INTERNATIONAL STANDARD

ISO 10301

First edition
1997-04-15

Water quality — Determination of highly volatile halogenated hydrocarbons — Gas-chromatographic methods

Qualité de l'eau — Dosage des hydrocarbures halogénés hautement volatils — Méthodes par chromatographie en phase gazeuse

Reference number
ISO 10301:1997(E)

Contents

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X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

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.

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.

International Standard ISO 10301 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annexes A to G of this International Standard are for information only.

Introduction

Highly volatile halogenated hydrocarbons are used in industrial, commercial and domestic fields, and can enter a water body via waste water and may consequently contaminate drinking water. Furthermore, they can originate from the use of chlorine as an oxidizing agent in water and waste-water treatment. They also can be introduced by inappropriate handling. In addition, they can be formed by decomposition of higher molecular mass organohalogen derivatives.

In uncontaminated ground water and rain water, the concentrations of halogenated hydrocarbons are generally below 0,1 µg/l. In surface water they may be higher, depending on the origin and quality of the water. In untreated waste water the concentrations may reach saturation of the aqueous phase. In general, the solubility of these compounds in organic solvents and in fatty material exceeds their solubility in water.

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Water quality — Determination of highly volatile halogenated hydrocarbons — Gas-chromatographic methods

Section 1 : General

1.1 Scope

This International Standard specifies two methods for the determination of highly volatile halogenated hydrocarbons using gas chromatography.

Section 2 specifies a method for the determination by liquid/liquid extraction of highly volatile halogenated hydrocarbons in drinking water, ground water, swimming pool water, most rivers and lakes and many sewage and industrial effluents. Typical values of "quantification limits" are given in table 1.

Table 1 — Typical values of "quantification limits" for some highly volatile halogenated hydrocarbons using liquid/liquid extraction

Compound	**Quantification limits** µg/l
Dichloromethane	50
Chloroform	0,05 - 0,3
Carbon tetrachloride	0,01 - 0,1
1,1-Dichloroethane	1,0 - 5
1,2-Dichloroethane	5 - 10
1,1,1-Trichloroethane	0,02 - 0,1
1,1,2,2-Tetrachloroethane	0,05 - 0,1
Hexachloroethane	0,01 - 0,05
cis-1,2-Dichloroethylene	5 - 50
trans-1,2-Dichloroethylene	1 - 10
Trichloroethylene	0,05 - 0,1
Tetrachloroethylene	0,1
Hexachlorobutadiene	0,01
Tribromomethane	0,1
1,1,2-Trichlorotrifluoroethane	0,1

Section 3 specifies a method for the determination of highly volatile halogenated hydrocarbons in drinking water, surface waters and ground water by a static head-space method. Typical values of "quantification limits" are given in table 2.

In practise, the head-space method is applicable for industrial effluents as a screening method, but in some cases it is necessary to confirm the result by the liquid-liquid extraction method.

NOTE : When applying this International Standard, the guide on analytical quality control for water analysis (see ISO/TR 13530) should be followed, especially for the calibration steps.

Table 2 — Typical values of "quantification limits" for some highly volatile halogenated hydrocarbons using static head-space method

Compound	Quantification limits µg/l
Dichloromethane	50
Chloroform	0,3
Carbon tetrachloride	0,1
1,1-Dichloroethane	100
1,2-Dichloroethane	100
1,1,1-Trichloroethane	0,1
1,1,2-Trichloroethane	20
1,1-Dichloroethylene	10
cis-1,2-Dichloroethylene	50
trans-1,2-Dichloroethylene	25
Trichloroethylene	0,2
Tetrachloroethylene	0,2
1,2-Dichloropropane	50
1,3-Dichloropropane	200
cis+trans-1,3-Dichloropropylene	10
Dibromomethane	0,3
Tribromomethane (Bromoform)	5
1,2-Dibromoethane	2
Bromochloromethane	1
Bromodichloromethane	0,2
Dibromochloromethane	0,3
1,1,3-Trifluoroethane	1

1.2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1:1980,	Water quality - Sampling - Part 1 : Guidance on the design of sampling programmes
ISO 5667-2:1991,	Water quality - Sampling - Part 2 : Guidance on sampling techniques
ISO/TR 13530:–[1]	Water quality - Guide to analytical quality control for water analysis

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[1] In preparation.

