
**General methods of tests for pigments
and extenders —**

Part 28:
**Determination of total content of
polychlorinated biphenyls (PCB) by
dissolution, cleanup and GC-MS**

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Méthodes générales d'essai des pigments et matières de charge —

*Partie 28: Détermination de la teneur totale en biphényles polychlorés
dans les pigments organiques par dissolution, purification et CG-SM*

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Foreword

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This document was prepared by Technical Committee ISO/TC 256, *Pigments, dyestuffs and extenders*.

A list of all parts in the ISO 787 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at <https://www.iso.org/members.html>.

Introduction

A number of methods to quantify PCBs in “environmental samples” or oil residues prove inadequate for pigments due to being merely extractive on the particle surface without taking into account occlusions of contaminants in the crystal lattice of pigments (see References [1] to [3]).

Occurrence and formation principles are referred to in References [5], [6] and [8].

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General methods of tests for pigments and extenders —

Part 28:

Determination of total content of polychlorinated biphenyls (PCB) by dissolution, cleanup and GC-MS

1 Scope

This document specifies a method for determining the total content of polychlorinated biphenyls (PCBs), checking for all 209 possible congeners in pigment materials.

This document is applicable to a working range from 1 mg/kg to 150 mg/kg. The lower quantitation limit of this method is 1 mg/kg per congener. Results below 1 mg/kg are considered to be qualitative only.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

ISO 18451-1, *Pigments, dyestuffs and extenders — Terminology — Part 1: General terms*

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3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18451-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at <https://www.iso.org/obp>

— IEC Electropedia: available at <http://www.electropedia.org/>

3.1

polychlorinated biphenyls

PCB

209 congeners, from mono- through deca-chlorinated biphenyls, which may be subdivided into homologue groups comprising PCB congeners with the same degree of chlorination, i.e. same gross formula

Note 1 to entry: The general CAS-Number for polychlorinated biphenyls is 1336-36-3. For a comprehensive congener list with CAS-Numbers, see [Annex A](#) or Reference [5].

3.2

internal reference material

mixture of defined quantities of ¹³C-Isotope-labelled PCBs added directly into the freshly weighed pigment sample

Note 1 to entry: No subsequent additions of internal reference materials are permitted. Surrogate standards reference materials can be added to assess recovery rates only, but these cannot be deemed an internal reference materials, nor can these be used for quantitation.

Note 2 to entry: Mass spectrometry assumes a vast linear range of detector sensitivity, thus a calibration with a single quantity will usually suffice.

Note 3 to entry: In case of major deviations between analytes and reference material concentrations, the quantitation might need to be confirmed by a second analysis (from the beginning) using an adequately adapted sample weight.

4 Principle

The principles have been developed from References [1] to [4], [6] and [7].

The use of solid surface extraction methods risks underestimating the actual content by orders of magnitude. Such errors are often further enhanced when the PCBs quantitation is carried out by using external or internal reference materials which do not undergo the same losses as the analytes that are occluded in the crystal lattice of the pigment.

5 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528.

Samples shall be of dry powder consistency. Volatiles should be less than 1 % (mass fraction), determined with a sample portion separated from the sample portions used for PCB analyses.

Samples shall be kept in the dark and in capped glass bottles or vials.

Samples suspected of having high impurities content shall be handled in dedicated glassware and kept separately from other laboratory equipment; sample mass may be reduced and internal reference materials amounts doubled in order to cope with the possible elevated levels of interferences by impurities. A screening pre-run is recommended to avoid detector overload.

Bromine detection or presence of partially brominated samples (e.g. C.I. Pigment Red 168, C.I. Pigment Green 36) require caution due to occurrence of "mixed" halogenated aromatic compounds. Analysis can proceed if results are checked for non-interference (see 9.5).

6 Procedure

6.1 General

This method requires a strict sequential application of the following steps:

- sample weighing;
- addition of internal reference material and thorough mixing;
- dissolution in concentrated sulfuric acid from 92 % (mass fraction) to 95 % (mass fraction);
- sonicate the mixture until fully dissolved and a homogenous dark solution is obtained in the sulfuric acid phase. The temperature shall be kept lower than 50 °C at all times, e.g. by circulating or continuously exchanging the water in the sonication bath.

