INTERNATIONAL STANDARD

ISO 12010

First edition
2012-03-15

Water quality — Determination of short-chain polychlorinated alkanes (SCCPs) in water — Method using gas chromatography-mass spectrometry (GC-MS) and negative-ion chemical ionization (NCI)

Qualité de l'eau — Détermination des alcanes polychlorés à chaîne courte (SCCP) dans l'eau — Méthode par chromatographie gazeuse-spectrométrie de masse (CG-SM) avec ionisation chimique négative (ICN)

Reference number
ISO 12010:2012(E)

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Published in Switzerland

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Foreword

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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.

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ISO 12010 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

The user should be aware that particular problems might require the specifications of additional marginal conditions.

Water quality — Determination of short-chain polychlorinated alkanes (SCCPs) in water — Method using gas chromatography-mass spectrometry (GC-MS) and negative-ion chemical ionization (NCI)

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.

IMPORTANT — It is absolutely essential that tests conducted in accordance to this International Standard be carried out by suitably qualified staff.

1 Scope

This International Standard specifies a method for the quantitative determination of the sum of short-chain polychlorinated *n*-alkanes, also known as short-chain polychlorinated paraffins (SCCPs), in the carbon bond range *n*-C_{10} to *n*-C_{13} inclusive, in mixtures with chlorine mass fractions ("contents") between 49 % and 67 %, including approximately 6 300 of approximately 8 000 congeners.

This method is applicable to the determination of the sum of SCCPs in unfiltered surface water, ground water, drinking water and waste water using gas chromatography-mass spectrometry with electron capture negative ionization (GC-ECNI-MS).

The method can be applied to samples containing 0,1 µg/l to 10 µg/l. Depending on the waste water matrix, the lowest detectable concentration is estimated to be >0,1 µg/l.

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 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 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO/TS 13530, *Water quality — Guidance on analytical quality control for chemical and physicochemical water analysis*

3 Principle

Determination of the sum of SCCPs in the carbon bond range *n*-C_{10} to *n*-C_{13} inclusive, in technical and environmental transposed mixtures with chlorine mass fractions ("contents") between 49 % and 67 % (e.g. approximately 3 to 10 chlorine atoms per molecule) and independent of the C-number distribution pattern of the congeners. No recognition of the chlorine content is necessary.

SCCPs in whole water samples are fortified with an internal standard and extracted using liquid-liquid extraction with an organic solvent. The sample enrichment procedure is followed by a clean-up procedure to eliminate interfering compounds. Gas chromatography (GC) is undertaken using a short capillary column within a short

retention time range. The detection of selected mass fragments is carried out using mass spectrometry (MS) in selected ion-monitoring mode using electron capture negative ionization mode (ECNI). The selection of the mass fragments is specific for the variety of technical mixtures as well as for their chlorine content and C-number distribution patterns. Alternative mass fragment combinations for qualification are also given in this International Standard.

The selected ion chromatogram is integrated over the full retention time range of the SCCPs. The quantification of the sum of SCCPs is carried out after establishing a calibration by multiple linear regression, measuring solutions of different technical mixtures fortified with an internal standard.

The calibration requires a minimum of three different composed standard mixtures, each of which resembles the C-number distribution pattern and chlorine content of different technical mixtures. This is to reflect the variety of chlorine contents and C-number distribution patterns of technical SCCP mixtures and SCCP levels found in environmental samples, which cannot be described by a single defined standard substance.

The method allows a quantification of the sum of SCCPs expected to be within an expanded measurement uncertainty of less than 50 %.

4 Interferences

Non-specific matrix interferences, as well as interferences from other environmental situations, are dealt with using the given clean-up procedure. Following the entire procedure, including the concentration factor of approximately 5 000, the following pollutants have been tested and found not to cause interferences below the following concentrations.

Potential interfering compounds	Highest concentration level at which no interferences higher than the limit of detection are detected
Aroclor 1262[a]	0,5 µg/l
Aroclor 1242[a]	0,5 µg/l
Aroclor 1221[a]	1 µg/l
Campheclor	0,2 µg/l
Halowax 1014[a]	1 µg/l
Halowax 1051[a]	1 µg/l
Technical chlordane	0,5 µg/l
MCCP (medium-chain chlorinated *n*-alkanes) 42 %	0,2 µg/l
MCCP (medium-chain chlorinated *n*-alkanes) 52 %	0,2 µg/l
MCCP (medium-chain chlorinated *n*-alkanes) 57 %	0,2 µg/l

[a] Product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

If the clean-up procedure is repeated, interferences can be further reduced.

5 Reagents and standards

Use solvents and reagents of sufficient purity, i.e. with negligibly low concentrations of SCCPs (e.g. lower than the limit of detection of the method).

NOTE Check blanks regularly over the entire procedure to ensure they are suitable and establish proper analytical control.

5.1 Solvents for extraction and preparation of stock solutions. The solvent for extraction is *n*-heptane. Other non-polar solvents, e.g. *n*-hexane (C_6H_{14}) or cyclohexane (C_6H_{12}), can be used if the extraction efficiency is comparable with those of *n*-heptane.

