

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

The European Standard EN ISO 18856:2005 has the status of a British Standard

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National foreword

This British Standard is the official English language version of EN ISO 18856:2005. It is identical with ISO 18856:2004.

The UK participation in its preparation was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, chemical and biochemical methods, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

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Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, the EN foreword page, the ISO title page, pages ii to v, a blank page, pages 1 to 32, an inside back cover and a back cover.

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English Version

Water quality - Determination of selected phthalates using gas chromatography/mass spectrometry (ISO 18856:2004)

Qualité de l'eau - Dosage de certains phtalates par chromatographie en phase gazeuse/spectrométrie de masse (ISO 18856:2004)

Wasserbeschaffenheit - Bestimmung ausgewählter Phthalate mittels Gaschromatographie/Massenspektrometrie (ISO 18856:2004)

This European Standard was approved by CEN on 20 July 2005.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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Foreword

The text of ISO 18856:2004 has been prepared by Technical Committee ISO/TC 147 "Water quality" of the International Organization for Standardization (ISO) and has been taken over as EN ISO 18856:2005 by Technical Committee CEN/TC 230 "Water analysis", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2006, and conflicting national standards shall be withdrawn at the latest by February 2006.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Endorsement notice

The text of ISO 18856:2004 has been approved by CEN as EN ISO 18856:2005 without any modifications.

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.

blank

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(<i>n</i> -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.

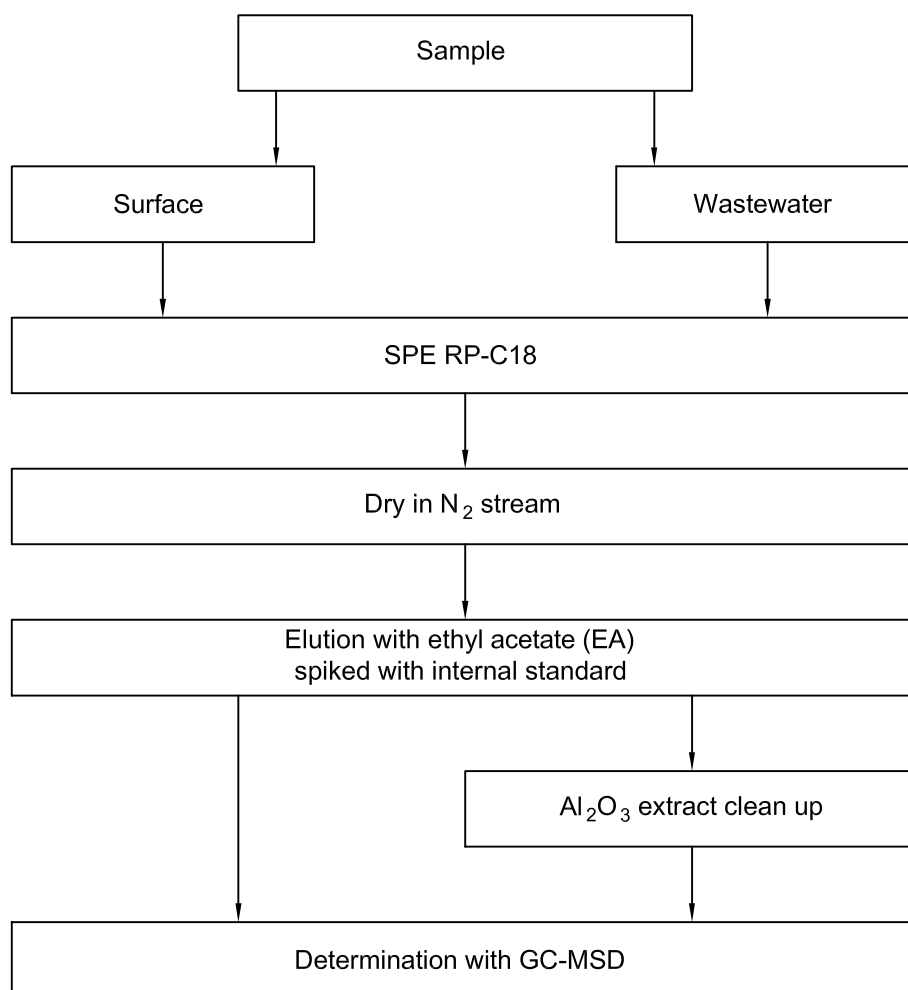


Figure 1 — Flowchart of the analysis

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, N₂ 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, C₄H₈O₂.

5.6 Methanol, CH₃OH.

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", $D_4-C_{16}H_{22}O_4$; D4-ring-deuterated di(*n*-octyl) phthalate, "D4-DOP", $D_4-C_{24}H_{38}O_4$, $^{13}C_{(6 \text{ to } 12)}$ -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.

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.