INTERNATIONAL STANDARD

ISO 23631

First edition
2006-02-01

Water quality — Determination of dalapon, trichloroacetic acid and selected haloacetic acids — Method using gas chromatography (GC-ECD and/or GC-MS detection) after liquid-liquid extraction and derivatization

Qualité de l'eau — Dosage du dalapon, de l'acide trichloroacétique et d'acides haloacétiques sélectionnés — Méthode par chromatographie en phase gazeuse (détection CG-DCE et/ou CG-SM) après extraction liquide-liquide et dérivatisation

Reference number
ISO 23631:2006(E)

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Published in Switzerland

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Foreword

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

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 23631 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

The user should be aware the particular problems could require the specifications of additional marginal conditions.

Water quality — Determination of dalapon, trichloroacetic acid and selected haloacetic acids — Method using gas chromatography (GC-ECD and/or GC-MS detection) after liquid-liquid extraction and derivatization

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.

Diazomethane is explosive, extremely toxic and severely irritating, causing pulmonary oedema when inhaled in high concentrations. Long-term, low-level exposure may lead to sensitization, resulting in asthma-like symptoms. Also, diazomethane and several of its chemical precursors have been cited as carcinogens.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for the determination of dalapon, trichloroacetic acid (TCA) and selected haloacetic acids (see Table 1) in ground water and drinking water by gas chromatography (GC-ECD and/or GC-MS detection) after liquid-liquid extraction and derivatization using diazomethane. Depending on the matrix, the method is applicable to a concentration range from 0,5 µg/l to 10 µg/l. The validated reporting limit of TCA and dalapon is about 0,05 µg/l (see Table C.1). Detection by electron-capture detector (ECD) in general leads to lower detection limits. Detection by mass spectrometry (MS) allows analyte identification.

This method may be applicable as well to compounds not mentioned in Table 1 or to other types of water. However, it is necessary to verify the applicability of this method for these special cases.

Table 1 — Haloacetic acids determined by this method

Name	Molecular formula	Relative molecular mass	CAS registry No.
Bromochloroacetic acid	$C_2H_2BrClO_2$	173,4	5589-96-8
Dalapon [a]	$C_3H_4Cl_2O_2$	143,0	75-99-0
Dibromoacetic acid	$C_2H_2Br_2O_2$	217,8	631-64-1
Dichloroacetic acid	$C_2H_2Cl_2O_2$	128,9	79-43-6
Monobromoacetic acid	$C_2H_3BrO_2$	138,9	79-08-3
Monochloroacetic acid	$C_2H_3ClO_2$	94,5	79-11-8
Trichloroacetic acid (TCA)	$C_2HCl_3O_2$	163,4	76-03-9

[a] 2,2-Dichloropropionic acid.

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 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

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

3 Principle

Dalapon, trichloroacetic acid (TCA) and selected haloacetic acids are extracted from the acidified water sample with methyl-*tert*-butyl ether (MTBE). The extract is concentrated by evaporation.

The analytes are methylated using diazomethane.

The methylated analytes are separated, identified and quantified by means of capillary gas chromatography with electron-capture detection (GC-ECD) and/or mass spectrometry (GC-MS).

4 Interferences

4.1 Interferences with the extraction procedure

Suspended particles in the water may interfere with the liquid-liquid-extraction procedure causing problems in layer separation. In this case, filter the water sample through a glass fibre filter (6.15) prior to enrichment.

4.2 Interferences with the gas chromatography and mass spectrometry procedure

Interferences may be caused e.g. by the injection system used or by inadequate separation of the analytes. Experienced operators, using the information given in the instrument manuals, may be able to minimize this type of interference. Regular checking of the chromatographic and spectrometric system is required to maintain adequate performance. Required system stability should be checked regularly by the use of a GC-standard.

Insufficiently purified solvents (5.6) as well as insufficiently purified sodium chloride (5.10) may cause severe interferences. Reagents used in the method to perform derivatization may lead to interferences in the ECD-chromatograms. Therefore, it is highly recommended that temperatures of the diazomethane building process be carefully kept in limits (see 5.19).

5 Reagents

Use solvents and reagents of sufficient purity, i.e. with negligibly low impurities compared with the concentration of analytes to be determined. As reagents use, as far as available, “residual grade” or better in order to obtain clean blanks. Check blanks regularly and establish proper charge control.

5.1 Water, complying to grade 1 as defined in ISO 3696:1987, or equivalent.

5.2 Operating gases for the gas chromatography/mass spectrometry, of high purity and in accordance with manufacturer's specifications.

5.3 Nitrogen, of high purity, i.e. minimum 99,996 % by volume, for concentration by evaporation.

5.4 Diethyl ether, $C_4H_{10}O$.

NOTE Stabilizers may cause interferences.

5.5 Ethanol, C_2H_5OH.

5.6 Solvents, e.g. ethyl acetate, $C_4H_8O_2$; acetone, C_3H_6O.

5.7 Methyl-*tert*-butyl ether (MTBE), $C_5H_{12}O$.

5.8 Benzoic acid, dissolved in ethanol, $c(C_7H_6O_2) = 0{,}2$ mol/l.

5.9 *N*-methyl-*N*-nitroso-4-toluenesulfonamide, $C_8H_{10}N_2O_3S$.

5.10 Sodium chloride, NaCl (e.g. heated at 550 °C for 4 h).

5.11 Potassium hydroxide solution, $w(KOH) = 60$ %.

5.12 Sodium hydroxide solution, $c(NaOH) = 0{,}1$ mol/l.

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

5.14 Phenolphthalein, $C_{20}H_{14}O_4$.

5.15 Acetic acid, $w(CH_3COOH) = 10$ %.

5.16 Mineral acid, e.g. hydrochloric acid, $w(HCl) = 25$ %.

5.17 Methylated reference substances.

Methylated reference substances (methyl esters of the acids listed in Table 1) of defined concentration suitable for the preparation of reference solutions for gas chromatography (9.2).

5.17.1 Stock solutions of individual methylated reference substances.

As an example, pipette 50 mg of each of the methylated reference substances into 100 ml volumetric flasks, dissolve in MTBE (5.7) and dilute to volume with MTBE.

Store stock solutions at about −18 °C, protected from light. They are stable for about 1 year.

5.17.2 Multiple-substance stock solutions of methylated reference substances.

As an example, transfer 2 ml of each of the solution of the individual substance (5.17.1) into a 100 ml volumetric flask and dilute to volume with MTBE (5.7).

Store stock solutions at about −18 °C, protected from light. They are stable for about 1 year.

