INTERNATIONAL STANDARD

ISO 18857-1

First edition
2005-01-15

Water quality — Determination of selected alkylphenols —

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

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

Partie 1: Méthode pour échantillons non filtrés par extraction en phase liquide-liquide et chromatographie en phase gazeuse avec détection sélective de masse

Reference number
ISO 18857-1:2005(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

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 18857-1 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: Method for filtered samples using solid phase extraction and gas chromatography with mass selective detection*

Water quality — Determination of selected alkylphenols —

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

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 with this part of ISO 18857 be carried out by suitably qualified staff.

1 Scope

This part of ISO 18857 specifies a method for the determination of 4-nonylphenol (mixture of isomers) and 4-(1,1,3,3-tetramethylbutyl)phenol in non-filtered samples of drinking water, ground water and surface water. The method is applicable in a concentration range from 0,005 µg/l to 0,2 µg/l for 4-(1,1,3,3-tetramethylbutyl)phenol and from 0,02 µg/l to 0,2 µg/l for 4-nonylphenol (mixture of isomers). Depending on the matrix, the method is also applicable to waste water containing the analyzed compounds in the concentration range from 0,1 µg/l to 50 µg/l. Higher concentrations can be measured after appropriate dilution of the sample.

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 reference document (including any amendments) applies.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

3 Principle

The compounds 4-(1,1,3,3-tetramethylbutyl)phenol and 4-nonylphenol (mixture of isomers) are extracted from the acidified water sample with toluene. The extract is cleaned, if necessary, with silica and the alkylphenols are separated by gas chromatography using capillary columns. The alkylphenols are identified by mass spectrometry and quantified using an internal standard over the total procedure. The response factor using 4-(1,1,3,3-tetramethylbutyl)phenol and a technical mixture of isomers of 4-nonylphenol is determined daily.

4 Interferences

The extent and the importance of interferences are sample-dependent.

There are many sources of sample contamination, including contamination of reagents during storage, contamination of equipment reused in the sequential extraction of samples and standards and carryover contamination from the septum seal on a sample bottle or vial and GC septa. Organic polymers can form alkyl phenols thus leading to elevated values. Avoid direct contact with plastics material as these can contain alkylphenols that can contaminate the sample.

5 Reagents

Use reagents with negligibly low concentrations of target alkyl phenols compared with the concentration to be determined and verify by blank determinations.

5.1 Water, grade 1, as specified in ISO 3696:1987.

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

5.3 Silica, medium pore size 6 nm (60 Å), grain-size 0,063 mm to 0,2 mm (230 mesh to 70 mesh).

Purify about 100 g of silica in a quartz beaker (6.5) by heating to 550 °C ± 20 °C in a muffle furnace (6.6) for at least 10 h. Let the silica cool to about 100 °C and transfer it to a wide-necked glass bottle. Let it cool to room temperature in a desiccator. Add water (5.1) to the silica to produce a concentration of about 3 % mass fraction. Homogenize on a shaking device for 2 h. Store tightly sealed.

5.4 Hexane, C_6H_{14}.

5.5 Toluene, C_7H_8.

Other extracting solvents may be used if equivalent recoveries can be achieved (see Annex C).

5.6 Sodium sulfate, Na_2SO_4, anhydrous, powdered.

5.7 Acetone, C_3H_6O.

5.8 4-*n*-nonylphenol(ring-$^{13}C_6$) solution, C_9H_{19}-[$^{13}C_6$]H_4-OH, 1 ng/µl, used as an internal standard.

Weigh 10 mg of 4-*n*-nonylphenol(ring-$^{13}C_6$) in a 100 ml measuring flask and bring to volume with acetone (5.7). Dilute this solution with acetone (5.7) in the ratio 1:100.

Alternative internal standards (e.g. 4-*n*-nonylphenol) that meet the internal standard requirements are acceptable. An internal standard should have the following characteristics: It should be stable and should not interfere with the analyte. It should be as similar in structure to the analyte as possible, to ensure that it will show the same properties relative to, for example, adsorption on glass surfaces, extraction, concentration as the analyte. It should not be present in the sample matrix.

5.9 4-nonylphenol solution, 1 ng/µl, used as a calibration standard.

Weigh 10 mg of 4-nonylphenol, $C_{15}H_{24}O$ (technical mixture of isomers), CAS No 84852-15-3, in a 100 ml measuring flask and bring to volume with toluene (5.5). Dilute this solution in the ratio 1:100 with toluene (5.5) or acetone (5.7) if a calibration over the total procedure (9.3, 9.4) is applied.

