INTERNATIONAL STANDARD

ISO 13913

First edition
2014-02-01

Soil quality — Determination of selected phthalates using capillary gas chromatography with mass spectrometric detection (GC/MS)

Qualité du sol — Détermination de phthalates sélectionnés en utilisant la chromatographie gazeuse capillaire avec détection par spectrométrie de masse

Reference number
ISO 13913:2014(E)

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Published in Switzerland

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Introduction

This International Standard is applicable and validated for several types of matrices as indicated in Table 1 (see also Annex A for the results of the validation).

Table 1 — Matrices for which this International Standard is applicable and validated

Matrix	Materials used for validation
Sludge	Municipal sludge
Biowaste	Fresh compost
Soil	Sludge amended soil

Soil quality — Determination of selected phthalates using capillary gas chromatography with mass spectrometric detection (GC/MS)

WARNING — Persons using this International Standard should be familiar with usual 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 selected phthalates in sludge, treated biowaste, and soil, after extraction and gas chromatographic analysis with mass spectrometric detection.

The method is applicable for the determination of phthalates (see Table 2) at the lowest mass content of 0,1 mg/kg to 0,5 mg/kg (expressed as dry matter), depending on the individual substance.

The applicability of the method to other phthalates not specified in Table 2 is not excluded except the isomeric mixtures, e.g. DiNP (Di-isononylphthalate), but shall be verified in each case.

Table 2 — Phthalates that can be determined according to this International Standard

No	Name	Formula	Abbreviation	Molar mass g/mol	CAS-RN[a]
1	Dimethylphthalate	$C_{10}H_{10}O_4$	DMP	194,2	00131-11-3
2	Diethylphthalate	$C_{12}H_{14}O_4$	DEP	222,2	00084-66-2
3	Dipropylphthalate	$C_{14}H_{18}O_4$	DPP	250,3	00131-16-8
4	Di-(2-methyl-propyl)phthalate	$C_{16}H_{22}O_4$	DiBP	278,4	00084-69-5
5	Dibutylphthalate	$C_{16}H_{22}O_4$	DBP	278,4	00084-74-2
6	Butylbenzylphthalate	$C_{19}H_{20}O_4$	BBzP	312,4	00085-68-7
7	Dicyclohexylphthalate	$C_{20}H_{26}O_4$	DCHP	330,4	00084-61-7
8	Di-(2-ethylhexyl)phthalate	$C_{24}H_{38}O_4$	DEHP	390,6	00117-81-7
9	Dioctylphthalate	$C_{24}H_{38}O_4$	DOP	390,6	00117-84-0
10	Didecylphthalate	$C_{28}H_{46}O_4$	DDcP	446,7	00084-77-5
11	Diundecylphthalate	$C_{30}H_{50}O_4$	DUP	474,4	03648-20-2

[a] Chemical Abstracts Service Registry Number.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5667-13, *Water quality — Sampling — Part 13: Guidance on sampling of sludges*

ISO 5667-15, *Water quality — Sampling — Part 15: Guidance on the preservation and handling of sludge and sediment samples*

ISO 10381-2, *Soil quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ISO 14507, *Soil quality — Pretreatment of samples for determination of organic contaminants*

ISO 22892, *Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry*

3 Principle

The dried sample, dried by freeze drying or with sodium sulfate, is extracted with ethyl acetate on the shaking device. An aliquot of the extract is cleaned with aluminium oxide (if necessary) followed by gas chromatographic separation using capillary columns and identification and quantification of the phthalates by mass spectrometry.

4 Interferences

4.1 General

Due to their use as plasticizer agents, phthalates are ubiquitous. The sources of phthalates are multiple and shall be checked and reduced by every laboratory itself. Therefore, special attention shall be paid to avoid contaminations.

4.2 Interferences during sampling

In order to avoid interferences and cross contaminations, do not use plastic materials (e.g. pipes, etc.).

4.3 Cross contamination

Chemicals and analytical equipment can be of various qualities. Cross contamination is likely to occur with laboratory air. Therefore, remove, as far as possible, plastic materials from the laboratory. Cleaning agents often contain phthalates and can severely contaminate the laboratory air if in use regularly. Therefore, refrain from using these agents during application of this procedure.

Using plastic gloves during pretreatment can increase the contamination.

4.4 Interferences in gas chromatography

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

Fittings, e.g. of syringes, or equipment and septa of the sampling bottles (6.5) can also contain phthalates.

5 Reagents

5.1 General

All reagents shall be of recognized analytical grade.

Use only reagents with negligibly low concentration of phthalates and verify by blank determinations and, if necessary, apply additional cleaning steps.

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

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

5.4 Ethyl acetate, $C_4H_8O_2$, phthalate-free, high purity.

5.5 Methanol, CH_3OH.

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

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

5.8 Aluminium oxide, Al_2O_3, neutral, 50 µm to 200 µm particle size, heated to 400 °C for at least 4 h.

Store heat-treated aluminium oxide in covered flask or desiccator. Use within five days after heat-treatment.

NOTE Alternative materials, like Florisil®[1)] or silica can be used, provided their properties and capacity to separate are similar to aluminium oxide and their properties are checked according to 8.6.

