
Kakovost vode - Določevanje polikloriranih naftalenov (PCN) - Metoda plinske kromatografije (GC) in masne spektrometrije (MS)

Water quality - Determination of polychlorinated naphthalenes (PCN) - Method using gas chromatography (GC) and mass spectrometry (MS)

iTeh STANDARD PREVIEW

Qualité de l'eau - Détermination des naphthalènes polychlorés (PCN) - Méthode par chromatographie en phase gazeuse (CG) et spectrométrie de masse (SM)

[SIST-TS ISO/TS 16780:2018](https://standards.iteh.ai/catalog/standards/sist/fef8487-94ff-49a9-b74c-3d5514d05e1d/sist-ts-iso-ts-16780-2018)

Ta slovenski standard je istoveten z: **ISO/TS 16780:2015**

ICS:

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances
71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis

SIST-TS ISO/TS 16780:2018**en**

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST-TS ISO/TS 16780:2018](https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018)

<https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018>

TECHNICAL
SPECIFICATION

ISO/TS
16780

First edition
2015-08-15

**Water quality — Determination of
polychlorinated naphthalenes (PCN)
— Method using gas chromatography
(GC) and mass spectrometry (MS)**

*Qualité de l'eau — Détermination des naphthalènes polychlorés
(PCN) — Méthode par chromatographie en phase gazeuse (CG) et
spectrométrie de masse (SM)*

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST-TS ISO/TS 16780:2018](https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018)

<https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018>



Reference number
ISO/TS 16780:2015(E)

© ISO 2015

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST-TS ISO/TS 16780:2018](https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018)
<https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2015, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

Foreword	v
1 Scope	1
2 Normative references	1
3 Terms, definitions, and abbreviated terms	2
3.1 Terms and definitions.....	2
3.2 Abbreviated terms.....	6
4 Principle	6
4.1 Extraction.....	6
4.2 Clean-up.....	7
4.3 Identification and quantification.....	7
4.4 Quality.....	8
5 Contamination and interferences	8
6 Reagents and standards	10
7 Apparatus and materials	16
8 Sample collection, preservation, storage and holding times	19
8.1 General.....	19
8.2 Storage times.....	19
9 Quality assurance and quality control	20
9.1 General.....	20
9.2 Spiking.....	20
9.3 Recovery of labelled compounds assessment.....	21
9.4 Method blanks.....	21
9.5 QC check sample.....	21
10 Calibration	21
10.1 Operating conditions.....	21
10.2 Mass spectrometer resolution.....	22
10.3 Ion abundance ratios, minimum levels, signal-to-noise ratios, and absolute retention times.....	22
10.4 Retention time.....	22
10.5 Column resolution performance check.....	23
10.6 Calibration by isotope dilution.....	23
10.7 Calibration by internal standard.....	23
10.8 Combined calibration.....	24
10.8.1 General.....	24
10.8.2 Data storage.....	24
10.8.3 Data acquisition.....	24
10.8.4 Response factors and multipoint calibrations.....	24
11 Sample preparation	25
11.1 General.....	25
11.2 Determination of solid particulate material.....	25
11.3 Preparation of aqueous samples containing 2 g/l of solid particulate material or less.....	25
11.3.1 General.....	25
11.3.2 Preparation of sample and QC aliquots.....	26
11.3.3 Filtration of particles.....	26
12 Extraction	26
12.1 Separating funnel extraction of filtrates and of aqueous samples that are visibly absent of particles.....	26
12.2 Solid phase extraction (SPE) of samples containing less than 2 g/l suspended particulate matter.....	27
12.2.1 Disk/cartridge preparation.....	27

ISO/TS 16780:2015(E)

12.2.2	Sample extraction	27
12.3	Soxhlet or PLE extraction of filters or disks	28
12.4	Macro-concentration	28
12.4.1	General	28
12.4.2	Rotary evaporation	28
12.4.3	Heating mantle	29
12.4.4	Kuderna-Danish (K-D)	29
12.5	Micro-concentration and solvent exchange	31
13	Extract clean-up	31
13.1	General	31
13.2	Back-extraction with acid and base	32
13.3	Gel permeation chromatography (GPC)	32
13.3.1	Column packing	32
13.3.2	Column calibration	32
13.3.3	Extract clean-up	33
13.4	Silica clean-up	33
13.5	Carbon column	34
13.6	Florisil clean-up	34
13.7	Silver nitrate–silica column	34
14	HRGC–HRMS analysis	35
14.1	General	35
14.2	MS resolution	35
14.3	Calibration verification	35
14.4	GC resolution	35
14.5	Blank	35
15	Qualitative determination	36
16	Quantitative determination	36
16.1	Isotope dilution quantification	36
16.2	Internal standard quantification	37
16.3	Determination of labelled compound recovery	37
16.4	Concentration in sample	38
16.4.1	General	38
16.4.2	Treatment of samples exceeding calibration range	38
16.5	Results and reporting	38
17	Test report	39
Annex A (informative) Use of alternate mass spectrometry detectors (LRMS, MS–MS)		40
Annex B (informative) Quality control and initial precision and recovery		43
Annex C (informative) Calculation of toxic equivalents		45
Annex D (informative) Pollution prevention		46
Annex E (informative) Waste management		47
Bibliography		48

iTeH STANDARD PREVIEW
(standards.iteh.ai)