5.10 4-(1,1,3,3-tetramethylbutyl)phenol solution, 1 ng/µl, used as a calibration standard.

Weigh 10 mg of 4-(1,1,3,3-tetramethylbutyl)phenol, $C_{14}H_{22}O$, CAS No 140-66-9, in a 100 ml measuring flask and bring to volume with toluene (5.5). Dilute this solution in the ratio 1:100 with toluene (5.5) or acetone (5.7) if a calibration over the total procedure (9.3, 9.4) is applied.

Store solutions 5.8, 5.9 and 5.10 in the refrigerator protected from light. Check the solutions weekly prior to use.

NOTE The solutions 5.8, 5.9 and 5.10 are commercially available.

5.11 Nitrogen, N_2, purity $\geqslant$ 99,996 %.

6 Apparatus

Clean all glassware by rinsing with acetone (5.7). Avoid detergents when using a labware-washing machine. Alternatively, prior to use, heat all glassware, except volumetric ware, to at least 250 °C for a minimum of 2 h.

The given volumes are chosen corresponding to the described extraction volume of 1 000 ml. Smaller volumes are possible.

Usual laboratory equipment, and the following.

6.1 Shaking device.

6.2 Flat-bottomed glass bottles, 1 000 ml, preferably of brown glass, with straight shoulders and a glass stopper or polytetrafluoroethene- (PTFE-) lined screw cap.

The sampling bottle shall allow direct extraction from the bottle.

6.3 Quartz wool, rinsed with hexane (5.4).

6.4 Clean up column, inner diameter 8 mm, length 120 mm, with glass or PTFE stopcocks.

6.5 Quartz beaker, 100 ml.

6.6 Muffle furnace, capable of maintaining a temperature of at least 600 °C.

6.7 Evaporation device, **rotary evaporator**, **turbo-evaporator** or **vacuum concentration device**.

6.8 Separator, for an example see Annex D, or another suitable device for phase separation.

6.9 Drying column, chromatographic column, length 600 mm, inner diameter 30 mm (or other convenient size), with coarse frit filter disk.

6.10 Tapered flask, 100 ml.

6.11 Vials, of brown glass, with a capacity of, for example 1,5 ml, compatible with the autosampler.

6.12 Gas chromatograph, temperature-programmable, with all required accessories, including gases, capillary columns, capillary injector and mass spectrometric detector.

The mass spectrometer should be capable of operating across the mass range of interest and incorporate a data system capable of quantifying ions using selected m/z values.

7 Sampling and sample pretreatment

Take samples in accordance with ISO 5667-1, ISO 5667-2 and ISO 5667-3.

For sampling, use bottles (6.2), and acidify the sample with acid (5.2) to pH 2.

Do not fill the sample bottles completely (e.g. fill them to the shoulder) in order to allow the addition of the extracting agent.

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

Carry out the extraction directly from the sampling bottle. Weigh the sample bottle with its contents to the nearest 1 g and record the mass for subsequent sample volume determination (8.1).

8 Procedure

8.1 Extraction and concentration

Add 100 µl to 1 000 µl of the internal standard (5.8) to 1 000 ml of the sample in the original sample bottle.

Choose the volume of the internal standard according to the matrix-dependent extraction end volume which may vary between 100 µl and 1 000 µl. The concentration should be approximately in the middle range of the calibration, e.g. 20 ng/l for ground and surface water or 500 ng/l for wastewater.

Add 40 ml of toluene (5.5) and extract for at least 4 h using the shaking device (6.1). Make sure that the phases are well mixed.

Let the phases separate and use a separator (6.8) to collect the toluene extract.

If an emulsion forms, break the emulsion by centrifuging the extract and/or by adding sodium sulfate.

Fill the drying column (6.9) with 1 cm to 2 cm with sodium sulfate (5.6) and clean it with 10 ml of toluene (5.5); discard this toluene portion.

Subsequently let the toluene extract run through the frit into a 100 ml tapered flask (6.10).

Rinse the frit with 10 ml of toluene (5.5) and add this toluene portion to the extract.

Evaporate the extract to about 2 ml using an evaporation device (6.7).

Using a gentle nitrogen (5.11) stream, carefully evaporate, at a temperature of < 40 °C, to 50 µl to 100 µl.

If necessary, e.g. in the case of wastewater and polluted surface water, continue with the clean-up as described in 8.2.

If a clean up is not necessary, transfer the extract to a vial, rinse using a glass pipette and evaporate the extract to a suitable volume (in general, 100 µl to 500 µl) using nitrogen (5.11).