Use 2,2,4-trimethylpentane (C_8H_{18}, isooctane) for conditioning of the glass bottles (6.1).

For preparation of the stock solutions, use dilutions in propanone (acetone), C_3H_6O.

For conditioning of the clean-up columns, use mixtures of *n*-heptane and propanone (acetone).

For the first elution step of the filtrated suspended matter, use methanol (CH_3OH).

5.2 Reference SCCP stock solutions. Use commercially available solutions, e.g. in cyclohexane or *n*-hexane, of the single mixtures of SCCP congeners with a defined carbon chain length and with different defined chlorine contents (see Table 1, first two columns). Alternatively, use commercially available ready-mixed solutions as described in Table 1.

Prepare the solutions Hordalub 17[1)]-s1, SCCP 51,5 %-s1, Hordalub 80[1)]-s1, Cereclor 60[1)]-s1, Hordalub 500[1)]-s1, and Cereclor 70[1)] -s1 according to Table 1. The suffix "-s1" denotes synthetically mixed standard solutions, which resemble the technical mixtures.

The chlorine content (third row) of the mixtures is calculated as the weighted mean.

Store the prepared solutions in a refrigerator at a temperature of 2 °C to 6 °C.

5.3 Internal standard stock solutions from individual congeners. Use commercially available individual congener standard solutions and prepare a stock solution in propanone (acetone) (5.1) at a concentration of, for example, 1 µg/ml.

Individual SCCP congeners with chlorine contents of between 49 % and 67 % are suitable as internal standards, e.g.

— 1,1,1,3,10,11-hexachlorundecane, with e.g. 0,1 µg/ml;

— 1,1,1,3,11,13,13,13-octachlorotridecane, with e.g. 0,1 µg/ml;

— 1,2,5,5,6,9,10-heptachlorodecane, with e.g. 0,01 µg/ml.

NOTE 1 The different individual SCCP congeners used as internal standard substances probably contribute to the sum of SCCPs in environmental samples. Nevertheless, the contribution is approximately <1 %, which means that the enhancement of the measurement uncertainty is negligible.

NOTE 2 Different individual SCCP congeners can produce different response factors, hence it can be necessary to use different concentrations.

If validated, other individual SCCP congeners can be used as the internal standard if the congener shows the same properties over the entire analytical process as the SCCPs being determined.

The solutions can be stored in a refrigerator at a temperature of 2 °C to 6 °C.

5.4 Copper powder, mesh size <63 µm. Copper powder is used in the clean-up procedure to remove sulfur and sulfur-containing matrix components.

5.5 Hydrochloric acid, 2 mol/l. Used for copper activation in the clean-up column.

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

5.6 Activated magnesium silicate,[2] MgO/3,75 SiO_2/(x) H_2O, for column chromatography.

Activated magnesium silicate is used in the clean-up procedure to separate organohalogenic compounds like polychlorinated biphenyls and naphthalenes.

Use activated magnesium silicate with the following characteristics: particle size 0,15 mm to 0,25 mm, of which 80 % >0,15 mm; surface area, determined according to the BET method, 170 m^2/g to 300 m^2/g; pH 9 to pH 10.

Activate the magnesium silicate by heating, for example, 200 g in a shallow dish at 140 °C for at least 4 h. Allow the activated magnesium silicate to cool to room temperature in a desiccator. Activated magnesium silicate can be stored in a closed bottle at room temperature for up to 1 month.

Table 1 — Reference substances stock solutions

Standard solutions			Synthetic mixed standard solutions, which resemble technical mixtures					
n-Alkane chain length	Chlorine content of the individual C-number mixtures, %	Mean number of chlorines in the molecules (calculated)	Hordalub 17 -s1	SCCP 51,5 % -s1	Hordalub 80 -s1	Cereclor 60 -s1	Hordalub 500 -s1	Cereclor 70 -s1
			Chlorine content calculated, %					
			49,0	51,5	56,0	59,0	62,0	66,7
			Composition, ng/ml					
C_{10}	44,82	3,22	500					
C_{10}	50,18	3,97	500	500	500			
C_{10}	55,00	4,79		500	500			
C_{10}	60,09	5,86				1 000	900	
C_{10}	65,02	7,16				500	300	2 000
C_{11}	45,50	3,63	1 200					
C_{11}	50,21	4,37	2 600	2 500		700		
C_{11}	55,20	5,31		1 000	2 000	1 300	400	
C_{11}	60,53	6,55			1 900	1 200	2 500	
C_{11}	65,25	7,94					2 500	3 200
C_{12}	45,32	3,93	1 000					
C_{12}	50,18	4,76	2 400	2 500	500			
C_{12}	55,00	5,74		1 500	2 500	2 000	1 000	
C_{12}	65,08	8,59			200	1 500	1 700	
C_{12}	69,98	10,62						3 100
C_{13}	44,90	4,19		500				
C_{13}	50,23	5,16	1 800	1 000				
C_{13}	55,03	6,22			1 000	400		
C_{13}	59,98	7,56			400	1 300	700	
C_{13}	65,18	9,34				100		1 700
Sum of SCCPs, ng/ml			**10 000**	**10 000**	**10 000**	**10 000**	**10 000**	**10 000**

5.7 Sodium sulfate, Na_2SO_4, anhydrous, granular.

5.8 Operating gases, for GC-MS, of high purity and in accordance with manufacturer's specifications.

2) Florisil is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

5.9 Nitrogen, N_2, purity ≥99,996 % volume fraction, for drying of the sorbent packing material and for concentrating solutions.

