
**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**

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*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*

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Foreword

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

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

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

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

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

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Introduction

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

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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.

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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).

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4 Interferences

4.1 Interferences with the extraction procedure

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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, $w(CH_3COOH) = 10$ %.

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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 $-18\text{ }^{\circ}\text{C}$, 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 $-18\text{ }^{\circ}\text{C}$, 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 $+10\text{ }^{\circ}\text{C}$ 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 $60\text{ }^{\circ}\text{C}$ (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 $-18\text{ }^{\circ}\text{C}$, 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, $\text{C}_3\text{H}_5\text{BrO}_2$ or 2,3-dichloropropionic acid $\text{C}_3\text{H}_4\text{Cl}_2\text{O}_2$ (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.

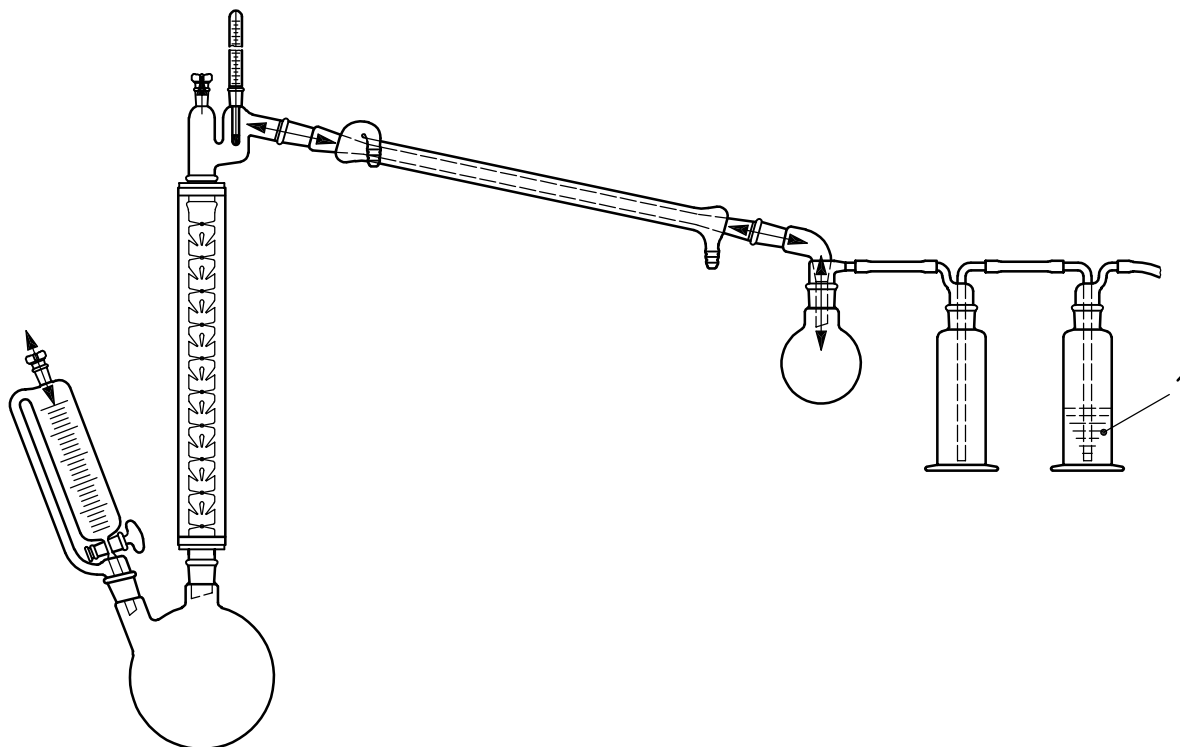
6.10.4 Distillation head.

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

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Figure 1 — Example of a distillation apparatus for preparing diazomethane

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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 ≥ 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 .