Discard the sample water and leave the empty bottle to drain for 5 min. Reweigh the empty sample bottle with the original cap and calculate the net weight of sample by difference to the nearest 1 g. This net weight (in grams) is equivalent to the volume (in millilitres) of water extracted. The volume of acid (5.2) added to acidify the sample is negligible.

8.2 Clean-up

8.2.1 Preparation of the clean up column

Fill the clean-up column (6.4), with the following, in the given sequence, and avoid trapping of air:

— quartz wool (6.3), about 0,5 cm;

— sodium sulfate (5.6), about 0,5 cm;

— prepared slurry of 2 g of silica (5.3) with hexane (5.4).

Condition the column with 5 ml of hexane (5.4).

8.2.2 Clean-up procedure

Dilute the extract with 1 ml of hexane (5.4) and transfer to the clean-up column.

Let the extract run through the column until the level of the extract is just above the layer of silica and then add 10 ml of hexane (5.4) and let it run through.

Elute the target compounds with 20 ml of toluene (5.5).

The toluene and hexane phases are clearly distinguishable.

Discard the hexane phase. As soon as the phase line is slightly above the stopcock, change the flask to collect the toluene extract.

Evaporate the toluene extract using the evaporation device (6.7), concentrate the extract to a volume of approximately 2 ml and subsequently concentrate the extract further to a volume of 50 µl to 100 µl using a gentle flow of nitrogen (5.11).

Transfer the extract to a suitable vial (6.11).

8.3 GC/MS operating conditions

Optimize the operating conditions of the GC-MS system in the electron-ionization mode in accordance with the manufacturer's instructions. The appropriate GC-oven-temperature programme is determined experimentally during method development and validation. For the sake of sensitivity, the ions listed in Table 1 are detected. The electron energy is set at 70 eV. An example of operating conditions is given in Annex B.

8.4 Blank determination

Treat the blank in exactly the same way as the sample, but replace the sample by the appropriate amount of pure water (5.1).

8.5 Identification

Identify the sample component by matching both retention times and relative intensities of the diagnostic ions of sample components and alkylphenol standards.

The target compound is present (e.g. is 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 ± 1 % (or a maximum of ± 6 s) in the chromatogram of the latest calibration standard, measured under identical conditions;

— the two diagnostic ions selected, *m/z* 135 and 107 (see Table 1), are present at the substance-specific retention time; and

— the pattern of 4-nonylphenol in the sample chromatogram is to a wide extent in agreement with the pattern of 4-nonylphenol (5.9) used as calibration standard, measured under identical conditions (to indicate the presence of the technical product 4-nonylphenol).

NOTE The external standard 4-nonylphenol used is a technical product. Therefore, the mass spectrogram shows an isomer pattern that usually consists of 8 to 10 main peaks (see Annex B). The isomer pattern may differ from batch to batch. Due to the different composition of the technical product, a fixed ratio of the relative intensities of the diagnostic ions selected, *m/z* 135 and 107, is not obtained for the whole peak pattern.

Table 1 — Diagnostic ions selected for identification and quantification

Substance	Ions
4-nonylphenol (mixture of isomers)	135, 107
4-(1,1,3,3-tetramethylbutyl)phenol	135, 107
4-*n*-nonylphenol(ring-$^{13}C_6$)	113

9 Calibration

9.1 General requirements

For practical reasons, the calibration is based on a solution containing 4-nonylphenol (mixture of isomers) and 4-(1,1,3,3-tetramethylbutyl)phenol.

Ensure there is a linear dependence between signal and concentration.

Determine the linear working range using at least five measurements at different concentrations (see ISO 8466-1).

The calibration function for a substance is valid only within the measured concentration range. Additionally, the calibration function depends on the condition of the gas chromatograph and shall be checked regularly. For routine analysis, a check of the calibration function by measurement of two points is sufficient.

There are three different possibilities to set up the calibration function:

— calibration of the GC-MS step only (not the total procedure) with an external standard; see 9.2;

— calibration of the total procedure with an external standard (including the extraction, concentration, clean-up and GC-MS steps); see 9.3;

— calibration of the total procedure with an internal standard (including the extraction, concentration, clean-up and GC-MS steps); see 9.4.

The first two possibilities serve to estimate the recovery. For routine analysis, only the calibration of the total procedure with an internal standard shall be applied.

Table 2 gives an explanation of the subscripts used in the equations and in the following text.

Table 2 — Explanation of subscripts

Subscript	Meaning
i	identity of the substance
e	calibration step
I	identity of internal standard
g	overall procedure

9.2 Calibration of the GC-MS step only (not the total procedure) with an external standard

For both alkylphenols establish a calibration function from at least five points.

Knowledge of the retention times of the respective single substances is a prerequisite. These are evaluated with the aid of the solutions of the single substances.

