SLOVENSKI STANDARD
SIST-TS CEN/TS 16183:2012

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Blato, obdelani biološki odpadki in tla - Določevanje izbranih ftalatov s kapilarno plinsko kromatografijo z masno selektivno detekcijo (GC/MS)

Sludge, treated biowaste and soil - Determination of selected phthalates using capillary gas chromatography with mass spectrometric detection (GC-MS)

Schlamm, behandelter Bioabfall und Boden - Bestimmung ausgewählter Phthalate mittels kapillarer Gaschromatographie mit massenspektrometrischer Detektion (GC-MS)

Boues, bio-déchets traités et sols - Détermination de certains phtalates par chromatographie en phase gazeuse capillaire avec détection par spectrométrie de masse (CG-SM)

Ta slovenski standard je istoveten z: **CEN/TS 16183:2012**

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TECHNICAL SPECIFICATION

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ICS 13.030.01

English Version

Sludge, treated biowaste and soil - Determination of selected phthalates using capillary gas chromatography with mass spectrometric detection (GC-MS)

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (CEN/TS 16183:2012) has been prepared by Technical Committee CEN/TC 400 “Project Committee - Horizontal standards in the fields of sludge, biowaste and soil”, the secretariat of which is held by DIN.

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

The preparation of this document by CEN is based on a mandate by the European Commission (Mandate M/330), which assigned the development of standards on sampling and analytical methods for hygienic and biological parameters as well as inorganic and organic determinants, aiming to make these standards applicable to sludge, treated biowaste and soil as far as this is technically feasible.

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

Introduction

This Technical Specification 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 Technical Specification is applicable and validated

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

WARNING — Persons using this Technical Specification should be familiar with usual laboratory practice. This Technical Specification 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 Technical Specification be carried out by suitably trained staff.

1 Scope

This Technical Specification 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 CEN/TS 16183

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 CAS-RN 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.

EN 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter fraction after determination of dry residue or water content*

EN 16179, *Sludge, treated biowaste and soil — Guidance for sample pretreatment*

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

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

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

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

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 (pipes, etc.).

4.3 Cross contamination

Chemicals and analytical equipment can be of various quality. 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 may 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 may increase the contamination.

4.4 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, e. g. of syringes, or equipment and septa of the sampling bottles (see 6.5) may 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 in covered flask or desiccator. Use within five days after heat-treatment.

NOTE Alternative materials, like Florisil®[1)] or silica may 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).

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

1) Florisil® is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by CEN of this product.

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) will be 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 volumetric flask, 250 ml (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 may 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, volume 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, volume 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

6.26 Agate mortar

6.27 Metallic clamp, for stopper.

6.28 Balance, e. g.: range 0,001 g to 100 g.

6.29 Pipette, volume 20 ml, 25 ml and 50 ml.