5.17.3 Reference solutions of methylated reference substances.

Solutions of defined concentration suitable for multipoint calibration (working solution for gas chromatography). Prepare the reference solutions by an adequate dilution of the stock solution (5.17.2) with MTBE (5.7).

Store reference solutions at a maximum of +10 °C or below (e.g. in a refrigerator), protected from light. They are stable for about 6 months.

5.18 Non-methylated reference substances.

5.18.1 General requirements.

Reference substances (acids, listed in Table 1) of defined concentration, suitable for the preparation of reference solutions used for spiking water samples. Spike samples for calibration of the total procedure (9.3 and 9.4) and calculation of the overall recovery, i.e. total of extraction recovery and recovery of the derivatization step (9.5).

5.18.2 Stock solutions of individual non-methylated reference substances.

As an example, place 50 mg each of a non-methylated reference substance into a 100 ml volumetric flask, dissolve with MTBE (5.7) and dilute to volume with MTBE.

Store stock solutions at about −18 °C, protected from light. They are stable for about 1 year.

5.18.3 Multiple substance stock solutions of non-methylated reference substances.

As an example, transfer 2 ml of each of the solution of the individual substance (5.18.2) into a 100 ml volumetric flask and dilute to volume with MTBE (5.7).

Store stock solutions at about −18 °C, protected from light. They are stable for about 1 year.

5.18.4 Reference solutions of non-methylated reference substances.

Prepare solutions of defined concentration suitable for multipoint calibration of the total procedure and spike water samples appropriately. Prepare the reference solutions by an adequate dilution of the stock solution (5.18.3) with MTBE (5.7).

Store reference solutions at a maximum of +10 °C or below (e.g. in a refrigerator), protected from light. They are stable for about 6 months.

5.19 Diazomethane solution (derivatization reagent).

WARNING — *N*-methyl-*N*-nitroso-4-toluenesulfonamide is an irritant and all skin contact shall be avoided.

Prepare diazomethane in a distillation apparatus, e.g. as shown in Figure 1. Pay attention to warning note in the clause “warning” on page 1.

For security reasons, install two wash bottles; keep the first one empty for the purpose of protecting the solution from backflush and fill the second with acetic acid (5.15).

Pipette 8 ml of KOH solution (5.11) and 10 ml of ethanol (5.5) in a 250 ml reaction flask.

Suspend 5,0 g of *N*-methyl-*N*-nitroso-4-toluenesulfonamide (5.9) in 45 ml of diethyl ether (5.4) or MTBE (5.7) in a pressure-equalizing funnel.

Cautiously warm the reaction flask to about 60 °C (water bath) and, within 20 min, dropwise add the *N*-methyl-*N*-nitroso-4-toluenesulfonamide suspension from the pressure-equalizing funnel. If MTBE is used as a solvent, slightly increase the temperature by some degrees in order to maintain a smooth distillation process.

Collect the diazomethane being formed during this process together with the distilled diethyl ether or MTBE in the trap (cooled with ice/NaCl).

After this reaction, add an additional 10 ml of the same ether (diethyl ether or MTBE) through the funnel and distil the remaining diazomethane.

Stopper the trap and store it at about −18 °C, protected from light. Check the stability of diazomethane solution regularly. It should always show an intensive yellow colour.

The solution is stable for at least 1 year.

Excess diazomethane and *N*-methyl-*N*-nitroso-4-toluenesulfonamide can be destroyed by adding a solution of acetic acid (5.15). It is recommended that reaction flask and pressure-equalizing funnel be rinsed with acetic acid. The remaining distillation apparatus may be cleaned by distilling 50 ml of ethanol (5.5).

The concentration of the diazomethane solution (derivatization reagent) can be checked by titration. If this step is desired, proceed as follows: Insert 3 ml of 0,2 mol/l of ethanolic benzoic acid solution (5.8) in a titration flask. Add 1 ml of etheric diazomethane solution (diethyl ether or MTBE) and phenolphthalein (5.14). Add 0,1 mol/l of sodium hydroxide solution (5.12) using a burette until the solution becomes permanently pink.

5.20 Internal standard, e.g. 2-bromopropionic acid, $C_3H_5BrO_2$ or 2,3-dichloropropionic acid $C_3H_4Cl_2O_2$ (9.4).

6 Apparatus

Equipment or parts of it, which are likely to come into contact with the water sample or its extract, shall be free from residues causing interferences. It is recommended to use vessels made of glass, stainless steel or polytetrafluoroethene (PTFE).

6.1 Flat-bottomed flasks, preferably brown glass, 250 ml, with glass stoppers.

6.2 Graduated cylinders, 250 ml.

6.3 Volumetric flasks, 10 ml, 25 ml, 50 ml and 100 ml.

6.4 Volumetric pipettes, different sizes between 1 ml and 50 ml.

6.5 Evaporation assembly, for sample enrichment and extract concentration.

6.6 Vials, suitable for automatic or manual injection. Glass vials with inert stopper, such as PTFE-coated septum, for storage of extracts.