1.3 Definition

For the purposes of this International Standard, the following definition applies :

1.3.1 highly volatile halogenated hydrocarbons: Fluorinated, chlorinated, brominated and/or iodinated mainly nonaromatic hydrocarbons composed of one to six atoms of carbon.

NOTE Their boiling points generally fall within the range of 20 °C to 220 °C at atmospheric pressure (see annex A).

Section 2 : Liquid/liquid extraction and analysis by gas chromatography

2.1 Principle

The highly volatile halogenated hydrocarbons are extracted into an organic solvent. The solution is then analysed by gas chromatography with an electron-capture detector or any other suitable detector.

2.2 Interferences

Interferences can be due to the sampling procedure, vials and stoppers, solvents, gases, organic compounds in the laboratory atmosphere and contamination from the autosampler. Procedures for minimizing contamination are given in 2.5 and 2.6.

2.3 Reagents

All reagents shall be of sufficient purity so as to not give rise to significant interfering peaks in the gas chromatogram of the solvent extract. The purity of reagents shall be verified by a suitable procedure, for example, by blank determinations (see 2.6.4).

Reagents can become contaminated by contact with air and other materials, particularly plastics, or by degradation caused by the action of light. Store all reagents in the dark in tightly sealed all-glass containers or other suitable vessels.

2.3.1 Water for the preparation of calibration solutions and blank

The quality of the water used shall be determined. 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 2.4.2.

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 (approximately 150-200 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 of another source and repeat the procedure.

2.3.2 Gases for gas chromatography

Nitrogen, ultrapure, volume concentration minimum 99,996 %, or argon-methane mixture, ultrapure. Other gases for gas chromatography shall be in accordance with the instrument manufacturer's instructions.

2.3.3 Extraction solvent (pentane) free from highly volatile chlorinated hydrocarbons

Analyse a sample of the extraction solvent by electron-capture gas chromatography to ensure that it does not contain material giving rise to interfering peaks in the chromatogram. If the compound of interest elutes in the same range as the extraction solvent, then use other solvents such as hexane, petroleum ether, heptane or xylene (for waste waters), providing that the validity of the result is maintained.

2.3.4 **Sodium sulfate,** anhydrous

Heat a portion of about 250 g to 300 g of Na_2SO_4 at 500 °C ± 20 °C for 4 h ± 30 min ; cool to about 200 °C in a muffle furnace and then to ambient temperature in a desiccator containing magnesium perchlorate (2.3.6) or equivalent alternative.

2.3.5 Sodium thiosulfate

Prepare a sodium thiosulfate solution (30 g/l) by dissolving 46 g ± 0,2 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) in 1 000 ml ± 5 ml water (see 2.3.1).

NOTE : Alternatively, solid sodium thiosulfate may be used.

2.3.6 Magnesium perchlorate

2.3.7 Water-miscible solvent

NOTE : Methanol, acetone or dimethylformamide may be used.

2.3.8 Reference substances

Pure examples of the highly halogenated hydrocarbons to be determined are required.

Store these reference substances in areas separate from sample extracts and the solvent used for the extraction.

NOTE : For reference substances which are gaseous at ambient temperature, it is recommended to use commercially available solutions.

2.3.9 Standard stock solutions

Prepare standard stock solutions by adding with a microlitre syringe defined quantities of each reference substance (see 2.3.8) under the surface of a suitable solvent.

NOTE : Suitable solvents for the preparation of standard stock solutions are acetone, pentane, hexane, dimethylbenzene or isooctane.

