compounds analysed according to the procedure of Annex B, their retention times and the selected ions for identification and quantitation

Compound	Retention time min: s	Primary ion	Secondary ions
1,1-dichloroethene	05:46	61	63,96,98
dichloromethane	06:06	49	51,84,86
trans-1,2-dichloroethene	06:20	61	63,96,98
1,1-dichloroethane	06:41	63	65,83
2,2-dichloropropane	07:18	77	96,79,97
cis-1,2-dichloroethene	07:18	61	63,96,98
trichloromethane	07:44	83	85
1,1,1-trichloroethane	07:58	97	99,61,117
1,1-dichloropropene	08:14	75	110,77,112
tetrachloromethane	08:14	117	119,121,82
benzene	08:33	78	77
1,2-dichloropropene	08:35	62	64,98
1,1-dichloropropene	09:40	76	77,83,85
trichloroethene	09:56	95	130,132,97
1,2-dichloropropane	10:25	62	63,76,78
2,3-dichloropropene	10:40	75	77,110,112
trans-1,3-dichloropropene	13:00	75	94,109,77
toluene	14:20	91	92
cis-1,3-dichloropropene	15:49	75	77,109,112
tetrachloroethene	16:55	166	131,164,129
1,3-dichloropropane	17:10	76	78,63,112
ethylbenzene	21:01	91	105,106
m-xylene	21:29	91	105,106
p-xylene	21:29	91	105,106
o-xylene	22:48	91	105,106
tribromomethane	23:17	173	171,175

Annex C
(informative)

Application of purge-and-trap concentration to the GC analysis of volatile compounds in water — Example 3: Validation study in the Netherlands

C.1 Purge-and-trap conditions[8)]

Sample volume:	100 ml
Purge gas flowrate:	40 ml/min
Purge time:	30 min
Purge temperature:	95 °C
Purge gas:	Helium
Sorbent:	Tenax TA
Desorption:	240 °C
Time:	15 min
Cryofocusing:	Yes

C.2 GC conditions

Column:	CP-Sil 5, 50 m length, 0,25 mm ID, 1,5 µm film thickness
Oven temperature:	80 °C for 2,5 min,10 °C/min to 280 °C, 280 °C for 10 min.

C.3 MS conditions[9)]

Type of MS:	Ion trap
Mode:	Full scan
Mass range:	20 u to 205 u
Scan speed:	1 scan/s
Multiplier:	1 600 V

8) The purge-and-trap equipment was an off-line combination of a self-built purge-and-trap instrument and a Chrompack thermal desorption unit. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

9) The purge-and-trap conditions are also applicable for GC analysis with detectors other than MS.

C.4 Performance

Table C.1 — Intralaboratory characteristics of the method at a concentration of approximately 200 ng/l water

Compound	Limit of detection (n = 8 to 10) ng/l	Drinking water $s_{rel,r}$	Surface water $s_{rel,r}$
dichloromethane	5	12	17
trichloromethane	8	4	8
1,1,1-trichloroethane	5	5	15
benzene	2	8	3
trichloroethylene	4	4	22
trans-1,3-dichloropropylene	4	5	12
toluene	7	24	70
tetrachloroethylene	5	4	6
monochlorobenzene	1	2	3
ethylbenzene	1	4	10
m-xylene	2	6	13
styrene	1	6	6
1,1,2,2-tetrachloroethane	11	9	6
1,2-dichlorobenzene	3	4	11
hexachloroethane	3	5	5
naphthalene	9	12	27
1,2,3-trichlorobenzene	3	7	14

NOTE $s_{rel,r}$ is the relative standard deviation for the repeatability.

