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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

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Contents

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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.

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.

Take the vial (see 2.4.4) filled according to 2.5 and insert a hypodermic syringe needle, through the septum, a distance of approximately 1 cm into the sample. Fill a 5 ml syringe with extraction solvent (see 2.3.3) and adjust the volume in the syringe to 2,5 ml, taking care to exclude any air bubbles. Insert the syringe needle, with syringe containing solvent now attached, through the septum, as far as possible into the vial. Invert the syringe plus vial (vial now above syringe) and inject the 2,5 ml of extraction solvent (see 2.3.3) into the vial. 2,5 ml of sample will be displaced via the open syringe needle. Withdraw both needles and shake the vial vigorously for 5 min.

Allow the layers to separate.

Then proceed to gas chromatographic analysis (see 2.6.3) or keep the extract with the water present for analysis. These extracts have proved stable for one month when stored in the vials, in the dark, at a temperature of about 4 °C.

NOTE : This method relies on the volume of the vials being reproducible. Nevertheless each vial should be checked and its volume noted for use in recovery checks.

2.6.3 Gas chromatography

Set up the gas chromatograph (see 2.4.1), fitted with an electron-capture detector or any other suitable detector and equipped with a suitable column, according to the manufacturer's instructions.

Normally, better resolution will be obtained with capillary columns.

The electron-capture detector is sensitive to halogenated hydrocarbons, but is not specific in its response. Its sensitivity to different halogenated hydrocarbons varies considerably (see annex D, table D.1) and the linearity of response to the compounds of interest and the useable working range of concentrations shall be determined by investigation using a series of calibration standard solutions of known concentrations.

Eliminate any contamination of the electron-capture detector which may cause a high or unsteady baseline according to the instructions of the manufacturer. Such contamination may be caused by contaminated gas (especially oxygen contamination) or a dirty detector due to a high column bleeding rate.

Should it be found necessary to clean the detector, the detector response and linearity shall be reconfirmed after cleaning and before further samples are analysed.

Inject an aliquot of the clear extract (see 2.6.1) into the injection port of the gas chromatograph or, in case of septum-vial extraction (see 2.6.2), withdraw aliquots of the solvent layer for gas chromatographic analysis through the septum using an appropriate microsyringe.

Compare the gas chromatogram obtained to those of the standard solutions (see 2.7).

Evaluate the gas chromatogram qualitatively and quantitatively (see 2.8). The requirements concerning the measurements, the calibration, evaluation and calculation techniques to be used are described in 2.7 and 2.8.

2.6.4 Blank determination

Prior to analysis and at regular intervals, carry out full blank determinations using water (see 2.3.1).

Take the blank through the complete analytical procedure, starting with sampling and including all steps until the evaluation of the gas chromatogram.

If the blank value is too high (> 10 % of the measured value for any of the compounds of interest), find the cause through step-by-step examination of the procedure. Decrease the blank value through suitable measures (for example, extraction of the "clean water" with the extraction solvent prior to analysis, elimination of contamination in the room air, checking of the gas chromatograph and integration parameters).

In the case of high blank values caused by laboratory air contamination, follow the method given in 2.6.2.

2.7 Calibration

Initially, determine the recovery ; obtain this recovery with the two following calibration steps :

a) calibration by direct injection of solvent standard solutions (see 2.7.1). This gives information on the linear working range of the detector, retention times and relative responses of the determinands.

b) calibration of the overall procedure (see 2.7.2) using spiked water samples, and extraction.

The data obtained from 2.7 a) are compared with those from 2.7 b) in order to calculate the recovery (see 2.7.3) of each determinand.

Carry out the daily recalibration (see 2.7.4) with solvent standard solutions according to a) or with spiked water extracts according to b).

The use of an internal standard is recommended (see 3.7.3.2) ; it allows some correction of differing extraction recovery and errors in the injected volume, for example :

- 1-bromo-2-dichloroethane ;
- 1,2-dibromoethane ;
- *trans*-1,2-dichloroethylene ;
- bromotrichloromethane ;
- 1,2-dibromo-1,1-dichloroethane.

Table 3 gives an explanation of the subscripts used in equations and the following text :

Table 3 — Explanation of the subscripts used in the symbols

Index	Meaning
i	Identity of the determinand
e	Measured value in calibration
g	Entire procedure
I	Internal standard

2.7.1 Calibration with an external standard, not using the overall procedure

Inject defined volumes in the range of 1 µl to 5 µl of the working standard solutions (see 2.3.11) into the gas chromatograph.
Measure the gas chromatograph signals for each substance (peak heights or peak areas or integration units respectively) and calculate concentrations.

For a graphic presentation of the calibration curve, plot the respective measured value y_{ie} on the ordinate against the respective mass concentrations ρ_{ie} of the substance i on the abscissa.

The injection volume used for calibration and for the measurement of the sample solutions shall be kept constant.

The series of measured values thus obtained shall be used to establish the linear regression function as follows :

$$y_{ie} = m_i \cdot \rho_{ie} + b_i \tag{1}$$

where :

y_{ie} is the (dependent variable) measured response of substance i, depending on ρ_{ie} ; the units depend on the evaluation, for example, area value ;

ρ_{ie} is the (independent variable) mass concentration of the substance i (external standard) in the calibration solution, in micrograms per litre ;

m_i is the slope of the calibration curve of substance i ; (corresponds to the substance-specific response factor f_i). The units depend on the evaluation, for example, area value x (l/µg) ;

b_i is the intercept of the calibration curve on the ordinate ; the unit depends on the evaluation for exemple, area value. As a rule, the intercept is very small. If it is large, the gas chromatographic system and the evaluation system shall be checked.

2.7.2 Calibration of the overall procedure using external standard

For each compound a separate calibration function (via the overall procedure) shall be established, consisting of at least five measurement points. It is permissible to examine several compounds in one calibration experiment.

To calibrate the entire procedure, prepare aqueous solutions by spiking water (see 2.3.1) with the compounds to be determined in an individual concentration range within the linear dynamic range of the detector as follows :

2.7.2.1 Preparation of spiked aqueous standard solutions

To a 100 ml volumetric flask, containing about 90 ml of water-miscible solvent (see 2.3.7), add, under the surface of the solvent using a microlitre syringe (see 2.4.2), known quantities of the standard stock solutions (see 2.3.9) of each determinand. Immediately make up to volume with the water-miscible solvent (see 2.3.7).

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

Calculate the respective concentration of each substance added.

The solution prepared in this way can be stored at a temperature of about 4 °C in the dark for several weeks. Prior to use, equilibrate at room temperature for at least 15 min.

Prepare at least 5 spiked aqueous standard solutions covering (depending on the compounds) the range 1 µg/l to 200 µg/l by adding different volumes of the above solution to water (see 2.3.1).

For the blank measurement, add to one bottle of water (see 2.3.1) the same quantity of solvent used for the preparation of the spiked aqueous standard solutions.

Use quantities such that the volume added is as small as possible ($\leqslant$ 1 ml/l of water), in order to minimize any effect on the partition equilibrium.

Prepare the spiked aqueous standard solutions on the day of use.

2.7.2.2 Calibration curve

Extract these spiked aqueous standard solutions (see 2.7.2.1) as described in 2.6.1 or 2.6.2.

The ratio of the volume of aqueous solutions to the volume of extraction solvent shall be identical to that of the flasks containing the samples.

Inject into the gas chromatograph the extract of the blank solution and then the calibration solutions with concentrations ρ_{ieg} in ascending order. Measure the peak values y_{ieg} of the the calibration samples.

Calculate a regression function for each substance using the pairs of values y_{ieg} and ρ_{ieg}. Deduct the value of the appropriate blank from each measured value y_{ieg}.

$$y_{\text{ieg}} = m_{\text{ig}} \cdot \rho_{\text{ieg}} + b_{\text{ig}} \tag{2}$$

where :

y_{ieg} is the (dependent variable) measured response of the substance i during calibration, depending on ρ_{ieg}. The units depend on the evaluation, for example area values ;

ρ_{ieg} is the (independent variable) mass concentration of the substance i in the calibration solution (external standard), in micrograms per litre ;

m_{ig} is the slope of the calibration curve of substance i ; corresponds to the substance-specific response factor, often referred to as f_{i}. The units depend on the evaluation, for example, area values x (l/µg) ;

b_{ig} is the axis intercept of the calibration curve on the ordinate. The units depend on the evaluation, for example, area values.

Plot the reference functions with the ordinate as the substance-specific measured signals y_{ieg} and the abscissa as the mass concentration ρ_{ieg} of the substance i in the spiked aqueous calibration solution. With the aid of the calibration curve, define the working range of the procedure.

2.7.3 Determination of the recovery

Determine by means of the calibration procedure according to 2.7.1 and 2.7.2 the substance-specific mean recovery A_{i}, for the substance i [see equation (3)].

$$A_{\text{i}} = \frac{m_{\text{ig}}}{(m_{\text{i}}/F_{\text{v}})} = \frac{m_{\text{ig}} \cdot V_{\text{E}}}{m_{\text{i}} \cdot V_{\text{p}}} \tag{3}$$

where :

A_i is the mean recovery for the substance i ; dimensionless ;

m_i see equation (1) ;

m_{ig} see equation (2) ;

F_v is the volume ratio of extraction solvent to sample. This factor has to be calculated taking into account sample volume, extractant volume, dilution factors (if applicable).

The following equation applies :

$$F_v = \frac{V_E}{V_p} \qquad (4)$$

where :

V_E is the final extraction solvent volume, in millilitres ;

V_p is the sample volume, in millilitres.

The recovery thus obtained is valid only under the experimental conditions used.

A high recovery is an essential prerequisite for good precision and accuracy of the analytical result. Variations of these values will indicate problems in extraction and preparation of standards. The recovery depends on determinands and is generally greater than 60 %. If not, the procedure should be checked.

Annex E (see table E.1) gives examples showing typical recovery data for drinking water.

2.7.4 Recalibration

For routine recalibration of the method, it is essential to work within the previously established linear range (see 2.7.1 or 2.7.2). This shall be updated regularly, especially when contaminated samples such as sewage or industrial effluents are analysed, as these may affect the detector and hence the linear range.

The minimum requirement for daily recalibration shall be injections of two standard solvent solutions (see 2.3.11) or two spiked water extracts (see 2.7.2). The concentration of the first solution shall be about 20 % of the selected linear working range, the concentration of the second solution about 80 %.

Calculate a regression function.

Compare this function to the previous established calibration curve (see 2.7.1 or 2.7.2). If the values are within the range of the confidance limits of the previously established calibration curve (see 2.7.1 or 2.7.2), use the new calibration for evaluation. If not, check the system and establish a complete new calibration curve.

2.8 Identification and evaluation

2.8.1 Identification of individual compounds

If, in the chromatogram of the sample extract run on a particular capillary column, no peak appears at the substance-specific retention time, consider the compound as not being detected.

If a peak appears at a particular substance-specific retention time, the presence of the compound is possible. Confirm the identity of this compound:

Repeat the complete comparison procedure, using a capillary column with a different polarity.

Normally, the reliability of the identification increases with increasing difference in the polarities of the column applied. If the comparative study with two capillary columns of differing polarities reveals the presence of peaks at the expected substance-specific retention times, consider the identity of the substance as highly probable.

NOTE : If necessary, mass spectrometry can be used for further confirmation.

2.8.2 Evaluation of individual compounds

2.8.2.1 Evaluation using (re)calibration according to 2.7.1

Calculate the mass concentration ρ_i of the substance i in the water sample, using equation (5) after solving equation (1) for the mass concentration ρ_i :

$$\rho_i = \frac{y_i - b_i}{m_i} \qquad (5)$$

where :

ρ_i is the mass concentration of the substance i in the water sample (uncorrected by recovery), units µg/l ;

y_i is the measured value of the substance i in the extract of the water sample (on condition that the same procedure is applied as with the calibration and the sample measurement) ; units depend on the evaluation, for example, area values ;

m_i is the slope of the calibration curve (see 2.7.1 or 2.7.4) of the substance i ; units depend on the evaluation, for example, area value x (l/µg) ;

b_i is the axis intercept of the reference line on the ordinate ; units depend on the evaluation, for example, area values.

If data taking into account recovery are required, the mass concentration ρ_{ic} of the substance i is calculated using equation (6) after solving equation (1) for the mass concentration ρ_{ic} :

$$\rho_{ic} = \frac{y_i - b_i}{m_i A_i} \tag{6}$$

where :

ρ_{ic} is the mass concentration of the substance i in the water sample (corrected by mean recovery), units µg/l ;

y_i is the measured value of the substance i in the extract of the water sample (on condition that the same procedure is applied as with the calibration and the sample measurement) ; units depend on the evaluation, for sample, area values ;

m_i is the slope of the calibration curve (see 2.7.1 or 2.7.4) of the substance i ; units depend on the evaluation, for example, area value x (l/µg) ;

b_i is the axis intercept of the reference line on the ordinate ; units depend on the evaluation, for example, area values ;

A_i is the specific mean recovery for the substance i.

2.8.2.2 Evaluation using (re)calibration according to 2.7.2

Calculate the mass concentration ρ_{ig} of the substance i in the water sample using equation (7) after solving equation (2) for the mass concentration ρ_{ig} :

$$\rho_{ig} = \frac{y_{ig} - b_{ig}}{m_{ig}} \tag{7}$$

where :

ρ_{ig} is the mass concentration of the substance i in the water sample (corrected by recovery), units µg/l ;

y_{ig} is the measured value of the substance i in the extract of the water sample (on condition that the same procedure is applied as with the calibration and the sample measurement) ; units depend on the evaluation, for example, area values ;

m_{ig} is the slope of the calibration curve (see 2.7.2 or 2.7.4) of the substance i ; units depend on the evaluation, for example area values x (l/µg) ;

b_{ig} is the axis intercept of the reference line on the ordinate ; units depend on the evaluation, for example area values.

2.8.3 Summary of the results

When the procedure described is applied, gas chromatography provides one individual result for each column used. Derive the final quantitative result from these two individual results as follows :

a) take the arithmetic mean, provided the differences between the individual results are less than 10 %, related to the lower result ;

b) choose the smaller value in the event of larger differences, provided that the smaller value is not caused by leakage in the gas chromatograph system. The larger value may be the result of peak overlap. Such a result shall be reported as a measured value, obtained from a single separation only.

2.9 Expression of results

Report the results, in micrograms per litre, to not more than two significant digits, as follows :

- at mass concentrations < 10 µg/l, report to the nearest 0,1 µg/l ;
- at mass concentrations ⩾ 10 µg/l, report to the nearest 1 µg/l.

EXAMPLES :

- trichloroethylene	0,8 µg/l ;
- tetrachloroethylene	110 µg/l.

2.10 Precision data

Data of interlaboratory tests are given in tables 4, 5 and 6.

Table 4 — Standard deviations of tap water

	a) Low spike				**b) High spike**			
Compound	**Spike level** µg/l	**Mean conc. found**	**Standard deviation** %	**Recovery** %	**Spike level** µg/l	**Mean conc. found**	**Standard deviation** %	**Recovery** %
1,1-Dichloroethylene	2,00	2,09	7,9	105	20,0	18,4	3,7	92,2
1,1,1-Trichloroethane	0,500	0,453	9,1	91	5,0	4,72	2,3	94
1,1,2-Trichloroethane	10,00	8,18	3,5	82	100,0	72,2	4,2	77
Tetrachloroethylene	0,500	0,600	11,2	120	5,0	5,26	3,4	105
1,1,1,2-Tetrachloroethane	0,500	0,385	7,2	77	5,0	4,85	2,2	97
1,1,2,2 Tetrachloroethane	2,00	1,68	6,4	84	20,0	17,1	4,0	86
Carbon tetrachloride	0,250	0,200	8,8	80	2,5	2,53	3,2	101
Chloroform	2,50	2,15	6,2	86	25,0	19,5	4,9	98
Trichloroethylene	0,500	0,479	10,4	96	5,0	4,89	4,2	78
Bromodichloromethane	2,50	1,85	9,8	74	25,0	21,1	3,4	84
Dibromochloromethane	2,50	1,80	6,2	72	25,0	22,3	3,7	89
Bromoform	2,50	2,26	10,5	90	25,0	22,2	5,1	89
Pentachloroethane	0,500	0,215	47,6	42	5,0	4,47	3,8	89

NOTES

1 These data are taken from "*Determination of very low concentrations of hydrocarbons and halogenated hydrocarbons in water,* 1984-5, Table 6", in the series: Methods for the Examination of Waters and Associated Materials, Her Majesty's Stationery Office.

2 Extraction conditions : 10 ml petroleum ether per 200 ml sample, extraction in separatory funnel, shaking for 5 min by hand.

Table 5 — Precision data for drinking water

Parameter	l	n	n_a %	x_{ref} µg/l	$\overline{x}$ µg/l	R %	σ_r µg/l	VC_r %	σ_R µg/l	VC_R %
Trichloromethane	18	70	0	14,7	16,1	110	1,6	9,9	2,99	18,6
Tetrachloromethane	18	70	0	15,9	16,8	106	2,0	12,0	4,8	28,6
1,1,1 - trichloroethane	17	63	10	13,1	13,7	105	0,96	7,0	2,1	14,9
Trichloroethylene	16	60	14	14,6	15,2	104	1,0	6,8	2,6	17,0
Tetrachloroethylene	17	65	7	16,1	15,9	99	1,2	7,7	3,1	19,1
Tribromomethane	17	65	7	14,3	13,2	92	1,2	8,7	2,2	16,3

l	is the number of laboratories	R	is the percentage recovery
n	is the number of values	σ_r	is the repeatability standard deviation
n_a	is the percentage of outliers	VC_r	is the repeatability variation coefficient
x_{ref}	is the reference concentration	σ_R	is the reproducibility standard deviation
$\overline{x}$	is the total mean concentration	VC_R	is the reproducibility variation coefficient

NOTES

1 Interlaboratory test carried out in Germany in 1986.

2 Extraction solvent used : pentane. The performance data are generated using the calibration according to 2.7.2 and by a phase-volume ratio with the extraction of 50 : 1. Therefore in some cases the extracts had to be diluted for final measurement. All participants received the same standard stock solution.

