SLOVENSKI STANDARD
SIST ISO 24293:2011

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Kakovost vode - Določevanje posameznih izomer nonilfenola - Metoda plinske kromatografije/masne spektrometrije (GC/MS) po ekstrakciji na trdni fazi (SPE)

Water quality - Determination of individual isomers of nonylphenol - Method using solid phase extraction (SPE) and gas chromatography/mass spectrometry (GC/MS)

Qualité de l'eau - Détermination des isomères individuels de nonylphénol - Méthode par extraction en phase solide (SPE) et chromatographie en phase gazeuse/spectrométrie de masse (GC/MS)

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Water quality — Determination of individual isomers of nonylphenol — Method using solid phase extraction (SPE) and gas chromatography/mass spectrometry (GC/MS)

Qualité de l'eau — Détermination des isomères individuels de nonylphénol — Méthode par extraction en phase solide (SPE) et chromatographie en phase gazeuse/spectrométrie de masse (GC/MS)

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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.

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.

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.

ISO 24293 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 could require the specifications of additional marginal conditions.

Water quality — Determination of individual isomers of nonylphenol — Method using solid phase extraction (SPE) and gas chromatography/mass spectrometry (GC/MS)

WARNING — Persons using this International Standard 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.

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

1 Scope

This International Standard specifies a method for the determination of selected individual isomers of nonylphenol in non-filtered samples of drinking water, waste water, ground water and surface water. The method is applicable in concentrations between 0,001 µg/l and 0,1 µg/l for individual isomers and from 0,01 µg/l to 0,2 µg/l for the sum of 4-nonylphenol (mixture of isomers). Depending on the matrix, the method is also applicable to waste water in concentrations between 0,1 µg/l and 50 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 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 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Principle

Extraction of the analytes listed in Table 1 from the acidified water sample by solid phase extraction, solvent elution and determination by gas chromatography with mass spectrometric detection.

The thirteen isomers listed (eleven identified isomers and two isomers with tentative identification) constitute more than 90 % of the 4-nonylphenol isomers that are detectable in technical products and in environmental samples in general. Water samples containing more than 500 mg/l of suspended matter and waste water samples are extracted by passing 100 ml of the sample through the solid phase extraction cartridge (5.2).

Table 1 — Analytes determinable by this method

Analyte	Formula	Abbreviation
4-(2,4-Dimethylheptan-4-yl)phenol	$C_{15}H_{24}O$	NP1
4-(2,4-Dimethylheptan-2-yl)phenol	$C_{15}H_{24}O$	NP2
4-(3,6-Dimethylheptan-3-yl)phenol	$C_{15}H_{24}O$	NP3
4-(3,5-Dimethylheptan-3-yl)phenol	$C_{15}H_{24}O$	NP4[a]
4-(2,5-Dimethylheptan-2-yl)phenol	$C_{15}H_{24}O$	NP5
4-(3,5-Dimethylheptan-3-yl)phenol	$C_{15}H_{24}O$	NP6 [a]
4-(3-Ethyl-2-methylhexan-2-yl)phenol	$C_{15}H_{24}O$	NP7
4-(3,4-Dimethylheptan-4-yl)phenol[b]	$C_{15}H_{24}O$	NP8[c]
4-(3,4-Dimethylheptan-3-yl)phenol	$C_{15}H_{24}O$	NP9[e]
4-(3,4-Dimethylheptan-4-yl)phenol	$C_{15}H_{24}O$	NP10[c]
4-(2,3-Dimethylheptan-2-yl)phenol	$C_{15}H_{24}O$	NP11
4-(3-Methyloctan-3-yl)phenol	$C_{15}H_{24}O$	NP12
4-(3,4-Dimethylheptan-3-yl)phenol[d]	$C_{15}H_{24}O$	NP13[e]

[a] Possible enantiomer.

[b] Information from MAKINO et al. [6]

[c] Possible enantiomer.

[d] Information from KATASE et al. [5]

[e] Possible enantiomer.

4 Reagents

Use reagents with negligible concentrations of the compounds of interest compared with the concentrations to be determined. Verify by blank determinations and, if necessary, apply additional cleaning steps.

4.1 **Water**, grade 1, as specified in ISO 3696.

4.2 **Acid**, e.g. hydrochloric acid, w(HCl) = 37 %, or sulfuric acid, $c(H_2SO_4)$ = 1 mol/l.

4.3 **Acetone**, C_3H_6O.

4.4 **Methanol**, CH_3OH.

4.5 **Hexane**, C_6H_{14}.

4.6 **Sodium sulfate**, anhydrous, Na_2SO_4, powdered.

4.7 Internal standard solution, 4-*n*-Nonylphenol (ring-$^{13}C_6$), C_9H_{19}-$^{13}C_6H_4$-OH solution, $\rho = 1$ ng/µl.

Weigh 10 mg of 4-*n*-nonylphenol in a 100 ml measuring flask and bring to volume with methanol (4.4). Dilute this solution with methanol in the ratio of 1:100. Acetone is not suitable for preparation of standard solution in this method. Alternative internal standards [e.g. 4-*n*-nonylphenol (deuterium label)] may be used if internal standard requirements can be met.