6.7 Magnetic stirrer, including PTFE-coated stirrer bar of suitable size.

6.8 Microseparator, device for phase separation.

6.9 Separating funnel, 250 ml and 500 ml.

6.10 Apparatus for preparing diazomethane, (see example in Figure 1), comprising the following:

6.10.1 Round-bottomed flask, double-necked, 250 ml.

6.10.2 Pressure-equalizing funnel, 100 ml.

6.10.3 Distillation column, for example, Vigreux column.

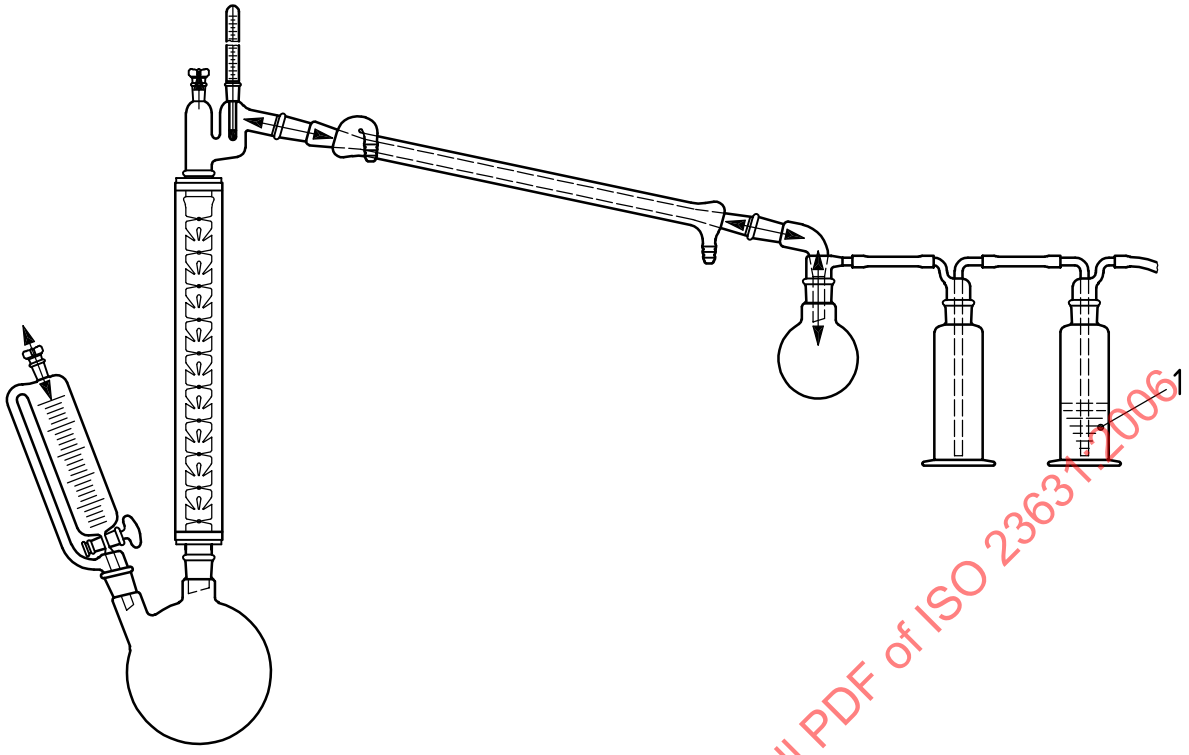
6.10.4 Distillation head.

6.10.5 Condenser, for example, Liebig condenser.

6.10.6 Round bottomed flask, 100 ml.

6.10.7 Flask for absorption of diazomethane, 250 ml.

6.10.8 Security flask, 250 ml, or a commercial distillation apparatus.



Key

1 acetic acid (w = 10 %) for absorption of diazomethane

Figure 1 — Example of a distillation apparatus for preparing diazomethane

6.11 Capillary gas chromatograph with electron-capture detector (ECD), equipped with a non-discriminating injection system (6.13), gas supply in accordance with the respective manufacturer's instructions.

Proper identification of the methylated dalapon and haloacetic acids according to Table 1 requires analysis on a minimum of two capillary columns of significantly differing polarity for both sample solution and standard solution. It is advantageous to connect both columns to one injector for simultaneous sample application. However, with this technique, misinterpretation caused by peak overlapping cannot completely be ruled out. In this event, two quantitative results will be obtained, with the lower value probably being more accurate.

6.12 Capillary gas chromatograph with mass spectrometric detector (MS), equipped with a non-discriminating injection system (6.13), electron impact ionization, gas supply in accordance with the respective manufacturer's instructions.

6.13 Non-discriminating GC-Injector, e.g. split/splitless injection system, programmable temperature vaporizer (PTV) or on-column-injection system.

6.14 Capillary columns, for gas chromatography (for examples of gas chromatograms, see Annex A). It is advantageous to use columns of a length $\geqslant$ 50 m.

6.15 Borosilicate glass fibre filter, diameter of fibres 0,75 µm to 1,5 µm, with inorganic binding material.

6.16 pH meter with electrodes.

6.17 Injection syringes, nominal capacity 5 µl or 10 µl.

7 Sampling and sample pre-treatment

Collect samples as specified in ISO 5667-1, ISO 5667-2 and ISO 5667-3.

For sampling, use thoroughly cleaned, preferably brown, flat-bottomed glass flasks (6.1), usually 250 ml. Rinse flasks and stoppers with the water to be sampled.

Fill the bottles completely with the water to be examined. Dechlorinate water samples containing chlorine by immediately adding approximately 25 mg of sodium thiosulfate pentahydrate (5.13).

If storage is unavoidable, store the sample at 4 °C in the dark. Treat and analyse the samples as soon as possible after sample collection (within 3 days).

8 Procedure

8.1 Sample preparation and extraction

8.1.1 Sample preparation

For the extraction, measure 200 ml ± 10 ml of the water sample under investigation in a graduated cylinder (6.2) or calculate the exact volume of the water sample after weighing.

Add the internal standard (5.20), if calibration with an internal standard covering the total procedure is to be performed.

Adjust with mineral acid (5.16) to a pH of (1,0 ± 0,2).

Add about 20 g of sodium chloride (5.10) to the water sample.

Extract the water sample according to 8.1.2 or 8.1.3.

8.1.2 Extraction by stirring with a magnetic stirrer and a microseparator

Place a magnetic stirring rod in the sample container (e.g. 250 ml flat-bottomed flask; 6.1) and add 20 ml of MTBE (5.7), stir the water sample using a magnetic stirrer (6.7) at about 1 000 min^{-1} for 5 min to 10 min, and then allow to stand for about 5 min.

Separate the organic phase in the microseparator as follows: Place the microseparator (6.8) on the sample container and pour water (5.1) into the funnel until the liquid level of the organic phase has risen high enough to allow the sample extract to be removed with a pipette for further procedure.

8.1.3 Extraction by shaking in the separating funnel

Shake the water sample twice in the separating funnel (6.9) with 20 ml of MTBE (5.7) for 20 min each time. Separate and collect the organic phase after each extraction step. After completion of the extraction, combine the organic phases.

8.2 Concentration and derivatization

Concentrate the extract (8.1.2 or 8.1.3) carefully to a final volume of about 0,8 ml to 0,9 ml (e.g. in a nitrogen stream or on a rotary evaporator under reduced pressure, 400 hPa, 30 °C). There is no extract-drying step necessary as long as MTBE is used for extraction purposes.

Add a sufficient volume (about 100 µl to 200 µl) of diazomethane solution (5.19) until a persistent yellow colouration appears.

Stopper the flask and keep in the dark for about 15 min.

At the end of the reaction time, concentrate the solution with nitrogen to a volume of not less than 0,8 ml in order to remove excess diazomethane.

If a calibration is being performed with an external standard (9.3), bring to volume (exactly 1 ml) with MTBE (5.7).

8.3 Gas chromatography analysis of individual compounds

8.3.1 Procedure with electron capture detector (GC-ECD)

Individual compounds in the sample are detected by means of an electron capture detector (ECD), by comparing the retention times (RT) corresponding to the respective peaks in the sample chromatograms with the retention times of substance peaks in the gas chromatograms of a reference solution measured under the same conditions.

The necessary assignment certainty by comparison of the retention times is achieved when the retention time of the respective substance in the ECD chromatogram is within a tolerance of RT = ± 0,02 min, compared with the retention time of the respective substance in the chromatogram of a methylated reference solution (5.17.3) measured under the same conditions.