Table 6 — Precision data for waste water

Parameter	l	n	n_a %	x_{ref} µg/l	$\bar{x}$ µg/l	R %	σ_r µg/l	VC$_r$ %	σ_R µg/l	VC$_R$ %
Trichloromethane	18	70	0	-	79,2	-	4,2	5,3	18,7	23,6
Tetrachloromethane	18	70	0	79,3	76,2	96	7,2	9,4	18,3	23,9
1,1,1 Trichloroethane	18	70	0	65,7	71,2	108	6,3	8,9	12,3	17,2
Trichloroethylene	17	66	6	73,0	74,7	102	7,3	9,7	14,8	19,8
Tetrachloroethylene	18	70	0	80,5	81,3	101	6,4	7,8	14,7	18,1
Dichloromethane	9	33	13	65,8	101	153	11,9	11,8	46,5	46,2

l is the number of laboratories
n is the number of values
n_a is the percentage of outliers
x_{ref} is the reference concentration
$\bar{x}$ is the total mean concentration
R is the percentage recovery
σ_r is the repeatability standard deviation
VC$_r$ is the repeatability variation coefficient
σ_R is the reproducibility standard deviation
VC$_R$ is the reproducibility variation coefficient

NOTES

1 Interlaboratory test carried out in Germany in 1986.

2 Extraction solvent used : pentane. The performance data are generated using the calibration according to 2.7.2 or with internal standard. The phase-volume ratio during extraction was 20 : 1. Therefore in some cases the extracts had to be diluted for final measurement. All participants received the same standard stock solution.

The measurement of dichloromethane content was part of the performance test. With a reference concentration of 65 µg/l the results were insufficient.

2.11 Test report

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

a) identity of the water sample ;

b) method used (by reference to the relevant section of this International Standard) ;

c) sample preparation, if performed ;

d) extraction solvent used, procedure used for the extraction (by reference to the relevant clauses of this International Standard) ;

e) evaluation function used according to 2.8.2 (uncorrected by recovery or corrected by recovery) ;

f) expression of the results according to 2.9 ;

g) all deviations from this method and all circumstances which might have affected the result.

Section 3: Static headspace method and analysis by gas chromatography

3.1 Principle

Samples are taken from sealed vials in which the ratio of volume of water taken to the volume of air, is fixed. The temperature of the vials is stabilized in a thermostatted system to within the range 50 °C - 80 °C to achieve specified equilibrium conditions.

Chromatographic analysis of the gaseous phase in equilibrium with the water in the sampling vials is carried out using an electron-capture detector or any other suitable detector.

3.2 Interferences

The method described in this standard requires scrupulous care when sampling and analysing. Contamination of the sample by air of the laboratory can occur. It is recommended that blank determinations be carried out (see 3.6.3).

3.3 Reagents

Use the reagents specified in 2.3.2, 2.3.5, 2.3.7, 2.3.8, as well as the following reagents.

3.3.1 Water, for the preparation of calibration solutions and blank solution

Use the water specified in 2.3.1 and in addition :

If the total dissolved solids content of the samples is less than 5 g/l, distilled or demineralized water is suitable. For samples whose total dissolved solids content is more than 5 g/l, the matrix effects can influence the equilibrium conditions. In this case, calibration solutions and blank solution with a total dissolved solids content near to that of the sample analysed shall be prepared by adding sodium chloride (see 3.3.2).

3.3.2 Sodium chloride

3.3.3 Sodium carbonate

3.4 Apparatus

3.4.1 Gas chromatograph, fitted with an electron-capture detector or any other suitable detector and with suitable columns

See 2.4.1.

3.4.2 Ordinary laboratory glassware

See 2.4.2.

3.4.3 Glass sampling vials with suitable septum

Glass vials fitted with a PTFE-coated septum and crimped metallic cap are recommended.

The fill level shall be marked and be identical on all vials. Vials which enable at least 10 ml of water to be taken are suitable.

NOTE : Stoppers of the "penicillin type" may be used. The stoppers should be disposable and their quality verified (see annex F for an example of a suitable procedure).

3.4.4 Crimping pliers

3.4.5 Thermostatted system for controlling the temperature of the vials (to between 50 °C and 80 °C) or equipment at a predetermined temperature.

3.5 Sampling

Take at least two samples for each analysis. Rinse the vials with the water to be analysed just before collecting the sample. Fill the vials to the mark (for example, the graduation mark or upper level of the cylindrical part of the vials). Stopper the vials, put the metallic cap into position and crimp (see annex G).

Take a full sample bottle for further dilutions if concentrations outside the calibration range are expected.

When sampling from pipework, allow a sufficient amount of water to flush to waste before sampling in order to avoid any contamination from the sampling point/tap.

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 glass sampling vial after rinsing 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 30 g/l solution (see 2.3.5) or a few crystals (3 mg to 5 mg) of solid sodium thiosulfate will be appropriate.

In the special case of sparkling water containing a high content of dissolved CO_2, add a sufficient quantity of sodium carbonate (see 3.3.3) to the sampling vials prior to sampling to obtain a carbonate concentration of 1 % (*m/m*) in the sample. The calibration solutions and the blank solution shall be prepared with identical sodium carbonate concentrations.

If an internal standard is needed (see 3.7.3.2), it shall be added immediately after sampling.

NOTE : The analysis of a blank atmosphere in the sampling area may enable the quality of the analysis to be better assessed when interpreting the results.

During transport of the samples, avoid sudden changes in temperature. The analysis shall be carried out without delay. If storage is unavoidable, cool the sample to about 4 °C and carry out the analysis within 48 h.

3.6 Procedure

3.6.1 Stabilization of sample temperature

Place the vials of samples (see 3.5) in the thermostatted system (see 3.4.5) at a fixed temperature in the range 50 °C to 80 °C, for at least 30 min and for the same time for all the vials.

NOTE : For specific equipment working at equilibrium, the time required to reach equilibrium can vary, particulary as regards the substance and the volume of the vials used; experience shows that a period of 90 min is necessary.

3.6.2 Gas chromatography

Set up the gas chromatograph (see 3.4.1), fitted with an electron-capture detector or any other suitable detector and equipped with a suitable column, according to the manufacturer's instructions.

Normally, better resolution will be obtained with capillary columns.

NOTE : For analysis of well-known water (for example, monitoring a water source), identification using one column is permissible.

The electron-capture detector is sensitive to halogenated hydrocarbons, but is not specific in its response. Its sensitivity to different halogenated hydrocarbons varies considerably (see annex D, table D.1) and the linearity of response to the compounds of interest and the useable working range of concentrations shall be determined by investigation using a series of calibration standard solutions of known concentrations.

Eliminate any contamination of the electron-capture detector which may cause a high or unsteady baseline according to the instructions of the manufacturer. Such contamination may be caused by contaminated gas (especially oxygen contamination) or a dirty detector due to a high column bleeding rate.

Should it be found necessary to clean the detector, the detector response and linearity shall be reconfirmed after cleaning and before further samples are analysed.

Inject an aliquot of the head-space vapour from the vials containing samples into the gas chromatograph column. Use automatic injection with the vials maintained at the selected temperature or manual injection with a gas syringe preheated to the selected temperature.

