SLOVENSKI STANDARD
SIST EN 15936:2012

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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

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English Version

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

Boues, bio-déchets traités, sols et déchets - Détermination de la teneur en carbone organique total (COT) par combustion sèche

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Foreword

This document (EN 15936:2012) 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.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.

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

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 implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, 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

This European Standard 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 European Standard is applicable and validated

Matrix	Materials used for validation
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 usual 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 %).

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

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 15002, *Characterization of waste — Preparation of test portions from the laboratory sample*

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*

3 Terms and definitions

For the purposes of this document, 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 elementary 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 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 sample is converted to carbon dioxide by combustion in an oxygen-containing gas flow free of carbon dioxide. To ensure complete combustion, catalysts and/or modifiers can be used. The released amount of carbon dioxide is measured by infrared spectrometry, thermal conductivity detection, flame ionisation detection after reduction to methane, or by gravimetry, coulometry, conductometry after absorption.

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).

4.2 Method B (direct procedure)

In this procedure, the carbonates present in the 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 4.1 and indicates the TOC directly.

4.3 Applicability of Methods A or B

Methods A and B have the same applicability for the determination of TOC and/or the determination of the 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).

NOTE 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 may 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, elementary carbon, carbides, cyanides, cyanates, isocyanates, isothiocyanates and thiocyanates are determined as organic carbon using the methods described in this European 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 method 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

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

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 · 4 H_2O ($C_{10}H_{12}N_2O_8Na_4$ · 4 H_2O), heated at 80 °C for 2 h.

Other forms of Na_4-EDTA hydrates may be used if the water content is exactly known. In these cases, 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 · 4 H_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 · 4 H_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 · 4 H_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 · 4 H_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. Tin crucibles are suitable only for Method A.

8 Sample pretreatment

Pretreat the sample according to EN 16179 or EN 15002, if not otherwise specified.

For soil, dried samples shall be used.

Moist or paste-like samples may be mixed with aluminium oxide (6.9) until granular material is obtained and then be comminuted. In this case, the ratio of aluminium oxide to sample shall be considered in the calculation of TOC (according to 9.4 or 10.4).

If samples contain – depending on the accuracy of the method – negligible amounts of volatile compounds except water, the samples may be dried.

9 Procedure - Method A (Indirect method)

9.1 Determination

9.1.1 General

The mass of the test portion should be as large as possible and shall be chosen so that the liberated quantity of carbon dioxide lies within the working range of the equipment/calibration.

9.1.2 Determination of the TC

The sample prepared according to Clause 8 is weighed into a suitable vessel (7.4). To minimize carbon blank values the vessel may be pre-treated by heating (in a muffle furnace or the TC apparatus itself).

The sample is burned or decomposed in a flow of carrier gas containing oxygen (6.13).

The combustion temperature shall be high enough to convert all carbon completely to carbon dioxide. For samples containing carbonates, which are difficult to decompose, e.g. barium carbonate, the release of the carbon dioxide may be improved by increasing the temperature or by the use of modifiers, e.g. tin, copper.

The temperature range of commercially available instruments is between 900 °C and 1 500 °C.

During the combustion of reactive samples explosion or fuming may be prevented by covering the sample with inert material e.g. silica sand.

The carbon dioxide released during the analysis is measured using one of the detection methods infrared spectrometry, gravimetry, coulometry, conductometry, thermal conductivity detection, flame ionisation detection after reduction to methane, or other suitable techniques, and is expressed as carbon.

9.1.3 Determination of the TIC

The sample prepared according to Clause 8 is weighed into the purging unit (7.3).

The system is closed gas-tight and flushed with carrier gas until no more carbon dioxide from ambient air is present. Then acid (6.12) is added and the carbon dioxide is stripped by purging or stirring and/or heating. The released carbon dioxide is transferred to the detector by the carrier gas.

The addition of anti-foaming agents, e.g. silicone oil, may be helpful in the case of strongly foaming samples.

The addition of wetting agents, e.g. surfactants, may improve wetting of the surface of the sample.

The carbon dioxide released during the gas evolution is immediately measured using one of the detection methods infrared spectrometry, gravimetry, coulometry, conductometry, thermal conductivity detection, flame ionisation detection after reduction to methane, or other suitable techniques and is expressed as carbon.

TIC may alternatively be determined according to ISO 10693.

Samples containing persistent carbonates (e.g. concrete, cement) require treatment with hot acid for complete release of carbon dioxide.

9.2 Calibration

If a relative method is used for detection, e.g. infrared detection, calibration is necessary.

Examples of calibration substances suitable for TC are calcium carbonate (6.1), potassium hydrogen phthalate (6.4), acetanilide (6.5), atropine (6.6), spectrographic graphite powder (6.7).

Sodium carbonate (6.2) and Na_4-EDTA (6.3) as well as all compounds with EDTA-structure shall not be used for TC-calibration as they are used as control substances.

Sodium carbonate (6.2) or calcium carbonate (6.1) are suitable for the calibration of TIC. Other calibration substances may be used provided their suitability is checked.

The following procedure should be applied for calibration:

— Establish the preliminary working range.

— Measure a minimum of five standard samples. The concentration of these standard samples shall be distributed evenly over the working range.

— Calculate mean values for each concentration.

— Carry out a linear regression analysis with the mean values and test the linearity of the calibration function (see also ISO 8466-1).

The function shall be linear. Otherwise the working range shall be restricted to the linear range.

If an absolute method is used for detection, e.g. coulometry, only control measurements according to 9.3 shall be carried out.

This calibration should be carried out for initial validation purposes or after major changes of the equipment.

9.3 Control measurements

Control measurements should be carried out using control mixture A (6.10) for the procedures according to 9.1.2. (TC) and 9.1.3 (TIC). Analysis of one concentration from the middle of the respective working range, possibly repeated two or three times, is sufficient. For the TC and TIC the mean recovery shall be between 90 % and 110 % with a coefficient of variation ≤ 5 %.

Blank values shall be taken into account if necessary.

If the required recoveries are not achieved, the following measures may be helpful.

For TC analysis: