SLOVENSKI STANDARD
oSIST prEN 15936:2011

01-januar-2011

Blato, obdelani biološki odpadki, tla in odpadki - Določevanje celotnega organskega ogljika (TOC) s suhim sežigom

Sludge, treated biowaste, soil and waste - Determination of total organic carbon (TOC) by dry combustion

Schlamm, behandelter Bioabfall, Boden und Abfall - Bestimmung des gesamten organischen Kohlenstoffs (TOC) mittels trockener Verbrennung

Boue, biodéchet traité, sol et déchets - Détermination de la teneur en carbone organique total (COT) par combustion sèche

Ta slovenski standard je istoveten z: **prEN 15936**

ICS:

13.030.20	Tekoči odpadki. Blato	Liquid wastes. Sludge

oSIST prEN 15936:2011 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

DRAFT
prEN 15936

December 2010

ICS 13.030.01

English Version

Sludge, treated biowaste, soil and waste - Determination of total organic carbon (TOC) by dry combustion

Boue, biodéchet traité, sol et déchets - Détermination de la teneur en carbone organique total (COT) par combustion sèche

Schlamm, behandelter Bioabfall, Boden und Abfall - Bestimmung des gesamten organischen Kohlenstoffs (TOC) mittels trockener Verbrennung

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Foreword

This document (prEN 15936:2010) 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 second CEN Enquiry.

This draft European Standard prEN 15936 was completely technically and editorially revised following the comments made during the 1st CEN-Enquiry in 2009 and the discussions from CEN/TC 400/WG 4 "Inorganic elements and compounds".

This European Standard 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 draft standard prEN 15936 is acceptable for its intended use and is ready for CEN enquiry.

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 CEN enquiry therefore asks for special attention by the NSBs to assure that the relevant and interested parties are consulted during the CEN enquiry, i. e. to assure that one single consolidated enquiry reply on this draft standard prEN 15936 can be presented by the NSB that covers the entire scope of this draft standard.

Introduction

This European Standard is (applicable and) validated for several types of matrices as indicated below (see also Annex A for the results of the validation):

Table 1 — Matrices for which this European Standard is (applicable and) validated

Matrix	Validated for
Sludge	Municipal sludge
Biowaste	Compost, Fresh Compost
Soil	Sludge amended soil, Agricultural soil
Waste	Filter cake, Bottom ash, Electro-plating sludge, Dredged sludge, Rubble

WARNING — Persons using this European Standard should be familiar with normal laboratory practice. This European 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 according to this European Standard be carried out by suitably trained staff.

1 Scope

This European Standard specifies two methods for the determination of total organic carbon (TOC) in sludge, treated biowaste, soil, waste and sediment samples containing more than 1 g carbon per kg of dry matter (0,1%).

Coal, charcoal and inorganic carbon compounds except carbonates will be determined as organic carbon when present in the sample.

For sludge, treated biowaste and soil only method A is validated.

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

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

ISO 10693, *Soil quality – Determination of carbonate content – Volumetric method*

3 Terms and definitions

For the purposes of this European Standard, the following terms and definitions apply:

3.1
total carbon
TC
quantity of carbon present in the sample in the form of organic, inorganic and elemental carbon

3.2
total inorganic carbon
TIC
quantity of carbon that is liberated as carbon dioxide by acid treatment

3.3
total organic carbon
TOC
quantity of carbon that is converted into carbon dioxide by combustion and which is not liberated as carbon dioxide by acid treatment

4 Principle

4.1 General

The TOC can be measured either by Method A (indirect procedure) or by Method B (direct procedure).

4.2 Method A (indirect procedure)

In this procedure the TOC is obtained by the difference between the results of the measurements of TC and TIC.

The total carbon (TC) present in the un-dried sample or dried sample is converted to carbon dioxide by combustion in an oxygen-containing gas flow free of carbon dioxide. For soil dried samples are used. To ensure complete combustion, catalysts and/or modifiers can be used. The released amount of carbon dioxide is measured by infrared spectrometry, gravimetry, coulometry, conductometry, thermal conductivity detection, flame ionisation detection after reduction to methane, or other suitable techniques.

The TIC is determined separately from another sub-sample by means of acidification and purging of the released carbon dioxide. The carbon dioxide is measured by one of the techniques mentioned above. Alternatively, for soil the total organic carbon content may be calculated by determining the total carbon content and subtracting the carbon present as carbonate, which can be determined according to ISO 10693 (volumetric method).

4.3 Method B (direct procedure)

In this procedure the carbonates present in the un-dried or dried sample are previously removed by treating the sample with acid. The carbon dioxide released by the following combustion step is measured by one of the techniques mentioned in 4.2 and indicates the TOC directly.

