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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, $w(\text{HCl}) = 37\ \%$, 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.

Add the internal standard solution (4.7), in a known amount (e.g. 50 µl) dependent on the sample matrix, to the water sample (e.g. 1 000 ml) in the sample bottle and mix thoroughly. Let this sample run through the cartridge, conditioned as specified in 7.1.2, at a flow rate of 5 ml/min to 10 ml/min. Extract samples containing more than 500 mg/l of suspended matter and waste water samples by passing a 100 ml sample through the cartridge. Rinse the cartridge with 10 ml of water (4.1), acidified with acid (4.2) to pH 3,5.

Remove the residual water in the sorbent packing by passing nitrogen through the cartridge at a flow rate of about 500 ml/min for about 1 h.

NOTE Depending on the colour of the moist adsorbent, the end of the removal of water from the cartridge can be recognized by the change of colour of sorbent material. The colour of the moist adsorbent is brown; the dry material is light orange. The end of the removal of water from the cartridge can usually be recognized by brightening of the sorbent packing.

Reweigh the empty sample bottle with its original cap or stopper and calculate the net weight of sample by difference to the nearest 1 g. For an assumed density of 1 g/ml, this net weight (in grams) is equivalent to the volume (in millilitres) of water extracted. The amount of the added volume of acid (4.2) to acidify the sample is negligible.

7.1.4 Elution

Add 1 ml of acetone (4.3) to the completely dried cartridge, allow to equilibrate for e.g. 10 min and elute through the cartridge, followed by adding five 1 ml aliquots of acetone (4.3) to the cartridge, but do not allow the acetone to elute below the top of the sorbent packing during the elution steps.

7.2 Clean up

Concentrate the eluate using a gentle stream of nitrogen to almost dryness. Add 1 ml of hexane (4.5) and transfer all into a clean up cartridge column (5.10). In general, 500 mg of silica in the cartridge requires the following extraction procedure. Wash with 10 ml of ethyl acetate (4.12) and subsequently with 15 ml of hexane. Add the sample and immediately elute with 15 ml of hexane followed by 10 ml of 30 % of diethyl ether (4.13) in hexane.

To confirm elution profiles of 4-nonylphenol, carry out a separation test using 4-nonylphenol for each batch of cartridges before analysis. Evaporate the cleaned extract using the evaporation device, concentrate the extract to a volume of approximately 2 ml and spike 50 µl to 100 µl of corresponding internal standard substance for syringe spike (4.14) into the extract, then subsequently concentrate the extract further to a volume of 50 µl to 100 µl using a gentle flow of nitrogen. Transfer the extract to a suitable vial.

7.3 GC/MS operating conditions

Optimize the operating conditions of the GC/MS system in electron ionization mode in accordance to the manufacturer's instructions. Determine the appropriate GC oven temperature programme experimentally during method development and validation. For the sake of sensitivity, selected ions (Table 2) are detected. An example of operating conditions is given in Annex C.

7.4 Blank determination

Treat the blank in exactly the same way as the sample, but replace the sample by the appropriate amount of pure water (4.1).

7.5 Identification

Identify the sample component by matching both the retention times and relative intensities of the diagnostic ions (Table 2) of sample components and calibration standard (4.8). It is a critical issue to identify individual isomers in order to obtain a similar chromatogram to Annex C that enables accurate identification. Old column material and inadequate temperature control may result in shifting of retention time between isomers. Reliable measurements of the thirteen peaks can be enabled by using isomer-specific single ion monitoring. Because of the absence of all of the fragment ions, 4-*n*-NP is not suitable. Major ions obtained from 4-*n*-NP are 107 and 220; detectable ions are obtained for 121, 135 and 149. It is difficult to use 4-*n*-NP to obtain ions 163 and 191. It is necessary to use a specific pair of ions (target M_1 and qualifier M_2 in Table 2) for the quantification of each resolved peak.

The target compound is present (identified) in the sample if:

- the relative or the absolute sample component retention time measured in the selected ion current chromatogram matches the relative or absolute retention time of the authentic compound within ± 0,2 % (or a maximum of ± 6 s) in the chromatogram of the latest calibration standard, measured under identical conditions;
- the selected diagnostic ions (see Table 2) are present at the substance specific retention time;
- the relative intensities of all selected diagnostic ions measured in the sample do not deviate by more than ± (0,1 Q + 10) % from the relative intensities determined in the external standard solution. (Q is the relative intensity of the diagnostic ion in the external standard solution.)

Table 2 — Selected diagnostic ions for identification and quantification

No	Analyte	Abbreviation	Selected diagnostic ions	
			Target	Qualifier
			M_1 [a]	M_2 [a]
1	4-(2,4-Dimethylheptan-4-yl)phenol	NP1	121	163
2	4-(2,4-Dimethylheptan-2-yl)phenol	NP2	135	220
3	4-(3,6-Dimethylheptan-3-yl)phenol	NP3	135	107 or 121
4	4-(3,5-Dimethylheptan-3-yl)phenol	NP4 [b]	149	191
5	4-(2,5-Dimethylheptan-2-yl)phenol	NP5	135	163
6	4-(3,5-Dimethylheptan-3-yl)phenol	NP6 [b]	149	191
7	4-(3-Ethyl-2-methylhexan-2-yl)phenol	NP7	135	220
8	4-(3,4-Dimethylheptan-4-yl)phenol[c]	NP8[d]	163	121
9	4-(3,4-Dimethylheptan-3-yl)phenol	NP9[f]	149	107
10	4-(3,4-Dimethylheptan-4-yl)phenol	NP10[d]	163	121
11	4-(2,3-Dimethylheptan-2-yl)phenol	NP11	135	220
12	4-(3-Methyloctan-3-yl)phenol	NP12	191	163
13	4-(3,4-Dimethylheptan-3-yl)phenol[e]	NP13[f]	135	107
	4-*n*-Nonylphenol (ring-$^{13}C_6$)	—	113	—

[a] M_1 is used for quantification; M_2 may be used for identification.

[b] Possible enantiomer.

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

[d] Possible enantiomer.

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

[f] Possible enantiomer.