INTERNATIONAL STANDARD

ISO 15680

First edition
2003-11-01

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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Reference number
ISO 15680:2003(E)

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Foreword

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

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*.

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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

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.

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

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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.

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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).

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

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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.

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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).

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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.

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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.

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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

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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.

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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.

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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.

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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).

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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.

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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

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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.

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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.

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The purge-and-trap apparatus should include:

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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.

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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.

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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).

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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.

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