4.4 Applicability of Methods A or B

Methods A and B have the same applicability in the terms of TOC content and/or TIC to TOC ratio. In samples with relatively high inorganic carbon contents method B should be applied.

Method B may lead to incorrect results in the following cases:

— the sample contains volatile substances that evaporate during the acidification (e.g. volatile hydrocarbons from sludge of oil separators);

— side reactions between the sample and the acid take place (e.g. decarboxylation, volatile reaction products).

The quality of results of Method B is dependent on experience and practice, especially regarding the steps before the determination of TOC. Use of automatic dispensing units regarding removal of carbonates prior to determination of TOC may improve the performance of Method B.

5 Interferences

Volatile organic substances may be lost during sample preparation. If necessary, the carbon content resulting from volatile organic substances shall be determined separately.

Depending on the laboratory experience with samples containing high amounts of carbonate the procedures may lead to unreliable TOC results if the TIC to TOC ratio is very high (e.g. ≥ 10).

Depending on the detection method used, different interferences may occur, for instance:

— the presence of cyanide can interfere with the coulometric detection of TIC by modifying the pH value (dissolution of HCN);

— high content of halogenated compounds may lead to an overestimation of TOC when coulometric detection is used; in some cases the classical silver or copper trap can be insufficient to absorb all halides.

When present, elemental carbon, carbides, cyanides, cyanates, isocyanates, isothiocyanates and thiocyanates are determined as organic carbon using the methods described in this standard. An interpretation of the measured value may therefore be problematic in cases where the sample contains relevant levels of the above-mentioned components. If needed, these components shall be determined separately by means of a suitable validated procedure and be recorded in the test report.

Elementary carbon, determined separately, may be subtracted if required for the sample. If this is done this shall be reported by the laboratory.

6 Reagents

All reagents used shall be at least of analytical grade.

Hygroscopic substances shall be stored in a desiccator.

6.1 Calcium carbonate, $CaCO_3$.

6.2 Sodium carbonate, Na_2CO_3, anhydrous.

6.3 Tetrasodium ethylenediamine tetraacetate-tetra-hydrate, Na_4-EDTA · $4H_2O$ ($C_{10}H_{12}N_2O_8Na_4 \cdot 4H_2O$), heated at 80 °C for 2 h.

NOTE Other forms of Na_4-EDTA hydrates may be used if the water content is exactly known. Then the composition of the control mixtures has to be recalculated accordingly (see also 6.10 and 6.11).

6.4 Potassium hydrogen phthalate, $C_8H_5O_4K$

6.5 Acetanilide, C_8H_9NO.

6.6 Atropine, $C_{17}H_{23}NO_3$.

6.7 Spectrographic graphite powder, C.

6.8 Sodium salicylate, $C_7H_5O_3Na$.

6.9 Aluminium oxide, Al_2O_3, neutral, granular size < 200 µm, annealed at 600 °C.

6.10 Control mixture A prepared from sodium carbonate (6.2), Na_4-EDTA · $4H_2O$ (6.3) and aluminium oxide (6.9) in a mass ratio of 2,34: 1,00:1,97.

The mixture shall be homogenized. It should contain 50,00 g/kg TIC and 50,00 g/kg TOC (e. g. 44,13 g of sodium carbonate, 18,83 g Na_4-EDTA · $4H_2O$, 37,04 g of aluminium oxide).

6.11 Control mixture B prepared from sodium salicylate (6.8), calcium carbonate (6.1), Na_4-EDTA · $4H_2O$ (6.3) and aluminium oxide (6.9) in a mass ratio of 1,00:4,36:1,97:8,40.

The mixture shall be homogenized. It should contain 33,3 g/kg TIC and 66,6 g/kg TOC (e.g. 6,36 g of sodium salicylate, 27,78 g of calcium carbonate, 12,50 g of Na_4-EDTA · $4H_2O$, 53,36 g of aluminium oxide).

6.12 Non-oxidizing mineral acid used for carbon dioxide expulsion, e. g. phosphoric acid H_3PO_4 (w = 85 %)

NOTE Due to possible corrosion by hydrochloric acid, phosphoric acid is preferred.

6.13 Carrier gas, e. g. synthetic air, nitrogen, oxygen or argon, free of carbon dioxide and organic impurities in accordance with the manufacturer's instructions.

7 Apparatus

7.1 Precision balance, accurate to at least 0,5 % of test portion weight.

7.2 Equipment for determination of carbon in solids, with accessories.

7.3 Purging unit for TIC determination, for Method A only.

7.4 Crucibles or boats, made of e.g. ceramics, silica glass, silver or platinum.

NOTE Tin and nickel crucibles are not acid-resistant.