
Blato, obdelani biološki odpadki in tla - Določevanje polikloriranih bifenilov (PCB) s plinsko kromatografijo z masno selektivno detekcijo (GC/MS) in s plinsko kromatografijo z detekcijo z zajetjem elektronov (GC/ECD)

Sludge, treated biowaste and soil - Determination of polychlorinated biphenyls (PCB) by gas chromatography with mass selective detection (GC-MS) and gas chromatography with electron-capture detection (GC-ECD)

Schlamm, behandelter Bioabfall und Boden - Bestimmung von polychlorierten Biphenylen (PCB) mittels Gaschromatographie mit Massenspektrometrie-Kopplung (GC-MS) und Gaschromatographie mit Elektroneneinfangdetektion (GC-ECD)

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Boues, bio-déchets traités et sols - Détermination des biphényles polychlorés (PCB) par chromatographie en phase gazeuse-spectrométrie de masse (CG-SM) et chromatographie en phase gazeuse avec détection par capture d'électrons (CG-DCE)

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Sludge, treated biowaste and soil - Determination of polychlorinated biphenyls (PCB) by gas chromatography with mass selective detection (GC-MS) and gas chromatography with electron-capture detection (GC-ECD)

Boues, bio-déchets traités et sols - Détermination des biphényles polychlorés (PCB) par chromatographie en phase gazeuse-spectrométrie de masse (CG-SM) et chromatographie en phase gazeuse avec détection par capture d'électrons (CG-DCE)

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This European Standard was approved by CEN on 24 May 2012.

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Foreword

This document (EN 16167:2012) 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.

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of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.

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This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

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 implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, 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.

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Introduction

Polychlorinated biphenyls (PCB) have been widely used as additives in industrial applications where chemical stability has been required. This stability on the other hand creates environmental problems when PCBs are eventually released into the environment. Since some of these PCB compounds are highly toxic, their presence in the environment (air, water, soil, sediment and waste) is regularly monitored and controlled. At present determination of PCB is carried out in these matrices in most of the routine laboratories following the preceding steps for sampling, pretreatment, extraction, clean-up by measurement of specific PCB by means of gas chromatography in combination with mass spectrometric detection (GC-MS) or gas chromatography with electron capture detector (GC-ECD).

This European Standard was developed in the European project 'HORIZONTAL'. It is the result of a desk study "3-12 PCB" and aims at evaluation of the latest developments in assessing PCBs in sludge, soil, treated biowaste and neighbouring fields. Taken into account the different matrices and possible interfering compounds, this European Standard does not contain one single possible way of working. Several choices are possible, in particular relating to clean-up. Detection with both MS-detection and ECD-detection is possible. Two different extraction procedures are described and 11 clean-up procedures. The use of internal and injection standards is described in order to have an internal check on choice of the extraction and clean-up procedure. The method is as far as possible in agreement with the method described for PAHs (see CEN/TS 16181). It has been tested for ruggedness.

This European 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 European Standard is applicable and validated

| Matrix | Materials used for validation |
|----------|-------------------------------|
| Sludge | Municipal sewage sludge |
| Biowaste | Compost |

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

1 Scope

This European Standard specifies a method for quantitative determination of seven selected polychlorinated biphenyls (PCB28, PCB52, PCB101, PCB118, PCB138, PCB153 and PCB180) in sludge, treated biowaste and soil using GC-MS and GC-ECD (see Table 2).

Table 2 — Target analytes of this European Standard

| Target analyte | | CAS-RN ^a |
|----------------|--------------------------------------|---------------------|
| PCB28 | 2,4,4'-trichlorobiphenyl | 7012-37-5 |
| PCB52 | 2,2',5,5'-tetrachlorobiphenyl | 35693-99-3 |
| PCB101 | 2,2',4,5,5'-pentachlorobiphenyl | 37680-37-2 |
| PCB118 | 2,3',4,4',5-pentachlorobiphenyl | 31508-00-6 |
| PCB138 | 2,2',3,4,4',5'-hexachlorobiphenyl | 35056-28-2 |
| PCB153 | 2,2',4,4',5,5'-hexachlorobiphenyl | 35065-27-1 |
| PCB180 | 2,2',3,4,4',5,5'-heptachlorobiphenyl | 35065-29-3 |

^a CAS-RN Chemical Abstracts Service Registry Number.

