SLOVENSKI STANDARD
SIST-TS CEN/TS 16189:2012

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Blato, obdelani biološki odpadki in tla - Določevanje linearnih alkilbenzen sulfonatov (LAS) z uporabo tekočinske kromatografije visoke ločljivosti (HPLC) s fluorescenčno detekcijo (FLD) ali masno selektivno detekcijo (MS)

Sludge, treated biowaste and soil - Determination of linear alkylbenzene sulfonates (LAS) by high-performance liquid chromatography (HPLC) with fluorescence detection (FLD) or mass selective detection (MS)

Schlamm, behandelter Bioabfall und Boden - Bestimmung von Linearen Alkylbenzolsulfonaten (LAS) mittels Hochleistungs-Flüssigkeitschromatographie (HPLC) mit Fluoroszenzdetektion (FLD) oder massenselektiver Detektion (MS)

Boues, bio-déchets traités et sols - Détermination des alkylbenzènesulfonates linéaires (LAS) par chromatographie liquide à haute performance (CLHP) avec détection par fluorescence (FLD) ou détection sélective de masse (SM)

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English Version

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The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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Foreword

This document (CEN/TS 16189:2012) 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.

Introduction

The anionic surfactant LAS (Linear Alkylbenzene Sulfonate) is found in the environment due to the use of LAS in detergents. For more than 30 years LAS has been the largest single surfactant used in detergents, and the use continues on a high level.

Although LAS is readily biodegradable during wastewater treatment, considerable amounts may still be found in sludge of municipal origin. By the use of sludge for soil improvement LAS may end up in the agricultural soil, where a rapid biodegradation takes place.

The method describes the determination of LAS in sludge, soil, treated biowaste and neighbouring fields. LAS is the sodium salt of alkylbenzene sulfonic acids, and it consists of a mixture of the homologues C_{10}-LAS, C_{11}-LAS, C_{12}-LAS, C_{13}-LAS and C_{14}-LAS. LAS is determined as the sum of the homologues.

This Technical Specification is applicable and validated for several types of matrices as indicated in Table 1 (see also Annex A for the results of the validation).

Table 1 — Matrices for which this Technical Specification is applicable and validated

Matrix	Materials used for validation
Sludge	Municipal sewage sludge
Biowaste	Fresh compost
Soil	Sludge amended soil

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.

1 Scope

This Technical Specification specifies a method for the determination of linear alkylbenzene sulfonate (LAS) in sludge, treated biowaste and soil using high-performance liquid chromatography (HPLC) with a fluorescence detector (FLD) or a mass selective detector (MS).

This Technical Specification specifies the determination of the sum of LAS. Under the conditions specified in this Technical Specification, typically a limit of detection of 20 mg/kg (expressed as dry matter) for sludge and of 0,2 mg/kg to 0,5 mg/kg for soil and treated biowaste may be achieved.

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

NOTE The single LAS homologues C_{10} to C_{14} can be determined by this Technical Specification.

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 22892, *Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry (ISO 22892)*

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 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
analyte
mixture of homologues (i. e. C_{10}-LAS, C_{11}-LAS, C_{12}-LAS, C_{13}-LAS and C_{14}-LAS) where each homologue consists of a mixture of four to six isomers depending on the length of the alkyl group

Note 1 to entry: The dominant homologues in detergents and environmental samples are C_{11}-LAS and C_{12}-LAS. C_{10} to C_{14} refers to the chain length of the linear alkyl group.

4 Principle

After pretreatment, the test sample is extracted by shaking with methanol. If necessary, interfering compounds are removed from the extract by a clean-up on a suitable column.

The extract is analysed by high performance liquid chromatography (HPLC) on a C_8- or C_{18}-column and detection by fluorescence (FLD) or mass spectrometry (MS).

The identification is based on the retention times of the homologues and of the isomers of each homologue. Another identification point is the pattern/fingerprint of the homologues, and the isomer fingerprint of each homologue if a C_{18}-column is used for HPLC. By use of MS detection the relative intensities of two diagnostic ions may also be used for the identification (optional).

