SLOVENSKI STANDARD
oSIST ISO/DIS 16780:2014

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Kakovost vode - Določevanje poliklooriranih 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)

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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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)

ICS 13.060.50

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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

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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.

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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.

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ISO 16780 was prepared by Technical Committee 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 document should be familiar with normal laboratory practice. This 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. 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 document be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for the determination of mono- to octa-polychlorinated naphthalenes (PCNs) 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). 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 may be modified to include other co-planar compounds such as polychlorinated dioxins and furans (PCDDs/PCDFs) and dioxin-like tetra- to hepta-chlorinated biphenyls (dlPCBs). This method may be used to determine PCNs in other matrices (e.g. biota, sediments, air), however additional clean-up steps and techniques may be required for samples with high organic loadings. Low resolution mass spectrometry (LRMS) and mass spectrometry/mass spectrometry (MS/MS) may be used and conditions are summarized in Annex A. Both LRMS and MS/MS may 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. The minimum levels (ML) in Table 2 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. The requirements for establishing method validation / 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/TS 13530, *Water quality — Guidance on analytical quality control for chemical and physicochemical water analysis*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

3 Terms, definitions and abbreviations

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

3.1 Terms and definitions

3.1.1
analyte
polychlorinated naphthalene (PCN) congener 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

[SOURCE: ISO 17858:2007,[2], definition 3.1.2]

3.1.3
calibration verification standard (VER)
midpoint calibration standard that is used to verify calibration

[SOURCE: ISO 17858:2007,[2], definition 3.1.3]

3.1.4
congener
a member of the same kind, class or group

EXAMPLE Any one of the 75 individual PCNs.

3.1.5
critical pair
a pair of isomers that must be separated to a predefined degree (e.g. 50 % valley) to ensure chromatographic separation meets minimum quality criteria

NOTE 1 to entry Adapted from ISO 17858:2007.

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 6)

3.1.7
homologue group
the complete group of isomers

EXAMPLE Tetrachloronaphthalenes.

[ISO 17858:2007,[2], definition 3.1.8]

3.1.8
isotope dilution
method using labelled (usually ^{13}C) internal standards to correct for losses during sample preparation and analysis

NOTE 1 to entry Adapted from ISO 17858:2007.

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

NOTE 1 to entry Adapted from ISO 17858:2007.

3.1.10
recovery standard
$^{13}C_{10}$-labelled PCN or alternate compound with similar properties, added before injection into the GC, to monitor variability of instrument response

3.1.11
solid particulate material (SPM, also 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,[2], definition 3.1.17]

3.1.13
toxic equivalent quantity
TEQ
sum of toxic equivalents of each individual congener

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 may or may not have the same chemical formula.

3.2 Abbreviations

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 (see Table 2)
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 acetone) 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 described 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 separatory 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) diskor 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 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 may include washes with acid and/or base, gel permeation, silica, florisil 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/quantification

An individual PCN 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 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 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. If the sample extract is being analysed for multi-component analyte groups (PCDD/Fs, PCBs, PCNs), a resolution of 10 000 is necessary. Resolutions of less than 10 000 may be used for specific analytes groups (PCBs, PCNs) where the matrix and potential interferences such as chlordane and related compounds are well characterized.

4.4 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 (round-robin) 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 Reagents

Solvents, reagents, labware, and other sample processing hardware can yield artefacts and/or elevated baselines causing misinterpretation of chromatograms. Reagents should be checked for potential interfering compounds and labware must be cleaned and checked to ensure that analytes of interest are not present in labware. 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 labware, to meet the method blank requirements of this method (9.5.).

An example of a cleaning procedure is given below.

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 may aid in cleaning.

After detergent washing, rinse labware immediately with hot tap water. The tap water rinse shall be followed by solvent rinse/soak (use suitable solvent (6.3.1) to remove contaminants. For known contaminated labware, use toluene as a final rinse/soak.

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

NOTE 1 Proper cleaning of labware is extremely important, because labware 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 may 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 2 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 2.

6 Reagents and standards

If not stated otherwise, use reagent grade chemicals and water according to grade 3 in ISO 3696.

6.1 pH adjustment and back-extraction

6.1.1 Potassium hydroxide solution

Dissolve 20 g of potassium hydroxide (KOH) in 100 ml of water.

6.1.2 Sulfuric acid, $\rho(H_2SO_4)$ = 1,84 mg/l.

6.1.3 Hydrochloric acid, c(HCl) = 6 mol/l.

6.1.4 Sodium chloride solution

Dissolve 5 g of sodium chloride (NaCl) in 100 ml of water.

6.1.5 Sodium thiosulfate, $Na_2S_2O_3$.

6.2 Reagents for drying and evaporation

6.2.1 Sodium sulfate, Na_2SO_4, granular, anhydrous, baked at 300 °C for 24 h minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.

If, after heating, the sodium sulfate develops a noticeable greyish cast (due to the presence of carbon in the crystal matrix), discard that batch of reagent as it is not suitable for use. Rinse with about 20 ml of dichloromethane (6.3.1) per gram of Na_2SO_4 or extract with dichloromethane (6.3.1) if background contamination is detected.

6.2.2 Prepurified nitrogen, N_2, volume fraction 99,999 %.

6.3 Solvents for extraction and clean-up, in glass, pesticide quality, free of interferences.

6.3.1 2-propanone, C_3H_6O.

6.3.2 Toluene, C_7H_8.

6.3.3 Cyclohexane, C_6H_{12}.

6.3.4 Hexane, C_6H_{14}.

6.3.5 Methanol, CH_3OH.

6.3.6 Dichloromethane, CH_2Cl_2.

6.3.7 Diethyl ether, $C_4H_{10}O$.

6.3.8 Ethanol, C_2H_6O.

6.3.9 Nonane, C_9H_{20}, distilled.

6.4 Gel permeation chromatography (GPC) calibration

6.4.1 GPC calibration solution, containing 300 mg/ml of corn oil, 15 mg/ml of bis(2-ethylhexyl) phthalate ($C_{24}H_{38}O_4$), 1,4 mg/ml of pentachlorophenol, (C_6Cl_5OH), 0,1 mg/ml of perylene, ($C_{20}H_{12}$), and 0,5 mg/ml of sulfur, (S).

6.5 Adsorbents for sample clean-up

6.5.1 Silica, 70 µm to 230 µm.

Prepare each type of silica at least every 2 weeks.

6.5.1.1 Activated silica, baked at 180 °C for a minimum of 1 h, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.

6.5.1.2 Acid silica

To prepare 30 % mass fraction acid silica, thoroughly mix 44,0 g of sulfuric acid (6.1.2) with 100 g of activated silica in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw cap. Prepare 22 % acid silica and 44 % acid silica in a similar manner using 29 g and 80 g of sulfuric acid, respectively.

6.5.1.3 Basic silica

Thoroughly mix 30 g of 1 mol/l sodium hydroxide solution with 100 g of activated silica in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw cap.

6.5.1.4 **Potassium silicate**, 36 % mass fraction.

Dissolve 56 g of high purity potassium hydroxide (6.1.1) in 300 ml of methanol (6.3.1) in a 750 ml flat-bottom flask. Add 100 g of silica (6.5.1) and a stirring bar, and stir on a hotplate at 60 °C to 70 °C for 1 h to 2 h. Decant the liquid and rinse the potassium silicate twice with 100 ml portions of methanol, followed by a single rinse with 100 ml of dichloromethane (6.3.1). Spread the potassium silicate on solvent-rinsed aluminium foil and dry for 2 h to 4 h in a hood. Activate overnight at 200 °C to 250 °C. Store in a bottle with a fluoropolymer-lined screw cap.