Table C.2 — Interlaboratory characteristics of the method at a concentration of approximately 200 ng/l water

Compound	Limit of detection	Drinking water			Surface water		
	ng/l	$s_{rel,r}$	$s_{rel,R}$	n	$s_{rel,r}$	$s_{rel,R}$	n
dichloromethane	5	6	55	11	8	68	10
trichloromethane	8	10	29	15	7	30	13
1,1,1-trichloroethane	5	5	29	16	6	14	15
benzene	2	11	14	23	6	15	20
trichloroethene	4	4	18	14	7	15	15
trans-1,3-dichloropropene	4	13	41	9	6	15	8
toluene	7	6	11	18	6	16	19
tertrachloroethene	5	5	23	14	7	23	15
monochlorobenzene	1	5	9	15	7	10	13
ethylbenzene	1	6	14	20	7	20	21
m-xylene	2	5	14	18	6	26	17
styrene	1	7	28	15	10	18	14
1,1,2,2-tetrachloroethane	11	3	16	6	6	16	8
1,2-dichlorobenzene	3	10	18	9	6	16	9
hexachloroethane	3	18	58	3	9	66	3
naphthalene	9	6	19	5	12	32	17
1,2,3-trichlorobenzene	3	7	27	5	5	35	4

$s_{rel,r}$ is the relative standard deviation for the repeatability;

$s_{rel,R}$ is the relative standard deviation for the reproducibility;

n is the number of laboratories.

NOTE The intralaboratory data were obtained according to the experimental conditions on the previous page; the interlaboratory data were obtained by various purge-and-trap GC-MS instruments.

Annex D
(normative)

Criteria for the GC-MS identification of target compounds

D.1 GC-MS criteria

D.1.1 Quality assurance

A certain quality of the GC-MS instrumentation is assumed for the application of the following criteria. The quality assurance protocols available at local laboratories (tuning, etc.) shall be followed. A detailed description is beyond the scope of this annex.

Minimum requirements are:

a) *Ionization mode:* electron impact;

b) *Electron energy:* depends on the application (generally 70 eV);

c) *Mass range:* depends on the application;

d) *Scan speed:* a minimum of 7 scans per chromatographic peak;

e) *Scan mode:* full scan or selected-ion monitoring;

f) *Mass resolution:* to be tuned on nominal resolution, the peak width at half-height of every tuned mass shall not exceed 0,7 u.

D.1.2 Retention times

The relative retention time of the target compound shall be determined in an external standard solution. The relative retention times are calculated using the retention-time standard(s). The calculated relative retention time shall have a value between 0,5 and 2.

D.1.3 Mass spectra

If available, select three diagnostic ions for each target compound. Determine their intensities I_1, I_2, I_3 in the external standard solution as the peak area or peak height of the corresponding extracted ion current chromatograms. Calculate the relative intensities as the ratio of the determined peak heights (or areas) and the peak height (or area) of the most intensive diagnostic ion.

D.1.4 Mass spectra with fewer than three diagnostic ions

If the mass spectrum of a target compound contains fewer than three diagnostic ions, the criteria of D.6 apply.

D.1.5 Peak maxima of the extracted ion current chromatograms

Diagnostic ions are supposed to originate only from the analyte under investigation. This implies that theoretically all diagnostic ions belonging to one and the same analyte have the same retention times. If the retention time of one selected diagnostic ion differs from the retention times of the other diagnostic ions from the same analyte, a co-eluting substance or a partly separated substance giving the same mass may be present. If such is the case, the particular diagnostic ion cannot be use.

The accuracy of the retention time depends upon the number of scans within the chromatographic peak and hence on the scan speed. Because the scan speed is limited, small differences in the retention times of the diagnostic ions shall be allowed. A suitable criterion for the allowed difference in retention times of all diagnostic ions of an analyte is 20 % of the peak width at half the peak height. Therefore the differences in retention times of the peak maxima of the selected diagnostic ions in the extracted ion current chromatograms belonging to the same analyte shall not be greater than 20 % of the peak width at half the peak height. The peak shape of all measured diagnostic ions shall be identical. These criteria apply for both the external standard solution and the sample

D.1.6 Overloading

When the mass spectrometer is overloaded, the GC-MS analysis shall be repeated with less sample.

NOTE Overloading can be recognized as the relative intensities of all of the diagnostic ions are significantly higher than in the external standard solution.

D.2 Identification

The analysed target compound is identified if:

— the relative retention time measured in the sample differs by less than $\pm$ 0,2 % from the relative retention time in the last measured external standard solution

and

— the relative intensities of all the selected diagnostic ions measured in the sample do not deviate by more than $\pm$ (0,1 $\times$ I_{std} + 10) % from the relative intensities determined in the external standard solution.