5.10 Calibration working solutions. Use a minimum of three different composed standard mixtures according to Table 1, Hordalub 17 -s1, Hordalub 80 -s1, and Cereclor 70 -s1. Prepare a minimum of nine calibration solutions (see bold figures in Table 2) with concentrations that correspond the detection capability of the mass spectrometer. Combine and dilute the solutions (5.2) and the internal standard solution (5.3) with *n*-heptane to produce solutions for the calibration range, e.g. as shown in Table 2.

The solutions may be stored in a refrigerator for up to 4 weeks. Check the concentration of the calibration solutions against an independently prepared standard prior to use.

Table 2 — Calibration working solutions

Mixture	Hordalub 17 -s1	SCCP 51,5 -s1	Hordalub 80 -s1	Cereclor 60 -s1	Hordalub 500 -s1	Cereclor 70 -s1	Internal standard: e.g. 1,1,1,10,11,13-hexachloro-decane
Sum of SCCPs, µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml
0,15	**0,15**						**0,1**
0,15		0,15					0,1
0,15			**0,15**				**0,1**
0,15				0,15			0,1
0,15					0,15		0,1
0,15						**0,15**	**0,1**
0,6	**0,6**						**0,1**
0,6		0,6					0,1
0,6			**0,6**				**0,1**
0,6				0,6			0,1
0,6					0,6		0,1
0,6						**0,6**	**0,1**
1,0	**1,0**						**0,1**
1,0		1,0					0,1
1,0			**1,0**				**0,1**
1,0				1,0			0,1
1,0					1,0		0,1
1,0						**1,0**	**0,1**

5.11 Quality control multi-component stock solution of SCCP for assuring calibration procedure. Quality control check solutions should be prepared to check the calibration independently. Prepare a minimum of three different solutions; see Table 3 or Annex A. These mixtures are also commercially available (e.g. in cyclohexane or *n*-hexane).

The solutions can be stored in a refrigerator for up to 4 weeks.

5.12 Test solution for checking linearity of internal standards. Prepare solutions of the internal standard used at concentrations of 0,1 µg/ml, 0,5 µg/ml, and 1 µg/ml.

6 Apparatus

Glassware and equipment which may come into contact with water samples or their extracts should be free from interfering compounds.

Clean all glassware by rinsing with propanone (acetone) (5.1).

6.1 Flat-bottomed glass bottles, conical shoulder, 1 000 ml capacity, for collecting water samples, preferably with glass stoppers.

The sample bottle shall enable direct extraction of the sample.

Before use, to condition it, rinse the dry sample bottle with e.g. 2 ml of isooctane (5.1), invert it and allow the solvent to drain and evaporate from it.

Table 3 — Calibration assurance solutions

***n*-Alkane chain length**	**Chlorine content of the individual C-number mixtures according to the manufacturer**, %	**SCCP 51,5 -s2**	**SCCP 55,5 -s2**	**SCCP 63 -s2**	**Hordalub 17 -s2**	**Hordalub 80 -s2**	**Hordalub 500 -s2**	**Cereclor 60 -s2**
		Calculated mean chlorine content, %						
		51,45	55,77	63,22	49,07	55,91	61,87	59,07
		Composition, ng/ml						
C_{10}	44,82				50			
C_{10}	50,18	50			50			
C_{10}	55	50	100			100		
C_{10}	60,09			50			90	150
C_{10}	65,02			50			20	
C_{11}	45,5	200	200		100			
C_{11}	50,21				280	50		
C_{11}	55,2	150				250		200
C_{11}	60,53		150	200		140	350	120
C_{11}	65,25			300			200	
C_{12}	45,32	150	100		100			
C_{12}	50,18	150	50	50	240	50		
C_{12}	55					250	100	200
C_{12}	65,08	100	200	100		20	170	150
C_{12}	69,98			50				
C_{13}	44,9	50						
C_{13}	50,23	100	50		180			
C_{13}	55,03		100			100		
C_{13}	59,98		50	100		40	70	170
C_{13}	65,18			100				
Sum of SCCPs, ng/ml		**1 000**	**1 000**	**1 000**	**1 000**	**1 000**	**1 000**	**990**

6.2 Evaporation device, e.g. rotary evaporator or nitrogen evaporating system.

6.3 Separator, for example micro-separator or other suitable device for phase separation.

6.4 Vials, compatible with the GC-autosampler (e.g. with a capacity of 1,5 ml).