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Description

Please find enclosed the first working draft of WI 00223111, Soil improvers and growing media - Determination of total organic carbon (TOC) by dry combustion.

As agreed during the meeting of CEN/TC 223/WG 4 on 2022-03-09, the enclosed 1st working draft and the forms for the activation of the new work item will be circulated to CEN/TC 223 as soon as the call for tender for the project leaders is completed and the project leaders are known.

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Soil improvers and growing media— Determination of total organic carbon (TOC) by dry combustion

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

CCMC will prepare and attach the official title page.

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European foreword

This European Standard has been prepared by Technical Committee CEN/TC 223 "Soil improvers and growing media", the secretariat of which is held by NEN.

This document is a working document.

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

1 Scope

This European Standard specifies a method for the determination of total organic carbon (TOC) in soil improvers and growing media containing more than 1 g carbon per kg of dry matter (0,1 %).

NOTE Samples with a low dry matter content can have an influence on the achievable limit of quantification as defined in the scope (i.e. 1 g carbon per kg of dry matter).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

EN 13040-1:—[1], *Soil improvers and growing media – Sample preparation – Part 1: Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory bulk density*

3 Terms and definitions

For the purposes of this document the terms and definitions given in CEN/TS 00223137:—[2] and EN 13040-1:— apply.

3.1

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 Process

4.1 Principle

The carbon dioxide released by the following combustion in an oxygen containing gas flow free of carbon dioxide, is measured by infrared spectrometry, thermal conductivity detection, or by the detector provided by the equipment used. To ensure complete combustion, catalysts and/or modifiers can be used. The released amount of carbon dioxide indicates the TOC.

The carbonates present in the sample shall be previously removed by treating the sample with acid.

4.2 Interferences

In the case of experience with samples containing high amounts of carbonates (e.g. carbonates to TOC ratio higher than 10) the operator shall take care to correctly eliminate all the carbonates to make sure to produce reliable TOC results.

When present, carbon from urea and urea-condensates carbides is determined as organic carbon using the method described in this document. 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.

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[1] Under preparation. Stage at the time of publication: EN 13040-1:20**.

[2] Under preparation. Stage at the time of publication: prCEN/TS 00223137:20**.

5 Reagents

All reagents shall be of recognized analytical grade.

5.1 Potassium hydrogen phthalate, $C_8H_5O_4K$.

5.2 Acetanilide, C_8H_9NO.

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

5.4 Sodium salicylate, $C_7H_5O_3Na$.

5.5 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.

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 shall be recalculated accordingly (see also 5.8).

5.6 Aluminum oxide, Al_2O_3, neutral, granular size < 200 µm, annealed at 600 °C.

5.7 Calcium carbonate, $CaCO_3$.

5.8 Control mixture

Control mixture prepared from sodium salicylate (5.4), calcium carbonate (5.7), Na_4-EDTA · $4H_2O$ (5.5) and aluminum oxide (5.6) in a mass ratio of 1,00 : 4,36 : 1,97 : 8,40.

The mixture shall be homogenised. It should contain 33,3 g/kg total inorganic carbon 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 aluminum oxide).

5.9 Inert absorbent material for determination on fluid samples, e.g., Chromosorb®[3].

5.10 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.

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

6 Apparatus

6.1. Laboratory grinder, capable of grinding to a particle size less than 0,5 mm.

6.2. Precision balance, capable of weighing to the nearest 0,5 % of test portion mass.

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

6.4 Crucibles, capsules or boats, made of e.g. silver, tin, ceramics or platinum.

[3] Chromosorb® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product.

Tin and nickel crucibles are not acid-resistant. In case of the necessity to remove inorganic carbon (see 7.2.4), silver or ceramics vessels shall be used.

6.5 Pasteur pipettes.

6.6 Drying system, thermostatically controlled and capable of maintaining temperature of (105 ± 2) °C.

6.7 Desiccator, with an active drying agent such as silica gel.

6.8 Evaporating dish or crucible, temperature tolerant laboratory vessel with a temperature resistance of at least 110 °C. Suitable materials are metallic, ceramic, borosilicate glass or quartz, porcelain, etc.

7 Procedure

7.1 Sample preparation

Solid samples are milled using a laboratory grinder (6.1) according to EN 13040-1 and homogenized. Liquid samples are homogenized by thorough mixing before weighing the test portion.

7.2 Determination

7.2.1 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 and calibration. See example in table A1 Annex A.

7.2.2 Preparation of solid samples

For solid materials dried samples shall be used.

