INTERNATIONAL STANDARD

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Water quality — Determination of selected phthalates using gas chromatography/mass spectrometry

Qualité de l'eau — Dosage de certains phtalates par chromatographie en phase gazeuse/spectrométrie de masse

Reference number
ISO 18856:2004(E)

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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 18856 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

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

INTERNATIONAL STANDARD **ISO 18856:2004(E)**

Water quality — Determination of selected phthalates using gas chromatography/mass spectrometry

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.

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 phthalates in water after solid phase extraction and gas chromatography/mass spectrometry.

This method is applicable to the determination of phthalates (see Table 1) in ground water, surface water, wastewater and drinking water in mass concentrations ranging from above 0,02 µg/l up to 0,150 µg/l, depending on the individual substance and the value of the blank.

The applicability of this method to other phthalates not specified in Table 1 is not excluded, but it is necessary to determine its applicability in each case (see Annex A for the list of phthalates).

General remarks concerning the recovery and use of internal standards is given in Annex B.

Table 1 — Phthalates determined by this method

No	Name	Formula	Abbreviation	Molar mass g/mol	CAS[a] number
1	Dimethyl phthalate	$C_{10}H_{10}O_4$	DMP	194,2	131-11-3
2	Diethyl phthalate	$C_{12}H_{14}O_4$	DEP	222,24	84-66-2
3	Dipropyl phthalate	$C_{14}H_{18}O_4$	DPP	250,3	131-16-8
4	Diisobutyl phthalate	$C_{16}H_{22}O_4$	DiBP	278,4	84-69-5
5	Dibutyl phthalate	$C_{16}H_{22}O_4$	DBP	278,4	84-74-2
6	Butyl benzyl phthalate	$C_{19}H_{20}O_4$	BBzP	312,4	85-68-7
7	Dicyclohexyl phthalate	$C_{20}H_{26}O_4$	DCHP	330,4	84-61-7
8	Di(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	DEHP	390,6	117-81-7
9	Di(*n*-octyl) phthalate	$C_{24}H_{38}O_4$	DOP	390,6	117-84-0
10	Didecyl phthalate	$C_{28}H_{46}O_4$	DDcP	446,7	84-77-5
11	Diundecyl phthalate	$C_{30}H_{50}O_4$	DUP	474,4	3648-20-2

[a] CAS: Chemical Abstracts System.

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 reference document (including any amendments) applies.

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

Extraction of the compounds from the water by solid-phase extraction. Then separation is accomplished using capillary columns by gas chromatography and followed by identification and quantification of the phthalates by mass spectrometry. The principle of this method is outlined in Figure 1.