If the gas chromatogram of the sample extract does not contain a peak at the substance-specific retention time on a capillary column, the compound is considered to be not detected.

If, on the other hand, a peak occurs at a certain substance-specific retention time, the presence of the target compound is possible. Its identity shall be verified by further investigation, however. If a peak likewise occurs in the comparison testing on a second capillary column of a different polarity group [1)] at the substance-specific retention time, the identity of the substance is very probable.

In only slightly polluted waters or waters for which information about the origin of the sample and its matrix is available, the identity may be considered as certain.

In water samples with a complex matrix, the compound may be identified with certainty on a third capillary column or else by means of mass spectrometry (GC-MS).

The sensitivity of the electron capture detector (ECD) varies for the methyl esters of the substances in Table 1. Therefore, in all quantitative measurements, care shall be taken to assure that the signals for the respective substance are within the working range of the ECD. If necessary, prepare dilutions of the solutions or the sample extracts.

In certain cases the detector signal of the electron capture detector (ECD) shows no linear dependence on the concentration of a substance. In such cases a quadratic regression function may be plotted as a reference curve from the pairs of values obtained in a multipoint calibration (see [2] in Bibliography).

8.3.2 Procedure with mass spectrometry (GC-MS)

The individual compound in the sample is considered to be identified if

— the retention times (RT) of the respective substance in the total ion chromatogram or single mass chromatogram lie within a limit deviation of RT = ± 0,02 min, compared with the retention times of the respective substance in the total ion chromatogram or single mass chromatogram of a reference solution measured under the same conditions

1) As a rule, the larger the difference in polarity between the two capillary columns, the more certain the information is (see example chromatogram in Annex A).

and if either

— complete mass spectra of the reference compounds (after background correction) correspond to the mass spectra present at the respective retention time in the total ion chromatogram of the water sample (likewise after background correction), within limits to be established from experience

or

— if the relative peak intensities of at least sufficiently characteristic molecule and fragment ions of the reference compounds (see Table 2) correspond to those of the compounds to be identified, within limits to be established from experience. Identification via the molecule ion or a main fragment ion alone is frequently insufficient; at least one further typical fragment mass (see Table 2) shall be used for validation.

No ion of significant intensity should be present in the mass spectrum after background subtraction with a larger mass than the highest possible mass for a compound to be identified.

While it is true that identification using the SIM (selected ion monitoring) method enables lower detection limits, it is based on a considerably lower information content and may therefore only be used in investigations where information is available about the origin of the sample and its matrix. If there is insufficient information about the water sample, at least two further characteristic masses should be used for validation (see Table 2).

8.4 Blank value measurements

Check that the instruments and reagents are in perfect condition by carrying out regular blank value measurements.

To carry out the blank value measurements, prepare and analyse 200 ml of water (5.1) in the same way as the sample.

If interfering blank values occur, find the reason for this by systematic investigations, so that the source of contamination can be eliminated.

Table 2 — Selected diagnostic ions for identification and quantification in mass spectrometric detection (informative)

Name	Selected ions for identification and quantification *m/z*
Bromochloroacetic acid (methyl ester)	127, 129, 131
Dalapon (methyl ester)	61, 97, 99
Dibromoacetic acid (methyl ester)	171, 173, 175
Dichloroacetic acid (methyl ester)	83, 85, 87
Monobromoacetic acid (methyl ester)	93, 95, 121, 123
Monochloroacetic acid (methyl ester)	77, 79, 108, 110
Trichloroacetic acid (methyl ester)	117, 119, 121
Examples of internal standard (informative)	
2-Bromopropionic acid (methyl ester)	87, 107, 109
2,3-Dichloropropionic acid (methyl ester)	97, 99, 121

9 Calibration

9.1 General requirements

For practical reasons, the calibration is based on multi-component solutions. Make sure to achieve a linear dependence of signal to concentration. Calibration of the GC-MS step (not including the total procedure) is described in 9.2.

Determine the linear working range using at least five measuring points of different concentration (see Bibliography [1]).

The calibration function for a substance is valid only for the measured concentration range. Additionally, the calibration function depends on the condition of the gas chromatograph and shall be checked regularly. For routine analysis, a check of the linear calibration function by measurement of two points is sufficient.

There are two different possibilities to set up the calibration function. In each case, adjust the working range of reference solutions to the given demands (5.17.3 and 5.18.4, reference substances):

— Calibration of the total procedure with external standard (including the extraction and derivatization step), (9.3).

— Calibration of the total procedure with internal standard (including the extraction and derivatization step), (9.4).

If setting up the method for the first time, check retention time (RT) and identity of each single compound carefully. It is recommended that each methyl ester of the acids mentioned in Table 1 be single-injected for checking retention time and/or mass spectrum (for examples of chromatograms and mass spectra see Annex A and Annex B) (5.17).

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

Table 3 — Definition of subscripts

Subscript	Meaning
e	Calibration step
fnd	Found
i	Substance *i*
is	Internal standard
j	Consecutive figure for pairs of values
nom	Nominal
tot	Total procedure

9.2 Calibration of the GC step not covering the total procedure

For each analyte, establish a calibration function from at least five points; it is practicable to include in one step all compounds mentioned in Table 1.

Establish the calibration function by injecting the calibration solution (5.17.3 or 5.18.4 following methylation).

The injection volume in the calibration step and in the measurement shall be the same.

For a graphic presentation of the calibration curve, plot the respective measured values $y_{i,\mathrm{e},j}$ (integration units e.g. for area or height) on the ordinate against the respective mass concentrations $\rho_{i,\mathrm{e},j}$ of the substance i on the abscissa.

Use the series of measured values thus obtained to establish the linear regression function as follows:

$$y_{i,\mathrm{e}} = m_i \cdot \rho_{i,\mathrm{e}} + b_i \tag{1}$$

where

$y_{i,\mathrm{e}}$ is the (dependent variable) measured response of substance i depending on $\rho_{i,\mathrm{e}}$. The unit is arbitrary, e.g. area unit;

m_i is the slope of the calibration function of substance i. The unit is arbitrary, e.g. area unit × litres per micrograms;

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

b_i is the ordinate intercept of the calibration curve. The unit is arbitrary, e.g. area unit.

9.3 Calibration with external standard covering the total procedure

To calibrate the total procedure, transfer 1 ml of reference solution (5.18.4) to 200 ml of water (5.1).

Treat and analyse the solution as given in Clause 8.

