
Blato, obdelani biološki odpadki in tla - Določevanje nonilfenolov (NP) ter nonilfenol-monoetoksilatov in dietoksilatov z uporabo plinske kromatografije z masno selektivno detekcijo (GC/MS)

Sludge treated biowaste and soil - Determination of nonylphenols (NP) and nonylphenol-mono- and diethoxylates using gas chromatography with mass selective detection (GC-MS)

Schlamm, behandelter Bioabfall und Boden - Bestimmung von Nonylphenolen (NP) und Nonylphenol-Mono- und Diethoxylaten mittels Gaschromatographie mit massenselektiver Detektion (GC-MS)

Boues, bio-déchets traités et sols - Détermination des nonylphénols et nonylphénol-mono- et di-éthoxylates par chromatographie en phase gazeuse avec détection sélective de masse (GC-MS)

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Diethoxylaten mittels Gaschromatographie mit
massenselektiver Detektion (GC-MS)

This Technical Specification (CEN/TS) was approved by CEN on 24 April 2011 for provisional application.

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Foreword

This document (CEN/TS 16182:2012) has been prepared by Technical Committee CEN/TC 400 "Project Committee - Horizontal standards in the fields of sludge, biowaste and soil", the secretariat of which is held by DIN.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

The preparation of this document by CEN is based on a mandate by the European Commission (Mandate M/330), which assigned the development of standards on sampling and analytical methods for hygienic and biological parameters as well as inorganic and organic determinants, aiming to make these standards applicable to sludge, treated biowaste and soil as far as this is technically feasible.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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CEN/TS 16182:2012 (E)**Introduction**

Nonylphenols (NP) are mainly found in the environment as degradation products of nonylphenol polyethoxylates (NPEO). NPEO have many applications as non-ionic detergents in washing and cleaning agents.

After use NPEO are degraded by de-ethoxylation, resulting in polyethoxylates with fewer ethoxy-groups. Nonylphenol-diethoxylates (NP2EO), nonylphenol-monoethoxylates (NP1EO) and nonylphenols (NP) are the last three products in the degradation chain. Due to their significant presence in sewage sludge, all three components are included in this Technical Specification.

This Technical Specification is applicable for several types of matrices and validated for municipal sewage sludge (see also Annex A for the results of the validation).

WARNING — Persons using this Technical Specification should be familiar with usual laboratory practice. This Technical Specification 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 according to this Technical Specification be carried out by suitably trained staff.

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1 Scope

This Technical Specification specifies a method for the determination of nonylphenols (NP), nonylphenol-monoethoxylates (NP1EO) and nonylphenol-diethoxylates (NP2EO) in sludge, treated biowaste and soil using GC-MS.

For sludge a limit of detection of 0,1 mg/kg and for soil and treated biowaste 0,02 mg/kg (expressed as dry matter) may be achieved.

Lower limits of detection may be achieved by concentrating the extract by solvent evaporation.

NOTE 4-tert-octylphenol can also be analysed with this method.

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.

EN 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter fraction after determination of dry residue or water content*

EN 16179, *Sludge, treated biowaste and soil — Guidance for sample pretreatment*

EN ISO 16720, *Soil quality — Pretreatment of samples by freeze-drying for subsequent analysis (ISO 16720)*

EN ISO 22892, *Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry (ISO 22892)* [SIST-TS CEN/TS 16182:2012](https://standards.iteh.ai/catalog/standards/sist/fcac209f-dbf6-4bc3-b1a6-1717309d2e40/iso-22892-2012)

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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

After pretreatment, the test sample is extracted by shaking with a mixture of acetone and petroleum ether (1:1). If necessary, interfering compounds are removed from the extract by a clean-up on a suitable column.

The extract is treated with *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (MSTFA) reagent for the derivatization (silylation) of the analytes, and subsequently analysed by gas chromatography and mass selective detection (GC-MS).

Nonylphenols and nonylphenol-mono- and diethoxylates are identified from the GC fingerprint, the relative retention times and the relative intensities of two diagnostic ions. The quantification is based on an internal standard procedure. The internal standards (¹³C-labelled 4-n-NP and ¹³C-labelled 4-n-NP2EO) are taken through the whole analytical procedure.

4 Interferences

4.1 Interferences from sampling

Use sampling containers of materials (preferably glass or steel) that do not significantly affect the sample during the contact through sampling and storage. Plastic containers may be used if it has been proven that they do not significantly affect the sample.