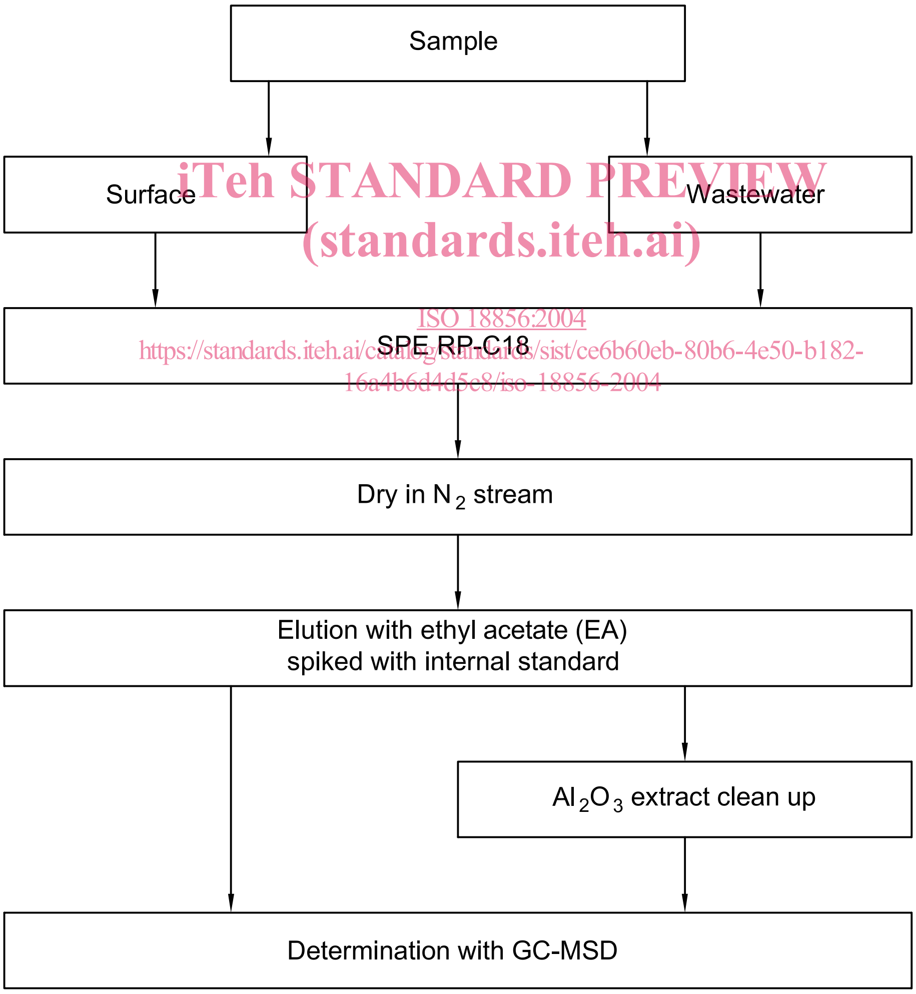

Figure 1 — Flowchart of the analysis

4 Interferences

IMPORTANT — Due to their use as plasticizer agents, phthalates are ubiquitous. Therefore, pay special attention to avoid any contamination.

4.1 Interferences during sampling

In order to avoid interferences and cross-contamination, do not use plastics materials (pipes, etc.).

4.2 Interferences during enrichment

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 of single substances may vary with concentration. Therefore, check the recovery regularly at different concentration levels and whenever new batches are used. Perform calibration and analysis with material from the same batch.

Cross-contamination is likely to occur with laboratory air. Therefore, remove, as far as possible, plastics materials from the laboratory. Cleaning agents often contain phthalates and may severely contaminate the laboratory air if in use regularly. Therefore, refrain from using these agents during application of this procedure.

The use of plastics gloves during pre-treatment may increase the contamination.

The maximum allowed blank level for each phthalate is 80 ng/l with reference to water (see Annex C).

4.3 Interferences in gas chromatography

Phthalates may bleed from the septa of the injector into the gas chromatograph, therefore use septa that are not likely to contaminate the system.

Fittings of syringes, for example, or equipment and septa of the sampling bottles (see 6.7) may as well contain phthalates. Therefore make sure that uncontaminated septa are used.

5 Reagents

Use, as far as available, reagents of analytical quality, or better. Use only reagents with negligibly low concentrations of phthalates and verify by blank determinations and, if necessary, apply additional cleaning steps.

5.1 Water, having a negligibly low concentration of phthalates.

In some cases, it may be preferable to use surface water instead of distilled water, because the concentration levels of the blank of surface water can be lower (9.3). Other waters with negligibly low concentrations of phthalates may be used as well.

5.2 Nitrogen, N_2 of high purity, at least a volume fraction of 99,9 %, for drying and eventually for concentration by evaporation.

5.3 Helium, He of high purity, at least a volume fraction of 99,999 %.

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

5.5 Ethyl acetate, highest purity, $C_4H_8O_2$.

5.6 Methanol, CH_3OH.

5.7 Isooctane, C_8H_{18} (2,2,4-trimethylpentane).

5.8 Quartz wool, heated to 400 °C for at least 4 h.

5.9 Reversed-phase C18 (RP-C18) **material**.

Alternative material and commercial glass cartridges may be used, provided the properties are similar to the material described in this International Standard and the properties are checked in accordance with 4.2.

Check break-through rates prior to starting the analysis and each time a new batch of RP-C18 is used.

5.10 Aluminium oxide, alumina, Al_2O_3, neutral, 50 µm to 200 µm, heated to 400 °C for at least 4 h.

Bring the aluminium oxide to ambient temperature within 6 h. Store in a covered flask. Use within 5 d after baking.

Alternative materials, such as Florisil1) or silica may be used, provided their properties and capacity to separate are similar to aluminium oxide and their properties are checked in accordance with 4.2.