(I_{std} is the relative intensity of the diagnostic ion in the external standard solution)

EXAMPLE Three selected diagnostic ions have the following relative intensities: 100 %, 50 % and 15 %.

The maximum allowed deviation for I_2 and I_3 in the sample is (I_1 is by definition 100 % in both the sample and the external standard):

I_2: $\pm$ (0,1 $\times$ 50 + 10) % = $\pm$ 15 %; in the sample I_2 shall lie between 35 % and 65 %

I_3: $\pm$ (0,1 $\times$ 15 + 10) % = $\pm$ 11,5 %; in the sample I_3 shall lie between 3,5 % and 26,5 %

Only if identification of the target compound has been performed accordingly, is the target compound considered as being identified.

D.3 Indication

If the requirements mentioned in D.2 are not met, but a peak is present, an indication of the presence of the analysed target compound requires that:

— the relative retention time in the sample differs by more than 0,2 % and by less than $\pm$ 1 % from the relative retention time determined in the last measured external standard solution;

and one of the following:

— above the lowest concentration for identification: all selected diagnostic ions are present in the mass spectrum;

— below the lowest concentration for identification: the most intensive diagnostic ion is present in the mass spectrum.

D.4 Negative result (absence of the target compound)

The target compound is absent in the sample (not identified and no indication of its presence), if:

— the relative retention time in the sample deviates by more than 1 % from the relative retention time determined in the last measured external standard solution;

or one of the following:

— above the lowest concentration for identification: not all selected diagnostic ions are present in the mass spectrum;

— below the lowest concentration for identification: the most intensive diagnostic ion is absent in the mass spectrum.

D.5 Suggestions for the selection of the diagnostic ions

— the m/z values should be as high as possible;

— even mass fragments are preferred over odd ones;

— if possible the molecular ion should be selected as one of the diagnostic ions;

— the “uniqueness value” should be as high as possible [11];

— if characteristic isotope clusters are present in the mass spectrum (e.g. chlorine), not more than two diagnostic ions should be selected from one isotope cluster;

— if during the sample preparation, the target compounds have been derivatized with a reagent with low specificity, only one of the ions M^+ and $[MDer]^+$ may be selected as a diagnostic ion (M^+ is the molecular ion of the derivatized target compound);

— in the selection of the diagnostic ions, possible column artefacts shall be taken into consideration, avoiding corresponding masses (e.g. m/z 73, 207, 281).

D.6 Target compounds with fewer than three fragments

In general, if a target compound has fewer than three masses in its mass spectrum, the reliability of identification is limited when no very specific mass fragments are available. However, for volatile compounds, the specificity of the mass fragments in combination with their retention time generally will be sufficient. Their volatility corresponds to a low molecular mass, limiting the number of possible false positive results: there are not many compounds of low molecular mass with the same retention time on a GC column and similar mass spectra.

Compounds with fewer than three mass fragments should be analysed in the full-scan mode. Identification is then based on the comparison of the full-scan mass spectra of the sample and of the external standard solution. In addition to the mass fragments present, the absence of any other fragments in the mass spectrum also serves as important information for identification.

For compounds with fewer than three mass fragments (especially if the available masses are not very specific), the reliability of the identification can be improved by separation on a column of different polarity and/or the application of a second (selective) detector (ECD, AED, PID).

Annex E
(informative)

Procedures for the cleaning of glassware and the preparation of contaminant-free water

E.1 Procedure for the cleaning of glassware

E.1.1 Routine cleaning

The following cleaning procedure is suggested.