According to 9.2, set up a calibration curve from the values $y_{i,\mathrm{e,tot},j}$ and $\rho_{i,\mathrm{e,tot},j}$.

$$y_{i,\mathrm{e,tot}} = m_{i,\mathrm{tot}} \cdot \rho_{i,\mathrm{e,tot}} + b_{i,\mathrm{tot}} \tag{2}$$

where

$y_{i,\mathrm{e,tot}}$ is the (dependent variable) measured response of substance i during calibration, depending on $\rho_{i,\mathrm{e,tot}}$. The unit is arbitrary, e.g. area unit;

$m_{i,\mathrm{tot}}$ is the slope of the calibration curve of substance i. The unit is arbitrary, e.g. area unit × litres per micrograms;

$\rho_{i,\mathrm{e,tot}}$ is the (independent variable) mass concentration of substance i in the spiked aqueous reference solution, in micrograms per litre, µg/l;

$b_{i,\mathrm{tot}}$ is the ordinate intercept of the calibration curve. The unit is arbitrary, e.g. area unit.

9.4 Calibration with internal standard covering the total procedure

The use of an internal standard procedure helps minimizing unavoidable minor errors that may occur throughout the total procedure, e.g.:

— Precision by GC-measurement is independent from minor deviations during probe injection.

— Minor sample losses throughout sample preparation as well as insufficient adjusting of small sample extract volumes to a precise level do not cause any problems in reproducibility.

— Determination is up to a certain degree independent of matrix effects in the sample, as long as recovery of both the internal standard and the analyte are comparable.

As internal standard, choose a substance with similar physical-chemical properties as the substance to be determined (enrichment behaviour, retention time, derivatization ability) (5.20). The internal standard should not be present in the sample to be analysed. The choice of a substance may be difficult and it depends on the problem to be resolved, in any case, the suitability should be checked. It may be advantageous to use more than one internal standard.

Add the internal standard (is) in a known amount to the water sample prior to analysis. The mass concentration ρ_{is} should be equal for both calibration and sample measurement. All reference solutions suitable for multipoint calibration should contain equal amounts of internal standard.

For calibration covering the total procedure, add 1 ml of reference solution (5.18.4) to 200 ml water (5.1) and analyse the samples as given in Clause 8.

According to 9.2, set up a calibration curve from the values $y_{i,\text{e,tot},j} / y_{\text{is,e,tot},j}$ and $\rho_{i,\text{e,tot},j} / \rho_{\text{is,e,tot},j}$ and establish a linear regression function using Equation (3):

$$\frac{y_{i,\text{e,tot}}}{y_{\text{is,e,tot}}} = m_{i,\text{is,tot}} \cdot \frac{\rho_{i,\text{e,tot}}}{\rho_{\text{is,e,tot}}} + b_{i,\text{is,tot}} \tag{3}$$

where

$y_{i,\text{e,tot}}$ is the (dependent variable) measured response of the substance i in the calibration, depending on $\rho_{i,\text{e}}$. The unit is arbitrary, e.g. area unit;

$y_{\text{is,e,tot}}$ is the measured response of the internal standard (is) in the calibration. The unit is arbitrary, e.g. area unit. All reference solutions contain equal amounts of internal standard;

$\rho_{i,\text{e,tot}}$ is the (independent variable) mass concentration of the substance i in the spiked aqueous reference solution, in micrograms per litre, µg/l;

$\rho_{\text{is,e,tot}}$ is the (independent variable) mass concentration of the internal standard (is), in micrograms per litre, µg/l;

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

$b_{i,\text{is,tot}}$ is the axis intercept of the calibration curve on the ordinate.

9.5 Determination of procedural recovery values

Reliable recovery data are obtained from analysis of spiked water samples (5.1) at different concentration levels, equidistantly spread over the working range. From these individual results, a mean specific recovery $\bar{A}_i$ is calculated.

As an example, add 1,0 ml of the respective reference solution (5.18.4) to 200 ml of water (5.1) and analyse the samples as given in Clause 8.

Using the calibration function in 9.2, calculate the single mass concentration $\rho_{i,N,\text{fnd}}$ for each concentration level N and for each substance i.

Calculate the single recovery $A_{i,N}$ according to Equation (4).

$$A_{i,N} = \frac{\rho_{i,N,\text{fnd}}}{\rho_{i,N,\text{nom}}} \cdot f \tag{4}$$

where

$A_{i,N}$ is the recovery of substance i on the concentration level N in percent, %;

$\rho_{i,N,\text{fnd}}$ is the recovered mass concentration of substance i on the concentration level N, calculated according to Equation (1), in micrograms per litre, µg/l;

$\rho_{i,N,\text{nom}}$ is the original mass concentration of substance i on the concentration level N, in micrograms per litre, µg/l;

f is the conversion factor, here: $f = 100$.

Calculate with these single results the mean recovery $\bar{A}_i$ according to Equation (5).

$$\bar{A}_i = \frac{\sum_{N=1}^{n} A_{i,N}}{n} \tag{5}$$

where

$\bar{A}_i$ is the mean recovery of substance i, in percent, %;

$A_{i,N}$ is the recovery of substance i on the concentration level N in percent, %;

n is the number of individual measurement values $A_{i,N}$.

With the described procedure stated in Clause 8, recoveries (> 65 % up to 70 %) are usually achieved. Low or unstable recoveries indicate matrix effects or difficulties during extraction.

10 Calculation

10.1 Calculation of single results by calibration with external standard covering the total procedure

Calculate the mass concentration $\rho_{i,\text{tot}}$ of the substance i in the water sample using Equation (6):

$$\rho_{i,\text{tot}} = \frac{y_{i,\text{tot}} - b_{i,\text{tot}}}{m_{i,\text{tot}}} \tag{6}$$

where

$\rho_{i,\text{tot}}$ is the mass concentration of the substance i in the water sample, in micrograms per litre, µg/l;

$y_{i,\text{tot}}$ is the measured value of the substance i in the extract of the water sample, for example, area unit;

$m_{i,\text{tot}}$, $b_{i,\text{tot}}$ see Equation (2).

10.2 Calculation of single results by calibration with internal standard covering the total procedure

Calculate the mass concentration $\rho_{i,\text{tot}}$ of the substance according to Equation (7) with regard to Equation (3).

$$\rho_{i,\mathrm{tot}} = \frac{\dfrac{y_{i,\mathrm{tot}}}{y_{\mathrm{is,tot}}} - b_{i,\mathrm{is,tot}}}{m_{i,\mathrm{is,tot}}} \cdot \rho_{\mathrm{is,tot}} \qquad (7)$$

where

$\rho_{i,\mathrm{tot}}$, $y_{i,\mathrm{tot}}$ see Equation (6);

$y_{\mathrm{is,tot}}$ is the measured response of the internal standard (is) in the water sample. The unit depends on the evaluation, for example area unit;

$\rho_{\mathrm{is,tot}}$ is the mass concentration of the internal standard (is), in micrograms per litre, µg/l;

$b_{i,\mathrm{is,tot}}$, $m_{i,\mathrm{is,tot}}$ see Equation (3).