Establish the calibration function by injecting the calibration solutions. For a calibration range of 0,005 µg/l to 0,2 µg/l, example mass concentrations are given in Table 3.

Table 3 — Examples for reference solutions

Aliquot of the diluted stock solution (1 ng/µl)	Absolute mass	Corresponding to a mass concentration (for 1 l of reference solution)
µl	µg	µg/l
5	0,005	0,005
10	0,01	0,01
20	0,02	0,02
50	0,05	0,05
75	0,075	0,075
100	0,1	0,1
200	0,2	0,2

The injection volume in the calibration step and in the measurement shall be the same.

For a graphic presentation of the calibration curve, plot the respective measured values, $y_{i\mathrm{e}}$, on the ordinate against the respective mass concentrations, $\rho_{i\mathrm{e}}$, of the substance, i, on the abscissa.

The series of measured values thus obtained shall be used to establish the linear regression function in accordance with Equation (1):

$$y_{i\mathrm{e}} = a_i \times \rho_{i\mathrm{e}} + b_i \tag{1}$$

where

$y_{i\mathrm{e}}$ is the dependent variable corresponding to the measured response, expressed in units dependant on the analytical method, e.g. area value, for a given $\rho_{i\mathrm{e}}$ of substance i;

$\rho_{i\mathrm{e}}$ is the independent variable corresponding to the mass concentration, expressed in micrograms per litre, of substance i, the external standard, in the working standard solution;

a_i is the slope of the calibration function for substance i, expressed in unit dependent on the analytical method, e.g. area value, times the reciprocal of the concentration, expressed in litres per microgram;

b_i is the ordinate intercept of the calibration curve, expressed in units dependent on the analytical method, e.g. area value.

9.3 Calibration of the total procedure with an external standard

To calibrate the entire procedure, add aliquots of each calibration solution (5.9 and 5.10) to 1 000 ml of water (5.1).

Treat and analyse the solution as given in Clause 8.

Set up a calibration curve, as specified in 9.2, using the values $y_{i\text{eg}}$ and $\rho_{i\text{eg}}$, in accordance with Equation (2):

$$y_{i\text{eg}} = a_{i\text{g}} \times \rho_{i\text{eg}} + b_{i\text{g}} \quad (2)$$

where

$y_{i\text{eg}}$ is the dependent variable corresponding to the measured response, expressed in units dependent on the analytical method, e.g. area value, for a given $\rho_{i\text{eg}}$ of substance i during calibration;

$\rho_{i\text{eg}}$ is the independent variable corresponding to the mass concentration, expressed in units of micrograms per litre, of substance i in the spiked aqueous standard solution;

$a_{i\text{g}}$ is the slope of the calibration curve for substance i, expressed in units dependent on the analytical method, e.g. area value times the reciprocal of the concentration, expressed in litres per microgram;

$b_{i\text{g}}$ is the ordinate intercept of the calibration curve, expressed in units dependent on the analytical method, e.g. area values.

9.4 Calibration of the total procedure with an internal standard

When using the internal standard (5.8), the determination of the concentration is independent of possible errors made during injection. Apart from this, errors caused by sample losses during individual steps of sample pretreatment or the difficult adjustment for a low sample volume can be avoided. Additionally, the concentration determination is independent of matrix effects in the sample, provided the recoveries of the substances analysed and the internal standard are approximately the same.

Prior to analysis, add the internal standard (5.8), in a known amount dependent on the sample matrix (8.1), to the water sample. The mass concentration ρ_I shall be the same for calibration and sample measurement.

For calibration over the total procedure, add aliquots of calibration solutions (5.9 and 5.10) and the internal standard (5.8) ρ_I always in the same concentration to each of 1 000 ml of water (5.1).

Pretreat and analyse the samples as specified in Clause 8.

Use the same solvent composition and internal standard concentration for the working standard solutions and the extracts.

Plot the values of the ratio $y_{i\text{eg}}/y_{I\text{eg}}$ (as peak areas, peaks heights or integration units) for each substance i on the ordinate and the associated ratio of the mass concentrations $\rho_{i\text{eg}}/\rho_{I\text{eg}}$ on the abscissa.

