



**SLOVENSKI STANDARD**  
**SIST ISO 17858:2010**

**01-september-2010**

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**Kakovost vode - Določevanje dioksinu podobnih polikloriranih bifenilov - Metoda s plinsko kromatografijo z masno selektivnim detektorjem**

Water quality - Determination of dioxin-like polychlorinated biphenyls - Method using gas chromatography/mass spectrometry

**iTeh STANDARD PREVIEW**

Qualité de l'eau - Dosage des biphényles polychlorés de type dioxine - Méthode par chromatographie en phase gazeuse/spectrométrie de masse

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**ICS:**

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances
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**Water quality — Determination of dioxin-  
like polychlorinated biphenyls — Method  
using gas chromatography/mass  
spectrometry**

*Qualité de l'eau — Dosage des biphényls polychlorés de type  
dioxine — Méthode par chromatographie en phase  
gazeuse/spectrométrie de masse*

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Case postale 56 • CH-1211 Geneva 20  
Tel. + 41 22 749 01 11  
Fax + 41 22 749 09 47  
E-mail [copyright@iso.org](mailto:copyright@iso.org)  
Web [www.iso.org](http://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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 17858 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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## Introduction

When using this International Standard, it may be necessary in some cases to determine whether and to what extent particular problems will require the specification of minor additional conditions.

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# Water quality — Determination of dioxin-like polychlorinated biphenyls — Method using gas chromatography/mass spectrometry

**WARNING** — Persons using this International Standard should be familiar with normal 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.

Attention is drawn to any relevant national safety regulations. The non-*ortho* and mono-*ortho* PCBs are co-planar and are among the most toxic of chemicals. All work with dioxin-like PCBs requires therefore the utmost care; the national safety measures which correspond to those for toxic substances shall be strictly adhered to.

**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 dioxin-like tetra- to hepta-chlorinated biphenyls (PCBs) in waters and wastewaters (containing less than 1 % suspended solids) using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). The method is optimized for dioxin-like PCBs, but can include other co-planar compounds such as polychlorinated dioxins and furans (PCDDs/PCDFs) and polychlorinated naphthalenes (PCNs). This method can be used to determine dioxin-like PCBs in other matrices (e.g. biota, sediments, air); however, additional clean-up steps and techniques can be required for samples with high organic loadings.

This method is applicable to the twelve non- and mono-*ortho* PCBs designated by the World Health Organization, as well as to other PCBs and co-planar compounds.

The detection limits and quantification levels in this method are dependent on the level of interferences as well as instrumental limitations. The minimum levels (ML) in Table 2 are the levels at which the dioxin-like PCBs can typically be determined with no interferences present.

This method is “performance based”. The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met. The requirements for establishing method equivalency are given in 9.2.

## 2 Normative references

The following referenced documents are indispensable for the application 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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

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**3 Terms, definitions and abbreviated terms****3.1 Terms and definitions**

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

**3.1.1****analyte**

dioxin-like polychlorinated biphenyl tested for by this method

See Table 1.

**3.1.2****calibration standard**

solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration

**3.1.3****calibration verification standard****VER**

midpoint calibration standard that is used to verify calibration

**3.1.4****certified reference material****CRM**

quality control sample used to determine accuracy and precision of method

**3.1.5****congener**

member of the same kind, class or group

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EXAMPLE Any one of the 209 individual PCBs

**3.1.6****critical pair**

pair of isomers that must be separated to a predefined degree (e.g. 25 % valley) to ensure chromatographic separation meets minimum quality criteria

**3.1.7****dioxin-like isomer**

PCB with identical chemical composition but different structure

**3.1.8****homologue group**

complete group of isomers

EXAMPLE

Tetrachlorobiphenyls.

**3.1.9****isotope dilution**

method using labelled (usually  $^{13}\text{C}_{12}$ ) internal standards to correct for losses during sample preparation and analysis

**3.1.10****keeper solvent**

high boiling point solvent added to the sampling standard solution

**3.1.11****method blank**

aliquot of reagent water that is treated exactly as a sample through the complete analytical procedure including extraction, clean-up, identification and quantification including all the relevant reagents and materials

**3.1.12****operational performance characteristics**

influence of the physical and chemical environment and maintenance problems, for example, mains voltage, temperature, supply of certain substances, set-up time, period of unattended operation

**3.1.13****pattern**

chromatographic fingerprint of any series of PCB isomers

**3.1.14****profile**

graphic representation of the sums of the isomer concentrations of the PCBs

**3.1.15****spiking**

addition of  $^{13}\text{C}_{12}$ -labelled PCB standards of which the recovery is calculated and used to correct values of native analytes of interest

**3.1.16****statistical performance characteristics**

quantification, for measured values, of the possible deviations resulting from the random part of the measuring process, e.g. repeatability or instability

**3.1.17****toxic equivalent factor****TEF**

relative toxicity to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)

**3.1.18****toxic equivalent quantity****TEQ**

sum of toxic equivalents of each individual congener

**3.2 Abbreviated terms**

<b>CRM</b>	certified reference material
<b>GC/MS</b>	gas chromatography/mass spectrometry
<b>GPC</b>	gel permeation chromatography
<b>HPLC</b>	high-performance liquid chromatography
<b>HRGC</b>	high-resolution gas chromatography
<b>HRMS</b>	high-resolution mass spectrometry
<b>IPR</b>	initial precision and recovery
<b>LRMS</b>	low-resolution mass spectrometry
<b>MDL</b>	method detection limit
<b>ML</b>	minimum level (see Table 2)
<b>PAR</b>	precision and recovery
<b>PCB</b>	polychlorinated biphenyl