11 Expression of results

The described gas chromatography method with EC detection gives a single individual result for each of the columns and/or types of detection used. The quantitative end result is ascertained from the individual results as follows:

Calculate the average, if the difference between the individual values is less than 10 % (relative to the lower result).

If the difference is greater than 10 %, select the lower value, provided that the lower value is plausible and not attributable e.g. to a problem in the gas chromatography system. The higher value may be the result of insufficient substance separation.

All measurement results suffer from a certain lack of reproducibility; this relative lack of reproducibility is frequently greatest in the lower range of application of the method.

In this standard, water samples were spiked with various concentrations of selected haloacetic acids for calculating the reproducibility (expressed as reproducibility coefficient of variation, CV_R). As can be seen from the values of Table C.1, CV_R is between 11,8 % and 48,9 %.

CV_R in a different concentration range may be estimated in individual cases from the quality management data documentation of a laboratory (e.g. range control cards in double determination procedures). Another possible method for estimating CV_R is to use external analytical quality control procedures, in which CV_R can be found by comparison of the results of several laboratories in interlaboratory trials. Matrix influences may cause higher values of CV_R.

The mass concentration of the individual compounds according to Table 1 in micrograms per litre (µg/l) should be reported with two significant figures. In case of mass concentration $< 0{,}1$ µg/l, only one significant figure should be reported.

EXAMPLES

Trichloroacetic acid	23 µg/l
Monobromoacetic acid	1,4 µg/l
Bromochloroacetic acid	0,37 µg/l
Dalapon	0,08 µg/l

12 Test report

The test report shall include, as a minimum, the following information:

a) reference to this International Standard (ISO 23631:2006);

b) the method used;

c) sample identity;

d) expression of the results, according to Clause 11;

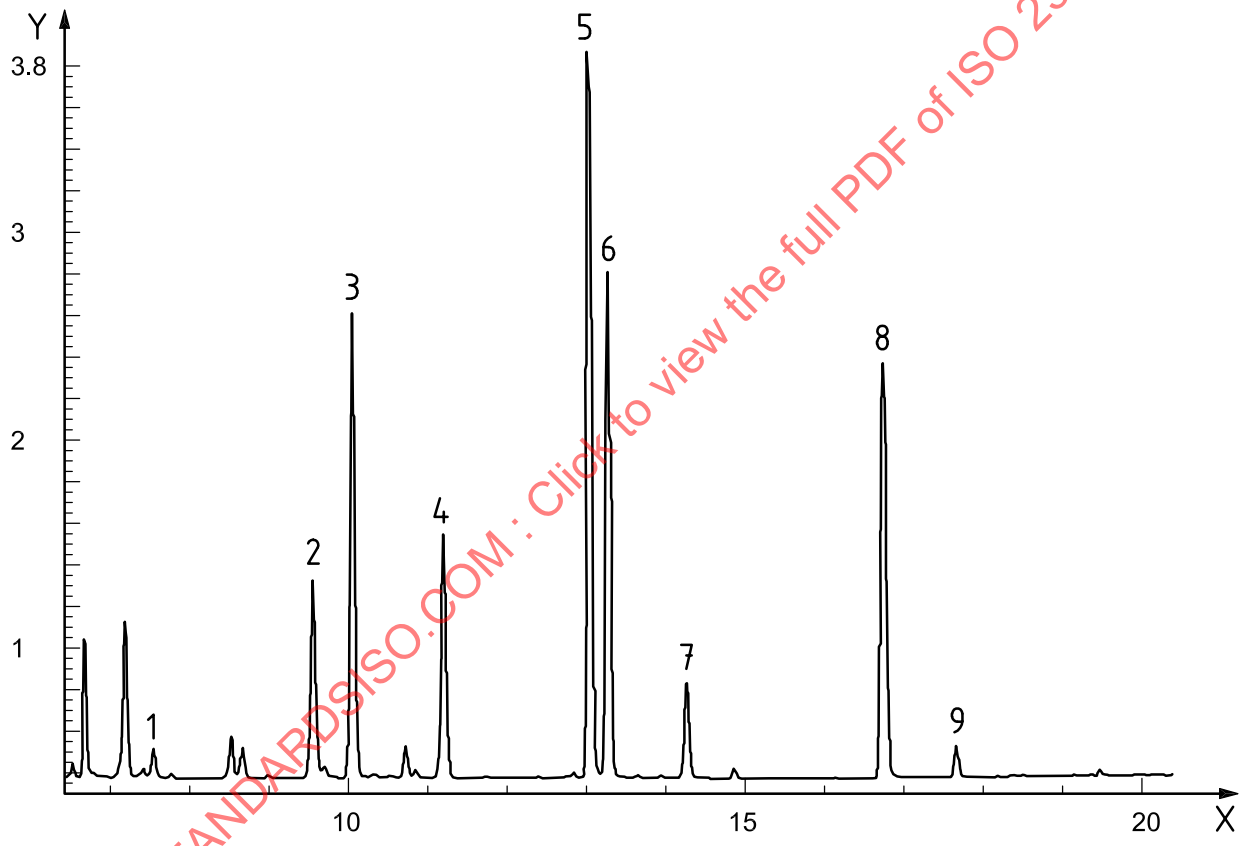
e) any deviations from this procedure and all circumstances which may have affected the results.