Establish the linear regression function using the corresponding pairs of values $y_{i\text{eg}}/y_{I\text{eg}}$ and $\rho_{i\text{eg}}/\rho_{I\text{eg}}$ of the measured series in accordance with Equation (3):

$$\frac{y_{i\text{eg}}}{y_{I\text{eg}}} = a_{i\text{g}I} \frac{\rho_{i\text{eg}}}{\rho_{I\text{eg}}} + b_{i\text{g}I} \quad (3)$$

where

$y_{i\text{eg}}$ is the dependent variable corresponding to the measured response, expressed in units depending on the analytical method, e.g. area value, for a given $\rho_{i\text{eg}}$ of substance i in the calibration;

$y_{I\text{eg}}$ is the dependent variable corresponding to the measured response, expressed in units depending on the analytical method, e.g. area value, for a given $\rho_{I\text{eg}}$ of the internal standard I in the calibration;

$\rho_{i\text{eg}}$ is the independent variable corresponding to the mass concentration, expressed in micrograms per litre, of substance i in the calibration solution;

$\rho_{I\text{eg}}$ is the independent variable corresponding to the mass concentration, in micrograms per litre, of the internal standard I;

$a_{i\text{g}I}$ is the slope of the calibration curve from $y_{i\text{eg}}/y_{I\text{eg}}$ as a function of the mass concentration ratio $\rho_{i\text{eg}}/_{I\text{eg}}$, often called the response factor;

$b_{i\text{g}I}$ is the ordinate intercept of the calibration.

9.5 Determination of procedural recovery values

Reliable recovery data are obtained from the analysis of water and spiked control water samples (5.1) at different concentrations, equidistantly spread over the working range. From these individual results a mean specific recovery, $\overline{A}_i$, is calculated.

Add to 1 000 ml of water (5.1) an aliquot of each of the respective calibration solutions (5.9 and 5.10) and proceed in the same way as described for a natural sample.

a) Using the calibration function in 9.2, calculate the individual mass concentration, $\rho_{i,\text{f}n\text{d}}$, for each concentration for each substance i.

b) Calculate the individual recovery, $A_{i,n}$, in accordance with Equation (4).

$$A_{i,n} = \frac{\rho_{i,\text{f}n\text{d}}}{\rho_{i,n\text{nom}}} \cdot f \tag{4}$$

where

$\rho_{i,\text{f}n\text{d}}$ is the recovered mass concentration, in micrograms per litre, of substance i at concentration n, determined in accordance with Equation (1);

$\rho_{i,n\text{nom}}$ is the original mass concentration, in micrograms per litre, of substance i at concentration n;

f is the conversion factor, in this case f = 100.

The recovery $A_{i,n}$ shall be between 50 % and 120 %, otherwise the analysis shall be repeated or improved.

Use these individual results to calculate the mean recovery, $\overline{A}_i$, in accordance with Equation (5).

$$\overline{A}_i = \frac{\sum_{n=1}^{N} A_{i,n}}{N} \tag{5}$$

where

n is the sequence number of the analysis of the individual value $A_{i,n}$;

$A_{i,n}$ is the recovery of the nth analysis of substance i;

$\overline{A}_i$ is the mean recovery, in percent, of substance i;

N is the total number of individual measurement values A_i.

With the ratio of mass to phase material as specified in Clause 8, high recoveries are usually achieved. Low or unstable recoveries indicate matrix effects or difficulties during extraction.

10 Calculation

10.1 Calculation of single results (not over the total procedure) after calibration with external standard

Calculate the mass concentration, ρ_i, of the substance i in accordance with Equation (6).

$$\rho_i = \frac{(y_i - b_i)V_\mathrm{o}}{a_i \cdot V_\mathrm{p} \cdot \overline{A}_i} f \tag{6}$$

where

ρ_i is the mass concentration, in micrograms per litre, of substance i in the water sample;

y_i is the measured value, for example, area value of substance i in the sample;

a_i, b_i see Equation (1);

V_o is the volume, expressed in millilitres, of the measured extract;

$\overline{A}_i$ see Equation (5);

f conversion factor, in this case f = 100;

V_p is the sample volume, in millilitres.

10.2 Calculation of single results after calibration with external standard over the total procedure

Calculate the mass concentration, $\rho_{i\mathrm{g}}$, of the substance i in the water sample in accordance with Equation (7):

$$\rho_{i\mathrm{g}} = \frac{y_{i\mathrm{g}} - b_{i\mathrm{g}}}{a_{i\mathrm{g}}} \tag{7}$$

where

$y_{i\mathrm{g}}$ is the measured value, for example, area value, of the substance i in the extract of the water sample;

$a_{i\mathrm{g}}$,$b_{i\mathrm{g}}$ see Equation (2).