NOTE This procedure is an example, and its applicability depends on the specific instrument used.

a) Remove the purge vessel from the purge-and-trap instrument. Ensure that the PTFE ferrules are not damaged during this stage.

b) Flush the purge vessel with clean water, using at least 10-fold its volume. If a water pump is used, suck the water through the vessel rather than pumping it.

c) Fill the purge vessel with a further quantity of clean water, ensuring that the sample portion of the vessel is completely filled. Place the purge vessel in a beaker.

d) Place the beaker in an ultrasonic bath and sonicate for a minimum of 20 min.

e) Discard the water from the purge vessel and repeat steps c) and d), sonicating for another 5 min.

f) Discard the water, dry the outside of the vessel and place immediately into an oven at a temperature greater than 200 °C. The vessels should be heated at this temperature for a minimum of 6 h or preferably overnight.

g) After the purge vessels have dried, cool to 100 °C and transfer immediately to an airtight storage container.

h) The purge vessels should be fitted to the purge-and-trap system while still slightly above ambient temperature, to minimize any adsorption of volatile compounds onto the glassware.

E.1.2 Glassware cleaning processes

For the analysis of samples containing volatile organic compounds in the low microgram per litre range, the preparation of scrupulously clean glassware is essential. Failure to do so can lead to problems in the interpretation of the final chromatogram due to the presence of extraneous peaks. The process of concentrating compounds of interest may similarly concentrate compounds resulting from contamination.

Basic cleaning steps include the following.

a) Remove surface residuals immediately after use. As soon as possible after glassware has come into contact with the sample or standard solutions, rinse the glassware with methanol before placing it in a hot detergent soak. If this is not carried out, the soaking process may serve to contaminate other glassware.

b) Hot-soak the vessel to loosen most of the particulate material which may be present. The hot soak comprises a bath of a suitable detergent in water at 50 °C or higher. The detergent should be entirely synthetic and not of a fatty acid base. Hard-water scum has an affinity for many chlorinated compounds,

and, being almost wholly water-insoluble, can cause deposits to occur as a thin film on all glassware in the bath.

c) Rinse the vessel in hot water to flush away any particulate matter.

d) Soak the vessel in an oxidizing agent to destroy traces of organic matter. The most common (and highly effective) oxidizing agent for removal of traces of organic compounds is chromic acid solution made up of sulfuric acid and potassium or sodium dichromate. For maximum efficiency, the soak solution should be warm (40 °C to 50 °C). Safety precautions should be rigidly observed in the handling of this solution.

e) Rinse the vessels in hot water to flush away loosened materials.

f) Rinse in distilled water to remove any metallic deposits.

g) Rinse with methanol to flush away any final traces of organic materials and to remove water.

h) Flush the vessels immediately before use with a suitable solvent and dry before use.

There is always a possibility that between the time of washing and subsequent use, the glassware may be be contaminated from either the atmosphere or by direct contact with volatile organic compounds. For checking, it is good practice to flush the vessels immediately before use with a suitable solvent, for example methanol.

E.2 Preparation of interference-free water

Verify the quality of the water to be used. For example, use the following procedure as a suitable preparation method.

Place water in a bottle with a conical shoulder, nominal capacity 2 litres, fitted with a ground-glass stopper, pretreated according to this annex.

Determine the content of the highly volatile halogenated hydrocarbons in this water.

If the water is contaminated, purify as follows:

— position a glass delivery tube with a sintered glass distributor a few millimetres above the bottom of the bottle;

— heat the water to approximately 60 °C;

— pass a stream of clean nitrogen (flowrate approximately 150 ml/min to 200 ml/min) through the water for 1 h via the bubbler. Let the water cool to room temperature and stopper the bottle;

— store the water in a glass bottle in the dark.

Subsequently verify again the absence of highly volatile halogenated hydrocarbons. If contamination is found, use a purge gas from another source and repeat the procedure.

NOTE Procedure taken from ISO 10301.

Annex F
(informative)

Preparation of standard solutions of volatile organic compounds

F.1 General

The amounts and volumes given below are examples; depending on the desired working range, different values may be taken.

F.2 Preparation of stock and spiking solutions

F.2.1 Stock solution for liquid substances

Add approximately 90 ml of solvent (6.2) to a 100 ml graduated flask.

Dose with a microlitre syringe defined volumes of 100 µl to 300 µl or defined quantities of between 100 mg and 300 mg of each VOC under the surface of the solvent.

Immediately make up to volume with the solvent (6.2).

Stopper the flask with a ground-glass stopper and cautiously shake the solution.

Calculate the respective concentrations of the compounds added by using their densities.