The operator shall weigh an aliquot of sample prepared according to 7.1 into a suitable vessel (6.4) using the precision balance (6.2).

Moist or paste-like samples may be mixed with aluminum oxide (5.6) until granular material is obtained and then be comminuted and homogenised. In this case, the ratio of the used masses of aluminum oxide to sample shall be considered in the calculation of TOC (according to Clause 8).

The following tasks shall be performed:

- Close the vessel (6.4) according to the manufacturer's specifications, taking care not to break it and not to touch it with hands.
- Take the mass when the vessel is closed.

7.2.3 Preparation of liquid samples

7.2.3.1 Procedure A

For liquid matrices the operator shall put a little Chromosorb® (5.9) in the vessel (6.4) in order to have a layer of inert material on the bottom of the vessel (6.4).

The operator shall tare the vessel with Chromosorb®, and then, using the Pasteur pipette (6.5) shall put a small aliquot of liquid sample into the vessel (6.4).

The following tasks shall be performed:

- Close the vessel (6.4) according to the manufacturer's specifications, taking care not to break it and not to touch it with hands.
- Take the mass when the vessel (6.4) is closed.

7.2.3.2 Procedure B

Alternatively, without using Chromosorb®, the operator shall dry an amount of liquid sample in an evaporating dish or crucible (6.8) into the drying system (6.6) set at (105 ± 2) °C until the residue appears dry, typically overnight.

After cooling the sample in the desiccator (6.7) the operator shall homogenise the dried sample and shall proceed as described for solid samples in 7.2.2.

7.2.4 Removal of inorganic carbon and determination of the TOC

In order to remove the inorganic carbon prior to the determination of TOC, the sample is carefully treated with a small volume of non-oxidizing mineral acid (5.10). After massing the sample in the crucible (6.4), add the acid slowly (dropwise) to avoid foaming and splashing of the sample. Add as little acid as possible but enough to soak the entire sample and to remove the inorganic carbon completely.

An automatic dispenser system allowing small increments of non-oxidizing acid diluted with water (1 : 10) to be added at a time may be used.

Generally, 4 h of waiting is enough time for the complete removal of carbon dioxide. If moistening with the acid is difficult, the sample may be dampened beforehand with as little water as possible.

The moisture can be partly removed before combustion. The temperature during this sample treatment shall not exceed 40 °C.

Burn the sample in the carrier gas containing oxygen (5.11).

The combustion temperature shall be high enough to convert the organic carbon completely to carbon dioxide. The use of catalysts e.g. copper may increase the recovery.

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

During the combustion of reactive samples explosion or fuming can be prevented by covering the sample with inert material e.g. silica sand after removal of the inorganic carbon.

The total carbon dioxide released during the combustion is measured using one of the detection methods infrared spectrometry, thermal conductivity detection, or other suitable techniques, and is expressed as carbon.

NOTE 1 The quality of results 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 can improve the performance of the method.

NOTE 2 Corrosion of the combustion device can occur as a result of the acid remaining in the sample. Salt deposits can contaminate the system.

7.3 Calibration

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

Examples of calibration substances suitable for TOC are potassium hydrogen phthalate (5.1), acetanilide (5.2), atropine (5.3).

Na_4-EDTA (5.5) as well as all compounds with EDTA-structure shall not be used for calibration as they are used as control substances.

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.

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

7.4 Control measurements

Control measurements should be carried out using control mixture (5.8) for the procedure according to 7.1.4. Analysis of one concentration from the middle of the respective working range, possibly repeated two or three times, is sufficient. For the TOC, 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 can be helpful.

For TOC analysis:

- checking the homogeneity of the control mixture;
- increase the oxygen content in the reaction chamber, so as to work in excess of oxygen;
- clean the instrument by cleaning the oxidation tube: removal of ashes from the oxidation tube;
- 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.

8 Calculation and expression of results

The TOC mass contents of the samples prepared according to Clause 7 are calculated from:

- calibration function and sample mass if relative detection methods are used;
- specific constants and sample mass if absolute detection methods are used.

The TOC is calculated on dry matter basis by Formula (2). For this purpose the water content determined separately and, if necessary, the dilution factor resulting from sample preparation is used (see Formula (1)).