10.3 Calculation of single results after calibration with internal standard over the total procedure

Calculate the mass concentration, $\rho_{i\mathrm{g}}$, of the substance in accordance with Equation (8) after solving Equation (3).

$$\rho_{i\mathrm{g}} = \frac{\dfrac{y_{i\mathrm{g}}}{y_{I\mathrm{g}}} - b_{i\mathrm{g}I}}{a_{i\mathrm{g}I}} \cdot \rho_{I\mathrm{g}} \tag{8}$$

where

y_{ig} is the measured value, for example area value, of substance i in the water sample;

y_{Ig} is the measured value, expressed in units depending on the analytical method, e.g. area value, of the internal standard I in the water sample;

ρ_{ig} is the mass concentration, in micrograms per litre, of the substance i in the water sample;

ρ_{Ig} is the mass concentration, in micrograms per litre of the internal standard I;

b_{igI} see Equation (3);

a_{igI} see Equation (3).

11 Expression of results

For drinking water and surface water, report the results in nanograms per litre to two significant figures. For waste water, report the results in micrograms per litre as follows:

— $<$ 1 µg/l: one significant figure;

— $\geqslant$ 1 µg/l: two significant figures (at most).

12 Test report

The report shall refer to this part of ISO 18857. The documentation shall contain the following:

a) identity of the sample;

b) sample storage and pretreatment;

c) complete description of the procedure;

d) identification and quantification of single components;

e) expression of results in accordance with Clause 11;

f) any deviation from this procedure and all circumstances that may have influenced the result.

Annex A
(informative)

Suitable capillary columns

DB-1701[1)]**:** (14 %-cyanopropyl-phenyl)-methylpolysiloxane phase, low-/mid-polarity, bonded and cross-linked, low bleed

DB–5[1)]**:** (5 %-phenyl)-methylpolysiloxane phase, non-polar, bonded and cross-linked, low bleed

HP-Ultra1[1)]**:** 100 % dimethylpolysiloxane phase, non-polar, bonded and cross-linked, low bleed

1) DB-1701, DB–5 and HP-Ultra1 are examples of suitable products available commercially. This information is given for the convenience of users of this part of ISO 18857 and do not constitute an endorsement by ISO of these products.

Annex B
(informative)

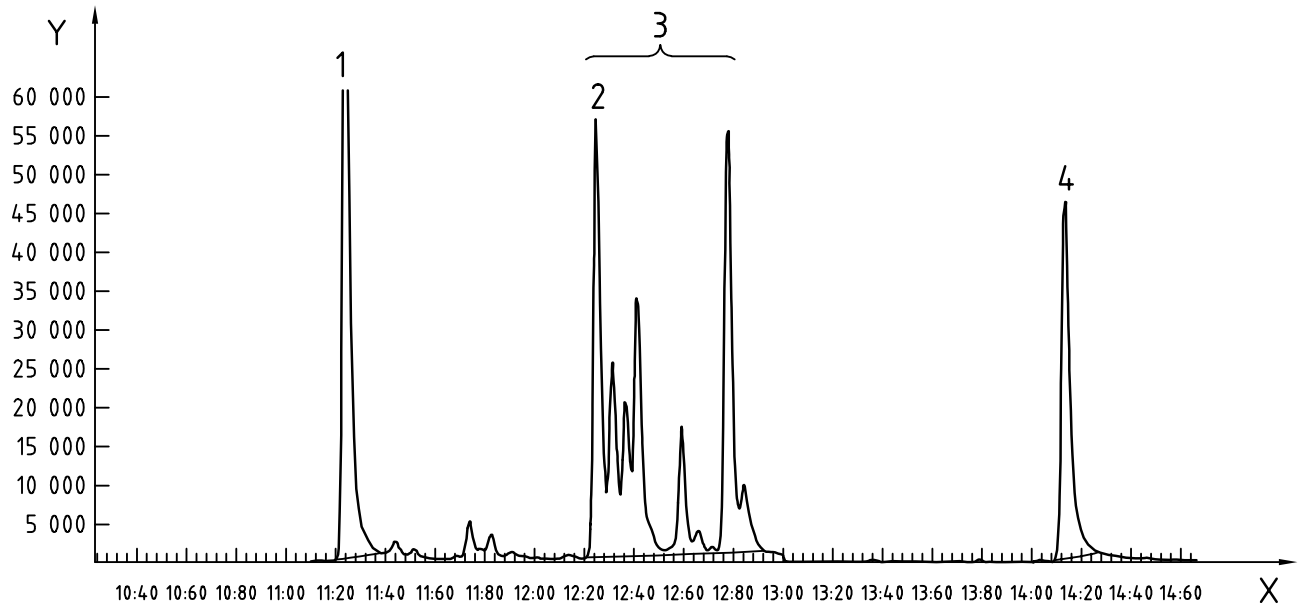
Examples of chromatograms

GC conditions for Figures B.1 and B.2

injection:	splitless	
injector temperature:	250 °C	
injection volume:	1 µl to 2 µl	
transfer line temperature:	280 °C	
flow rate:	1 ml/min to 1,5 ml/min	
carrier gas:	helium, pre-pressure 69 kPa (10 psi)	
capillary column:	stationary phase:	DB-5
	length:	30 m
	inner diameter:	0,25 mm
	film thickness:	0,25 µm
temperature programme	at 100 °C for 1 min; then to 200 °C at 10 °C/min; then to 250 °C at 7 °C/min; then at 250 °C for 10 min	

