INTERNATIONAL STANDARD

ISO 15913

First edition
2000-04-01

Water quality — Determination of selected phenoxyalkanoic herbicides, including bentazones and hydroxybenzonitriles by gas chromatography and mass spectrometry after solid phase extraction and derivatization

Qualité de l'eau — Dosage de certains herbicides phénoxyalcanoïques, y compris bentazones et hydroxybenzonitriles, par chromatographie en phase gazeuse et spectrométrie de masse après extraction en phase solide et dérivatisation

Reference number
ISO 15913:2000(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 734 10 79
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

Contents

Page

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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15913 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annexes A, B, C and D of this International Standard are for information only.

Water quality — Determination of selected phenoxyalkanoic herbicides, including bentazones and hydroxybenzonitriles by gas chromatography and mass spectrometry after solid phase extraction and derivatization

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

1 Scope

This International Standard specifies a method for the determination of phenoxyalkanoic acids in ground and drinking water in mass concentrations $\geqslant$ 50 ng/l (detailed information is given in Table A.1 of annex A). Examples of phenoxyalkanoic acids which can be determined by this method are given in Table 1.

This method may be applicable 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 (see annex B).

Table 1 — Plant treatment agents determined by this method

Name	Molecular formula	Relative molecular mass	CAS registry No.
(2,4-Dichlorophenoxy) acetic acid	$C_8H_6Cl_2O_3$	221,0	94-75-7
Mecoprop	$C_{10}H_{11}ClO_3$	214,65	93-65-2
Dichlorprop	$C_9H_8Cl_2O_3$	235,06	120-36-5
MCPA	$C_9H_9ClO_3$	200,6	94-74-6
MCPB	$C_{11}H_{13}ClO_3$	228,67	94-81-5
(2,4,5-Trichlorophenoxy)acetic acid	$C_8H_5Cl_3O_3$	255,5	93-76-5
Bentazone	$C_{10}H_{12}N_2O_3S$	240,3	25057-89-0
Bromoxynil	$C_7H_3Br_2NO$	276,9	1689-84-5
4-(2,4-Dichlorophenoxy)-butanoic acid	$C_{10}H_{10}Cl_2O_3$	249,1	94-82-6
Fenoprop	$C_9H_7Cl_3O_3$	269,51	93-72-1

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC 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 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*.

3 Term, definition, abbreviations and subscripts

3.1 Term and definition

For the purposes of this International Standard, the following term and definition applies.

3.1.1
phenoxyalkanoic herbicides
herbicides which undergo derivatization with diazomethane and which may subsequently be determined by gas chromatography

EXAMPLE Typical phenoxyalkanoic herbicides include alkylhalogenated phenoxy acids, hydroxybenzonitriles and bentazone.

3.2 Abbreviations

2,4-D (2,4-dichlorophenoxy) acetic acid

2,4-DB 4-(2,4-dichlorophenoxy) butanoic acid

2,4-DP dichlorprop

MCPP mecoprop

2,4,5-T (2,4,5-trichlorophenoxy) acetic acid

2,4-TP fenoprop

3.3 Subscripts

c calibration step using an external standard

g overall procedure

i identity of the substance *i*

is internal standard

j consecutive figure *j* for pairs of values

sam sample

sol solvent

4 Principle

After acidification, substances are enriched on solid phase adsorbent material [for example RP[1)]-C18 material], eluted with solvent, methylated with diazomethane and then determined by gas chromatography using a mass spectrometric detector. In some cases, the substances may be present as their esters, for example octanoic esters. Hydrolysis of the water sample (see annex C) may lead to higher concentrations of the free acids.

5 Interferences

5.1 Occurrence

Interferences may occur especially when examining other types of water, for example surface water.

5.2 Sampling

To avoid interferences collect the sample as described in clause 8.

5.3 Enrichment

The commercially available adsorbent materials are often of varying quality. Considerable batch-to-batch differences in quality and selectivity of this material are possible. The recovery may vary with the concentration. Therefore, check recovery regularly at different concentrations. Perform calibration and analysis with material taken only from the same batch. Suspended matter in the water sample (such as iron hydroxide, calcium carbonate) occurring during sampling, storage and sample preparation, or an increase in the concentration of microorganisms may clog the packing. In this case, filter the water sample through a glass fibre filter prior to enrichment.

5.4 Gas chromatography and mass spectrometry

Use the operational conditions set in accordance with manufacturer's instructions. Check these settings at regular intervals.

General interferences, caused by the injection system or insufficient separation can be eliminated with the help of special laboratory experience and the instrument's manuals.

