
Organska in organsko-mineralna gnojila - Določevanje celotnega organskega ogljika (TOC) s suhim sežigom

Organic and organo-mineral fertilizers - Determination of the total organic carbon (TOC) content by dry combustion

Organische und organisch-mineralische Düngemittel - Bestimmung des Gehalts an gesamtem organischem Kohlenstoff (TOC) durch trockene Verbrennung

Engrais organiques et organo-minéraux - Détermination de la teneur en carbone organique total (COT) par combustion sèche

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**Organic and organo-mineral fertilizers - Determination of
the total organic carbon (TOC) content by dry combustion**

Engrais organiques et organo-minéraux -
Détermination de la teneur en carbone organique

Organische und organisch-mineralische Düngemittel -
Bestimmung des Gehalts an organischem Kohlenstoff
(TOC) durch trockene Verbrennung

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European foreword

This document (CEN/TS 17776:2022) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

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1 Scope

This document is applicable to fertilizing products, which are classified as PFC 1(A) and PFC 1(B) or the PFC 1(A) and PFC 1(B) component in PFC 7 of Regulation (EU) 2019/1009 [5]. However, the present method was not validated for blends.

This document specifies a method for the determination of total organic carbon (TOC) by elemental analysis using dry combustion. The method is applicable to organic and organo-mineral fertilizers containing more than 1 g carbon per kg of dry matter (0,1 %), with the exclusion of organo-mineral fertilizers containing urea-formaldehyde polymers as long as there is no method available to assess carbon in urea-formaldehyde polymers.

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.

CEN/TS 17771, *Organic and organo-mineral fertilizers — Determination of the nitrogen content*

CEN/TS 17773, *Organic and organo-mineral fertilizers — Determination of the dry matter content*

EN 15705, *Fertilizers — Determination of urea condensates using high-performance liquid chromatography (HPLC) — Isobutylidenediurea and crotonylidenediurea (method A) and methylen-urea oligomers (method B)*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696: 1987)*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

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

Note 1 to entry: In agreement with Regulation (EU) 2019/1009 [5], carbon derived from urea and polymers containing urea are not considered as organic in this document.

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 Applicability

The method is applicable to organic and organo-mineral fertilizers both solid and liquid.

The present method is not selective, because combustion occurs for both organic and inorganic carbon.

4.3 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.

Carbon from urea and urea-condensates (crotonyliden diurea, CDU and isobutyliden diurea, IBDU), determined separately using CEN/TS 17771 and EN 15705 may be subtracted if required for the sample. If this is done this shall be reported by the laboratory.

5 Reagents

All water used shall be grade 3 according to EN ISO 3696:1995. 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, $Na_4-EDTA \cdot 4H_2O$ ($C_{10}H_{12}N_2O_8Na_4 \cdot 4H_2O$), 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, $CaCO_3$.

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5.8 Control mixture

Control mixture prepared from sodium salicylate (5.4), calcium carbonate (5.7), $\text{Na}_4\text{-EDTA} \cdot 4\text{H}_2\text{O}$ (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 $\text{Na}_4\text{-EDTA} \cdot 4\text{H}_2\text{O}$, 53,36 g of aluminum oxide).

5.9 Chromosorb®¹ (inert absorbent material for determination on fluid samples).

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

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

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

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.

6.4 Pasteur pipettes.

6.5 Drying system, thermostatically controlled and capable of maintaining temperature of $(105 \pm 2) ^\circ\text{C}$.

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

6.7 Evaporating dish or crucible, temperature tolerant laboratory vessel with a temperature resistance of at least $110 ^\circ\text{C}$. Suitable materials are metallic, ceramic, borosilicate glass or quartz, porcelain, etc.

7 Procedure**7.1 Sampling and sample preparation**

Sampling and sample preparation should be performed carefully, following the principles described in EN 1482 (all parts) with appropriate adaptations, required to account for specificities of organic and organo-mineral fertilizers. Grinding of the laboratory sample is recommended for homogeneity reasons. The sample shall then pass through a sieve of 0,5 mm.

¹ Chromosorb® is the trade name of a product. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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 A.1.

7.2.2 Preparation of solid samples

For solid fertilizers dried samples shall be used.

The operator shall weigh an aliquot of sample prepared according to 7.1 into a suitable vessel (6.3) using the precision balance (6.1).

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 (6.3) 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

Procedure A

For liquid fertilizers the operator shall put a little Chromosorb® (5.9) in the vessel (6.3) in order to have a layer of inert material on the bottom of the vessel (6.3).

The operator shall tare the vessel with Chromosorb®, and then, using the Pasteur pipette (6.4) shall put a small aliquot of liquid sample into the vessel (6.3).

The following tasks shall be performed:

- Close the vessel (6.3) 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 (6.3) is closed.

Procedure B

Alternatively, without using Chromosorb®, the operator shall dry an amount of liquid sample in an evaporating dish or crucible (6.7) into the drying system (6.5) set at $(105 \pm 2) ^\circ\text{C}$ until the residue appears dry, typically overnight.

After cooling the sample in the desiccator (6.6) 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 weighing the sample in the crucible (6.3), 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.

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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).

Na₄-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.