The limit of detection depends on the determinants, the equipment used, the quality of chemicals used for the extraction of the sample and the clean-up of the extract.

Under the conditions specified in this European Standard, limit of application of 1 µg/kg (expressed as dry matter) can be achieved.

Sludge and treated biowaste may differ in properties and also in the expected contamination levels of PCBs and presence of interfering substances. These differences make it impossible to describe one general procedure. This European Standard contains decision tables based on the properties of the sample and the extraction and clean-up procedure to be used.

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

EN ISO 16720, *Soil quality — Pretreatment of samples by freeze-drying for subsequent analysis (ISO 16720)*

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

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 18512, *Soil quality — Guidance on long and short term storage of soil samples*

EN 16167:2012 (E)**3 Terms and definitions**

For the purposes of this document, the following terms and definitions apply.

3.1**polychlorinated biphenyl****PCB**

biphenyl substituted by one to ten chlorine atoms

[SOURCE: EN 15308:2008, 3.1]

3.2**congener**

member of the same kind, class or group of chemicals, e.g. anyone of the two hundred and nine individual PCB

Note 1 to entry: The IUPAC congener numbers are for easy identification; they do not represent the order of chromatographic elution.

[SOURCE: EN 15308:2008, 3.2]

3.3**critical pair**

pair of congeners that will be separated to a predefined degree (e.g. $R = 0,5$) to ensure chromatographic separation meets minimum quality criteria

[SOURCE: EN 15308:2008, 3.6]

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4 Principle

Due to the horizontal character of this European Standard, different procedures for different steps (modules) are allowed. Which modules should be used depends on the sample. A recommendation is given in this European Standard. Performance criteria are described and it is the responsibility of the laboratories applying this European Standard to show that these criteria are met. Using of spiking standards (internal standards) allows an overall check on the efficiency of a specific combination of modules for a specific sample. But it does not necessarily give the information upon the extensive extraction efficiency of the native PCB bonded to the matrix.

After pretreatment according to the methods referred to in 9.2, the test sample is extracted with a suitable solvent.

The extract is concentrated by evaporation: If necessary, interfering compounds are removed by a clean-up method suitable for the specific matrix. The eluate is concentrated by evaporation.

The extract is analyzed by gas chromatography. The various compounds are separated using a capillary column with a stationary phase of low polarity. Detection occurs with mass spectrometry (MS) or an electron capture detector (ECD) (see 8.2.1).

PCBs are identified and quantified by comparison of relative retention times and relative peak heights (or peak areas) with respect to internal standards added. The efficiency of the procedure depends on the composition of the matrix that is investigated.

5 Interferences

5.1 Interference with sampling and extraction

Use sampling containers of materials (preferably of steel, aluminium or glass) that do not change the sample during the contact time. Avoid plastics and other organic materials during sampling, sample storage or extraction. Keep the samples from direct sunlight and prolonged exposure to light.

During storage of the samples, losses of PCBs may occur due to adsorption on the walls of the containers. The extent of the losses depends on the storage time.

5.2 Interference with GC

Substances that co-elute with the target PCB may interfere with the determination. These interferences may lead to incompletely resolved signals and may, depending on their magnitude, affect accuracy and precision of the analytical results. Peak overlap does not allow an interpretation of the result. Asymmetric peaks and peaks being broader than the corresponding peaks of the reference substance suggest interferences.

Chromatographic separation between the following pairs can be critical. The critical pair PCB28 and PCB31 is used for selection of the capillary column (see 8.2.2). If molecular mass differences are present, quantification can be made by mass selective detection. If not or using ECD, the specific PCB is reported as the sum of all PCBs present in the peak. Typically, the concentrations of the co-eluting congeners compared to those of the target congeners are low. When incomplete resolution is encountered, peak integration shall be checked and, when necessary, corrected.

- PCB28 – PCB31
- PCB52 – PCB73
- PCB101 – PCB89 / PCB90
- PCB118 – PCB106
- PCB138 – PCB164 / PCB163

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Presence of considerable amounts of mineral oil in the sample may interfere with the quantification of PCB in GC-MS. In presence of mineral oil, GC-ECD may be preferred or mineral oil can be removed using clean-up procedure G (see 10.4.8) using DMF/*n*-hexane.

Presence of tetrachlorobenzyltoluene (TCBT)-mixtures may disturb the determination of the PCB with GC-ECD.