5.11 Internal standards, for example diallyl phthalate, DAIP, $C_{14}H_{14}O_4$; D4-ring-deuterated dibutyl phthalate, “D4-DBP”, D4-$C_{16}H_{22}O_4$; D4-ring-deuterated di(*n*-octyl) phthalate, “D4-DOP”, D4-$C_{24}H_{38}O_4$, $^{13}C_{(6\text{ to }12)}$-labelled standard (as far as available).

5.12 Reference substances of the phthalates, mentioned in Table 1, with defined mass concentrations, for the preparation of reference solutions for the gas chromatographic procedure.

5.13 Solutions of single substances.

In a 10 ml volumetric flask (6.15), dissolve, for example, 10 mg of each of the reference substances in ethyl acetate (5.5) and bring to volume with ethyl acetate (mass concentration: 1 g/l).

Store the solutions in glass bottles at –18 °C, protected from light, and check the concentration at least every three months.

5.14 Stock solution.

In a 10 ml volumetric flask (6.15), add a volume between 100 µl and 500 µl of the single substance solutions (5.13) and bring to volume with ethyl acetate (mass concentration 10 mg/l to 50 mg/l).

Store the solution in a glass bottle at –18 °C, protected from light, and check the concentration at least every three months.

5.15 Reference solutions for multipoint calibration.

Prepare solutions by adequate dilution of the stock solution (5.14) and internal standards (5.17) with ethyl acetate (5.5).

Store the solutions in a glass bottle at –18 °C, protected from light and check the concentration at least every three weeks.

5.16 Reference solution for the determination of the recovery.

Prepare solutions by adequate dilution of the stock solution (5.14) with ethyl acetate.

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1) Florisil is a trade name of prepared magnesium silicate. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

5.17 Solution of the internal standards (see Annex D).

5.17.1 Internal standard stock solution of D4-ring-deuterated-di(*n*-octyl) phthalate (D4-ring-DOP).

Weigh for example 0,1 g of D4-DOP (5.11) in a 10 ml volumetric flask (6.15) filled with about 5 ml of ethyl acetate (5.5), and bring to volume with ethyl acetate.

5.17.2 Internal standard stock solution of D4-ring-deuterated-dibutyl phthalate (D4-ring-DBP).

Weigh for example 0,1 g of D4-DBP (5.11) in a 10 ml volumetric flask (6.15) filled with about 5 ml of ethyl acetate (5.5) and bring to volume with ethyl acetate.

5.17.3 Solution I internal standard.

Combine both solutions (5.17.1 and 5.17.2), for example, by dilution 1:100 by pipetting 0,1 ml of each solution into a 10 ml volumetric flask (6.15) filled with about 5 ml of ethyl acetate (5.5). Bring to volume with ethyl acetate.

5.17.4 Solution II internal standard.

From Solution I (5.17.3), for example take 250 µl and transfer it to a volumetric flask of 250 ml (6.15) and bring to volume with ethyl acetate (5.5).

The final concentrations of D4-DBP and of D4-DOP will be 0,1 mg/l in ethyl acetate.

5.17.5 Solution III internal standard.

Transfer 1 ml of Solution I internal standard (5.17.3) to a 10 ml volumetric flask (6.15), filled with 5 ml of ethyl acetate and bring to volume with ethyl acetate (5.5).

The final concentrations of D4-DBP and of D4-DOP will be 10 mg/l in ethyl acetate.

5.18 Standard solution for the determination of the retention times.

Dilute the solutions of the single substances (5.13) for example 1:1 000 with ethyl acetate (5.5).

NOTE Example of solutions, see Annex D.

6 Apparatus

Equipment or parts likely to come into contact with the water sample or its extract shall be free from phthalates. This may be achieved by thorough cleaning of all glass apparatus (see 8.1). Examples of equipment to avoid contamination are given in Annex E.

6.1 Narrow-neck flat bottomed flasks with glass stoppers, preferably brown glass, of 1 000 ml and 2 000 ml capacities.

6.2 Drying oven, capable of being maintained at a temperature of (105 ± 10) °C.

6.3 Muffle furnace, adjustable for temperatures of up to 400 °C, with a capacity of at least 60 l.

6.4 Vacuum device for solid phase extraction (vacubox, extraction box, see E.4).

6.5 Stainless steel cock, with stainless steel cone or polytetrafluoroethene (PTFE) cock with a Luer2)-connection for separate vacuum connection.