NOTE : With capillary columns, the volume of sample which can be injected is limited. It is recommended to follow the manufacturer's instructions. A 1 ml injection sample is usually satisfactory.

If the concentrations of the samples measured are too high (or too low), it is preferable to first inject a smaller (or higher) volume of the gaseous phase rather than to dilute. In fact, any dilution involves operations that can cause a loss of determinand through volatilization and contamination from the outside air. Then carry out a recalibration corresponding to the volume of air injected.

Compare the gas chromatogram obtained to those of the standard solutions (see 3.7).

Evaluate the gas chromatogram qualitatively and quantitatively (see 3.8).

The requirements concerning the measurements, the calibration, evaluation and calculation techniques to be used are described in 3.7 and 3.8.

3.6.3 Blank determination

Prior to and between analyses, full blank determinations shall be performed using water (see 2.3.1) and, if applicable (see 3.5), internal standard and salts. These examinations shall comprise the entire course of the analysis, including all reagents, from sampling to evaluation of the gas chromatogram. If the blank is too high (> 10 % of the measured value for any of the compounds of interest), an investigation of all procedural steps shall be performed, in order to trace the cause. Efforts shall be made to reduce the level of the blank (such as elimination of the contamination of the ambient air, examination of the reagents and checking of the settings of the gas chromatograph and integration parameters). If measurements have to be made near the limit of detection, the blank levels may prevent the evaluation.

If the "empty-value" (vial only, without water, salt and internal standard) is of the same order of magnitude as the blank or higher, other conditions for the handling of the sample (clean air) must be applied.

Deduction of the blank value is allowed only in those cases where the standard deviation of the blank measurement does not exceed the standard deviation of the total procedure, otherwise the systematic errors shall be eliminated.

3.7 Calibration

Two different approaches are described to establish the reference function for the head-space analysis :

a) calibration of the overall procedure using an external standard (see 3.7.1 ; 3.7.2 ; 3.7.3 ; 3.7.3.1) ;

b) calibration of the overall procedure using an internal standard (see 3.7.1 ; 3.7.2 ; 3.7.3 ; 3.7.3.2).

The calibration function obtained for a particular determinand is valid only for the established concentration range and the respective sample preparation used. It further depends on the operational conditions of the entire analytical system. It requires frequent verification at regular intervals.

For each determinand, a separate calibration function shall be established, consisting of at least five measurement points. It is permissible to examine several compounds in one calibration. A knowledge of the retention times of the determinands is essential. The retention times can be determined with the aid of single standard solutions, analyzed under defined analytical conditions.

The head space analysis requires a calibration using the entire procedure. This is accomplished by preparing aqueous solutions of the compounds to be determined over an individual concentration range which shall be within the linear dynamic range of the detector.

Dimethylformamide, acetone or methanol can be used as water-miscible solvent. These solvents provide rapid, uniform distribution of the halogenated hydrocarbons in water. The quantities shall be such that the volume added is as small as possible (≤ 1 ml/l of water), in order to minimize the effect on the partition equilibrium.

NOTE : Calibration with an external standard, as described in 3.7.3.1, may independently be checked using the method of standard addition (not described here).

For an explanation of the subscripts used in the equations, see table 3 in 2.7.

3.7.1 Preparation of the standard stock solution and the spiking solutions

To a 100 ml graduated vial containing about 90 ml of water-miscible solvent (see 2.3.7), add under the surface of the solvent.using a microlitre syringe (see 2.4.2), known quantities of 100 µl to 300 µl of each substance in question (see 2.3.8)

Immediately make up to volume with the water-miscible solvent (see 2.3.7).

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

Calculate the respective concentration of each substance added.

The solution prepared in this way can be stored at a temperature of about 4 °C in the dark for several weeks. Prior to use, equilibrate at room temperature for at least 15 min.

Prepare at least five spiking solutions from this solution by dilution with the same water-miscible solvent. The individual dilution step shall not exceed the ratio of 1:100.

3.7.2 Preparation of calibration solutions

Make ready a graduated vial containing water (see 2.3.1) and a magnetic stirrer rod (see 2.4.6) on a magnetic stirrer (see 2.4.5).Turn on the stirrer.

Stir vigorously and add a suitable volume (< 1ml/l of water) of a spiking solution (see 3.7.1) directly into the vortex of the water. If needed, add the same quantity of the internal standard to all vials. Add the same quantity of internal standard also to the sample itself.

Reduce the rotational speed of the magnetic stirrer until the vortex disappears. With the graduated vial stoppered, keep stirring for approximately 1 h.

Prepare calibration solutions of higher or lower concentrations by appropriately prepared standard solutions (spiking solutions according to 3.7.1). It is not permitted to dilute the aqueous spiked solutions.

Prepare the calibration solutions on the day of use.

3.7.3 Calibration curve

To examine the location of sample preparation, fill a glass vial (see 3.4.3) with ambient air and stopper the vial.

Fill a second glass vial (see 3.4.3) with the same quantity of water (see 2.3.1) as was taken for the calibration or the sample measurement respectively, and stopper the vial. If salt and internal standard are required for the analysis, add these too.

This sample serves as the blank.

Prepare at least five glass vials (see 3.4.3). Add salt if necessary, and the respective aqueous calibration solution (see 3.7.2). Stopper the vials.

Carry out the procedures described in 3.6.1 and 3.6.2.

The ratio of the volume of calibration solutions to the volume of air shall be identical to that of the vials containing the samples. The volume of the gaseous phase injected into the chromatograph shall be the same as for the water sample, blank and calibration solutions.

Beginning with the sample of the ambient air, determine, in ascending order of the concentration ρ_{ieg}, the peak values y_{ieg} of the calibration solutions.

Plot the substance-specific measured signals y_{ieg} on the ordinate and the mass concentration ρ_{ieg} of the substance i in the aqueous calibration solution on the abscissa.

Calculate a regression line for each substance, using the pairs of values y_{ieg} and ρ_{ieg}. If an internal standard, I, is used, use the values y_{ieg}/y_{Ieg} and ρ_{ieg}. Deduct the value of the appropriate blank from each measured value y_{ieg} (see 3.6.3).