CEN/TS 16182:2012 (E)**4.2 Interferences by GC-MS**

Substances that co-elute with NP, NP1EO or NP2EO and give the same ion(s) may interfere with the determination. This may have a large influence on the result, since all three analytes are determined from the sum of a cluster of five to nine chromatographic peaks. It is essential that the interfering peaks are not included in the calculations. A peak is excluded if the retention times are not the same as expected from the calibration standard and if the relative peak areas from the two diagnostic ions differ more than 30 % from the same peak in the calibration standard. Interfering peaks may usually be spotted by comparing the fingerprints of the sample with the fingerprints of the calibration standard, although the isomer distribution in the environmental samples may differ from the distribution in the calibration standard.

5 Reagents**5.1 General**

All reagents shall be of recognised analytical grade.

The purity of the reagents used shall be checked by running a blank determination as described in 8.5.

5.2 Acetone, C₃H₆O.**5.3 Hexane-like solvent**

Any aliphatic hydrocarbon solvent with a boiling point or boiling range between 34 °C and 100 °C may be applied.

5.4 Anhydrous sodium sulphate, Na₂SO₄, powdered.

Heated for at least 6 h to (550 ± 20) °C, cooled to about 200 °C in the furnace and then to ambient temperature in a desiccator containing magnesium perchlorate or a suitable alternative. The anhydrous sodium sulphate shall be kept carefully sealed.

5.5 N-methyl-N-(trimethylsilyl)-trifluoroacetamide, C₆H₁₂F₃NOSi, (MSTFA), CAS-RN¹⁾ 24589-78-4, for derivatization.

5.6 Isooctane, C₈H₁₇, boiling point 99 °C.

5.7 Derivatization solution, 5 % MSTFA (5.5) in isooctane (volume fraction).

Dissolve e. g. 1 ml of MSTFA (5.5) in isooctane (5.6) in a 20 ml volumetric flask and make up to volume with isooctane (5.6).

Store the derivatization solution in a dark place at a temperature of (4 ± 3) °C. The solution is stable for at least two months.

5.8 Operating gas for gas chromatography with MS-detector

Helium of sufficient purity and in accordance with the manufacturer's specification.

5.9 Nitrogen, N₂, for solvent evaporation.

Nitrogen of sufficient purity.

1) CAS-RN Chemical Abstracts Service Registry Number.

5.10 Standards for calibration

The following standard substances shall be used:

- 4-Nonylphenols (NP), mixture of isomers, CAS-RN 84852-15-3;
- 4-Nonylphenol monoethoxylates (NP1EO), mixture of isomers, CAS-RN 26027-38-3;
- 4-Nonylphenol diethoxylates (NP2EO), mixture of isomers, CAS-RN 20427-84-3.

The two nonylphenol ethoxylates may contain small amounts of other ethoxylates. It is important to check the purity of all the standards used for calibration.

The standards may be taken from pure compounds or from solutions with a guaranteed concentration.

The standards shall be stored in a freezer at a temperature of (-18 ± 3) °C.

NOTE 1 If 4-tert-octylphenol is included: 4-(1,1,3,3-tetramethylbutyl)phenol, CAS-RN 140-66-9.

NOTE 2 For NP, NP1EO and NP2EO conflicting information about CAS-RN may be found.

5.11 Internal standards

The following internal standard substances may be used:

- ¹³C-labelled 4-n-nonylphenol (4-n-NP), C₉H₁₉[¹³C₆]H₄-OH;
- ¹³C-labelled 4-n-nonylphenol-diethoxylate (4-n-NP2EO).

The internal standards shall be stored in a freezer at a temperature of (-18 ± 3) °C.

D₄-labelled 4-n-nonylphenol or 4-n-nonylphenol (non-labelled) may be used as an alternative internal standard to ¹³C-labelled 4-n-nonylphenol. 4-n-nonylphenol-diethoxylate (non-labelled) may be used as an alternative internal standard to ¹³C-labelled 4-n-nonylphenol-diethoxylate. Non-labelled compounds may only be used if it is shown that they are not present in the sample.

For ion trap MS deuterated internal standards shall not be used.

5.12 Internal standard solution

Prepare an internal standard solution with the two internal standards in isooctane (5.6). The concentrations are 20 mg/l for 4-n-NP and 100 mg/l for 4-n-NP2EO.

It is essential that the same internal standard solution is used for calibration standard solutions and for samples, blank and internal quality control samples.