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 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

[SIST-TS ISO/TS 16780:2018](#)

<https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018>

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST-TS ISO/TS 16780:2018](#)

<https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018>

Water quality — Determination of polychlorinated naphthalenes (PCN) — Method using gas chromatography (GC) and mass spectrometry (MS)

WARNING — Persons using this Technical Specification should be familiar with normal 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.

Attention is drawn to any relevant national safety regulations. A number of PCN congeners have dioxin-like properties and are toxic chemicals. All work with PCNs requires the utmost care; the national safety measures which correspond to those for toxic substances shall be strictly followed.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this Technical Specification be carried out by suitably trained staff.

1 Scope

This Technical Specification specifies a method for the determination of polychlorinated naphthalenes (PCNs), where “poly” means “mono” to “octa”, in waters and waste waters [containing less than 2 g/l solid particulate material (SPM)] using high resolution gas chromatography–high resolution mass spectrometry (HRGC–HRMS).

NOTE 1 The congeners analysed by this method are listed in [Table 1](#).

The working range of the method is 20 pg/l to 8 ng/l. The method is optimized for PCNs, but can be modified to include other coplanar compounds such as polychlorinated dioxins and furans (PCDDs/PCDFs) and dioxin-like tetra- to heptachlorinated biphenyls (dlPCBs). This method can be used to determine PCNs in other matrices (e.g. biota, sediments, air); however, additional clean-up steps and techniques can be necessary for samples with high organic loadings. Low resolution mass spectrometry (LRMS) and mass spectrometry–mass spectrometry (MS–MS) can be used.

NOTE 2 LRMS and MS–MS conditions are summarized in [Annex A](#).

Both LRMS and MS–MS can be less selective than HRMS and there is a possibility of bias due to interfering compounds if these techniques are used.

The detection limits and quantification levels in this method are dependent on the level of interferences as well as instrumental limitations.

NOTE 3 The minimum levels (ML) in [Table 4](#) are the levels at which the PCNs can typically be determined with no interferences present.

This method is performance based. The analyst is permitted to modify the method, e.g. to overcome interferences, provided that all performance criteria in this method are met.

NOTE 4 The requirements for establishing method validation or equivalency are given in [Clause 9](#).

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/TS 16780:2015(E)

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 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 8466 (all parts), *Water Quality — Calibration and evaluation of analytical methods and estimation of performance characteristics*

3 Terms, definitions, and abbreviated terms

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

3.1 Terms and definitions

3.1.1

analyte

substance to be determined

EXAMPLE A polychlorinated naphthalene (PCN) congener tested for by the method specified in this Technical Specification.

Table 1 — PCNs determined by this method

PCN No. (Reference[4])	Chlorine substitution	CAS Registry No.
Total MonoCNs	Mono congener total	
2	2-MonoCN	91-58-7
Total DiCNs	Di congener total	
6	1,5-DiCN	1825-30-5
Total TriCNs	Tri congener total	
13	1,2,3-TriCN	50402-52-3
Total TetraCNs	Tetra congener total	
27	1,2,3,4-TetraCN	20020-02-4
28	1,2,3,5-TetraCN	53555-63-8
36	1,2,5,6-TetraCN	67922-22-9
42	1,3,5,7-TetraCN	53555-64-9
46	1,4,5,8-TetraCN	3432-57-3
48	2,3,6,7-TetraCN	34588-40-4
Total PentaCNs	Penta congener total	
49	1,2,3,4,5-PentaCN	67922-25-2
50	1,2,3,4,6-PentaCN	67922-26-3
52/60	1,2,3,5,7-/	53555-65-0/
	1,2,4,6,7-PentaCN	150224-17-2
53	1,2,3,5,8-PentaCN	150224-24-1
54	1,2,3,6,7-PentaCN	150224-16-1
Total HexaCNs	Hexa congener total	
63	1,2,3,4,5,6-HexaCN	58877-88-6
64/68	1,2,3,4,5,7-/	67922-27-4/
	1,2,3,5,6,8-HexaCN	103426-95-5

Table 1 (continued)

