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

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

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Foreword

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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).

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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*.

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 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

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

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 "$^{13}C_{12}$".]

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
$^{13}C_{10}$-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
$^{13}C_{10}$-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
$^{13}C_{10}$-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.

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, Florisil[1)] 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 ^{13}C 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
	m/z		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 ^{13}C-labeled PCN standards is limited, ^{13}C-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.

Table 3 *(continued)*

Function group	Quantitation ions	Compound	Dwell	Delay	Theoretical isotopic ratio	Acceptable range
	m/z		ms	ms		
2	299,8648[a], 297,8677	PentaCNs	50	10	1,62	1,38 to 1,86
	309,8983[a], 307,9013	$^{13}C_{10}$-PentaCNs	25	10	1,62	1,38 to 1,86
	292,9824[b]	PFK Lock Mass	30	10		
3	333,8258[a], 335,8229	HexaCNs	50	10	1,23	1,01 to 1,45
	343,8594[a] 345,8564	$^{13}C_{10}$-HexaCNs	25	10	1,23	1,01 to 1,45
	337,9207[a],335,9236	$^{13}C_{12}$-PentaCB [b]	25	10	1,62	1,38 to 1,86
	342,9792	PFK Lock Mass	30	10		
4	367,7868[a], 369,7839	HeptaCNs	50	10	1,02	0,87 to 1,17
	377,8204[a], 379,8174	$^{13}C_{10}$HeptaCNs	50	10	1,15	0,98 to 1,32
	380,9760	PFK Lock Mass	30	10		
5	403,7449[a], 401,7479	OctaCN	50	10	1,15	0,98 to 1,32
	413,7785[a], 411,7814	$^{13}C_{10}$-OctaCN	25	10	1,15	0,98 to 1,32
	405,8428[a],407,8398	$^{13}C_{12}$-HeptaCB [b]	25	10	1,02	0,87 to 1,17
	392,9760	PFK Lock Mass	30	10		

[a] Most abundant ion.

[b] Injection standard.

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

4.4 Quality

The quality of the analysis is ensured 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 (round-robin) studies, certified reference materials (CRMs) and spiked matrix samples (SMSs). 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 Reagents. Solvents, reagents, laboratory-ware, and other sample processing hardware can yield artefacts or elevated baselines causing misinterpretation of chromatograms. Check reagents for potential interfering compounds and clean and check laboratory-ware to ensure that analytes of interest are not present. Specific selection of reagents and purification may be required. When a clean reference matrix that simulates the sample matrix under test is not available, use reagent water (6.6) or a matrix that most closely resembles the sample.

5.2 Clean laboratory-ware, to meet the method blank requirements of this method (9.4).

An example of a cleaning procedure follows.

Dismantle laboratory-ware with removable parts, particularly separating funnels with fluoropolymer stopcocks, prior to detergent washing. Rinse laboratory-ware with solvent and wash with a detergent solution as soon after use as is practical. Sonication of laboratory-ware containing a detergent solution for approximately 30 s may aid in cleaning.

After detergent washing, rinse laboratory-ware immediately with hot tap water. The tap water rinse shall be followed by solvent rinse or soak, using a suitable solvent (6.3) to remove contaminants. For known contaminated laboratory-ware, use toluene as a final rinse or soak.

Number each piece of re-usable laboratory-ware or minimally identify each set of specific type of laboratory-ware (e.g. Soxhlet extractors, round-bottomed flasks) to associate that specific laboratory-ware with the processing of a particular sample or set of samples. This practice assists the laboratory in tracking possible sources of contamination for individual samples, identifying laboratory-ware associated with highly contaminated samples that may require extra cleaning, and determining when laboratory-ware shall be discarded.

IMPORTANT — Proper cleaning of laboratory-ware is extremely important, because laboratory-ware can contaminate the samples, but can also remove the analytes of interest by surface adsorption if the surface is activated during the cleaning procedure. Glassware can be checked for contamination by analysing solvent rinses.

Demonstrate that all materials used in the analysis are free from interferences by running reference matrix method blanks initially and with each sample batch (to a maximum of 20 samples); (see 9.4, 14.5).

The reference matrix shall simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix shall not contain analytes in detectable amounts, but shall contain matrix compounds and potential interferents in the concentrations expected to be found in the samples to be analysed.

NOTE Interferences co-extracted from samples can vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds, including PCBs of higher degrees of ^{37}Cl substitution, dibenzofurans of lower degrees of ^{37}Cl substitution, chlordane and related compounds and labelled dibenzo-*p*-dioxins can be present at concentrations orders of magnitude higher than the PCNs being analysed. Because the levels of PCNs are measured by this method are typically lower than these compounds, the elimination of interferences is essential. The example clean-ups given in Clause 13 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCNs at the levels shown in Table 4.

Table 4 — Suggested quantification relationships

PCN	Quantification reference	Minimum level[a]	Minimum level[a]
		Waters (pg/l)	Extract (pg/µl)
Total MonoCNs	$^{13}C_{10}$-PCN 42	20	1,0
2-MonoCN (2)	$^{13}C_{10}$-PCN 42	20	1,0
Total DiCNs	$^{13}C_{10}$-PCN 42	20	1,0
1,5-DiCN (6)	$^{13}C_{10}$-PCN 42	20	1,0
Total TriCNs	$^{13}C_{10}$-PCN 42	20	1,0
1,2,3-TriCN (13)	$^{13}C_{10}$-PCN 42	20	1,0
Total TetraCNs	Mean of $^{13}C_{10}$-PCN 27/42	20	1,0
1,2,3,4-TetraCN (27)	$^{13}C_{10}$-PCN 27	20	1,0
1,2,3,5-TetraCN (28)	Mean of $^{13}C_{10}$-PCN 27/42	20	1,0
1,2,5,6-TetraCN (36)	Mean of $^{13}C_{10}$-PCN 27/42	20	1,0
1,3,5,7-TetraCN (42)	$^{13}C_{10}$-PCN 42	20	1,0
1,4,5,8-TetraCN (46)	Mean of $^{13}C_{10}$-PCN 27/42	20	1,0
2,3,6,7-TetraCN (48)	Mean of $^{13}C_{10}$-PCN 27/42	20	1,0

[a] The minimum level ML for each analyte is defined as the level for which the entire analytical system shall give a recognizable signal and acceptable calibration point. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specific sample masses/volumes and clean-up procedures have been used. i.e. based on 1 l of sample.

NOTE Minimum levels are given for guidance only. Mean refers to mean recovery of both internal standards.