3.7.3.1 Calibration function using an external standard

$$y_{ieg} = m_{ig} \cdot \rho_{ieg} + b_{ig} \qquad (8)$$

where :

y_{ieg}	is the (dependent variable) measured response of the substance i during calibration, depending on ρ_{ieg}. The units depend on the evaluation, for example area values ;
ρ_{ieg}	is the (independent variable) mass concentration of the substance i in the calibration solution (= external standard), in micrograms per litre ;
m_{ig}	is the slope of the calibration curve of substance i ; corresponds to the substance-specific response factor, often referred to as f_i ; the units depend on the evaluation, for example area values x (l/µg) ;
b_{ig}	is the axis intercept of the reference line on the ordinate ; the units depend on the evaluation, for example area values.

3.7.3.2 Calibration function using an internal standard

This procedure eliminates errors due to variable injection volume and, to a certain extent also from the ratio of the phase volumes and from matrix interferences in the sample.

Choose as internal standard, I, a substance which exhibits physical and chemical properties (such as phase equilibrium, vapour pressure, retention time, detector response) similar to the determinand. This substance, or another one with an equal retention time, shall not be present in the sample. The choice of an appropriate substance is often difficult, and its effectiveness shall be checked every time (see examples of internal standards in 2.7). The use of several internal standards is not excluded.

Prior to analysis, add the internal standard I to the sample. The mass concentration of the internal standard ρ_{Ieg} shall be the same in the blank, the water sample and the calibration solutions.

Calculate the calibration function by regression using the ratio of $y_{\text{ieg}}/y_{\text{leg}}$ as a function of the ratio of $\rho_{\text{ieg}}/\rho_{\text{leg}}$:

$$\frac{y_{\text{ieg}}}{y_{\text{leg}}} = m_{\text{ilg}} \cdot \frac{\rho_{\text{ieg}}}{\rho_{\text{leg}}} + b_{\text{ilg}} \qquad (9)$$

where :

y_{ieg}	see equation (8) ;
y_{leg}	is the (dependent variable) measured value of the internal standard I on calibrating, dependent on ρ_{leg}; the units depend on the evaluation, for example area values ;
ρ_{ieg}	see equation (8);
ρ_{leg}	is the (independent variable) mass concentration of the internal standard I in the calibration solution, in micrograms per litre;
m_{ilg}	is the slope of the calibration curve of the ratio of the measured values $y_{\text{ieg}}/y_{\text{leg}}$ as a function of the corresponding ratio of the mass concentration $\rho_{\text{ieg}}/\rho_{\text{leg}}$ (corresponds to the substance-specific response factor, often referred to as f_{i}); nondimensional;
b_{ilg}	is the axis intercept of the calibration curve on the ordinate; nondimensional.

3.8 Identification and evaluation

3.8.1 Identification of individual compounds

See 2.8.1.

3.8.2 Evaluation of individual compounds

3.8.2.1 Evaluation using an external standard

Calculate the mass concentration ρ_{ig} of the substance i in a water sample using equation (10), obtained after solving equation (8) :

$$\rho_{\text{ig}} = \frac{y_{\text{ig}} - b_{\text{ig}}}{m_{\text{ig}}} \qquad (10)$$

where :

ρ_{ig}	is the mass concentration of the substance i in the water sample, in micrograms per litre;

y_{ig} is the measured value of the substance i in the water sample (on condition that the same procedure is applied as with the calibration and the sample measurement); the units depend on the evaluation, for example area values [see also key to equation (8)];

m_{ig} is the slope of the calibration curve of the substance i ; the units depend on the evaluation, for example area value x (l/µg);

b_{ig} is the axis intercept of the calibration curve on the ordinate; the units depend on the evaluation, for example, area values.

[For m_{ig} and b_{ig} : see equation (8)]

3.8.2.2 Evaluation using an internal standard

Calculate the mass concentration ρ_{ig} of the substance i in a water sample using equation (11) after solving equation (9) and provided that the concentration of the internal standard is always the same :

$$\rho_{ig} = \frac{(y_{ig}/y_{lg}) - b_{ilg}}{m_{ilg}} \cdot \rho_{lg} \qquad (11)$$

where :

ρ_{ig} is the mass concentration of the substance i in the water sample; same units as ρ_{ieg}, for example µg/l [see equation (9)];

ρ_{lg} is the mass concentration of the internal standard I in the water sample; same units

as ρ_{leg}, for example µg/l [see equation (9)];

y_{ig} is the measured value of the substance i in the water sample; (on condition that the same procedure is applied as with the calibration and the sample measurement); same units as y_{ieg}, depending on the method of evaluation, for example area values [see also equation (9)];

y_{lg} is the measured value of the internal standard I in the water sample; same units as y_{leg}, depending on the method of evaluation, for example area values [see also equation (9)];

m_{ilg}, b_{ilg}see equation (9).

3.8.3 Summary of the results

See 2.8.3.

3.9 Expression of results

See 2.9.

3.10 Precision data

Data from interlaboratory tests carried out in Germany in 1989 are given in tables 7 and 8.

Table 7 — Precision data for drinking water

Parameter	l	n	n_a %	x_{ref} µg/l	$\bar{x}$ µg/l	R %	s_r µg/l	VC_r %	s_R µg/l	VC_R %
Tetrachloroethylene	22	85	0	3,084	2,25	72,8	0,147	6,56	0,622	27,7
Tetrachloromethane	9	32	0	0,151	0,19	122,5	0,007	3,9	0,103	55,7
Trichloroethylene	18	65	0	4,169	2,90	69,6	0,123	4,23	0,472	16,3
1,1,1-Trichloroethane	21	80	0	8,928	6,05	67,7	0,188	3,11	1,288	21,3
Trichloromethane	20	76	0	12,59	9,55	75,8	0,493	5,17	1,757	18,4
Tribromomethane	14	49	0	2,684	2,39	88,8	0,210	8,81	0,419	17,6
Bromodichloromethane	22	79	5	7,577	5,84	77,0	0,345	5,91	1,055	18,1
Dichloromethane	13	39	24	25,12	21,4	85,1	1,28	5,99	3,889	18,2
cis-1,2-Dichloroethylene	10	32	18	48,73	31,51	64,7	3,302	10,68	4,950	15,9

l is the number of laboratories
n is the number of values
n_a is the percentage of outliers
x_{ref} is the reference concentration
$\bar{x}$ is the total mean concentration
R is the percentage recovery
s_r is the repeatability standard deviation
VC_r is the repeatability variation coefficient
s_R is the reproducibility standard deviation
VC_R is the reproducibility variation coefficient