PCN No. (Reference[4])	Chlorine substitution	CAS Registry No.
66/67	1,2,3,4,6,7-/	103426-96-6
	1,2,3,5,6,7-HexaCN	103426-97-7
69	1,2,3,5,7,8-HexaCN	103426-94-4
70	1,2,3,6,7,8-HexaCN	17062-87-2
71/72	1,2,4,5,6,8-/	90948-28-0
	1,2,4,5,7,8-HexaCN	103426-92-2
Total HeptaCNs	Hepta congener total	
73	1,2,3,4,5,6,7-HeptaCN	58863-14-2
74	1,2,3,4,5,6,8-HeptaCN	58863-15-3
75 (OctaCN)	1,2,3,4,5,6,7,8-OctaCN	2234-13-1

Note: PCN numbering nomenclature is detailed in Reference[4]. The CAS Registry Number is a unique numerical identifier assigned by Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature.

3.1.2**calibration standard**

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

[SOURCE: ISO 17858:2007, 3.1.2 — modified]

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

midpoint calibration standard that is used to verify calibration

[SOURCE: ISO 17858:2007, 3.1.3]

3.1.4**congener**

member of the same kind, class or group

[SOURCE: ISO 17858:2007, 3.1.5]

EXAMPLE Any one of the 75 individual PCNs.

3.1.5**critical pair**

pair of isomers that must be separated to a predefined degree (e.g. 50 % valley) to ensure chromatographic separation meets minimum quality criteria

[SOURCE: ISO 17858:2007, 3.1.6, modified — “50 %” replaces “25 %”.]

3.1.6**dioxin-like isomer**

PCN for which a relative potency to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) has been calculated see [Table 2](#)

Table 2 — Examples of relative potencies^[16]

Compound	REP
1,3,5,7CN(42)	0,000 01
1,2,5,6CN(36)	0,000 01

ISO/TS 16780:2015(E)

Table 2 (continued)

Compound	REP
1,2,3,5CN(28)	0,000 001
1,2,3,4CN(27)	0,000 01
2,3,6,7CN(48)	0,001
1,4,5,8CN(46)	0,000 000 1
1,2,3,5,7CN/1,2,4,6,7CN(52/60)	0,000 1
1,2,3,4,6CN(50)	0,000 1
1,2,3,6,7CN(54)	0,000 1
1,2,3,5,8CN(53)	0,000 01
1,2,3,4,5CN(49)	0,000 001
1,2,3,4,6,7CN/1,2,3,5,6,7CN(66/67)	0,01
1,2,3,4,5,7CN/1,2,3,5,6,8CN(64/68)	0,001
1,2,3,5,7,8CN(69)	0,001
1,2,4,5,6,8CN/1,2,4,5,7,8CN(71/72)	0,001
1,2,3,4,5,6CN(63)	0,001
1,2,3,6,7,8CN(70)	0,01
1,2,3,4,5,6,7CN(73)	0,01
1,2,3,4,5,6,8CN(74)	0,01
1,2,3,4,5,6,7,8CN(75)	0,1

3.1.7**homologue group**

complete group of isomers

SIST-TS ISO/TS 16780:2018

<https://standards.iteh.ai/catalog/standards/sist/fefc8487-94ff-49a9-b74c-5d5514d65e1d/sist-ts-iso-ts-16780-2018>

EXAMPLE Tetrachloronaphthalenes.

[SOURCE: ISO 17858:2007, 3.1.8 — modified]

3.1.8**isotope dilution**method using labelled (usually ^{13}C) internal standards to correct for losses during sample preparation and analysis[SOURCE: ISO 17858:2007, 3.1.9, modified — “ ^{13}C ” replaces “ $^{13}\text{C}_{12}$ ”.]**3.1.9****method blank**

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

[SOURCE: ISO 17858:2007, 3.1.11, modified — “free of analytes” replaces “that is”.]

3.1.10**recovery standard** $^{13}\text{C}_{10}$ -labelled PCN added before injection into the GC, to monitor variability of instrument response, and determine recovery of surrogate/internal standards

Note 1 to entry: An alternate compound with similar properties can be used if a labelled PCN standard is not available.

3.1.11**solid particulate material****SPM****suspended solids**

non dissolved particle matter present in the sample

3.1.12**toxic equivalent factor****TEF**

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

[SOURCE: ISO 17858:2007, definition 3.1.17]

3.1.13**toxic equivalent quantity****TEQ**

sum of toxic equivalents of each individual congener

[SOURCE: ISO 17858:2007, 3.1.18]

3.1.14**surrogate standard**

$^{13}\text{C}_{10}$ -labelled PCN added to the sample prior to analysis and used to correct for losses of the PCN analytes during sample extraction or clean-up

Note 1 to entry: Surrogate standards have the same chemical formula and structure as the analyte of interest.