In case of mixing the sample with aluminium oxide (see 7.2.2) a dilution factor following Formula (1) shall be used:

$$f = (m_s + m_a)/m_s \quad (1)$$

where

m_s is the mass of the sample, in g;

m_a is the mass of aluminium oxide, in g.

$$m_{TOC,dm} = \frac{f \times m_{TOC}}{100 - w} \times 100 \quad (2)$$

where

$m_{TOC,dm}$ is the TOC content as carbon, calculated on dry matter basis, in g/kg;

m_{TOC} is the TOC content as carbon in the sample, in g/kg;

w is the water content of the sample as mass fraction in %, according to EN 13040-1;

f is the dilution factor resulting from the sample preparation of the sample according to 7.1 (see Formula (1)).

If directly using liquid samples, the dry matter content has to be taken into account.

The TOC content is reported as carbon on a dry matter basis. According to Formula (2) results are obtained in grams per kilogram (g/kg), but other units may be used.

9 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) test method used with reference to this document (prEN 00223111:2022);

c) information on applied pre-treatment procedure;

d) test results obtained expressed as grams per kilogram (g/kg) of TOC in the sample;

e) date of sampling and sampling procedure (if known);

f) date when the analysis was finished;

g) all operating details not specified in this document, or regarded as optional, together with details of any incidents occurred when performing the method, which might have influenced the test result(s).

Annex A
(informative)

Example of operational information

Table A.1 — Table of examples

Parameters	Laboratory 1	Laboratory 2	Laboratory 3
Sample preparation: grinding modality	Retsch® SM300 Knife Mill + Retsch® ZM200 Cyclone Rotor Mill	RETSCH® GM-200 knife mill	Retsch® MM400 ball mill
Sample preparation: type and size of the sieve	Sieved at 0,5 mm	Giuliani® sieve, UNI 2331-2 with 0,5 mm sieve	Sieved at 0,5 mm
Sample mass massed for analysis	TOC VARIO SELECT (macro) TOC 1 to 5 % mass 50 to 10 mg TOC 5 to 10 % mass 35 to 10 mg TOC 10 to 20 % mass 15 to 5 mg TOC 20 to 40 % mass 7 to 2.5 mg CHNS-O, Carlo Erba (micro) TOC 1 to 5 % mass 50 to 10 mg TOC 5 to 10 % mass 20 to 3.5 mg TOC 10 to 20 % mass 10 to 2 mg TOC 20 to 40 % mass 10 to 1 mg	TOC 1 to 10 % mass 200 to 150 mg TOC 10 to 30 % mass 100 to 110 mg TOC 30 to 50 % mass 60 to 80 mg TOC > 50 % mass 30 to 40 mg	TOC 1 to 5 % mass 10 to 5 mg TOC 5 to 10 % mass 5 to 2 mg TOC 10 to 20 % mass 3 to 1 mg TOC 20 to 40 % mass 1 to 0,5 mg
Size of the crucible used	40 mm × 40 mm The sample is closed in a silver sheet.	35 mm × 35 mm The sample is closed in tin sheet.	5 mm × 9 mm tin crucible Silver crucible, in case of acid attack.
Tool used for analysis	TOC VARIO SELECT® Elementar (macro) CHNS-O, Carlo Erba® (micro)	CNS, ELEMENTAR, VARIO MACRO® model	CHNS-O, Flash 2000 (Thermo Fisher Scientific®)
Temperature of combustion	Combustion temperature 950 °C	- Combustion temperature: 1 050 °C; - Post-combustion temperature: 800 °C;	- Combustion in excess of oxygen; - Combustion temperature: 1 000 °C.

Parameters	Laboratory 1	Laboratory 2	Laboratory 3
		- Reduction temperature: 850 °C.	
Catalyst	Combustion pipe packed with copper oxide and quartz flakes.	- Combustion catalyst: tungsten oxide; - 5 % CuO + Pt post-combustion catalyst; - Reduction catalyst: copper.	- Combustion pipe packed with chromium oxide and silver-plated cobalt oxide; - Reduction tube at 650 °C packed with reduced copper wires.
Gas carrier	Oxygen	Helium	Helium
Detector	IR (Infrared) detector	TCD (Thermal Conductivity Detector)	TCD (Thermal Conductivity Detector)

Bibliography

[1] EN 15936, *Sludge, treated biowaste, soil and waste — Determination of total organic carbon (TOC) by dry combustion*

[2] EN 1482:2007, *Fertilizers and liming materials - Sampling and sample preparation*

[3] 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*

[4] UNI 2331-2, *WOVEN METAL WIRE CLOTHS FOR SIEVING - WOVEN WIRE CLOTHS FOR TEST*

[5] CEN/TS 00223137, *Soil improvers and growing media - Terminology*