F.2.2 Stock solution for substances of semi-gaseous state at room temperature (vinyl chloride, fluorochlorohydrocarbons)

Fill a headspace vial to between 50 % and 80 % with e.g. 20 ml of dimethylformamide (DMF) (6.2); seal the vial with a PTFE-laminated crimp cap and weigh to an accuracy of 0,2 mg.

Inject a fixed volume of vinyl chloride gas into the headspace of the headspace vial using a gas-tight syringe.

Do not allow the injection needle to come in contact with the solvent.

Ensure pure gas is added in the following way: e.g. evacuate a gas sample tube, fill it with vinyl chloride gas and take it out using a syringe.

Prepare at least five standard stock solutions of vinyl chloride, preferably evenly distributed over the working range, for the calibration function. As the preparation of gaseous standards is a very delicate procedure, replicate standard stock solutions are strongly recommended to allow a check on proper preparation.

Weigh the added vinyl chloride to an accuracy of 0,2 mg and determine the quantity of vinyl chloride using the difference in masses.

To prepare mass concentrations < 100 µg/l, prepare standard solutions of higher concentration and dilute with dimethylformamide.

NOTE The procedure as described here may also be applied to substances of liquid state at room temperature.

Store the stock standard solutions in screw-top flasks with PTFE-coated screw caps. Methanol solutions of the liquid substances remain stable for at least 4 weeks at about 4 °C.

Solutions of vinyl chloride in methanol or DMF remain stable for up to one week, provided they are stored at temperatures below 5 °C.

F.2.3 Preparation of spiking solutions

Allow the stock solution to equilibrate to room temperature for about 15 min, shaking occasionally with care.

Prepare at least 5 spiking solutions of different concentrations by dilution of small volumes of the stock standard solution into an appropriate solvent, preferably the same solvent used for preparing the stock solutions. See also 6.6.

The individual dilution steps should not exceed a ratio of 1:100.

F.3 Preparation of the aqueous calibration solutions

For the measuring range of a substance of between e.g. 0,03 µg/l and 3,0 µg/l, take the following steps:

Place a 250 ml graduated flask containing water (6.1) and a glass-coated magnetic stirring rod on a magnetic stirrer.

While stirring, dose with up to 25 µl of a spiking solution (F.2.3) directly into the turbulence funnel under the water surface.

Reduce the rotational speed of the magnetic stirrer until the vortex disappears.

Stopper the graduated flask and continue stirring for another 15 min.

For blank determination, prepare another graduated flask with water and with only the same volume of solvent.

Prepare a fresh aqueous calibration solution when needed.

Annex G
(informative)

Determination of the (absolute) recovery of substances analysed by purge-and-trap concentration

The purge-and-trap performance of the compound can be verified according to the procedure below, which is applicable to on-line and off-line purge-and-trap GC analysis. Depending on the working range of interest and the instrument in use, different volumes or amounts can be applied. The values given below are examples.

Put 5 µl of the spiking solution (concentration close to half of the linear range) on an adsorbent trap. Remove the solvent by passing a purge gas through the absorbent trap for 5 min to 10 min and then analyse the adsorption tube. Compare the results with those of a spiked water sample with an addition of 5 µl of the same spiking solution. The absolute purge-and-trap recovery for analyte i [η_i(abs)] is determined as follows:

$$\eta_i(\text{abs}) = y_{i,\text{p}} / y_{i,\text{s}} \times 100\ \%$$

where

η_i(abs) is the absolute purge-and-trap recovery for analyte i;

$y_{i,\text{p}}$ is the response of analyte i after purging, e.g. peak area;

$y_{i,\text{s}}$ is the response of analyte i after direct spiking, e.g. peak area.

As the standard itself applies calibration over the entire procedure, no corrections for incomplete recovery should be carried out.

NOTE Incomplete recovery may result in poor sensitivity for the specific compound or in poor repeatability and reproducibility. To improve the recovery of specific compounds, the purge time can be prolonged or the purge temperature can be increased. An alternative determination of the recovery is to carry out repeated purge-and-trap analyses of the same sample. From the decrease of the peak area, the initial analyte concentration in the sample can be calculated. This procedure is particularly suitable for on-line systems.

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