6.6 Wash bottle, for example of 5 l capacity.

6.7 Sampling vial, glass, with inert stopper, e.g. septum, lined with PTFE for storage of the extracts, and glass sampling bottles, with inert septum, of 2 ml capacity, for storage of the extracts for GC autosampler operation.

6.8 Glass cartridges, with Luer2)-cone and conical joint in accordance with ISO 383, DN 14/23 (see E.1).

6.9 Sample reservoir, column, having an inner diameter of 4 cm, length of about 35 cm, conical joint in accordance with ISO 383, DN 14/23 (e.g. see E.3).

6.10 PTFE-frits for cartridges, of 6 ml capacity.

6.11 Disk to cover the sample reservoir, with an inner diameter of 4,5 cm, and with a circular depression in the range 3,4 cm to 4,5 cm; in the centre of the aluminium disc a hole for the Luer[2] cone, having a diameter of 0,5 cm (see E.2).

6.12 Aluminium foil, heated to 400 °C.

6.13 Stainless steel reservoir, for storage of smaller glass apparatus.

6.14 Measuring cylinders, of 250 ml and 500 ml capacities.

6.15 Volumetric flasks, of 1 ml, 2 ml, 10 ml, 25 ml and 250 ml capacities.

6.16 Pasteur-pipettes, e.g. 2 ml.

6.17 Syringes, of 2 µl, 5 µl, 10 µl, 50 µl, 100 µl and 500 µl capacities with a maximum permitted error of ± 2 %.

6.18 Gas chromatograph (GC), with capillary column, temperature-controlled and with mass spectrometric detection.

6.19 Fused silica capillary columns, with non-polar stationary phase (see Annex F); inner diameter $\leqslant$ 0,32 mm, length about 30 m, film thickness of 0,10 µm to 0,50 µm.

Check the quality of the column, for example by injecting the reference solution (5.16) and ensure that the separation is satisfactory.

6.20 Glass tubes, graduated, and with a capacity of 10 ml.

6.21 Nitrogen device for drying.

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2) Luer cone is a special conical joint and is the trade name of a commercially available product. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

7 Sampling and sample pre-treatment

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

Use for sampling pre-treated sampling bottles (6.1 and 8.1) and make sure that the stoppers are pretreated as well.

Fill the bottles almost completely with the sample.

In general, sampling should be carried out using stainless steel containers or glass vessels.

In order to avoid contamination, do not use any plastics material (tubes and other). If plastics parts in the sampling apparatus are unavoidable, flush the apparatus with at least five times the volume of the sample. If applicable, state this step in the test report.

Extract and analyse the sample as soon as possible after sample collection. If storage is unavoidable, store the samples in the dark at 4 °C no longer than 4 d.

In general, samples are examined without pretreatment, i.e. suspended solids are not removed prior to analysis.

Prior to analysis, homogenize the sample.

8 Procedure

8.1 Pretreatment of glass apparatus

Clean all glass apparatus used during analysis in the dishwasher with water and subsequently dry in the oven (6.2) at 105 °C.

Heat the pre-rinsed glass apparatus in the muffle furnace (6.3) using for example the following temperature programme.

Heat to 100 °C at a rate of 2,5 °C/min; then to 250 °C at a rate of 10 °C/min; finally to 400 °C and maintain 75 min isothermally. Subsequently let the apparatus cool to room temperature within 12 h.

NOTE Glassware for volumetric purposes can change its properties due to the heating process.

Close the cooled glass apparatus (bigger vessels) with the respective stoppers or with aluminium foil (6.12). Store smaller glass apparatus in decontaminated (heated) and appropriately closed stainless steel containers (6.13).

In order to avoid losses by adsorption at the walls, rinse the walls with isooctane (5.7) by using Pasteur pipettes (6.16). Discard the solvent.

Let residual solvent evaporate under a fume hood.

Carry out this deactivation of the surface after heating and cooling or immediately prior to use.

8.2 Extraction

8.2.1 Conditioning of the solid phase material and enrichment

Prepare the cartridges as follows and fill them in the given sequence:

a) place a PTFE frit (6.10) in the cartridge;

b) add 250 mg of RP-C18 material (5.9);