6 Safety remarks

PCBs are highly toxic and shall be handled with extreme care. Avoid contact with solid materials, solvent extracts and solutions of standard PCB with the body shall not be allowed to occur. It is strongly advised that standard solutions are prepared centrally in suitably equipped laboratories or are purchased from suppliers specialised in their preparation.

Solvent solutions containing PCB shall be disposed of in a manner approved for disposal of toxic wastes.

For the handling of hexane precautions shall be taken because of its neurotoxic properties.

National regulations shall be followed with respect to all hazards associated with this method.

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7 Reagents

7.1 General

All reagents shall be of recognised analytical grade. The purity of the reagents used shall be checked by running a blank test as described in 10.1. The blank shall be less than 50 % of the lowest reporting limit.

7.2 Reagents for extraction

7.2.1 **Acetone (2-propanone)**, $(\text{CH}_3)_2\text{CO}$.

7.2.2 ***n*-heptane**, C_7H_{16} .

7.2.3 **Petroleum ether**, boiling range 40 °C to 60 °C.

Hexane-like solvents with a boiling range between 30 °C and 69 °C are allowed.

7.2.4 **Anhydrous sodium sulfate**, Na_2SO_4 . The anhydrous sodium sulfate shall be kept carefully sealed.

7.2.5 **Distilled water** or water of equivalent quality, H_2O .

7.2.6 **Sodium chloride**, NaCl , anhydrous.

7.2.7 **Keeper substance**. High boiling compound, i.e. octane, nonane.

7.3 Reagents for clean-up

7.3.1 Clean-up A using aluminium oxide

7.3.1.1 **Aluminium oxide**, Al_2O_3 . [SIST EN 16167:2013
https://standards.iteh.ai/catalog/standards/sist/aa56c54b-e8b4-4bd8-9984-e36b1ad77058/sist-en-16167-2013](https://standards.iteh.ai/catalog/standards/sist/aa56c54b-e8b4-4bd8-9984-e36b1ad77058/sist-en-16167-2013)

Basic or neutral, specific surface 200 m²/g, activity Super I according to Brockmann.

7.3.1.2 Deactivated aluminium oxide

Deactivated with approximately 10 % water.

Add approximately 10 g of water (7.2.5) to 90 g of aluminium oxide (7.3.1.1). Shake until all lumps have disappeared. Allow the aluminium oxide to condition before use for some 16 h, sealed from the air, use it for maximum two weeks.

NOTE The activity depends on the water content. It can be necessary to adjust the water content.

7.3.2 Clean-up B using silica gel 60 for column chromatography

7.3.2.1 **Silica gel 60**, particle size 63 µm to 200 µm.

7.3.2.2 **Silica gel 60**, water content: mass fraction $w(\text{H}_2\text{O}) = 10 \%$.

Silica gel 60 (7.3.2.1), heated for at least 3 h at 450 °C, cooled down in a desiccator and stored containing magnesium perchlorate or a suitable drying agent. Before use heat at least for 5 h at 130 °C in a drying oven. Then allow cooling in a desiccator and add 10 % water (mass fraction) in a flask. Shake for 5 min intensively by hand until all lumps have disappeared and then for 2 h in a shaking device. Store the deactivated silica gel in the absence of air, use it for maximum of two weeks.

7.3.3 Clean-up C using gel permeation chromatography (GPC)

7.3.3.1 **Bio-Beads^{®1)} S-X3.**

7.3.3.2 **Ethyl acetate, C₄H₈O₂.**

7.3.3.3 **Cyclohexane, C₆H₁₂.**

Preparation of GPC, for example: Put 50 g Bio-Beads[®] S-X3 (7.3.3.1) into a 500 ml Erlenmeyer flask and add 300 ml elution mixture made up of cyclohexane (7.3.3.3) and ethyl acetate (7.3.3.2) 1:1 (volume) in order to allow the beads to swell; after swirling for a short time until no lumps are left, maintain the flask closed for 24 h. Drain the slurry into the chromatography tube for GPC. After approximately three days, push in the plungers of the column so that a filling level of approximately 35 cm is obtained. To further compress the gel, pump approximately 2 l of elution mixture through the column at a flow rate of 5 ml · min⁻¹ and push in the plungers to obtain a filling level of approximately 33 cm.