4.8 4-nonylphenol solution, $\rho = 1$ ng/µl (calibration standard).

Weigh 10 mg of 4-nonylphenol, $C_{15}H_{24}O$ (technical mixture of isomers), CAS No 25154-52-3, in a 100 ml measuring flask and bring to volume with hexane (4.5). Dilute this solution in the ratio of 1:100 with hexane if a calibration over the total procedure is applied.

4.9 Solid phase material, on styrene-divinylbenzene polymer basis, e.g. commercially available packing material (see Annex A).

4.10 Nitrogen, N_2, purity $\geqslant$ 99,996 % volume fraction, for drying of the sorbent packing after sample extraction and for concentration of extracts by evaporation.

4.11 Sodium thiosulfate pentahydrate, $Na_2S_2O_3 \cdot 5\ H_2O$.

4.12 Ethyl acetate, $C_4H_8O_2$.

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

4.14 Corresponding internal standard solution for syringe spike, phenanthrene (d_{10}), $C_{14}D_{10}$ solution, CAS No 85-01-8, $\rho = 0{,}1$ ng/µl. Weigh 10 mg of phenanthrene (d_{10}) in a 100 ml measuring flask and bring to volume with hexane (4.5). Dilute this solution with hexane in the ratio of 1:1 000.

5 Apparatus

Equipment or parts which may come into contact with the water sample or the extract should be free from interfering compounds.

Clean all glasswares by rinsing with acetone (4.3). Avoid detergents when using a labware washing machine. Alternatively, heat all glassware, except volumetric wares, to at least 400 °C for at least 2 h prior to use.

5.1 Narrow-neck flat-bottomed glass bottles, conical shoulders, preferably brown glass, of capacity 1 000 ml, with glass stoppers or with PTFE-lined screw caps (PTFE = polytetrafluoroethene).

Keep samples away from light if brown glass bottles are not available. The bottle and cap liner or glass stopper should be rinsed with acetone (4.3) and dried before use in order to minimize contamination.

5.2 Solid phase extraction cartridges, inert non-leaching plastic, e.g. polypropene or glass.

The cartridges should be packed with a minimum of 200 mg of sorbent (4.9). The commercially available disk type may be used provided there is enough information available concerning the sample volume and the required quantity of elution solvent. These cartridges are used for extraction.

5.3 Vacuum or pressure assembly, for the extraction step.

5.4 Volumetric flasks, with inert stopper.

5.5 Quartz wool, rinsed with acetone (4.3).

5.6 Muffle furnace, capable of being maintained at a temperature of 400 °C.

5.7 Evaporation assembly, e.g. rotary evaporator with vacuum stabilizer and water bath.

5.8 Vials, brown glass with PTFE-lined septa, capacity e.g. 1,5 ml, according to the autosampler.

5.9 Gas chromatograph/mass spectrometer. The gas chromatograph shall be temperature-programmable, with all required accessories including gases, capillary columns, capillary injector and mass spectrometric detector.

The mass spectrometer should be capable of operating over the mass range of interest and it should be equipped with a data system capable of quantifying ions using selected *m/z* values.

5.10 Clean up cartridge column, inert non-leaching plastic, e.g. polypropene or glass.

The cartridges should be packed with a minimum of 200 mg of sorbent (reverse phase, silica). These cartridges are used for clean up.

5.11 Flame ionization detector.

6 Sampling and sample pretreatment

Take samples as specified in ISO 5667-1.

Use carefully cleaned bottles for sampling (5.1). Fill each bottle only to its shoulder with water to be sampled (approximately 1 000 ml). In the presence of free chlorine, immediately add approximately 80 mg of sodium thiosulfate pentahydrate (4.11). Other non-interfering substances may be used for dechlorination as well (e.g. sodium sulfite). Acidify the samples with acid (4.2) to pH 3,5.

If necessary, store the samples in a refrigerator (2 °C to 5 °C) and analyse them as soon as possible, but not later than 2 weeks after sampling.

7 Procedures

7.1 Solid phase extraction

7.1.1 General

In general, samples are examined without pretreatment; in other words, suspended solids are not removed prior to analysis. Before starting the analysis, homogenize the samples. If blocking of the cartridge packing is likely to occur, use a filter aid, e.g. quartz wool (5.5).

7.1.2 Conditioning of the solid phase material

The following procedures are described for commercially available 6 ml polypropylene cartridges (5.2) packed with 200 mg of sorbent (4.9) sandwiched between two polyethylene frits. The manufacturer's guidance for other materials of the SPE cartridge shall be preferred.

Rinse the cartridge with two 10 ml aliquots of acetone (4.3) and let the cartridge drain dry after the first rinsing. Before the acetone level of the second aliquot falls below the top edge of the packing, add 10 ml of water (4.1), acidified with acid (4.2) to pH 3,5, to the cartridge, and make sure that the sorbent packing in the cartridge does not run dry. Retain the water in the cartridge (water level just above the packing) to keep the sorbent activated.

7.1.3 Sample extraction

Start the extraction immediately after conditioning. Make sure that no air bubbles are trapped in the sorbent bed when changing from conditioning to extraction. Maintain the sorbent material in the cartridge immersed in water at all times.