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Water quality — Determination of short-chain polychlorinated alkanes (SCCPs) in sediment, sewage sludge and suspended (particulate) matter — Method using gas chromatography-mass spectrometry (GC-MS) and electron capture negative ionization (ECNI)

Qualité de l’eau — Détermination des alcanes polychlorés· à chaîne courte dans les sédiments, boues d’épuration et matières en suspension (particules) —

Méthode par chromatographie en phase gazeuse-spectrométrie de masse (CG-SM) et ionisation chimique négative par capture d’électron (ECNI)

Please see the administrative notes on page iii

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ISO/CEN PARALLEL PROCESSING

This final draft has been developed within the International Organization for Standardization (ISO), and processed under the **ISO-lead** mode of collaboration as defined in the Vienna Agreement. The final draft was established on the basis of comments received during a parallel enquiry on the draft.

This final draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel two-month approval vote in ISO and formal vote in CEN.

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Foreword

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The committee responsible for this document is 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 sediment, sewage sludge and suspended (particulate) matter — Method using gas chromatography-mass spectrometry (GC-MS) and electron capture negative ionization (ECNI)

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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 with this document 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 50 % and 67 %, including approximately 6 000 of approximately 8 000 congeners.

This method is applicable to the determination of the sum of SCCPs in sediment and suspended (particulate) matter, sewage sludge, and soil using gas chromatography-mass spectrometry with electron capture negative ionization (GC-ECNI-MS).

Depending on matrix and the detection capabilities of the GC-ECNI-MS, the method can be applied to samples containing, e.g. 0,03 µg/g to 3 µg/g sum of SCCPs.

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 5667-12, *Water quality — Sampling — Part 12: Guidance on sampling of bottom sediments*

ISO 5667-13, *Water quality — Sampling — Part 13: Guidance on sampling of sludges*

ISO 5667-17, *Water quality — Sampling — Part 17: Guidance on sampling of bulk suspended solids*

ISO 12010, *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)*

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 50 % 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 solid samples are fortified with an internal standard and extracted using pressurized liquid extraction with an organic solvent. The sample extraction procedure is followed by a clean-up procedure by column chromatography and gel permeation chromatography 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 mass fragments and the compositions of the calibration solutions used in this International Standard are essential for the analysis of the sum of SCCPs.

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 a multiple linear regression measuring solutions of different SCCP mixtures fortified with an internal standard.

The analysed sum of SCCPs includes the variety of SCCPs with their differing chlorine content and C-number distribution patterns as found in technical mixtures, as well as compositions in the environment. The calibration requires at least three differently composed standard mixtures.

These standard mixtures mimic different mixtures found in the environment. Only the multiple linear regression quantification with these specific mixtures enables the quantification of the variety of observed mixtures of SCCP in the environment and in technical compositions described in the scope and in Reference [6]. It is not possible to use only one reference mixture for that complex task.

4 Interferences

Non-specific matrix interferences, as well as interferences from other environmental situations, are dealt with using the given clean-up procedure. A further reduction of matrix effects can be achieved by reducing the mass spectrometric resolution to, e.g. 0,4 amu, which is often possible with a quadrupol mass spectrometer. The exact masses are 374,9588; 410,9169; and 422,9355 (see Reference [4]).

Applying the entire procedure, a selection of chlorinated pollutants has been tested and found not to cause interferences below the concentrations given in Table 1.

Table 1 — Highest concentration level which causes no interferences higher than the limit of quantification of 0,03 µg/g

Potential interfering compounds	Highest concentration level which causes no interferences higher tha the limit of quantification of 0,03 µg/g
Aroclor 1262[a]	0,25 µg/g
Aroclor 1242[a]	2 µg/g
Aroclor 1221[a]	2 µg/g
Campheclor (toxaphene)	0,35 µg/g
Halowax 1014[a]	2 µg/g
Halowax 1051[a]	0,08 µg/g
MCCP (medium-chain chlorinated *n*-alkanes) 42 %	2 µg/g
MCCP (medium-chain chlorinated *n*-alkanes) 52 %	1,2 µg/g
MCCP (medium-chain chlorinated *n*-alkanes) 57 %	2 µg/g

[a] Aroclor 1262, Aroclor 1242, Aroclor 1221, Halowax 1014, and Halowax 1051 are products commercially available. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

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.

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

5.1 Solvents for extraction, column chromatography, and preparation of stock solutions.

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

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

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 defined carbon chain length and with different defined chlorine contents (see Table 2, first two columns). Alternatively, use commercially available ready mixed solutions with the same composition.

Mixtures of synthetic solutions were used to simulate environmentally occurring SCCPs or technical products of SCCPs. For example, the synthetic mixed calibration stock solution “Lake Ontario water” is mixed to resemble a Lake Ontario water as reported in Reference [7]. Its characteristic is a relatively high content of C_{10} to C_{12}, especially C_{12} and a low chlorine content as partly reported in water samples too. The synthetic mixed calibration stock solution “Perch” simulates a C-number distribution found in a perch (see Reference [4]). The standard mixture “Sediment Drevnice” simulates a natural mixture reported about a sediment of the river Drevnice (see Reference [5]) with a high content of C_{13} and a higher chlorine content.

The compositions of the calibration mixtures, as well as of the independent quality assurance solutions, are mandatory to achieve the quantification of the variety of SCCP-mixtures. An example for recoveries of quality assurance solutions is given in Annex H.

Prepare the solutions “Lake Ontario water”, “Perch”, and “Sediment Drevnice” according to Table 2.

