SIST

SLOVENSKI STANDARD
kSIST-TS FprCEN/TS 16189:2011

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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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This draft Technical Specification is submitted to CEN members for Technical Committee Approval. It has been drawn up by the Technical Committee CEN/TC 400.

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (FprCEN/TS 16189:2010) 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.

This document is currently submitted to the Formal Vote.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

This Technical Specification is part of a modular horizontal approach in which this document belongs to the analytical step.

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.

Until now, test methods determining properties of materials within the environmental area were prepared in Technical Committees (TCs) working on specific products/matrices (e.g. soil, waste, sludge). However, it is understood that many steps within individual test procedures may also be used for the analysis of various other materials. By careful determination of these steps and selection of specific questions within these steps, elements of the test procedure can be described in a way that can be used for a variety of matrices and materials with certain specifications. This optimization is in line with the development among end-users of standards. A majority of routine environmental analyses are carried out by institutions and laboratories working under a scope that is not limited to one single environmental matrix but covers a wide variety of matrices. Availability of standards covering more matrices contributes to the optimization of laboratory procedures and standard maintenance costs, e.g. costs related to accreditation and recognition.

A horizontal modular approach was developed in the project "Horizontal". "Modular" means that a test standard developed in this approach concerns a specific step in assessing a property and not the whole "chain of measurement" (from sampling to analyses). A beneficial feature of this approach is that individual "modules" can be replaced by improved ones without jeopardizing the standard "chain".

The results of the desk study as well as the evaluation and validation studies have been subject to discussions with all parties concerned in the CEN structure during the development by project "Horizontal". The results of these consultations with interested parties in the CEN structure have been presented to and discussed in CEN/TC 400.

Based on data from interlaboratory studies and consultations with interested parties within CEN member bodies, it has been concluded that this CEN/TS 16189 is acceptable for its intended use and is ready for FV.

It is recognized that standardization in the environmental field in most national standardization bodies is organized in national standardization committees that mirror the vertical structure of technical committees in the environmental field in CEN. The present FV therefore asks for special attention by the NSBs to assure that the relevant and interested parties are consulted during the FV, i.e. to assure that one single consolidated enquiry reply on this CEN/TS 16189 can be presented by the NSB that covers the entire scope of this draft Technical Specification.

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 below (see also Annex C for the results of the validation):

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

Matrix	Validated for
Sludge	Municipal sewage sludge
Compost	Fresh compost
Soil	Sludge amended soil

WARNING — Persons using this Technical Specification should be familiar with normal 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 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.

prEN WI00400022, *Sludge, treated biowaste and soil — Guidance for sample pretreatment*

prEN 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter by determination of dry residue or water content*

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*

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

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 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 clean-up using 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 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 A.

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 bio-waste	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

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 9.4.

6.2 Methanol, CH_3OH; HPLC-grade.

6.3 Acetonitrile, C_2H_3N; HPLC-grade.

6.4 Ammonium acetate, [CH_3COO^- NH_4^+], *c*(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.