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Water quality — Determination of selected alkylphenols —

Part 2: Gas chromatographic-mass spectrometric determination of alkylphenols, their ethoxylates and bisphenol A in non-filtered samples following solid-phase extraction and derivatisation

Qualité de l'eau — Dosage d'alkylphénols sélectionnés —

Partie 2: Dosage par chromatographie en phase gazeuse-spectrométrie de masse d'alkylphénols, de leurs éthoxylates et de bisphénol A dans des échantillons non filtrés après extraction en phase solide et dérivation

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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 18857-2 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

ISO 18857 consists of the following parts, under the general title *Water quality — Determination of selected alkylphenols*:

— *Part 1: Method for non-filtered samples using liquid-liquid extraction and gas chromatography with mass selective detection*

— *Part 2: Gas chromatographic-mass spectrometric determination of alkylphenols, their ethoxylates and bisphenol A in non-filtered samples following solid-phase extraction and derivatisation*

Introduction

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

Water quality — Determination of selected alkylphenols —

Part 2:
Gas chromatographic-mass spectrometric determination of alkylphenols, their ethoxylates and bisphenol A in non-filtered samples following solid-phase extraction and derivatisation

WARNING — Persons using this part of ISO 18857 should be familiar with normal laboratory practice. This part of ISO 18857 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 part of ISO 18857 be carried out by suitably qualified staff.

1 Scope

This part of ISO 18857 specifies a gas chromatographic-mass spectrometric (GC-MS) determination of selected alkylphenols, their ethoxylates and bisphenol A in non-filtered samples of drinking, ground, surface, and waste waters following solid-phase extraction and derivatisation.

The lower limit of the working range depends on the matrix, on the specific compound to be analysed and on the sensitivity of the mass spectrometric detection unit. The method is applicable in a working range from 0,005 µg/l to 0,2 µg/l for 4-(1,1,3,3-tetramethylbutyl)phenol (OP), and its mono- (OP_1EO) and diethoxylate (OP_2EO), from 0,03 µg/l to 0,2 µg/l for 4-nonylphenol (mixture of isomers) (NP), and its mono- (NP_1EO) and diethoxylate (NP_2EO), and from 0,05 µg/l to 0,2 µg/l for bisphenol A (BPA).

Depending on the matrix, the method is also applicable to waste water in a working range from 0,1 µg/l to 50 µg/l for OP, OP_1EO, OP_2EO and BPA, and from 0,5 µg/l to 50 µg/l for NP, NP_1EO and NP_2EO. The working ranges are based on experimental work carried out in ruggedness testing. Water samples containing suspended matter at concentrations of more than 500 mg/l and waste water samples are extracted by passing a 100 ml sample through the cartridge.

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 5667-3, *Water quality — Sampling — Part 3: Guidance on the 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*

3 Principle

Extraction of the analytes listed in Table 1 from an acidified water sample by solid-phase extraction, solvent elution, derivatisation and determination by GC-MS detection.

Table 1 — Analytes determinable by GC-MS following solid-phase extraction and derivatisation

Analyte	Empirical formula	Abbreviation	CAS[a] No.
4-(1,1,3,3-Tetramethylbutyl)phenol	$C_{14}H_{22}O$	OP	140-66-9
4-(1,1,3,3-Tetramethylbutyl)phenol monoethoxylate	$C_{16}H_{26}O_2$	OP_1EO	—
4-(1,1,3,3-Tetramethylbutyl)phenol diethoxylate	$C_{18}H_{30}O_3$	OP_2EO	—
4-Nonylphenol (mixture of isomers)	$C_{15}H_{24}O$	NP	84852-15-3[b]
4-Nonylphenol monoethoxylate (mixture of isomers)	$C_{17}H_{28}O_2$	NP_1EO	—
4-Nonylphenol diethoxylate (mixture of isomers)	$C_{19}H_{32}O_3$	NP_2EO	—
Bisphenol A	$C_{15}H_{16}O_2$	BPA	80-05-7

[a] CAS: Chemical Abstracts Service.

[b] The commercially produced nonylphenols are predominantly 4-nonylphenol with a varied and undefined degree of branching in the alkyl groups. This mixture of isomers falls under the CAS number 84852-15-3, but CAS numbers 104-40-5 (4-nonylphenol, straight chain) and 25154-52-3 (nonylphenol, straight chain) have also been incorrectly used to denote this isomer mixture.