Annex A
(informative)

Examples of gas chromatograms

Operating conditions:

capillary column:	DB 1 (J&W) [2], 60 m × 0,25 mm × 0,25 µm
injection:	2 µl, splitless (0,5 min), 280 °C
range of concentration:	0,33 µg/ml to 1,00 µg/ml
carrier gas:	helium (5.0) 1,6 bar
GC oven temperature:	45 °C, 1 min; 4 °C/min to 95 °C, 4 min; 20 °C/min to 300 °C, 15 min
detector:	ECD, 300 °C



Key

X Time, min
Y Abundance

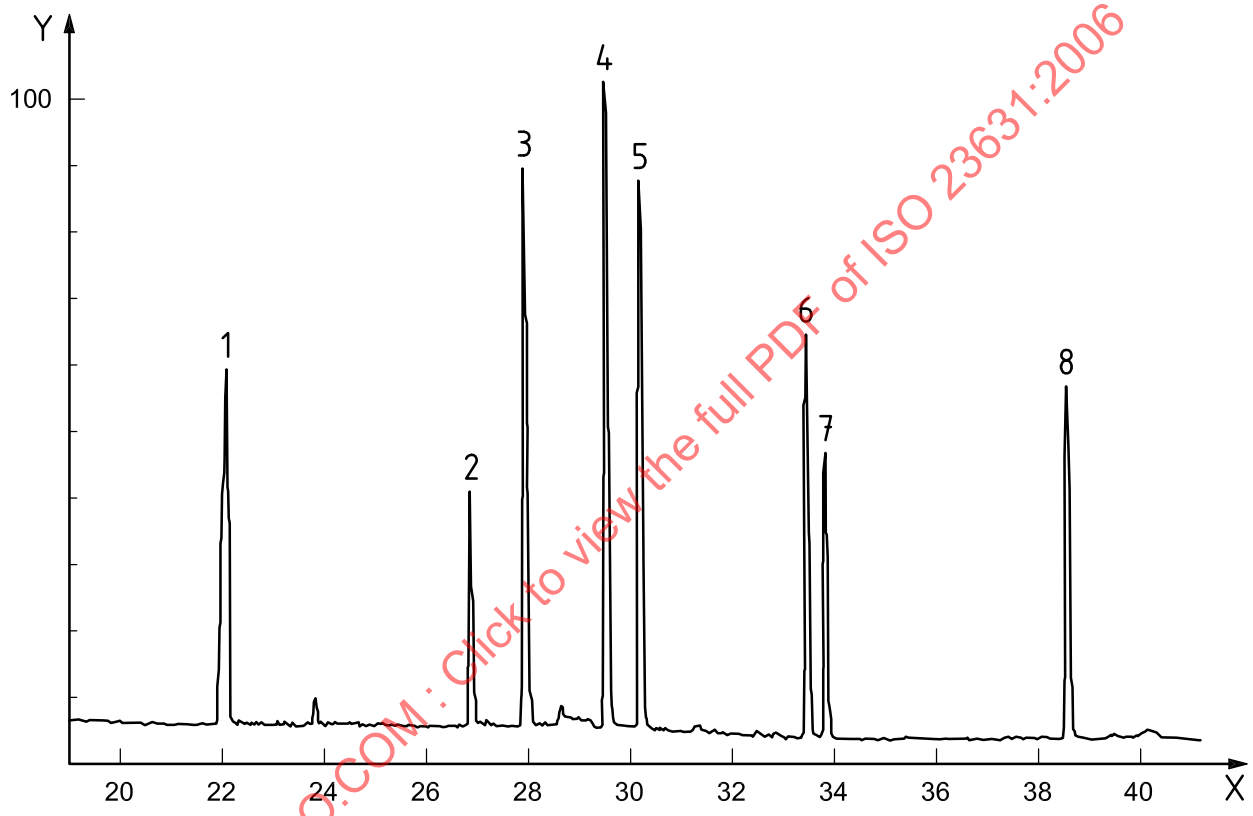
1 Monochloroacetic acid (methyl ester)
2 Monobromoacetic acid (methyl ester)
3 Dichloroacetic acid (methyl ester)
4 Dalapon (methyl ester)
5 Bromochloroacetic acid (methyl ester)
6 Trichloroacetic acid (methyl ester)
7 2,3-Dichloropropionic acid (methyl ester) /(internal standard)
8 Dibromoacetic acid (methyl ester)
9 1,3-Dichlorobenzene / (internal standard)

Figure A.1 — Gas chromatogram 1

2) DB 1 (J&W) is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

Operating conditions:

capillary column:	DB 1 (J&W) [3], 60 m × 0,25 mm × 1,0 µm
injection:	ATAS Optic 2 [3], 40 °C; 10 °C/s to 300 °C
	2 µl, splitless (1,0 min)
range of concentration:	0,2 µg/ml to 0,6 µg/ml
carrier gas:	helium (5.0), EPC: 1,0 bar to 1,7 bar
GC oven temperature:	40 °C, 10 min; 3 °C/min to 160 °C, 0 min;
	20 °C/min to 300 °C, 10 min
detector:	Finnigan MAT [3], GC/Q, ion-trap-MS, 70 eV, source temp. 200 °C



Key

X Time, min

Y Abundance, %

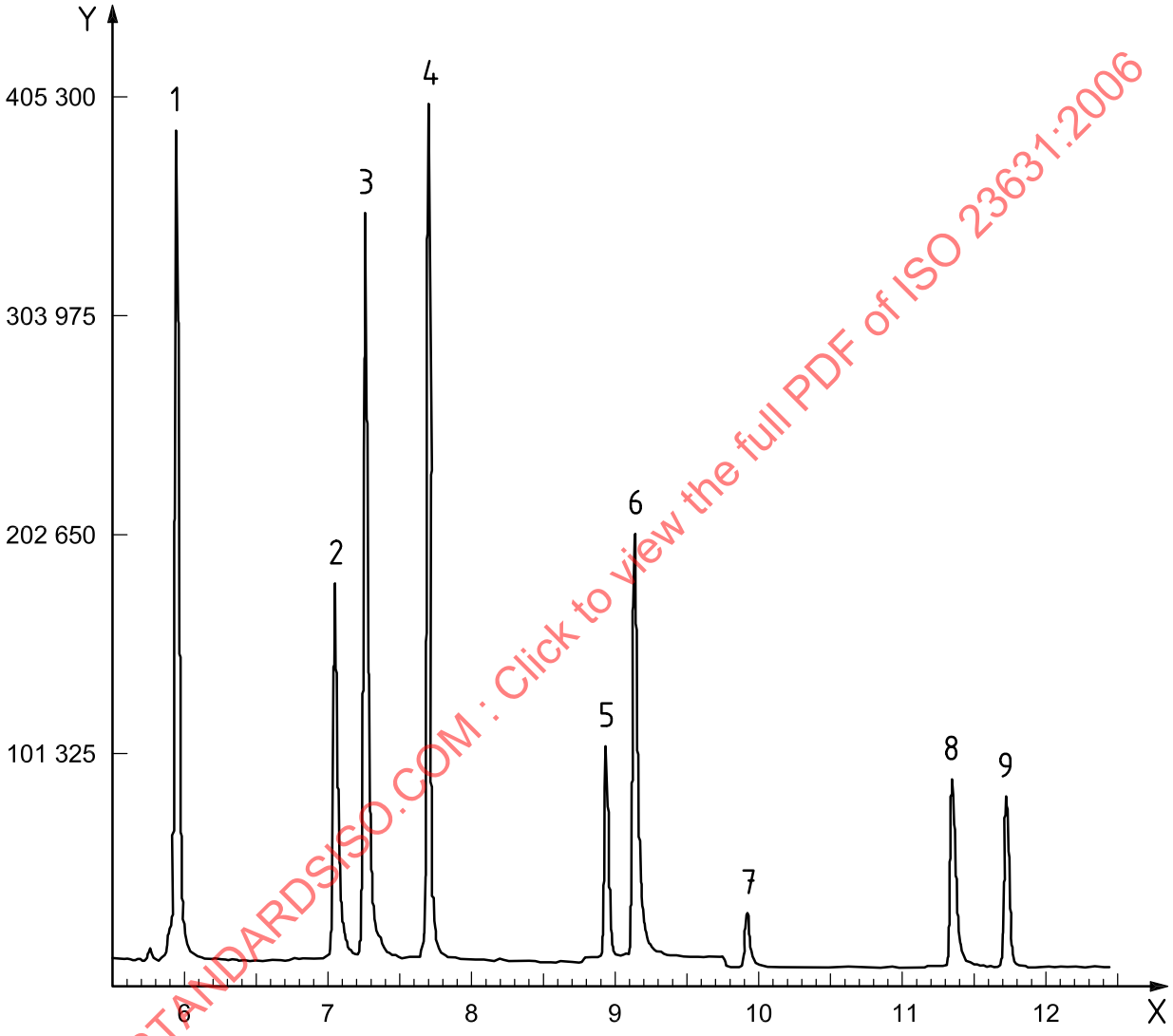
1 Monochloroacetic acid (methyl ester)
2 Monobromoacetic acid (methyl ester)
3 Dichloroacetic acid (methyl ester)
4 2-Bromopropionic acid (methyl ester) / (internal standard)
5 Dalapon (methyl ester)
6 Bromochloroacetic acid (methyl ester)
7 Trichloroacetic acid (methyl ester)
8 Dibromoacetic acid (methyl ester)