Table 2 — Reference substances stock solutions

Standard solutions, e.g. in *n*-heptane			Synthetic mixed standard solutions which resemble environmental mixtures		
n-alkane chain length	Chlorine content (%) of the individual C-number mixtures	Mean number of chlorines in the molecules (calculated)	“Lake Ontario water”	“Perch”	“Sediment Drevnice”
Chlorine content calculated (%)			**50,2**	**60,6**	**65,0**
Composition, ng/ml					
C_{10}	44,82	3,22			
C_{10}	50,18	3,97	1 000		
C_{10}	55,00	4,79	1 000		
C_{10}	60,09	5,86		500	
C_{10}	65,02	7,16		1 100	280
C_{11}	45,50	3,63	1 000		
C_{11}	50,21	4,37	1 000		
C_{11}	55,20	5,31		600	
C_{11}	60,53	6,55		1 000	500
C_{11}	65,25	7,94		3 000	660

Table 2 *(continued)*

Standard solutions, e.g. in *n*-heptane			**Synthetic mixed standard solutions which resemble environmental mixtures**		
n-alkane chain length	Chlorine content (%) of the individual C-number mixtures	Mean number of chlorines in the molecules (calculated)	"Lake Ontario water"	"Perch"	"Sediment Drevnice"
Chlorine content calculated (%)			**50,2**	**60,6**	**65,0**
Composition, ng/ml					
C_{12}	45,32	3,93	2 000		
C_{12}	50,18	4,76	2 000	800	
C_{12}	55,00	5,74	2 000	2 000	
C_{12}	65,08	8,59		900	1 000
C_{12}	69,98	10,62			830
C_{13}	44,90	4,19			
C_{13}	50,23	5,16			
C_{13}	55,03	6,22			
C_{13}	59,98	7,56		100	730
C_{13}	65,18	9,34			6 000
Sum of SCCP (ng/ml)			**10 000**	**10 000**	**10 000**

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

Store the prepared solutions in a refrigerator at 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 50 % and 67 % are suitable as internal standards if the mass trace in mass spectrometric detection is not affected by matrix components, e.g. 1,1,1,3,11,13,13,13-octachlorotridecane with e.g. 0,1 µg/ml.

NOTE 1 The different individual SCCP congeners used as internal standard substances probably contribute in environmental samples to the sum of SCCPs. 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 for different concentrations to be used.

The solutions should be stored in a refrigerator at 2 °C to 6 °C.

5.4 Calibration solutions.

Use the standard mixtures according to Table 2. Prepare a minimum of nine calibration solutions (see Table 3) with concentrations according to 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 3.

Table 3 — Calibration solutions

Mixture	"Lake Ontario" water	"Perch"	"Sediment Drevnice"	**Internal standard**
				1,1,1,3,11,13,13,13-octachlorotridecane
	µg/ml	µg/ml	µg/ml	µg/ml
Sum of SCCPs, µg/ml				
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
1	1			0,1
1		1		0,1
1			1	0,1
2	2			0,1
2		2		0,1
2			2	0,1
3	3			0,1
3		3		0,1
3			3	0,1

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

Quality control check solutions can be prepared to check the calibration independently. For that, use the calibration mixtures as given in ISO 12010 (see Annex K). These mixtures are commercially available (e.g. in cyclohexane or *n*-hexane).

5.5 Extraction auxiliary and clean-up materials.

5.5.1 High purity silica sand, grain size 600 µm to 850 µm, free of blanks.

5.5.2 Copper powder, grain size <63 µm.

5.5.3 2 mol/l hydrochloric acid.

5.5.4 Al_2O_3, neutral, high activity, (10 % water).

5.5.5 Glass wool.

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

5.7 Nitrogen, N_2, purity ≥99,996 % volume fraction for concentrating the solutions.

5.8 Sodium sulfate, anhydrous, Na_2SO_4, powdered.

6 Apparatus

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

6.1 Wide-necked bottle, 1 000 ml up to 5 000 ml capacity for wet sediment or sludge.

6.2 Freeze drying apparatus.

6.3 Deep freezer.

6.4 Mortar and pestle or a grinding mill.

6.5 Drying ovens, capable of maintaining temperatures in the ranges of 100 °C to 400 °C for baking and storage of clean-up materials, for baking of glassware, and for dry residue determination of samples.

6.6 Sieve shaker with appropriate sieve meshes (aperture size), e.g. 2 mm.

6.7 Desiccator.

6.8 Pressurized liquid extractor (PLE) and filter suited for the device.

6.9 Evaporation device.

For example, rotary evaporator, turboevaporator, or vacuum concentration device.

6.10 Glass columns for chromatographic clean-up.

6.11 GPC clean-up system (with modular design).

6.11.1 Pump, sampling injector, sample rack, fraction collector.

6.11.2 Column, Shodex CLNpakPAE 800 AC®[1)] 8,0 mm × 300 mm.

6.12 Volumetric cylinders, 250 ml and 500 ml.

6.13 Volumetric flasks, 1 ml, 2 ml, 10 ml, and 25 ml.

6.14 Pasteur pipettes, e.g. 2 ml.

6.15 Syringes, 2 µl, 5 µl, 10 µl, and 50 µl, volume precision ±2 %.

6.16 Sample vials.

Amber glass with fluoropolymer-lined screw-cap is most suitable.

6.17 Gas chromatograph, with a splitless injection port coupled to a mass spectrometer (GC-MS) with chemical ionization and appropriate reactant gas (e.g. CH_4).

1) Shodex CLNpakPAE 800 AC is a product commercially available. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