4 Interferences

4.1 Sampling and extraction

Sampling containers shall consist of materials that do not change the sample when in contact with it. Avoid contact with plastics and other organic materials during sampling, sample storage or extraction.

Commercially available adsorbent materials are often of varying quality. Considerable batch-to-batch differences in quality and selectivity of this material are possible. The recovery of single substances can vary with the concentration. Therefore, check the recovery regularly at different concentrations and whenever new batches are used. Perform calibration and analysis with material from the same batch.

4.2 Gas chromatography-mass spectrometry

Substances with retention times or which produce masses similar to the analytes to be determined can interfere with the determination.

These interferences may lead to incompletely resolved signals and to additional signals in the chromatographic pattern of NP, NP_1EO and NP_2EO. They may, depending on their magnitude, affect accuracy and precision of the analytical results, since all three analytes are determined from the sum of a cluster of eight to ten chromatographic peaks (Table 3 and Annex C). It is important that the interfering peaks are not included in the calculations.

The presence of interfering compounds can, if necessary, be detected by recording full mass spectra (range of mass fragments to monitor m/z = 50 to m/z = 350).

Matrix interferences can be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences varies considerably, depending on the nature of the sample. In drinking water and ground water, matrix interferences usually do not occur.

5 Reagents

The reagents shall not have blank values that would interfere with the GC-MS analysis.

Use solvents and reagents of sufficient purity, i.e. with negligibly low impurities compared with the concentration of analytes to be determined. As reagents, use, as far as available, “residual grade” or better in order to obtain clean blanks. Check blanks regularly and establish proper charge control.

5.1 Water, as specified in ISO 3696, grade 1, or equivalent.

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

5.3 Acetone, C_3H_6O.

5.4 Internal standard solutions.

Examples of suitable internal standards are given in Table 2.

Store solutions 5.4.1 and 5.4.2 in a refrigerator protected from light. Check the solutions weekly prior to use.

Table 2 — Internal standards

No.	Name	Abbreviation	CAS No.
1	4-(1,1,3,3-Tetramethylbutyl)phenol (ring-$^{13}C_6$)	OP-$^{13}C_6$	—
2	4-(1,1,3,3-Tetramethylbutyl)phenol monoethoxylate (ring-$^{13}C_6$)	OP_1EO-$^{13}C_6$	—
3	4-(1,1,3,3-Tetramethylbutyl)phenol diethoxylate (ring-$^{13}C_6$)	OP_2EO-$^{13}C_6$	—
4	4-(3,6-Dimethyl-3-heptyl)phenol (ring-$^{13}C_6$)	363 NP-$^{13}C_6$	—
5	4-(3,6-Dimethyl-3-heptyl)phenol monoethoxylate (ring-$^{13}C_6$)	363 NP_1EO-$^{13}C_6$	—
6	4-(3,6-Dimethyl-3-heptyl)phenol diethoxylate (ring-$^{13}C_6$)	363 NP_2EO-$^{13}C_6$	—
7	Bisphenol A-d16	BPA-d16	96210-87-6

5.4.1 Internal standard stock solution.

Use commercially available internal standard solutions or prepare a solution as follows.

Weigh 10 mg of each internal standard (Table 2) separately in a 100 ml one-mark volumetric flask and make up to the mark with acetone (5.3) to give a concentration of each internal standard of 100 ng/µl.

5.4.2 Internal standard working solution.

Dilute the solution (5.4.1) with acetone (5.3) 1→100 to give a final concentration of each internal standard of 1 ng/µl.

5.5 Solutions of reference standards of the analytes listed in Table 1.

Store solutions 5.5.1 and 5.5.2 in a refrigerator protected from light. Check the solutions weekly prior to use.

5.5.1 Reference standard stock solution.

Use commercially available reference standard solutions or prepare a solution as follows.

Weigh 10 mg of each reference substance separately in a 100 ml volumetric flask and bring to volume with acetone (5.3) to give a concentration of each reference standard of 100 ng/µl.

5.5.2 Reference standard working solution.

Dilute the solution (5.5.1) 1→100 with acetone (5.3) to give a final concentration of each reference substance of 1 ng/µl.