Figure A.2 — Gas chromatogram 2

3) DB 1 (J&W), ATAS Optic 2 and Finnigan MAT are examples of suitable products 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.

Operating conditions:

capillary column:	CP-Sil 8 CB MS (Chrompack) [4], 60 m × 0,25 mm × 0,15 µm
injection:	Gerstel KAS [4], 50 °C; 10 °C/s to 250 °C
	2 µl, splitless (1,5 min)
range of concentration:	0,25 µg/ml to 2,0 µg/ml
carrier gas:	helium (5.0); 0,70 ml/min
GC oven temperature:	40 °C; 5 °C/min to 150 °C;
	20 °C/min to 250 °C, 10 min
mass spectrometer:	Hewlett Packard, Quadrupole HP 5970 B MSD [4], 70 eV, SIM



Key

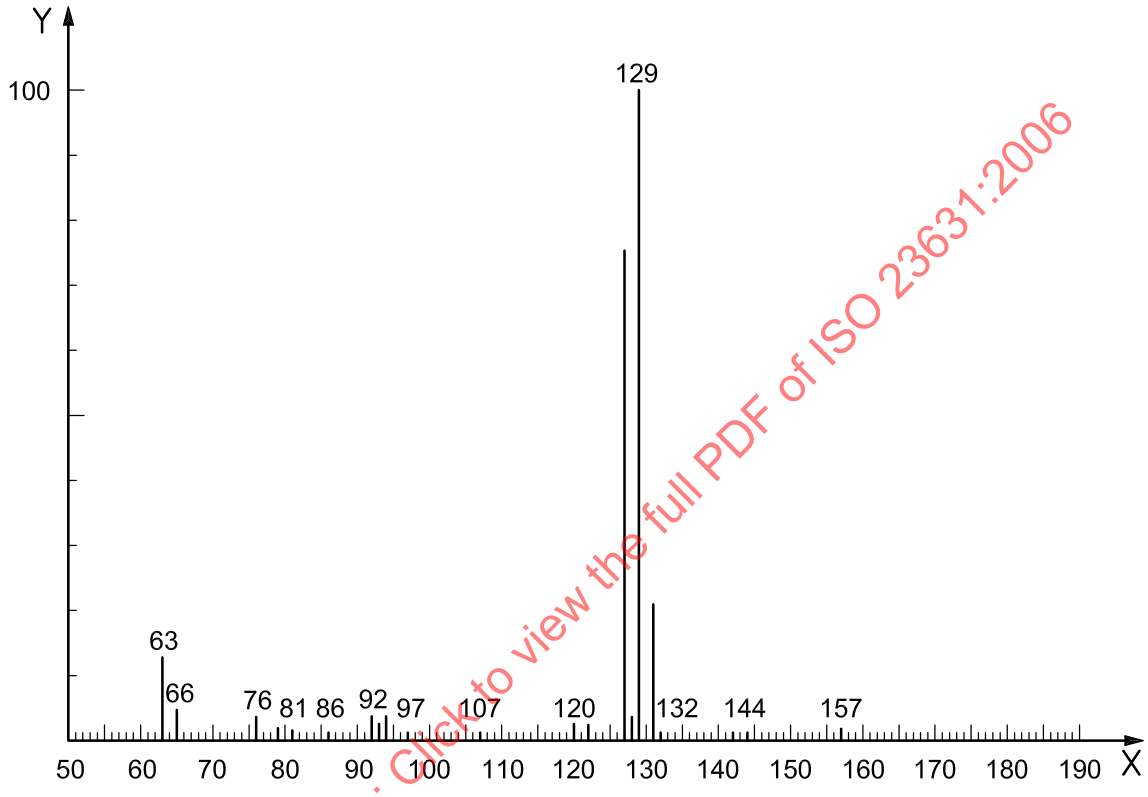
X	Time, min	Y	Abundance
1	Monochloroacetic acid (methyl ester)	6	Bromochloroacetic acid (methyl ester)
2	Monobromoacetic acid (methyl ester)	7	2,3-Dichloropropionic acid (methyl ester) /(internal standard)
3	Dichloroacetic acid (methyl ester)	8	Dibromoacetic acid (methyl ester)
4	Dalapon (methyl ester)	9	1,4-Dichlorobenzene d_4 / (internal standard)
5	Trichloroacetic acid (methyl ester)		

Figure A.3 — Gas chromatogram 3

4) CP-Sil 8 CB MS (Chrompack), Gerstel KAS and Hewlett Packard, Quadrupole HP 5970 B MSD are examples of suitable products 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.

Annex B
(informative)

Mass spectra of methylated dalapon and haloacetic acids



Key

X Mass / Charge ratio, *m/z*

Y Intensity, %

Figure B.1 — Bromochloroacetic acid (methyl ester)