Store the internal standard solution in a dark place at a temperature of (4 ± 3) °C. The solution is stable for at least two years, provided that evaporation of solvent is negligible.

5.13 Stock solutions

Prepare individual stock solutions of about 100 mg/l in isooctane (5.6), either from solid standard substances or from solutions with a certified concentration.

Store the stock solutions in a dark place at a temperature of (4 ± 3) °C. The solutions are stable for at least 2 years, provided that evaporation of solvent is negligible.

CEN/TS 16182:2012 (E)**5.14 Calibration standard solutions**

A mixed calibration standard solution is prepared from the stock solutions (5.13) by diluting the stock solutions with isooctane (5.6). Internal standard solution (5.12) is added to a concentration of 0,2 mg/l for 4-n-NP and 1,0 mg/l for 4-n-NP2EO. The calibration standards are made to concentrations from 0,01 mg/l to 5 mg/l.

Store the calibration standard solutions in a dark place at a temperature of (4 ± 3) °C. The solutions are stable for at least two weeks, provided that evaporation of solvent is negligible.

6 Apparatus**6.1 General**

All equipment that comes into contact with the sample or extract shall be free from nonylphenols and nonylphenol ethoxylates. Glassware may be cleaned by heating, at least for 2 h at 450 °C.

6.2 Usual laboratory glassware

6.2.1 Screw cap glass flask with polytetrafluoroethylene (PTFE) seal; volume 100 ml and 250 ml.

6.2.2 Round-bottom flasks, volume 100 ml and 250 ml.

6.2.3 Test tubes and vials

6.3 Shaking device

Reciprocating shaker, with horizontal movement (up to at least 250 strokes per minute).

6.4 Evaporator

Rotary evaporator. Other device like turbo evaporator or Kuderna Danish²⁾ may be used.

6.5 Clean-up column

Silica column. Commercial columns or freshly prepared columns may be used.

Alternative materials like aluminium oxide or Florisil^{®3)} may be used, provided that a sufficient recovery of the analytes has been proven.

6.6 Freeze drying apparatus

6.7 Gas chromatograph with mass selective detector equipped with a capillary column: 5 % phenyl-methyl silicone stationary phase coated onto fused silica or an equivalent chemically bonded phase.

The dimensions should be sufficient to separate the nonylphenols as described below. In general column length should be 25 m to 50 m. An example of a column is given in Annex B.

2) Kuderna Danish is an example of a suitable product available commercially. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by CEN of this product.

3) Florisil[®] is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by CEN of this product.

The first two peaks in the SIM chromatogram of the nonylphenols are selected as critical pairs for the quality criteria for the chromatographic system. The resolution shall be sufficiently high, so that the first two peaks in nonylphenols are baseline separated when measured at ion 207, see Table 2.

7 Sample storage and sample pretreatment

7.1 Sample storage

Store the samples in a dark place in a freezer or in a refrigerator. The samples can be stored up to three weeks in a freezer at a temperature of $(-18 \pm 3) ^\circ\text{C}$ or up to seven days in the refrigerator at $(4 \pm 3) ^\circ\text{C}$.

Determine the content of dry matter in the sample according to EN 15934.

NOTE Sludge samples with unusually high amounts of nonylphenol polyethoxylates (NPPEO) relative to the analytes can only be stored for seven days in the freezer at $(-18 \pm 3) ^\circ\text{C}$.

7.2 Sample pretreatment

Pretreat the samples according to EN 16179 if not otherwise specified.

Different pretreatment procedures are used for the different matrices. This is presented in Table 1.

Table 1 — Pretreatment methods used prior to nonylphenol analysis

Matrix	Freeze drying (EN ISO 16720)	No drying
Sludge dry matter > 2 % ^a	X	X
Sludge dry matter < 2 % ^b	X	
Soil ^c	X	X
Treated biowaste	X	X

^a Sludge samples with more than 2 % dry matter can be analysed as wet samples, or they can be analysed after freeze-drying.

^b Sludge samples with less than 2 % dry matter can only be analysed after freeze-drying.

^c Soil and treated bio-waste samples can be analysed as wet samples (field-moist samples), or they can be analysed after freeze-drying.

8 Procedure

8.1 Extraction

8.1.1 General

The wash of organic phase (extraction solvent) with water may be carried out directly in the extraction flask with the sample present.

Other extraction techniques than described in this Technical Specification, like ultrasonic extraction, microwave or pressurised liquid extraction may be suitable. If other extraction techniques are applied, the comparability to the method described in this Technical Specification shall be proven.