MS conditions for Figures B.1 and B.2

type:	quadrupole	
ionization:	EI 70 eV	
mode:	SIM	
temperatures:	MS source:	230 °C
	MS quadrupole:	150 °C



Key

X Time

Y Abundance

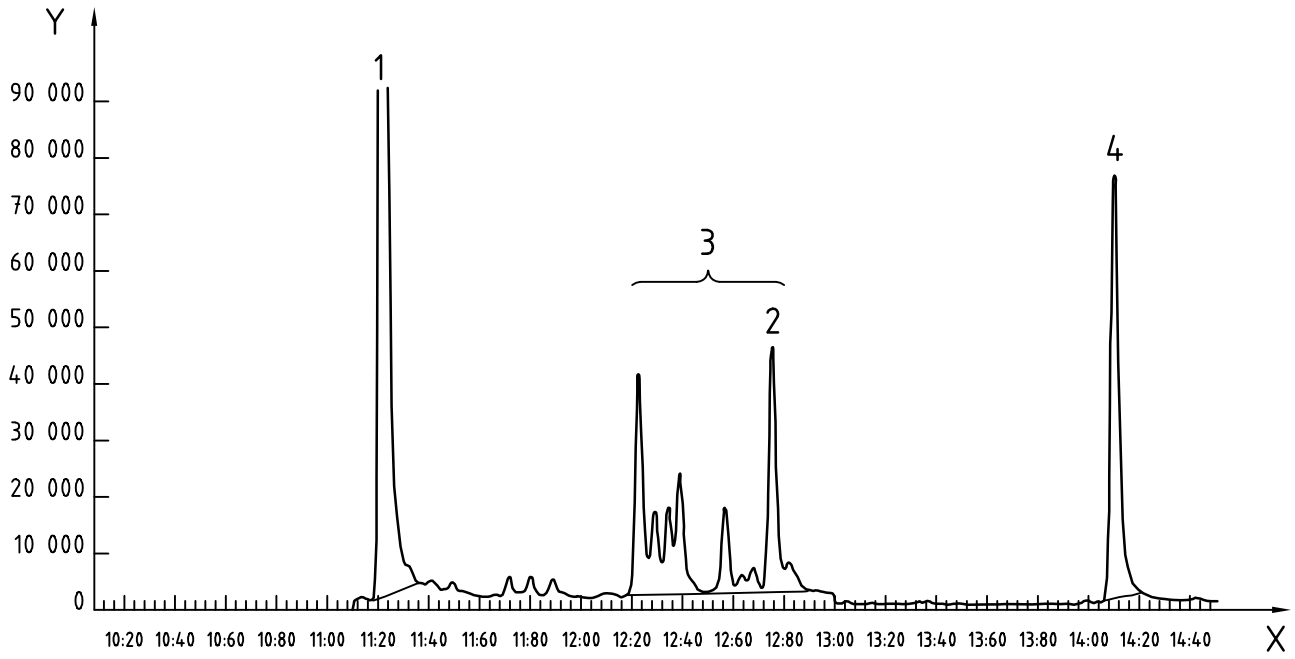
1 4-(1,1,3,3-tetramethylbutyl)-phenol;11:24

2 12:25

3 mixture of isomers of 4-nonylphenol; ion 135.00 (134.70 to 135.30); ion 113.00 (112.70 to 113.30);

4 internal standard; 14:15

Figure B.1 — Chromatogram of a standard solution in toluene (selected-ion mode)



Key

X Time

Y Abundance

1 4-(1,1,3,3-tetramethylbutyl)-phenol;11:22

2 12:76

3 mixture of isomers of 4-nonylphenol; ion 135.00 (134.70 to 135.30); ion 113.00 (112.70 to 113.30);

4 internal standard; 14:13

Figure B.2 — Chromatogram of a river water extract in toluene (selected ion mode)

Annex C
(informative)

Recovery tests — 4-nonylphenol (mixture of isomers)