3.1.15**internal standard**

$^{13}\text{C}_{10}$ -labelled PCN or analogue added to the sample prior to analysis and used to correct for losses of the PCN analytes during sample extraction or clean-up

Note 1 to entry: Internal standards do not have the same structure as the analyte of interest but can or may not have the same chemical formula.

ISO/TS 16780:2015(E)

3.2 Abbreviated terms

AR	analytical reagent
CRM	certified reference material
GC-MS	gas chromatography-mass spectrometry
GPC	gel permeation chromatography
HPLC	high performance liquid chromatography
HRGC	high resolution gas chromatography
HRMS	high resolution mass spectrometry
IPR	initial precision and recovery
LRMS	low-resolution mass spectrometry
MDL	method detection limit
ML	minimum level
PAR	precision and recovery
PCB	polychlorinated biphenyl
PCDD/PCDF	polychlorinated dibenzo-p-dioxin/dibenzofuran
PCN	polychlorinated naphthalene
PFK	perfluorokerosene
PLE	pressurized liquid extractor
SIM	selected ion monitoring
SMS	spiked matrix samples
SPE	solid-phase extraction
SPM	solid particulate material
TEF	toxic equivalent factor
TEQ	toxic equivalent quantity
VER	calibration verification standard

4 Principle

4.1 Extraction

4.1.1 Stable isotopically labelled analogues of PCNs (diluted in a suitable solvent such as 2-propanone) are spiked into a ~1 l aqueous sample. Sample size can be adjusted in order to meet required detection limits and data quality objectives. Where available, a minimum of one labelled standard per homologue group should be used and the sample extracted using the procedures as specified in [4.1.2](#) or [4.1.3](#).

4.1.2 Samples containing no visible particles are extracted using liquid/liquid extraction or by solid phase extraction (SPE) cartridge or disk. The extract is concentrated for clean-up.

4.1.3 Samples containing visible particles are vacuum filtered through a glass fibre filter. The filter is extracted in a Soxhlet extractor or a pressurized liquid extractor (PLE). The filtrate is extracted in a separating funnel. The extract is concentrated and combined with the Soxhlet extract prior to clean-up. Alternatively, the sample is vacuum filtered through a solid phase extraction (SPE) disk or cartridge. The disk is eluted with suitable solvent mixtures or extracted in a Soxhlet or a PLE, and the extract is concentrated for clean-up.

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

4.2 Clean-up

After extraction, sample extracts are cleaned to remove interfering components. Sample clean-up procedures may include washes with acid or base, gel permeation, silica, Florisil¹⁾ and activated carbon chromatography. Due to the large number of potential interfering compounds, efforts should be taken to ensure unique identification and accurate quantification of as many PCN congeners as possible.

4.3 Identification and quantification

An individual PCN is identified by comparing the GC retention time and ion abundance ratio of two exact masses monitored (see Table 3) with the corresponding retention time of a labelled internal standard (isotope dilution) and the theoretical or acquired ion abundance ratio of the two exact masses. The isomers and congeners for which there are no labelled analogues (internal standard method) are identified when retention times or relative retention times and ion abundance ratios agree within predefined limits.

NOTE Resolution of greater than or equal to 10 000 is recommended. High resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) at a resolution of greater than or equal to 10 000 is at present required to achieve adequate sensitivity and selectivity, and to allow the use of some ¹³C labelled standards. Resolutions of less than 10 000 can be used for specific analytes groups (PCBs, PCNs) where the matrix and potential interferences such as chlordane and related compounds are well characterized.

Table 3 — Congener function groups and ions

Function group	Quantitation ions	Compound	Dwell	Delay	Theoretical isotopic ratio	Acceptable range
	<i>m/z</i>		ms	ms		
0	162,0236 ^a , 164,0208	MonoCNs	50	10	0,33	0,17 to 0,48
	195,9847 ^a , 197,9818	DiCNs	50	10	0,65	0,50 to 0,80
	180,9888	PFK Lock Mass	30	10		
1	229,9457 ^a , 231,9428	TriCNs	50	10	1,02	0,87 to 1,17
	265,9038 ^a , 263,9067	TetraCNs	50	10	1,30	1,11 to 1,5
	275,9373 ^a , 273,9402	¹³ C ₁₀ -TetraCNs	25	10	1,30	1,11 to 1,5
	268,9824	PFK Lock Mass	30	10		

^a Most abundant ion.

^b Injection standard.

NOTE When the availability of ¹³C-labeled PCN standards is limited, ¹³C-labeled PCB standards can be used as injection standards

1) Florisil is the trade name of a product supplied by US Silica Co. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.