



SLOVENSKI STANDARD
SIST EN 13137:2002

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Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments

Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments

Charakterisierung von Abfall - Bestimmung des Gesamten Organischen Kohlenstoffs (TOC) in Abfall, Schlämmen und Sedimenten

Caractérisation des déchets - Dosage du carbone organique total (COT) dans les déchets, boues et sédiments

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ICS:

- 13.030.10 Trdni odpadki Solid wastes
- 13.030.20 V^ [ă å æ Æ |æ Liquid wastes. Sludge

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Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments

Caractérisation des déchets - Dosage du carbone organique total (COT) dans les déchets, boues et sédiments

Charakterisierung von Abfall - Bestimmung des Gesamten Organischen Kohlenstoffs (TOC) in Abfall, Schlämmen und Sedimenten

This European Standard was approved by CEN on 18 June 2001.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This European Standard has been prepared by Technical Committee CEN/TC 292 "Characterization of waste", the secretariat of which is held by NEN.

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of an identical text or by endorsement, at the latest by February 2002, and conflicting national standards shall be withdrawn at the latest by February 2002.

Annex A of this European Standard is informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

Organic carbon in waste as well as in sludges and sediments is found in various forms. Due to the diversity of possible organic carbon compounds, the quantitative determination of all individual organic components of natural and anthropogenic origin is not possible. Therefore, it is necessary to rely on the measurement of total quantities. One of these is total organic carbon (TOC).

This parameter may be used for assessing the suitability of waste for landfilling.

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1 Scope

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

This standard can be applied as well to sludges, sediments and comparable materials.

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 problematical in cases where the waste 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.

NOTE At the time of publication of this European Standard a standardized procedure for determination of elemental carbon in waste is not available.

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2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

ISO 3733, *Petroleum products and bituminous materials - Determination of water - Distillation method.*

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 6296, *Petroleum products - Determination of water – Potentiometric Karl Fischer titration method.*

ISO 11465, *Soil quality - Determination of dry matter and water content on a mass basis - Gravimetric method.*

EN 12880, *Characterization of sludges - Determination of dry residue and water content.*

3 Terms and definitions

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

3.1

total carbon (TC)

the quantity of carbon present in waste in the form of organic, inorganic and elemental carbon

3.2

total inorganic carbon (TIC)

the quantity of carbon that is liberated as carbon dioxide by acid treatment

3.3

total organic carbon (TOC)

the quantity carbon that is converted into carbon dioxide by combustion and which is not liberated as carbon dioxide by acid treatment

NOTE Be aware that the above definitions are valid for this European Standard only and do not comply completely with scientific definitions of TC, TOC and TIC.

4 Principle

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

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 undried 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, gravimetry, coulometry, conductometry, thermal conductivity detection, flame ionization 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.

4.2 Method B (direct procedure)

In this procedure the carbonates present in the undried 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 in the terms of TOC content and/or TIC to TOC ratio.

Method B may lead to incorrect results in 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).

If these restrictions can be excluded, Methods A and B lead to comparable results. In case of doubt, Method A should be preferred.

NOTE The quality of results of Method B is more dependant on experience and practice, especially regarding the steps before combustion.

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5 Interferences

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

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.

6 Hazards

Samples may be liable to fermentation and may be infectious. Due to this it is recommended to handle these samples with special care. The gases which may occur due to the microorganism activities are potentially flammable. Excessive pressure build-up may cause the sample container to burst, potentially resulting in the formation of infectious aerosols and contaminated shrapnel.

Harmful compounds may arise during the combustion process and during the acid treatment. The user has to take appropriate precautions (e.g. activated carbon filters) to avoid these getting into the laboratory environment.

Samples with a high organic content may explode at introduction into the furnace. This risk can be reduced by using less sample or covering the sample with inert material.

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7 Reagents**7.1 General**

All reagents used shall be at least of analytical grade and suitable for their specific purposes.

Hygroscopic substances shall be stored in a desiccator.

7.2 Calcium carbonate, CaCO_3 **7.3 Sodium carbonate**, Na_2CO_3 , anhydrous**7.4 Tetrasodium ethylenediamine tetraacetate-tetra-hydrate**, $\text{Na}_4\text{-EDTA}\cdot 4\text{H}_2\text{O}$,

$\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\text{Na}_4\cdot 4\text{H}_2\text{O}$, heated at 80 °C for two hours.

NOTE Other forms of $\text{Na}_4\text{-EDTA}$ 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 7.8 and 7.9).

7.5 Potassium hydrogen phthalate, $\text{C}_8\text{H}_5\text{O}_4\text{K}$ **7.6 Sodium salicylate**, $\text{C}_7\text{H}_5\text{O}_3\text{Na}$ **7.7 Aluminium oxide**, Al_2O_3 , neutral, granular size < 200 μm , annealed at 600 °C

7.8 Control mixture A: sodium carbonate (7.3), $\text{Na}_4\text{-EDTA}\cdot 4\text{H}_2\text{O}$ (7.4) and aluminium oxide (7.7) 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 of $\text{Na}_4\text{-EDTA}\cdot 4\text{H}_2\text{O}$, 37,04 g of aluminium oxide).