The quantification is based on an internal standard procedure. The internal standard (C_8-LAS) is taken through the whole analytical procedure.

Depending on the type of matrices from which LAS is extracted, different analytical pathways can be applied. An overview of the analytical procedure for the matrix of interest is shown in Table 2.

5 Interferences

5.1 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.

5.2 Interferences by HPLC-FLD and HPLC-MS

The chromatographic analysis can be done on a C_8- or a C_{18}-reverse phase column, and the choice of column determines the separation obtained. On the C_8-column (with methanol in mobile phase) the LAS homologues are separated, however, there is no separation of the isomers. On the C_{18}-column (with acetonitrile in mobile phase) the homologues are separated and there is a partial separation of the isomers of each homologue. This is illustrated by the chromatograms in Annex B.

The selectivity of the fluorescence as well as the mass selective detector is high; however, interference from co-eluting substances may occur. It is essential that the interfering peaks are not included in the calculations. A peak is excluded if the retention time differs from the LAS standard mixture. Interfering peaks can best be detected when a C_{18}-column is used for the LC analysis, due to the partial separation of the isomers. The C_{18}-column is mandatory when fluorescence is used, due to the higher selectivity obtained. The interfering peaks can usually be detected by comparing the fingerprints of the sample with the fingerprints of the LAS standard mixture, although the isomer and homologue distribution in the environmental samples may differ from the distribution in the standard mixture.

The highest selectivity is obtained by the use of a C_{18}-column and the MS detector. However, for most applications the separation on a C_8-column is sufficient, when MS is used. When all isomers are eluted in one peak, the integrations are less complicated, resulting in a higher precision and a lower limit of detection.

Table 2 — Choice of analytical procedure

Matrix	FLD		MS	
	C_8-column	C_{18}-column	C_8-column	C_{18}-column
Sludge	No	Yes	Yes	Yes
Soil	No	(Yes)[a]	Yes	Yes
Treated biowaste	No	(Yes)[a]	Yes	Yes
[a] For FLD the limit of detection will generally be inadequate for this type of matrix.				

6 Reagents

6.1 General

Use only reagents of recognized analytical grade, unless otherwise specified.

The purity of the reagents used shall be checked by running a blank determination as described in 9.4.

6.2 Methanol, CH_3OH; HPLC-grade.

6.3 Acetonitrile, C_2H_3N; HPLC-grade.

6.4 Ammonium acetate, $c(CH_3COO^- NH_4^+)$ = 0,01 mol/l.

6.5 Mobile phases for HPLC

6.5.1 For isomeric separation on C_{18}-column

— Mobile phase A: 0,01 mol/l ammonium acetate (6.4);

— Mobile phase B: Acetonitrile (6.3).

6.5.2 For homologue separation on C_8-column

— Mobile phase A: 0,01 mol/l ammonium acetate (6.4);

— Mobile phase B: Methanol (6.2).

6.6 Reagents for clean-up procedures

6.6.1 Clean-up procedure based on strong anion exchange (SAX)

6.6.1.1 SAX column

6.6.1.2 Acetic acid, CH_3COOH

6.6.1.3 Hydrochloric acid, HCl

6.6.1.4 Methanol, CH_3OH

6.6.2 Clean-up procedure based on graphitised carbon black (GCB)

6.6.2.1 GCB column

6.6.2.2 Hydrochloric acid, HCl

6.6.2.3 Tetramethylammonium hydroxide, $C_4H_{13}NO$ (CAS-RN 10424-65-4[1)]); pentahydrate.

6.6.2.4 Formic acid, HCOOH

6.6.2.5 Dichloromethane, CH_2Cl_2

6.6.2.6 Methanol, CH_3OH

6.7 Nitrogen, N_2, for solvent evaporation of sufficient purity.

6.8 Standards for calibration

6.8.1 General

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

1) CAS-RN Chemical Abstracts Service Registry Number.