NOTE 1 Using this concentration range avoids major disintegration and rearrangement of mono- and bichlorinated biphenyls.

NOTE 2 Sufficient dissolution is indicated by absence of the "tyndall-effect" (i.e. no scattering of a preferably blue light beam by the solution).

Upon dissolution in concentrated sulphuric acid, pigment molecules are protonated and may be considered in a simplified way as being pulled out of their crystal lattice one by one in drawer-like fashion, until all the solid matter has dissolved, without cleavage occurring at the molecular (chromophor) level.

Any possible inadvertent destruction of analytes is likely to occur also to the internal reference materials at a related, nearly equal rate, thus compensating for any destructive effects, at the expense of a slightly lower signal-to-noise ratio (see Reference [5]). There may be a slightly increased rate of destruction for low chlorinated biphenyls.

This may be offset by a preceding leaching step as described in the Note to 9.1.

6.2 Clean-up to eliminate interfering species

Interfering species such as aryl sulfuric acids, carboxylic acids, esters, polymeric surfactants, heterocyclic compounds are eliminated by a cleanup performed by sequential wet column-chromatography.

6.3 Separation and quantification

(Optional) separation from PCDD/PCDF, (which may be later eluted and analysed), as well as from other interfering substances on an alumina column.

Final separation and quantitation by gas chromatography (GC) using MS detection mode (see 8.18). The application of a 60 m column (see 8.3) will ensure that most PCB congeners are separated or recognizable at different retention times.

Exceptionally a 30 m column may be used for screening. The instrument should comprise automatic flow and pressure control, programmable temperature controls and auto sampling equipment (see 8.2).

MS detector should preferably be operated in SIM mode.

NOTE SIM is the most suitable mode for quantitation. SCAN is best for qualitative identification of the signals, but suffers from reduced sensitivity.

Quantitation is achieved by using the ratio of peak areas of analytes (identified as analyte by three or more specific mass traces as "qualifiers") versus the corresponding internal standards areas, to cope with overlapping ranges of chlorination groups and residual interfering peaks.

There are no intentional chemical reactions except for the dissolution step, which incurs protonation merely to cleave the crystal lattice, as all other steps are merely physical ones.

Chemical reaction leading to decay of analytes are considered to occur with both the internal reference material and the analytes alike, assuming full compensation of the resultant error. It is therefore essential to use internal reference materials matching the congeners distribution profile of the sample to a relatively high degree. Other approaches to assess artefacts in detail (see example in Reference [1]) shall be mentioned in the test report.

7 Reagents

7.1 Safety precautions

In case of spillage, apply 30 VA ultraviolet lamp for irradiation of spillage areas (254 nm wavelength emitted power maximum).

Staff is required to be qualified for and familiar with handling of hazardous substances in the laboratory.

All material, solvents, reagents, and standards shall be handled with appropriate care. Laboratory facilities, equipment and personnel shall comply with the latest legal and safety standards on PCB handling as may be locally applicable.

Upon accidental skin contact with PCB, triply wipe skin area with polyethylene glycol-wetted cloth (to be disposed of) and see emergency medical services immediately.

Major droplet spillages may result in shutdown of the entire laboratory facilities. Protect eyes when applying UV-lamp irradiation after spillages for decomposing contaminants.

7.2 Reagents, solvents and absorbents

Only reagents and solvents of acknowledged and certified analytical grade for pesticide analyses or comparable grades shall be used.

Solvents shall be used as delivered. New column adsorbents shall be purged by shaking in and decanting off dichloromethane (or a similarly suitable solvent), followed by drying under suitable cover.

7.2.1 **Sulphuric acid**, 92 % to 95 % (mass fraction).

7.2.2 **Phosphoric acid**, p.a., 85 % (mass fraction).

7.2.3 **Diatomaceous earth**.