7.9 Control mixture B: sodium salicylate (7.6), calcium carbonate (7.2), $\text{Na}_4\text{-EDTA}\cdot 4\text{H}_2\text{O}$ (7.4) and aluminium oxide (7.7) 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 $\text{Na}_4\text{-EDTA}\cdot 4\text{H}_2\text{O}$, 53,36 g of aluminium oxide).

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

7.11 Synthetic air, nitrogen, oxygen, argon, free of carbon dioxide and organic impurities in accordance with the manufacturer's instructions

8 Equipment

8.1 Homogenization device, for example mixers, stirrers, grinders, mills

8.2 Analytical balance, accurate to at least 0,5 % of test portion weight

8.3 Equipment for determination of carbon in solids; with accessories

8.4 Purging unit for TIC determination (to Method A only)

9 Sample storage

The samples are collected in glass or other suitable containers. Biologically active samples should be analysed immediately or stored at, at least - 18 °C. For biologically inactive samples special preservation may not be necessary.

10 Procedure Method A (indirect method)

10.1 Sample preparation

The samples supplied for analysis should be as homogeneous as possible and undried.

Depending on the nature and appearance of the sample different procedures can be used, for example:

- a) Solid samples may be directly comminuted (avoiding heat) and reduced to a granular powder, preferable particle size less than 200 µm.
- b) Moist or paste-like samples may be mixed with aluminium oxide (7.7) until granular material is obtained and then comminuted, preferable particle size less than 200 µm. In this case the ratio of aluminium oxide to sample shall be considered in the calculation of TOC (10.6 or 11.6).

If samples contain - according to the accuracy of the method - negligible amounts of volatile compounds except water, the samples may be dried at 105 °C before homogenization. For analysing liquid sludges, especially sewage sludge, freeze drying may also be used. In these cases the test report has to contain a clause: "sample dried at 105 °C" respectively "sample dried by freeze drying" (13d).

10.2 Water content

The determination of the water content shall be performed on a separate subsample.

For samples containing no or negligible amounts of volatile organic compounds the water content is calculated from the determination of the dry matter according to ISO 11465, respectively EN 12880.

In case of samples containing volatile organic compounds the water content should be determined in another way, for instance in accordance with ISO 3733 (distillation method) or ISO 6296 (Karl-Fischer-method).

10.3 Determination

10.3.1 General

This European Standard gives no recommendation concerning the construction of the apparatus and method of operation.

The operational characteristics should be selected and checked in accordance with the manufacturer's instructions.

The weight 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.

Measurements are made at least twice for TC as well as for TIC. The difference of the two values should be $\leq 10\%$ of the mean. If this is not the case, at least one further determination is necessary; the coefficient of variation should then be $\leq 10\%$. If this is not the case, the coefficient of variation shall be reported together with the result.

EN 13137:2001 (E)**10.3.2 Determination of the TC**

The sample prepared according to 10.1 is weighed into a suitable vessel (boat or crucible made of e.g. ceramics, silica glass, platinum or tin). The vessel may be pretreated by heating (in a muffle-oven or the TC apparatus itself) to minimize carbon blank values.

The sample is burned or decomposed in a flow of carrier gas containing oxygen (7.11).

The combustion temperature has to 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 1500 °C.

During the combustion of reactive samples, detonation 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 in accordance with clause 4 and is expressed as carbon.

10.3.3 Determination of the TIC

The sample prepared according to 10.1 is weighed into the purging vessel (8.4).

The system is closed gas-tight and flushed with carrier gas until no more carbon dioxide from ambient air is present. Then acid (7.10) 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.

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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 procedures in accordance with clause 4 and is expressed as carbon.

10.4 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 (7.2) or potassium hydrogen phthalate (7.5). Sodium carbonate (7.3) and Na₄-EDTA (7.4) as well as all compounds with EDTA-structure shall not be used for calibration as they are used as control substances.

Sodium carbonate (7.3) or calcium carbonate (7.2) are suitable for the calibration of TIC.

Other calibration substances may be used provided their suitability is checked.

The following procedure should be adopted during calibration:

- Establish the preliminary working range.
- Measure a minimum of five (recommended ten) standard samples at least in triplicate. 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 using ISO 8466-1.

The function should be linear. Otherwise the working range has to be restricted to the linear range.

If an absolute method is used for detection, e.g. coulometry, only control measurements according to 10.5 have to be carried out.

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

10.5 Control measurements

Control measurements shall be performed to check that the equipment is functioning correctly. They should be carried out each working day using the control mixture A (7.8) for the procedures according to 10.3.2 (TC) and 10.3.3 (TIC). Analysis of one concentration from the middle of the respective working range repeated three times is sufficient. For the TC and TIC the mean recovery has to be between 90 % and 110 % with a coefficient of variation ≤ 5 %.

When control charts are used one measurement per batch is sufficient.

A blank value shall be determined for all equipment and reagents used. It shall be taken into account if necessary.

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

TC analysis

- checking the homogeneity of the control mixture
- checking the calibration
- increasing the combustion temperature
- reducing the flow of the carrier gas
- encouraging a turbulent flow in the combustion tube
- using modifiers
- using post-oxidation of the combustion gases by catalysts

TIC analysis

- checking the homogeneity of the control mixture
- checking the calibration
- increasing the temperature during release of carbon dioxide
- optimizing the stirring speed and/or the gas flow in the purging vessel
- improving the gas exchange in the purging vessel
- avoiding condensation in the system.

10.6 Evaluation

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