5.9 Internal standards.

For example:

— deuterated di-n-butylphthalate, "D4-ring-DBP";

— deuterated D4-$C_{16}H_{22}O_4$;

— deuterated di-(2-ethylhexyl) phthalate "D4-ring-DEHP";

— deuterated D4-$C_{24}H_{38}O_4$; di-n-octylphthalate, "D4-ring-DOP";

— D4- $C_{24}H_{38}O_4$;

— ^{13}C-labelled standards can also be used, if available.

5.10 Reference substances.

Table 2 gives a list of phthalates with defined mass concentrations for the preparation of reference solutions for the gas chromatographic procedure.

5.11 Solutions of the single substances.

In a 10-ml volumetric flask (6.13), transfer e.g. 10 mg of each of the reference substances (5.10) in ethyl acetate (5.4) and bring to volume with ethyl acetate (5.4) (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.

5.12 Stock solution.

In a 10-ml volumetric flask (6.13), dissolve between 100 µl and 500 µl of the single substance solutions (5.11) and bring to volume with ethyl acetate (5.4) (concentration: 10 mg/l to 50 mg/l).

1) This information is given for the convenience of users of this document and does not constitute an endorsement by ISO TC 190/SC 3 of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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

5.13 Reference solutions for multipoint calibration (see Annex B).

Prepare solutions by adequate dilution of the stock solution (5.12) and internal standards (5.9) with ethyl acetate (5.4).

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

5.14 Solution of the internal standards (see Annex B).

5.14.1 Internal standard solution of D4-phthalates.

Weigh e.g. 0,1 g of an internal standard phthalate (D4) (5.9) in a 10-ml volumetric flask (6.13) filled with about 5 ml of ethyl acetate (5.4) and bring to volume with ethyl acetate (5.4). Store the solution in a glass bottle at −18 °C.

5.14.2 Solution I internal standard mix.

Combine the solutions of the single internal standard phthalates (5.9) e.g. by dilution 1:100 as follows: Transfer with a syringe 0,1 ml (6.15) of each solution into a 10-ml volumetric flask (6.13) filled with about 5 ml of ethyl acetate (5.4). Bring to volume with ethyl acetate. The final concentration of di-n-octylphthalate (D4), di-n-butylphthalate (D4), and di-(2-ethylhexylphthalate) is 100 mg/l in ethyl acetate (5.4).

5.14.3 Solution II internal standard mix.

Take from this 1:100 dilution (5.14.2) e.g. 250 µl, transfer into a 250-ml volumetric flask (6.13), filled with 250 ml of ethyl acetate (5.4).

The final concentration of di-n-octylphthalate (D4), di-n-butylphthalate (D4), and di-(2-ethylhexylphthalate) is 0,1 mg/l in ethyl acetate (5.4).

5.14.4 Solution III internal standard mix.

Dilute the solution I internal standard (5.14.2.) 1:10. Pipette 1 ml of the solution (5.14.2.) in a 10-ml volumetric flask (6.13) filled with about 5 ml of ethyl acetate (5.4). Bring to volume with ethyl acetate. The final concentration of di-n-octylphthalate (D4), di-n-butylphthalate (D4), and di-(2-ethylhexylphthalate) is 10 mg/l in ethyl acetate.

5.15 Sodium sulfate, Na_2SO_4, heated to 400 °C for at least 4 h.

6 Apparatus

6.1 General

Equipment or parts of it which are likely to come into contact with the sample or its extract shall be free from phthalates. This can be achieved by thorough cleaning of all glass apparatus and checked by the blank determination.

6.2 Wide-neck flat bottomed flasks with glass stoppers, preferably brown glass, volumes 500 ml and 1 000 ml.

6.3 Drying oven, capable of maintaining at a temperature of (105 ± 5) °C.

6.4 Muffle furnace, adjustable, up to temperatures of (400 ± 10) °C, with capacity of e.g. at least 60 l.

6.5 Sampling vial, glass, with inert stopper, e.g. septum, lined with polytetrafluoroethylene (PTFE) for storage of the extracts, and sampling bottles, glass, with inert septum, 2 ml, for storage of the extracts for auto sampler operation.

6.6 Vacuum device for clean-up, vacubox, extraction box.

6.7 Stainless steel cock, with stainless steel cone or polytetrafluoroethylene (PTFE) cock with Luer connection for separate vacuum connection.

6.8 Glass cartridges, with Luer cone.

6.9 Polytetrafluoroethylene (PTFE) frits, for cartridges, 6 ml.

6.10 Aluminium foil, heated to 400 °C.

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

6.12 Measuring cylinders, volumes 50 ml and 100 ml.

6.13 Volumetric flasks, volumes 10 ml, 25 ml, and 250 ml.

6.14 Pasteur pipettes, e.g. 2 ml.

6.15 Syringes, 2 µl, 5 µl, 10 µl, 50 µl, 100 µl, and 500 µl, maximum permitted error ±2 %.

6.16 Gas chromatograph, with capillary column, temperature controlled, with mass spectrometric detection.

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

6.18 Fused silica columns, with non-polar stationary phase (see Annex C for examples).

Check the quality of the column e.g. by injecting the reference solution (5.13) and ensure that the separation is satisfactory.

6.19 Glass tubes, graduated 5 ml or 10 ml.

6.20 Nitrogen device, for drying the glass cartridges (6.8).

6.21 Beaker, volumes 50 ml and 100 ml.

6.22 Erlenmeyer flask, volume 250 ml.

6.23 Shaking device, horizontal shaking movement.

6.24 Freeze drying apparatus.

6.25 Metal spoon.