7.2.4 **Silica gel**, 63 mesh to 200 mesh.

7.2.5 **Aluminium oxide** (alumina) (Basic, Activity: Super 1).

7.2.6 **Silver nitrate**, p.a., ultrapure.

7.2.7 **Cesium hydroxide**, hemihydrate.

7.2.8 **Sodium sulfate**, p.a., granulated.

NOTE Sodium sulfate (anhydrous) is used to eliminate residual aqueous and alcoholic matter in the hexane phase, as this can have detrimental effects on the GC column materials.

7.2.9 **Porous styrene divinylbenzene beads** for size exclusion chromatography.

7.2.10 ***n*-Hexane**.

7.2.11 **Dichloromethane**.

7.2.12 **Toluene**.

7.2.13 ***n*-Nonane**.

7.2.14 **Ethanol**.

7.2.15 **Ethyl acetate**.

7.2.16 **Cyclohexane**.

Original reference solutions shall be diluted by a factor 5 or 2 (MBP-MXP), using *n*-nonane, octane or similar high-boiling, non-aromatic solvents. Dilution should be carried out filling up vial content to 2 or 5 times its mass by adding the solvent. The error due to slightly different densities of reference concentrate and pure solvent is <0,5 %, hence negligible.

7.3 Internal reference materials for PCBs, 13C12-labelled

- PCB cong. ## 3, 15, 28, 52, 118, 153, 180, 194, 208, 209: LGC/Cambridge #CIL-EC-4189¹⁾
- PCB cong. ## 3, 8, 28, 52, 101, 118, 138, 153, 180, 194, 206, 209: Wellington-CAMPRO # MBP-MXP¹⁾
- PCB cong. ## 3, 8, 28, 52, 101, 114, 118, 138, 153, 180, 194, 206, 209: LGC/Cambridge #CIL-EC 5411¹⁾

These internal reference materials or similar are recommended with respect to the requirement of a “reporting threshold” value of 2 mg/kg for any resolvable PCB peak, covering in principle all 209 congeners.

Optional: To assess low-chlorinated biphenyls (Mono-CB-s, Di-CB-s) in detail, the user may counter-check these by using a spiking series for the particular homologue groups.

7.4 Cleaning/disposal agents

All glassware shall be purged with a suitable solvent prior to use and then washed intensively with a high-alkaline detergent or soap with readily soluble anionic and phosphate-containing surfactants in order to exclude any source of cross contamination. Joint grease shall be excluded from the laboratory. New glassware shall be purged by shaking in and decanting off dichloromethane (or a similarly suitable solvent), followed by drying under suitable cover.

Decontamination soap, brushes for all glassware, discharge bins (separate waste streams); polyethylene glycol pharmaceutical grade as first aid in case of skin contamination.

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8 Apparatus

8.1 Glassware, equipped with B (NS) 29 ground joints only as standard and inverse joint geometry.

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8.2 Column (for the clean-up procedure), 30 cm long, 14 mm internal diameter, B (NS) 29/32 shells, 250 ml top reservoir as integral part and PTFE stop cock at the bottom of the column.

8.3 Capillary column (for the gas chromatographic determination) of 60 meters length, internal diameter 0,25 mm coated with 0,25 µm thick film of 5 % phenylmethylsiloxane equivalent to a phenyl arylene polymer with the following characteristics:

- non-polar with very low bleed characteristics, ideal for GC-MS;
- excellent inertness for active compounds;
- improved signal-to-noise ratio for better sensitivity and mass spectral integrity;
- bonded and cross-linked;
- solvent rinsable to separate most of the 209 PCB congeners.

NOTE “Fast GC” permitted for particular congeners to be sought (i.e. a selection of the spectrum of 209 congeners for special purposes, to be mentioned in the final report).

8.4 Round-bottomed flasks, B (NS) 29, 1 000 ml, 500 ml and 250 ml.

8.5 Flat-bottomed flasks, 100 ml.

8.6 Cylinders, calibrated, 100 ml and 500 ml.

1) Examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.