The containers containing the solutions shall be marked or weighed so that any evaporation losses of the solvent may be recognized. The solutions shall be stored in volumetric flasks with ground glass stoppers at a temperature of 4 °C in the dark. Prior to use, they shall be brought to ambient temperature and the level of solvent shall be adjusted, if necessary.

NOTE 1: A convenient concentration of standard stock solution is obtained by weighing 50 mg of the reference substance and dissolving it in 100 ml of the solvent. The solution is stable for about 1 year.

NOTE 2: For practical reasons, it is recommended to use mixed standard stock solutions.

2.3.10 Intermediate standard solutions

Prepare intermediate standard solutions by a suitable dilution of the stock solution (see 2.3.9) with the extraction solvent (see 2.3.3).

A typical value is 10 µg/ml.

Store the intermediate standard solutions at about 4 °C in the dark. These solutions are stable for 6 months.

2.3.11 Working standard solutions

Prepare at least five different concentrations by suitable dilutions of the intermediate standard solutions (see 2.3.10) with the extraction solvent (see 2.3.3).

Suitable concentrations are in the ng/ml range. Store these solutions at about 4 °C in the dark. These solutions are stable for at least 1 month.

2.4 Apparatus

2.4.1 Gas chromatograph fitted with an electron-capture detector or any other suitable detector and with suitable columns.

Separation of the highly volatile halogenated hydrocarbons requires high separation power. The best separations are obtained with capillary columns.

Different reference columns (specific for volatiles compounds) are available from the chromatographic equipment suppliers. The choice depends on the variety of substances to be analysed, the sampling technique, gas chromatograph configuration, etc.

As a guide, the following rules may be applied to the gas chromatograph column:

a) nonpolar [(poly(dimethylsiloxane)] or semipolar [(poly(5 %-diphenyl-95 % dimethylsiloxane)] bonded phases ;

b) as the relation between internal diameter and film thickness is a critical parameter, choose a phase ratio around 80 - 100 (suitable for volatile, low molecular mass compounds) ;

c) length : generally, more than 30 m.

Annex B gives several examples of separation.

NOTE : Nonvolatile compounds, contained for example in waste water, may shorten the lifetime of the gas chromatographic column.

2.4.2 Ordinary laboratory glassware

As an example of preparation, glassware to be used may be washed with detergent, rinsed with deionized water and finally with the extraction solvent or heated in an oven at 150 °C for at least 1 h and cooled at room temperature before use.

In order to minimize contamination during transport or storage, close the vessels and protect the neck of the bottle, for example with aluminium foil.

All syringes shall be thoroughly cleaned and their cleanliness verified by gas chromatography before use.

2.4.3 Glass bottles, capacity about 250 ml, sealed with a solid glass stopper.

Prior to use, place the bottles upside down in a ventilated drying oven along with the stoppers and heat them for at least 1 h at 150 °C.

2.4.4 Glass vials of capacity approximately 30 ml to 40 ml, with polytetrafluoroethylene (PTFE) coated septum.

2.4.5 Magnetic stirrer or mechanical shaker

2.4.6 Magnetic stirrer rods (length approximately 4 cm), coated with PTFE. Store the magnetic stirrer rods separately for each concentration range.

2.4.7 Microseparator (see as an example annex C, figure C.1).

2.4.8 Glass wool washed with extraction solvent.

2.4.9 Bottles with PTFE-coated septum, capacity approximately 2 ml, to store the extract.

2.5 Sampling and sample preparation

Take samples according to ISO 5667-1 and ISO 5667-2.

Collect and store the water samples in bottles (see 2.4.3) cleaned as described in 2.4.2.

In the special case of septum-vial extraction (see 2.6.2), fill glass vials (see 2.4.4).

Collect the sample normally by immersion, by filling the bottle or the vial completely, discarding this water, refilling and stoppering so as to leave no headspace.

Loss of volatile compounds through degassing of the sample shall be avoided. Slowly fill the bottle at the sampling point until it overflows, avoiding turbulence.