Table 8 — Precision data for waste water

Parameter	l	n	n_a %	x_{ref} µg/l	$\bar{x}$ µg/l	R %	s_r µg/l	VC_r %	s_R µg/l	VC_R %
Tetrachloroethylene	17	64	0	38,18	27,63	71,3	0,62	2,26	7,03	25,8
Tetrachloromethane	10	36	0	0,625	0,29	45,7	0,05	17,59	0,110	38,5
Trichloroethylene	23	78	5	57,35	41,07	71,6	1,226	2,98	8,74	21,3
1,1,1-Trichloroethane	19	72	0	31,58	20,034	63,4	0,764	3,81	4,45	22,8
Trichloromethane	18	60	12	5,774	4,55	78,9	0,131	2,89	0,633	13,9
Dichloromethane	17	62	0	51,85	48,42	93,4	4,28	8,82	19,22	39,7
1,2-Dichloroethane	12	44	0	112	94,16	84,1	3,92	1,06	27,08	28,8

See table 7 for symbols.

3.11 Test report

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

a) identity of the water sample ;

b) method used (by reference to the relevant section of this International Standard) ;

c) sample preparation, if performed ;

d) evaluation function used according to 3.8.2 ;

e) expression of the results according to 3.9 ;

f) all deviations from this method and all circumstances which might have affected the result.

Annex A
(informative)

Characteristics of highly volatile halogenated hydrocarbons

Name	Formula	Molecular mass g/mol	Boiling point	Density g/cm^3	Solubility in water g/l	Percent by mass of halogens %
Chlorinated compounds						
Chloromethane	CH_3Cl	50,59	-24,2	0,92	7,2	70,2 Cl
Dichloromethane	CH_2Cl_2	84,93	39,6	1,32	16,7	83,5 Cl
Trichloromethane (chloroform)	$CHCl_3$	119,38	61,2	1,49	7,3	89,0 Cl
Tetrachloromethane (carbon tetrachloride)	CCl_4	153,82	76,6	1,59	1,16	92,2 Cl
Chloroethane	CH_2ClCH_3	64,52	12,3	0,89	4,5	54,9 Cl
1,1-Dichloroethane	$CHCl_2CH_3$	98,97	57,3	1,17	5,1	71,6 Cl
1,2-Dichloroethane	CH_2ClCH_2Cl	98,97	83,5	1,25	8,7	71,6 Cl
1,1,1-Trichloroethane	CCl_3CH_3	133,41	74,1	1,34	4,4	79,8 Cl
1,1,2-Trichloroethane	$CHCl_2CH_2Cl$	133,41	113,8	1,44	4,5	79,8 Cl
1,1,1,2-Tetrachloroethane	CCl_3CH_2Cl	167,85	130,2	1,54	1,1	84,5 Cl
1,1,2,2-Tetrachloroethane	$CHCl_2CHCl_2$	167,85	145,1	1,59	2,9	84,5Cl
Pentachloroethane	CCl_3CHCl_2	202,30	159,9	1,68	0,05	87,6 Cl
Hexachloroethane	CCl_3CCl_3	236,74	184,6	2,09	0,05	89,8 Cl
Chloroethylene	$CHCl=CH_2$	62,5	-13,3	0,91	0,06	56,7 Cl

Name	Formula	Molecular mass g/mol	Boiling point °C	Density g/cm^3	Solubility in water g/l	Percent by mass of halogens %
1,1-Dichloroethylene	$CCl_2=CH_2$	96,94	37,0	1,22	0,4	73,2 Cl
cis-1,2-Dichloroethylene	$CHCl=CHCl$	96,94	60,3	1,28	3,5	73,2 Cl
trans-1,2-Dichloroethylene	$CHCl=CHCl$	96,94	48,4	1,26	6,3	73,2 Cl
Trichloroethylene	$CCl_2=CHCl$	131,40	86,9	1,46	1,1	81,0 Cl
Tetrachloroethylene	$CCl_2=CCl_2$	165,83	121,2	1,62	0,1	85,6 Cl
1-Chloropropane	$CH_2ClCH_2CH_3$	78,54	46,6	0,89	2,7	45,1 Cl
2-Chloropropane	$CH_3CHClCH_3$	78,54	35,7	0,86	3,4	45,1 Cl
1,1-Dichloropropane	$CHCl_2CH_2CH_3$	112,99	88,1	1,13	---	62,8 Cl
1,2-Dichloropropane	$CH_2ClCHClCH_3$	112,99	96,4	1,15	2,8	62,8 Cl
1,3-Dichloropropane	$CH_2ClCH_2CH_2Cl$	112,99	120,4	1,19	2,7	62,8 Cl
2,2-Dichloropropane	$CH_3CCl_2CH_3$	112,99	69,3	1,11	---	62,8 Cl
1,1,1-Trichloropropane	$CCl_3CH_2CH_3$	147,43	106	1,29	---	72,2 Cl
1,1,2-Trichloropropane	$CHCl_2CHClCH_3$	147,43	132	1,34	---	72,2 Cl
1,1,3-Trichloropropane	$CHCl_2CH_2CH_2Cl$	147,43	145,5	1,35	---	72,2 Cl
1,2,2-Trichloropropane	$CH_2ClCCl_2CH_3$	147,43	123	1,32	---	72,2 Cl
1,2,3-Trichloropropane	$CH_2ClCHClCH_2Cl$	147,43	156,8	1,39	0,19	72,2 Cl
1,1,1,2-Tetrachloropropane	$CCl_3CHClCH_3$	181,88	150	1,47	---	78,0 Cl
1,1,1,3-Tetrachloropropane	$CCl_3CH_2CH_2Cl$	181,88	159	1,50	---	78,0 Cl
1,1,2,2-Tetrachloropropane	$CHCl_2CCl_2CH_3$	181,88	155	1,50	---	78,0 Cl
1,1,2,3-Tetrachloropropane	$CHCl_2CHClCH_2Cl$	181,88	178	1,51	---	78,0 Cl
1,1,3,3-Tetrachloropropane	$CHCl_2CH_2CHCl_2$	181,88	---	1,50	---	78,0 Cl
1,2,2,3-Tetrachloropropane	$CH_2ClCCl_2CH_2Cl$	181,88	164	1,49	---	78,0 Cl