6.8.2 C_{11}-LAS, sodium linear undecylbenzene sulfonate, $C_{17}H_{27}SO_3Na$; 99 %.

6.8.3 C_{12}-LAS, sodium linear dodecylbenzene sulfonate, $C_{18}H_{29}SO_3Na$; 99 % (CAS-RN 2211-98-5).

6.8.4 C_{13}-LAS, sodium linear tridecylbenzene sulfonate, $C_{19}H_{31}SO_3Na$; 99 %.

6.8.5 C_{10}-C_{14}-LAS mixture of homologues and isomers, highest possible purity (CAS-RN 69669-44-9, CAS-RN 25155-30-0).

6.9 Internal standard, C_8-LAS

Octylbenzene sulfonic acid, sodium salt $C_{14}H_{21}SO_3Na$ (CAS-RN 6149-03-7).

The internal standard shall be stored in the freezer at a temperature of (–18 ± 3) °C.

6.10 Internal standard solution

Prepare the internal standard solution of the internal standard (6.9) by dilution to about 1 000 mg/l in methanol (6.2).

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

6.11 Stock solutions

Prepare individual stock solutions of 1 000 mg/l to 5 000 mg/l in methanol (6.2), either from solid standard substances or from solutions with a certified concentration. Prepare stock solutions of C_{11}-LAS (6.8.2), C_{12}-LAS (6.8.3) and C_{13}-LAS (6.8.4).

Prepare a calibration mixture by mixing stock solutions of C_{11}-LAS, C_{12}-LAS and C_{13}-LAS containing equal concentrations of each homologue.

Prepare a stock solution of C_{10} to C_{14}-LAS mixture (6.8.5) of 1 000 mg/l to 5 000 mg/l in methanol (6.2). This solution is only for identification.

Store the stock solutions and the calibration mixture in a dark place at a temperature of (4 ± 3) °C. The solutions are stable for at least two years.

6.12 Calibration standard solutions

6.12.1 General

Calibration standard solutions are prepared from the calibration mixture (6.11) by diluting with a 1:1 mixture of methanol (6.2) and ammonium acetate (6.4).

The calibration range is different for sludge (see 6.12.2) and for soil or treated biowaste (see 6.12.3).

Store the calibration standard solutions in a dark place at a temperature of (4 ± 3) °C.

NOTE A diluted C_{10}- to C_{14}-mixture is prepared for the identification of the C_{10} and C_{14} homologues, which are not present in the calibration mixture.

6.12.2 Sludge samples

For sludge samples the calibration standards are prepared for concentrations from 5 mg/l to 500 mg/l. The internal standard solution (6.10) is added to a concentration of 10 mg/l.

6.12.3 Soil and treated biowaste samples

For samples of soil or treated biowaste the calibration standards are prepared for concentrations from 0,05 mg/l to 5 mg/l. The internal standard solution (6.10) is added to a concentration of 1 mg/l.

7 Apparatus

7.1 General

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

7.2 Usual laboratory glassware

7.2.1 Screw cap glass flask with polytetrafluoroethylene (PTFE) seal; volume 20 ml and 100 ml.

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

7.2.3 Test tubes and vials

7.3 Shaking device

Reciprocating shaker with horizontal movement (suitable for (250 ± 20) strokes per minute).

7.4 Evaporator

Rotary evaporator, turbo evaporator or Kuderna Danish[2)].

7.5 Freeze drying apparatus

7.6 High-performance liquid chromatograph with fluorescence or mass selective detector

The HPLC system is equipped with a C_8- or C_{18}-reverse phase chromatographic column. The dimensions should be sufficient to separate the LAS as described below.

NOTE Two examples for HPLC-columns are given in Annex B.

The fluorescence detector shall be suitable to measure at excitation wavelength of 230 nm and emission wavelength of 310 nm. If a fixed wavelength detector is used, the nearest possible wavelengths shall be used.

The mass selective detector shall be equipped with an atmospheric pressure ionization electro-spray (API-ES) interface. Use the negative ion mode.

The separation of LAS homologues shall fulfil the following requirements: The five homologues C_{10} to C_{14} shall all be separated to baseline.

Isomeric separation (mandatory for fluorescence detection): C_{11}-LAS shall be separated into at least four chromatographic peaks, although these are not separated to baseline.

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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.