6 Reagents

6.1 General

Use, as far as available, "for residual analysis" reagents. Use only reagents and water with negligibly low impurities, i.e. resulting in clean blanks.

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

6.3 Nitrogen, of high purity, i.e. minimum 99,996 % by volume, for drying and eventually for concentration by evaporation.

6.4 Hydrochloric acid, c(HCl) = 2 mol/l.

6.5 Diethyl ether, $C_4H_{10}O$, stabilized.

---

1) RP = reversed phase

6.6 Ethanol, C_2H_5OH.

6.7 Acetic acid, CH_3COOH, 10 % by volume, aqueous solution (used to destroy diazomethane).

6.8 Sodium hydroxide solution, c(NaOH) = 6 mol/l.

6.9 Solvents for the elution, for example acetone C_3H_6O, or methanol, CH_3OH.

6.10 Methanol, CH_3OH, as conditioning agent.

6.11 Potassium hydroxide solution, KOH, volumic mass of 60 %.

6.12 Diazald (*N*-methyl-*N*-nitroso-4-toluenesulfonamide), $C_8H_{10}N_2O_3S$.

6.13 Solid phase adsorbent material, most commonly RP-C18-material, in the form of commercially available cartridges or adequately glass columns filled according to 7.4 with a minimum packing of 1,0 g.

For selectivity of the material see 5.3.

6.14 Internal standard, preferably deuterated or ^{13}C-labelled compounds.

The standards are often commercially available at a concentration of 100 µg/ml. Dilute this standard with acetone. The final concentration in the water sample shall be for example about 100 ng/l.

6.15 Diazomethane solution.

WARNING — Diazald is an irritant and all skin contact should be avoided.

Prepare diazomethane in a distillation apparatus, such as the one shown in Figure 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 (6.7).

Insert 8 ml of the KOH solution (6.11) and 10 ml of ethanol (6.6) in a 250 ml reaction flask.

Suspend 5,0 g of diazald (6.12) in 45 ml of diethyl ether (6.5) in a pressure-equalizing funnel.

Cautiously warm the reaction flask to about 60 °C (water bath) and, within 20 min, dropwise add the diazald suspension from the filter funnel.

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

After this reaction, add an additional 10 ml of diethyl ether through the filter funnel and distil the remaining diazomethane.

Stopper the trap and store it at about −18 °C. Check the stability of the diazomethane which should have an intensive yellow colour.

NOTE Excess diazomethane may be destroyed by adding a solution of acetic acid (6.7).

Prior to cleaning, rinse all diazomethane glassware with acetic acid (6.7).