Name	**Formula**	**Molecular mass** g/mol	**Boiling point** °C	**Density** g/cm^3	**Solubility in water** g/l	**Percent by mass of halogens** %
cis-Chloropropylene,	$CHCl{=}CHCH_3$	76,53	32,8	0,93	---	76,4 Cl
trans-Chloropropylene,	$CHCl{=}CHCH_3$	76,53	37,4	0,93	---	76,4 Cl
2-Chloropropylene	$CH_2{=}CClCH_3$	76,53	22,6	0,90	---	76,4 Cl
3-Chloropropylene	$CH_2{=}CHCH_2Cl$	76,53	44,9	0,94	3,3	76,4 Cl
1,1-Dichloropropylene	$CCl_2{=}CHCH_3$	110,97	76	1,18	---	64 Cl
cis-1,2-Dichloropropylene	$CHCl{=}CClCH_3$	110,97	---	---	---	64 Cl
trans-1,2-Dichloropropylene	$CHCl{=}CClCH_3$	110,97	77	---	---	64 Cl
cis-1,3-Dichloropropylene	$CHCl{=}CHCH_2Cl$	110,97	104,3	1,22	---	64 Cl
trans-1,3-Dichloropropylene	$CHCl{=}CHCH_2Cl$	110,97	112	1,22	---	64 Cl
2,3-Dichloropropylene	$CH_2{=}CClCH_2Cl$	110,97	94	1,20	---	64 Cl
3,3-Dichloropropylene	$CH_2{=}CHCHCl_2$	110,97	84,4	1,17	---	64 Cl
1,1,2-Trichloropropylene	$CCl_2{=}CClCH_3$	145,42	118	1,38	---	73,2 Cl
1,1,3-Trichloropropylene	$CCl_2{=}CHCH_2Cl$	145,42	---	---	---	73,2 Cl
1,2,3-Trichloropropylene	$CHCl{=}CClCH_2Cl$	145,42	(142)	1,41	---	73,2 Cl
1,3,3-Trichloropropylene	$CHCl{=}CHCHCl_2$	145,42	---	---	---	73,2 Cl
2,3,3-Trichloropropylene	$CH_2{=}CClCHCl_2$	145,42	---	---	---	73,2 Cl
3,3,3-Trichloropropylene	$CH_2{=}CHCCl_3$	145,42	114	1,37	---	73,2 Cl
1,1,2,3-Tetrachloropropylene	$CCl_2{=}CClCH_2Cl$	179,87	---	---	---	78,9 Cl
1,1,3,3-Tetrachloropropylene	$CCl_2{=}CHCHCl_2$	179,87	---	1,53	---	78,9 Cl
1,2,3,3-Tetrachloropropylene	$CHCl{=}CClCHCl_2$	179,87	---	---	---	78,9 Cl
2,3,3,3-Tetrachloropropylene	$CH_2{=}CClCCl_3$	179,87	---	---	---	78,9 Cl
1,1,2,3,3-Pentachloropropylene	$CCl_2{=}CClCHCl_2$	214,31	185	1,63	---	82,7 Cl
1,1,3,3,3-Pentachloropropylene	$CCl_2{=}CHCCl_3$	214,31	---	---	---	82,7 Cl
1,2,3,3,3-Pentachloropropylene	$CHCl{=}CClCCl_3$	214,31	(183)	---	---	82,7 Cl
Hexachloropropylene	$CCl_2{=}CClCCl_3$	248,77	---	1,77	---	85,5 Cl

Name	Formula	Molecular mass g/mol	Boiling point °C	Density g/cm^3	Solubility in water g/l	Percent by mass of halogens %
1-Chlorobutane	$CH_2ClCH_2CH_2CH_3$	92,57	78,4	0,89	6,6	38,3 Cl
1,4-Dichlorobutane	$CH_2ClCH_2CH_2CH_2Cl$	127,03	153,9	1,14	---	55,8 Cl
3-Chlorobut-1-ene	$CH_2=CHCHClCH_3$	90,55	64,0	0,90	---	39,2 Cl
2-Chlorobuta-1,3-diene	$CH_2=CClCH=CH_2$	88,54	59,4	0,87	---	40,0 Cl
Hexachlorobuta-1,3-diene	$CCl_2=CClCCl=CCl_2$	260,78	221,0	1,67	0,001	81,5 Cl
Chlorobenzene	C_6H_5Cl	112,56	132,0	1,11	0,5	31,5 Cl
1,2-Dichlorobenzene	$C_6H_4Cl_2$	147,00	180,5	1,30	0,26	48,2 Cl
1,3-Dichlorobenzene	$C_6H_4Cl_2$	147,00	173,0	1,29	0,11	48,2 Cl
1,4-Dichlorobenzene	$C_6H_4Cl_2$	147,00	174,5	1,23	0,10	48,2 Cl
1,2,3-Trichlorobenzene	$C_6H_3Cl_3$	181,45	218,5	1,45	---	58,6 Cl
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	181,45	212,0	1,45	2,20	58,6 Cl
1,3,5-Trichlorobenzene	$C_6H_3Cl_3$	171,45	208,4	1,39	---	58,6 Cl

Name	Formula	Molecular mass g/mol	Boiling point °C	Density g/cm^3	Solubility in water g/l	Percent by mass of halogens %
Brominated compounds						
Bromomethane	CH_3Br	94,94	3,5	1,67	0,9	84,2 Br
Dibromomethane	CH_2Br_2	173,84	96,9	2,49	11,5	91,9 Br
Tribromomethane (bromoform)	$CHBr_3$	252,75	145,5	2,89	3,0	94,8 Br
Tetrabromomethane	CBr_4	331,65	189,5	2,96	2,24	96,4 Br
1,2-Dibromoethane	CH_2BrCH_2Br	187,87	131,4	2,18	4,31	85,1 Br
1,1,2,2-Tetrabromoethane	$CHBr_2CHBr_2$	345,67	235	2,68	0,65	92,5 Br
1,2-Dibromoethylene	$CHBr{=}CHBr$	185,86	110	2,27	---	86,0 Br
2,2-Dibromopropane	$CH_3CBr_2CH_3$	201,90	144	1,75	---	79,2 Br
1-Bromobutane	$CH_2BrCH_2CH_2CH_3$	137,03	101,6	1,27	0,58	58,3 Br
Iodinated compounds						
Methyl iodide	CH_3I	141,94	42,4	2,28	13,6	89,4 I
Methylene iodide	CH_2I_2	267,84	182	3,32	1,24	94,8 I
Iodoform	CHI_3	393,73	218	4,19	0,1	96,7 I