7.3.4 Clean-up D using Florisil^{®2)}

7.3.4.1 **Florisil[®], baked 2 h at 600 °C. Particle size 150 µm to 750 µm.**

7.3.4.2 **Iso-octane, C₈H₁₈.**

7.3.4.3 **Toluene, C₇H₈.**

7.3.4.4 **Iso-octane/Toluene 95/5.**

7.3.5 Clean-up E using silica H₂SO₄/silica NaOH

7.3.5.1 **Silica, SiO₂, particle size 70 µm to 230 µm, baked at 180 °C for a minimum of 1 h, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.**

7.3.5.2 **Silica, treated with sulfuric acid.**

Mix 56 g silica (7.3.5.1) and 44 g sulfuric acid (7.3.8.1).

7.3.5.3 **Sodium hydroxide solution, c(NaOH) = 1 mol/l.**

7.3.5.4 **Silica, treated with sodium hydroxide.**

Mix 33 g silica (7.3.5.1) and 17 g sodium hydroxide (7.3.5.3).

7.3.5.5 **n-hexane, C₆H₁₄.**

7.3.6 Clean-up F using benzenesulfonic acid/sulfuric acid

7.3.6.1 **3 ml silica gel column, of adsorbent mass 500 mg, particle size 40 µm.**

7.3.6.2 **3 ml benzenesulfonic acid column, of adsorbent mass 500 mg, particle size 40 µm.**

1) Bio-Beads[®] is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product. Equivalent products may be used if they can be shown to lead to the same results.

2) 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 European Standard and does not constitute an endorsement by CEN of this product. Equivalent products may be used if they can be shown to lead to the same results.

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7.3.7 Clean-up G using DMF/hexane partitioning

7.3.7.1 Dimethylformamide(DMF), C_3H_7NO .

7.3.8 Clean-up H using concentrated sulfuric acid

7.3.8.1 Sulfuric acid, H_2SO_4 of purity 96 % to 98 % (mass fraction).

7.3.9 Clean-up I using TBA sulfite reagent

7.3.9.1 Tetrabutylammonium reagent (TBA sulfite reagent)

Saturate a solution of tetrabutylammonium hydrogen sulfate in a mixture of equal volume of water and 2-propanol, $c((C_4H_9)_4NHSO_4) = 0,1 \text{ mol/l}$, with sodium sulfite.

NOTE 25 g of sodium sulfite should be sufficient for 100 ml of solution.

7.3.9.2 2-Propanol, C_3H_8O .7.3.9.3 Sodium sulfite, Na_2SO_3 .

7.3.10 Clean-up J using pyrogenic copper

WARNING — Pyrogenic copper is spontaneously inflammable. Suitable precautions shall be taken.7.3.10.1 Copper(II)-sulfate pentahydrate, $CuSO_4 \cdot 5 H_2O$.7.3.10.2 Hydrochloric acid, $c(HCl) = 2 \text{ mol/l}$.

7.3.10.3 Zinc granules, Zn particle size 0.3 mm to 1.4 mm.

7.3.10.4 Anionic detergent aqueous solution (e.g. 35 g/100 ml, n-dodecane-1-sulfonic acid sodium salt $(CH_3(CH_2)_{11}SO_3Na)$).

NOTE Other commercially available detergents may also be suitable.

7.3.10.5 Deoxygenated water

7.3.10.6 Pyrogenic copper

Dissolve 45 g copper(II)-sulfate pentahydrate (7.3.10.1) in 480 ml water containing 20 ml hydrochloric acid (7.3.10.2) in a 1 000 ml beaker.

Take 15 g of zinc granules size (7.3.10.3), add 25 ml water and one drop of anionic detergent solution (7.3.10.4) in another 1 000 ml beaker.

Stir with a magnetic stirrer at a high speed to form a slurry. Then whilst stirring at this high speed, carefully add the copper(II)-sulfate solution drop by drop using a glass rod.

Hydrogen is liberated and elemental pyrogenic copper is precipitated (red coloured precipitate).

Stirring is continued until the hydrogen generation almost ceases. Then the precipitated copper is allowed to settle. The supernatant water is carefully removed and the product washed with deoxygenated water (7.3.10.5) three times, to eliminate residual salts.

Then the water is carefully replaced with 250 ml acetone (7.2.1) (whilst continuously stirring the mixture). This operation is repeated twice more to ensure elimination of water.