The use of plastics tubing when taking samples shall be kept to a minimum in order to avoid losses or contamination of the sample.

If reaction between free halogens and organic matter in the sample, to produce trihalogenated methanes, is to be eliminated, add an excess of sodium thiosulfate (see 2.3.5) to the sampling bottle or vial after rinsing the bottle or the vial but prior to sampling.

NOTE : The quantity of sodium thiosulfate added to the sample is not critical but should be sufficient to react with all the chlorine present. Normally 0,1 ml to 0,2 ml of a 30 g/l solution (see 2.3.5) or a few crystals (3 mg to 5 mg) of solid sodium thiosulfate will be appropriate for a sample volume of about 250 ml.

If an internal standard is needed, it shall be added as soon as possible after sampling.

Avoid warming the sample during the transport.

If storage is unavoidable, cool the samples to about 4 °C and carry out the extraction within 48 h, if possible, since the extracts are much more stable than the water samples.

NOTE : If composite samples are being analysed, losses of highly volatile chlorinated hydrocarbons may occur when individual samples are mixed.Therefore, individual samples should be extracted separately and the solvent extracts combined before analysis.

2.6 Procedure

Use the extraction procedures described in 2.6.1 or 2.6.2. If in the laboratory, contamination of the sample by air cannot be excluded, use septum-vial extraction (see 2.6.2).

2.6.1 Extraction

Take the full sample bottle (see 2.5) and discard enough water so that there is a residual sample volume of 200 ml ± 10 ml. Weigh the bottle and sample in order to accurately determine the sample volume. Add the extraction solvent (see 2.3.3), close and mix vigorously with the sample using a magnetic stirrer or a mechanical shaker for 5 min (see 2.4.5), to ensure that the extractant is finely dispersed in the sample in order to obtain a reproducible recovery.

NOTE : The volume of solvent used depends upon the type of sample ; suitable volumes are 10 ml for drinking water and 50 ml for waste water.

After mixing, allow the sample container to stand until the layers separate. Draw off directly the upper solvent layer using a pipette or, if the phases are not well separated, a microseparator (see 2.4.7) as follows :

Insert a glass wool plug (about 2 cm) through the central tube of the microseparator until it reaches the wider part. Rinse the tube and the plug with extraction solvent and dry both. Place the microseparator on top of the bottle containing the extracted sample and slowly add through the side tube sufficient water (see 2.3.1) so that the extract rises in the central tube past the glass wool.

It is not necessary to filter all of the organic phase through glass wool to obtain sufficient liquid for analysis.

If this treatment is not successful, separate the phases by centrifugation of a few millilitres of the turbid organic phase in a closed glass vessel (such as a centrifuge tube with a screw cap) or by freezing.

Do not concentrate the sample extract by evaporation.

Immediately proceed to gas chromatographic analysis (see 2.6.3). If analysis cannot be carried out immediately, store the solvent extract in an airtight stoppered bottle (see 2.4.9) at a temperature of about 4 °C, no longer than one month.-

NOTE : For higher-boiling extraction solvents, such as hexane or 1,2-dimethylbenzene (*o*-xylene), cooling is not necessary; 1,2-dimethylbenzene extracts should be dried with anhydrous sodium sulfate (see 2.3.4) or magnesium perchlorate (see 2.3.6) (approximately 10 mg/ml) prior to gas chromatographic analysis.

The extraction shall be carried out in an environment as free as possible from volatile halogenated compounds. Often, interfering peaks will occur, especially at the beginning of the chromatogram. Contamination of the sample may be caused by sprays being used, solvents in the laboratory or refrigerants coming from chillers. Blank determinations (see 2.6.4) are necessary.

2.6.2 Septum-vial extraction

NOTE : Owing to the absence of a headspace, mixing with this technique is less efficient than using a bottle as in 2.6.1. Recoveries may be a little lower but are acceptable and reproducible.