6.5.2 Activated carbon

Thoroughly mix 9,0 g of carbon packing material and 41,0 g of Celite 545 to produce a mass fraction of 18 % of the mixture. Activate the mixture at 130 °C for a minimum of 6 h. Store in a desiccator.

6.5.3 **Florisil**, 70 µm to 250 µm.

Activate in an oven above 130 °C for a minimum of 24 h. Use as soon as possible after removal from oven. Activity of florisil may be dependant on relative humidity.

Prepare freshly for each use.

6.5.4 **Silver nitrate/silica**, (10 % mass fraction) for elimination of organosulfur and organohalogen compounds, made of silver nitrate ($AgNO_3$) analytical reagent (AR) grade or equivalent and silica (6.5.1.1).

Dissolve 10 g of silver nitrate in 40 ml water, add in portions 90 g silica and shake until the mixture is homogeneous. Let stand for 30 min. Transfer the mixture to a drying oven pre-heated to 70 °C and heat from 70 °C to 125 °C over a 2 h period. Activate at 125 °C for at least 10 h. Store the mixture in a brown glass bottle.

Prepare freshly for each use.

6.6 Blank reference matrices

Matrices in which PCNs and interfering compounds are not detected by this method, e.g. reagent water, bottled water purchased locally, HPLC grade water or water prepared by passage through activated carbon.

6.7 Standard solutions

Purchase standard solutions as final working / calibration solutions or mixtures with certification indicating their purity, concentration, and authenticity. Alternatively, prepare standard solutions from materials of known purity and composition.

NOTE 1 If the chemical purity is 98 % or greater, the mass may be used without correction to compute the concentration of analytes in the standard.

When not being used, store standards in the dark in sealed ampoules or screw capped vials with fluoropolymer lined caps. Check the concentrations regularly so that solvent loss by evaporation can be detected. If solvent loss has occurred, replace the solution.

NOTE 2 Standard preparation (6.7 to 6.15) and Tables 3 and 4 give examples of a standard scheme that are acceptable. Other concentrations and spiking schemes may be used provided the performance criteria of the method can be met.

Check stock standard solutions for signs of degradation prior to the preparation of calibration or performance test standards.

NOTE 3 Use certified reference standards and solutions to determine the accuracy of calibration standards if available.

6.8 Precision and recovery (PAR) stock solution

The PAR stock solution should contain PCNs at the concentrations shown in Table 4. When diluted to the final concentration, the solution is referred to as the PAR standard solution (6.12). If possible obtain this solution from an alternate supplier. This enables an ongoing verification and validation of the calibration (6.11) and labelled spiking solutions (6.9).

6.9 Surrogate spiking solution

Prepare the surrogate spiking solution to contain the labelled analytes in nonane at the concentrations shown in Table 4.

Dilute a sufficient volume of the labelled compound solution with acetone (6.3.1) to prepare a diluted spiking solution.

NOTE Each sample requires 1,0 ml of the diluted solution, but no more solution should be prepared than can be used within 1 d.

6.10 Recovery standard(s)

Prepare the recovery standard solution to contain $^{13}C_{10}$-labelled compounds(s), or alternate compound(s) with similar properties, in nonane at the concentration shown in Table 4 for the specific groups of compounds analysed.

6.11 Calibration standards

Combine the solutions in 6.8 to 6.10 to produce at least five calibration solutions for example, shown in Table 3 in nonane.

NOTE These solutions permit the relative response (labelled to native) and response factor to be measured as a function of concentration. A minimum of five solutions over the calibration range of the method should be used. Each concentration step should range between 3 times and 10 times the lower concentrated standard.

Use the mid-point standard for calibration verification (VER).

6.12 Precision and recovery (PAR) standard solution

Use this standard solution for determination of initial and ongoing precision and recovery. For each sample matrix, dilute the required amount the precision and recovery stock solution (6.8) to 2,0 ml with acetone (6.3.1). Use an amount that is representative of the levels being determined in the samples being analysed or at regulatory limit that the samples under test are governed by.