INTERNATIONAL STANDARD

ISO 13876

First edition
2013-11-15

Soil quality — Determination of polychlorinated biphenyls (PCB) by gas chromatography with mass selective detection (GC-MS) and gas chromatography with electron-capture detection (GC-ECD)

Qualité du sol — Détermination des polychlorobiphényles (PCB) par chromatographie en phase gazeuse avec détection sélective de masse (GC-MS) et chromatographie en phase gazeuse avec détection par capture d'électrons (GC-ECD)

Reference number
ISO 13876:2013(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

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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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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

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, and 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).

The European Standard EN 16167:2012 on which this International Standard is based, 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 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 and 11 clean-up procedures are described. 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 ISO 13859). It has been tested for ruggedness.

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 sewage sludge
Biowaste	Compost

Soil quality — Determination of polychlorinated biphenyls (PCB) by gas chromatography with mass selective detection (GC-MS) and gas chromatography with electron-capture detection (GC-ECD)

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 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 International 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] 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 International Standard, a limit of application of 1 µg/kg (expressed as dry matter) can be achieved.

Sludge and treated biowaste can 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 International 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.

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

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

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

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

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 209 individual PCBs

[SOURCE: EN 15308:2008, 3.2]

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

3.3
critical pair
pair of congeners that is separated to a predefined degree (e.g. R = 0,5) to ensure chromatographic separation meets minimum quality criteria

[SOURCE: EN 15308:2008, 3.6]

4 Principle

Due to the horizontal character of this International Standard, different procedures for different steps (modules) are allowed. Which modules should be used depends on the sample. A recommendation is given in this International Standard. Performance criteria are described and it is the responsibility of the laboratories applying this International Standard to show that these criteria are met. Use of spiking standards (internal standards) allows an overall check on the efficiency of a specific combination of modules for a specific sample. However, 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 analysed 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) (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 can 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 can interfere with the determination. These interferences can lead to incompletely resolved signals and, depending on their magnitude, can 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 (8.2.1). 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

Presence of considerable amounts of mineral oil in the sample can interfere with the quantification of PCB in GC-MS. In presence of mineral oil, GC-ECD can 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 can 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. It is strongly advised that standard solutions are prepared centrally in suitably equipped laboratories or are purchased from suppliers specialized 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.

7 Reagents

7.1 General

All reagents shall be of recognized 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), $(CH_3)_2$ 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, basic or neutral, specific surface of 200 m^2/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 $w(H_2O)$ = 10 %.

Silica gel 60 (7.3.2.1) is 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 for least 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, $C_4H_8O_2$.

7.3.3.3 Cyclohexane, C_6H_{12}.

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 of 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 for 2 h at 600 °C, particle size of 150 µm to 750 µm.

7.3.4.2 Iso-octane, C_8H_{18}.

7.3.4.3 Toluene, C_7H_8.

7.3.4.4 Iso-octane/Toluene 95/5.

7.3.5 Clean-up E using silica H_2SO_4/silica NaOH

7.3.5.1 Silica, SiO_2, particle size of 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 of silica (7.3.5.1) and 44 g of 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 of silica (7.3.5.1) and 17 g of sodium hydroxide (7.3.5.3).

7.3.5.5 *n*-hexane, C_6H_{14}.

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 of 40 µm.

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

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

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

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 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 mol/l.

7.3.10.3 Zinc granules, Zn, particle size of 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 can also be suitable.

7.3.10.5 Deoxygenated water.

7.3.10.6 Pyrogenic copper.

Dissolve 45 g of copper(II)-sulfate pentahydrate (7.3.10.1) in 480 ml of water containing 20 ml of 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 of 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 while 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 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.