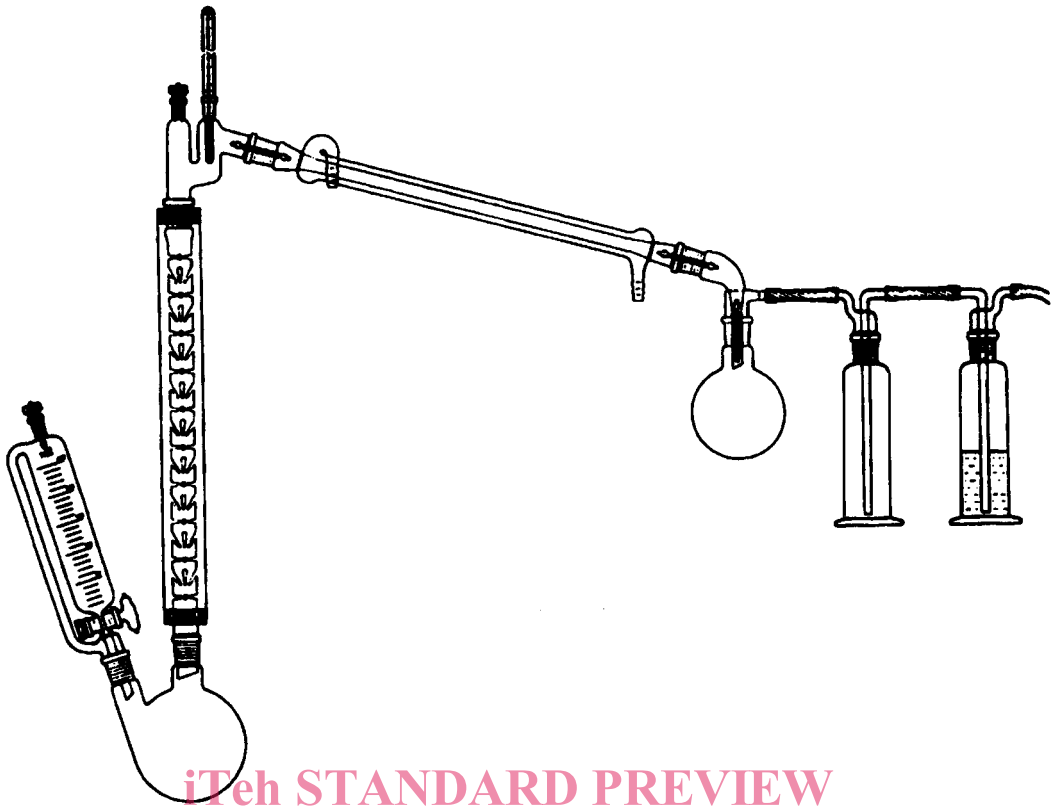

Figure 1 — Example of a distillation apparatus

6.16 Reference substances:

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

6.16.1.1 Solutions of individual methyl esters.

As an example, place 50,0 mg each of a reference substance into a 100 ml volumetric flask, dissolve with acetone (6.9) and dilute to volume.

Store the solution at −18 °C, protected from light.

Check the concentration regularly.

6.16.1.2 Methyl ester stock solutions.

As an example, pipette 1 ml of each of the solution of the individual substance (6.16.1.1) into a 100 ml volumetric flask and dilute to volume with acetone (see 6.9).

Store the solutions at −18 °C, protected from light.

Check the concentration of the stock solutions regularly.

6.16.1.3 Methyl ester reference solutions (working standard solution).

Prepare the reference solutions by an adequate dilution of the stock solution (6.16.1.2).

Store the reference solution in the refrigerator. Reference solutions are stable for about 6 months.

6.16.2 Free-acid reference substances:

6.16.2.1 Solutions of the individual free acid.

As an example, place 50,0 mg of each of the reference substance into a 100 ml volumetric flask, dissolve with acetone (6.9) and dilute to volume.

Store the solutions at −18 °C, protected from light.

Check the concentration of the stock solutions regularly.

6.16.2.2 Free-acid stock solution (intermediate standard solutions).

As an example, pipette 1 ml of each of the solutions of the individual free acid (6.16.2.1) into a 100 ml volumetric flask and dilute to volume.

Store the solutions at −18 °C, protected from light.

Check the concentration of the free-acid stock solutions regularly.

6.16.2.3 Free-acid reference solutions (working standard solutions).

Prepare the solutions by adequate dilution of the stock solution (6.16.2.2).

Store the free-acid reference solutions in a refrigerator. Their shelf-life is limited.

7 Apparatus

7.1 General requirements

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 or stainless steel.

7.2 Flat-bottomed flasks, preferably brown glass, 1 000 ml and 2 000 ml, with glass stoppers.

7.3 Graduated cylinders, 1 000 ml.

7.4 Cartridges, made of polypropene or glass, filled with solid-phase material, for example RP-C18 material, (6.13).

NOTE The cartridges are commercially available.

7.5 Vacuum pump or **pressure assembly**.

7.6 Vials, suitable for automatic or manual injection.

7.7 Volumetric flasks, 10 ml or 100 ml.

7.8 Capillary gas chromatograph, equipped with a non-discriminating injection system and a mass-spectrometric detector.

7.9 Capillary columns, for gas chromatography; for examples see annex D, Figures D.5 and D.6.

7.10 Glass-fibre filters, made of borosilicate glass, of fibre diameter for example from 0,75 µm to 1,5 µm, with inorganic binding material.

7.11 pH meter.

7.12 Injection syringes, nominal capacity 5 µl and higher.

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

— double-necked, round-bottomed flask, 250 ml capacity;

— pressure-equalizing funnel, 100 ml capacity;

— distillation column, for example Vigreux column;

— distillation head;

— condenser, for example Liebig condenser;

— flask for absorption of diazomethane;

— security flask;

or a commercial distillation apparatus.

8 Sampling

Collect samples in accordance with ISO 5667-1, ISO 5667-2, and ISO 5667-3.

Use thoroughly-cleaned, preferably brown, flat-bottomed glass flasks (see 7.2) for sampling.

Fill the bottles completely with the water to be examined.

Treat and analyse the samples as soon as possible after the sample collection.

If storage is unavoidable, store the sample at 4 °C in the dark, but not for longer than 3 days.

9 Procedure

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

It should be investigated whether and to what extent particular problems will require the specification of additional marginal conditions.

9.1 Solid phase adsorption and derivatization of test samples

9.1.1 Conditioning of the RP-C18 adsorbent material

Wash the RP-C18 material in the cartridge or glass column (7.4) with a volume of methanol (6.10) five times that of the column volume.

Rewash the column with a volume of water (6.1), five times that of the column volume and use the conditioned material for enrichment.

Do not let the cartridge/column run dry.