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<b>PCDD/PCDF</b>	polychlorinated dibenzo- <i>p</i> -dioxin/dibenzofuran
<b>PCN</b>	polychlorinated naphthalene
<b>PFK</b>	perfluorokerosene
<b>SIM</b>	selected ion monitoring
<b>SPE</b>	solid-phase extraction
<b>TEF</b>	toxic equivalent factor
<b>TEQ</b>	toxic equivalent quantity
<b>VER</b>	calibration verification standard

**4 Principle****4.1 Spiking and extraction**

Stable isotopically labelled analogues of dioxin-like PCBs (diluted in a suitable solvent such as acetone) are spiked into a 1 litre aqueous sample (a sample containing less than 1 % suspended solids). A minimum of one labelled standard per homologue group is used and the sample is extracted by one of three procedures noted in 4.1 a), 4.1 b) and 4.1 c). If the sample contains more than 1 % solid material, the solid portion can be analysed directly after filtration or drying and the aqueous portion can be discarded.

- a) Samples containing no visible particles are extracted with dichloromethane [6.4 f)] in a separatory funnel or by solid-phase extraction. The extract is concentrated for clean-up.
- b) Samples containing visible particles are vacuum filtered through a glass-fibre filter. The filter is extracted in a Soxhlet extractor using toluene and the filtrate is extracted with dichloromethane [6.4 f)] in a separatory funnel. The dichloromethane extract is concentrated and combined with the Soxhlet extract prior to clean-up.
- c) The sample is vacuum filtered through a glass-fibre filter on top of a solid-phase extraction (SPE) disk. The filter and disk are eluted with suitable solvent mixtures or extracted in a Soxhlet or pressure filtration extractor, and the extract is concentrated for clean-up.

Other solvents and extraction techniques may be substituted, provided that all the performance criteria can be met.

**4.2 Clean-up**

After extraction, sample extracts are cleaned to remove interfering components. Sample clean-up procedures can include washes with acid and/or base, gel permeation, alumina, silica, Florisil<sup>1)</sup> and activated carbon chromatography. High-performance liquid chromatography (HPLC) can be used for further isolation of other specific co-planar compounds if required. Due to the large number of potential interfering compounds, sample extracts shall be fractionated or analysed on at least two distinct GC column phases to ensure unique identification and accurate quantification of each dioxin-like PCB congener.

**4.3 Concentration**

After clean-up, the extract(s) is concentrated to near dryness. Prior to injection, recovery standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by GC and detected by a high-resolution mass spectrometer. Two exact masses are monitored for each analyte.

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1) Florisil 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.

Resolution greater than or equal to 10 000 is recommended. High-resolution gas chromatography/high-resolution mass spectrometry at a resolution greater than or equal to 10 000 is at present required to achieve adequate sensitivity and selectivity, and to allow the use of all  $^{13}\text{C}_{12}$ -labelled standards. If the sample extract is being analysed for multi-component analyte groups (PCDD/Fs, PCBs, PCNs), a resolution of 10 000 is necessary. At resolutions less than 10 000, some  $^{13}\text{C}_{12}$  PCDFs and PCBs interfere with native PCDDs of the same level of chlorination. Resolutions less than 10 000 can be used for specific analyte groups (PCBs, PCNs) where the matrix and potential interferences are well characterized.

#### 4.4 Identification

An individual dioxin-like PCB is identified by comparing the GC retention time and ion abundance ratio of two exact masses monitored (see Table 7) with the corresponding retention time of an authentic internal standard and the theoretical or acquired ion-abundance ratio of the two exact masses. The isomers and congeners for which there are no labelled analogues are identified when retention times or relative retention times and ion-abundance ratios agree within predefined limits. Masses of those PCBs with a degree of chlorination higher than three (e.g. PentaCB 110 for TetraCB 77) shall be monitored to ensure there is no contribution to the mass of interest.

#### 4.5 Quantification

Quantitative analysis is performed using selected ion monitoring (SIM) areas, in one of two ways.

- a) For the dioxin-like PCBs for which labelled analogues have been added to the sample (4.1), the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.
- b) For the dioxin-like PCBs for which labelled analogues are not added, the GC/MS system is calibrated for each compound using an isomer or congener with the most similar structure and the concentration of each compound is determined using the internal standard technique.

#### 4.6 Analytical quality

The quality of the analysis is assured through reproducible calibration and testing of the extraction, clean-up, and GC/MS systems. Interferences, biases and limitations should be determined and identified for each target analyte through intercalibration (interlaboratory) studies, certified reference materials (CRM) and spiked matrix samples (SMS). A series of quality control (QC) samples (CRM, SMS) should be analysed with each set of samples and monitored through control charting or other quality review procedures.

### 5 Contamination and interferences

**5.1** Where possible, monitor or clean reagents by extraction or solvent rinse.

Solvents, reagents, labware, and other sample processing hardware can yield artefacts and/or elevated baselines causing misinterpretation of chromatograms. (Example chromatograms showing typical retention times of native and labelled PCBs are given in Annex A.) Specific selection of reagents and purification of solvents by distillation in all-glass systems can be required. Many reagents, solvents and labware contain background levels of dioxin-like compounds, e.g. PCB118 and PCB105.

**5.2** Clean labware such that the method blank requirements given in 9.5.3 are met. An example of a cleaning procedure is given below in a) to c).

- a) Disassemble labware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, prior to detergent washing. Rinse labware with solvent and wash with a detergent solution as soon after use as is practical. Sonication of labware containing a detergent solution for approximately 30 s can aid in cleaning.
- b) After detergent washing, rinse labware immediately with hot tap water. The tap water rinse shall be followed by an acetone rinse, then a dichloromethane [6.4 f)] rinse/soak. For known contaminated labware, use toluene as a final rinse/soak.