Table C.1

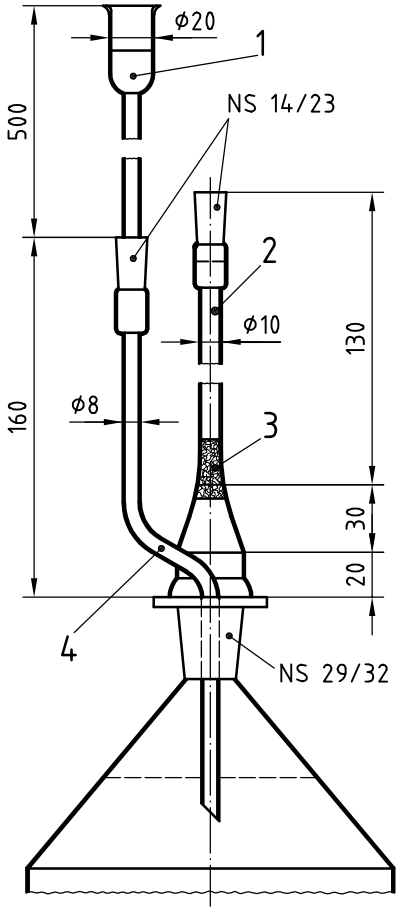
Extracting solvent	Recovery[a] %
hexane	64
cyclohexane	39
tert-butylmethyl ether	49
toluene	87
ethyl acetate	no phase separation

[a] Based on a single analysis using an analyte concentration of 0,5 µg/l.

Annex D
(informative)

Example of a separator

Dimensions in millimetres



Key

1 top, for pressure optimization
2 toluene extract
3 glass wool
4 water

Figure D.1 — Example of a separator

Annex E
(informative)

Method performance data

An interlaboratory trial carried out in March/April 2002 yielded the results given in Table E.1.

Table E.1 — Method performance data [a]

Sample	Matrix	Analyte	Parameter [b]									
			l	n	n_{AP}	$\bar{\bar{x}}$	x_{ref}	η	s_R	CV_R	s_r	CV_r
					%	µg/l	µg/l	%	µg/l	%	µg/l	%
alkyl 1	surface water	4-(1,1,3,3-tetramethyl-butyl)-phenol	13	26	7,1	0,016 6	0,019	87,3	0,004 16	25,1	0,001 96	11,8
		4-nonylphenol (mixture of isomers)	11 —	22 —	15,4 —	0,028 7 —	0,023 —	124,9 —	0,016 44 —	57,2 —	0,004 09 —	14,2 —
alkyl 2	surface water	4-(1,1,3,3-tetramethyl-butyl)-phenol	13	26	13,3	0,066 8	0,075	89,0	0,017 89	26,8	0,003 59	5,4
		4-nonylphenol (mixture of isomers)	11 —	22 —	26,7 —	0,082 8 —	0,090 —	92,0 —	0,015 59 —	18,8 —	0,006 24 —	7,5 —
alkyl 3	waste water	4-(1,1,3,3-tetramethyl-butyl)-phenol	15	30	0,0	1,40	1,40	100,1	0,449	32,0	0,132	9,4
		4-nonylphenol (mixture of isomers)	15 —	30 —	6,3 —	2,02 —	1,80 —	112,2 —	0,635 —	31,5 —	0,164 —	8,1 —

[a] The results of the interlaboratory trial show a high reproducibility variation coefficient of 57,2 % for the lowest tested concentration level (0,023 µg/l) for 4-nonylphenol (mixture of isomers).

Possible reasons are the following:

The tested concentration was near the limit of determination. Technical 4-nonylphenol is a complex mixture of various isomers reflected as a pattern of usually 8 to 10 peaks in the chromatogram. Consequently, the tested concentration of 0,023 µg/l is not represented by a single peak but is distributed over all peaks of the pattern. These, therefore, have significantly lower peak intensities, so that the integration of the peak pattern becomes more difficult. The method requires considerable personal skill and experience in the interpretation of the peak patterns of these complex mixtures. Furthermore, the influence of the blank increases with decreasing concentrations.

[b] The designation of the variables is as follows:

- l is the number of laboratories after outlier rejection;
- n is the number of analytical results after outlier rejection;
- n_{AP} is the number of outliers;
- $\bar{\bar{x}}$ is the total mean of all results after outlier rejection;
- x_{ref} is the reference value;
- η is the recovery rate;
- s_R is the reproducibility standard deviation;
- CV_R is the reproducibility variation coefficient;
- s_r is the repeatability standard deviation;
- CV_r is the repeatability variation coefficient.

Bibliography

[1] ISO 8466-1:1990, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ICS 13.060.50

Price based on 18 pages