5.6 2,2,2-Trifluoro-*N*-methyl-*N*-(trimethylsilyl)acetamide (MSTFA), $C_6H_{12}F_3NOSi$.

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

5.8 Sand, e.g. sea sand, acid washed and calcinated for analysis, particle size 0,1 mm to 0,3 mm.

5.9 Nitrogen, N_2, purity ⩾ 99,996 % volume fraction, for drying of the sorbent packing after sample extraction and for concentration by evaporation.

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

6 Apparatus

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

Clean all glassware by rinsing with acetone (5.3). Avoid detergents when using a labware washing machine. Alternatively, prior to use, heat all glassware, except volumetric ware, to at least 200 °C for a minimum of 2 h.

Usual laboratory equipment, and in particular the following.

6.1 Narrow-neck flat bottomed glass bottles, conical shoulders, preferably brown glass, 1 000 ml, with glass stoppers or with PTFE-lined screw caps (PTFE = polytetrafluoroethene). Protect samples from light if brown glass bottles are not available. Wash the bottle, cap liner or glass stopper, then rinse with acetone (5.3), and dry before use in order to minimise contamination.

6.2 Solid-phase extraction cartridges, of inert non-leaching plastic, e.g. polypropene, or glass. The cartridges should be packed with a minimum of 200 mg of sorbent (5.7).

6.3 Vacuum or pressure assembly, for the extraction step.

6.4 One-mark volumetric flasks, ISO 1042[1] class A, with inert stoppers.

6.5 Quartz wool, rinsed with acetone.

6.6 Pear-shaped flask, 10 ml, with inert stopper.

6.7 Evaporation assembly, e.g. rotary evaporator with vacuum stabiliser and water bath.

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

6.9 Stainless steel cocks, with stainless steel cone.

6.10 Gas chromatograph, temperature-programmable and with all required accessories including gases, capillary columns, capillary injector and mass spectrometer detector. The mass spectrometer should be capable of operating in electron impact mode over the mass range of interest and incorporate a data system capable of quantifying ions using selected m/z values (selected ion monitoring).

7 Sampling and sample pretreatment

Take samples as specified in ISO 5667-1 and ISO 5667-3.

For sampling, use carefully cleaned bottles (6.1). Fill bottles only to the shoulder, in which case the sample volume is approximately 1 l. This volume is completely used for extraction (8.1). If the presence of free chlorine is suspected, immediately add approximately 80 mg of sodium thiosulfate (5.10). Other non-interfering substances may be used for dechlorination as well (e.g. sodium sulfite). Acidify the sample with acid (5.2) to pH (2 ± 0,2).

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

Weigh the sample bottle with its contents to the nearest 1 g and record the mass for subsequent sample volume determination (8.1.2).

8 Procedure

8.1 Solid-phase extraction

In general, samples are examined without pretreatment, which means that suspended solids are not removed prior to analysis. Before starting the analysis, homogenise the sample. In cases where blocking of the cartridge packing is likely to occur, use some filter aid, e.g. quartz wool (6.5) or sand (5.8) e.g. 0,5 cm bed thickness.

8.1.1 Conditioning of the solid-phase material

The following procedure is described for commercially available 6 ml polypropene cartridges packed with 200 mg of sorbent sandwiched between two polyethene frits.

Rinse the cartridge with two 10 ml aliquots of acetone (5.3). Allow the first aliquot to drain from the cartridge. Before the acetone level of the second aliquot falls below the top edge of the packing, add 10 ml of water (5.1), acidified with acid (5.2) to pH (2 ± 0,2), to the cartridge, and make sure that the sorbent packing in the cartridge does not run dry, e.g. by using a stainless steel cock (6.9). Retain the water in the cartridge (water level just above the packing) to keep the sorbent activated.

8.1.2 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 mixture (5.4.2) well below the surface of the water sample (Clause 7) in the sample bottle [50 µl to 200 µl of the prepared mixture (5.4) dependent on the sample matrix] and mix thoroughly. Allow this sample to run through the cartridge (8.1.1) at a flow rate between 5 ml/min and 10 ml/min. Water samples containing suspended matter at a concentration of more than 500 mg/l and waste water samples are extracted by passing a 100 ml sample through the cartridge. Rinse the cartridge with 10 ml of water (5.1), acidified with acid (5.2) to pH (2 ± 0,2).

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