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

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National foreword

This British Standard is the UK implementation of EN 15936:2012.

The UK participation in its preparation was entrusted to Technical Committee H/-/4, Environmental testing programmes.

A list of organizations represented on this committee can be obtained on request to its secretary.

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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

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

This European Standard was approved by CEN on 24 May 2012.

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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of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

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:

- checking the homogeneity of the control mixture;
- checking the calibration;
- increasing the temperature during release of carbon dioxide;
- use of modifiers;

For TIC analysis:

- optimising 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.

9.4 Calculation and expression of results

The TC and TIC mass contents 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 calculation of TOC is achieved from the difference of the mean values of TC and TIC according to Formula (1):

$$m_{\mathrm{TOC}} = f\,(m_{\mathrm{TC}} - m_{\mathrm{TIC}}) \qquad (1)$$

In case of mixing the sample with aluminium oxide (see Clause 8) a dilution factor following Formula (2) shall be used:

$$f = \frac{m_{\mathrm{s}} + m_{\mathrm{a}}}{m_{\mathrm{s}}} \qquad (2)$$

where

m_{TOC}	is the TOC content as carbon in the sample expressed in grams per kilogram (g/kg);
m_{TC}	is the mean value of the TC content as carbon in the sample, prepared according to Clause 8 expressed in grams per kilogram (g/kg);
m_{TIC}	is the mean value of the TIC content as carbon in the sample prepared according to Clause 8 expressed in grams per kilogram (g/kg);
f	is the dilution factor resulting from the sample preparation of the sample according to Clause 8;
m_{s}	is the mass of the sample expressed in grams (g);
m_{a}	is the mass of aluminium oxide expressed in grams (g).

The TOC value resulting from Formula (1) is calculated on dry matter basis by Formula (3). For this purpose the water content, determined separately according to EN 15934, is used:

$$m_{\mathrm{TOC,dm}} = m_{\mathrm{TOC}} \times \frac{100}{100 - w} \qquad (3)$$

where

$m_{\text{TOC,dm}}$ is the TOC content as carbon, calculated on dry matter basis expressed in grams per kilogram (g/kg);

m_{TOC} is the TOC content as carbon in the sample expressed in grams per kilogram (g/kg);

w is the water content of the sample as mass fraction expressed in percent (%).

The TOC content is reported as carbon on a dry matter basis. According to Formula (3) results are obtained in grams per kilogram (g/kg), but other units may be used.

10 Procedure Method B (direct method)

10.1 Determination

10.1.1 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.

10.1.2 Removal of the inorganic carbon and determination of the TOC

The sample prepared according to Clause 8 is weighed into a suitable vessel (7.4). The vessel may be prepared by thermal treatment (in a muffle furnace or the combustion apparatus itself) to minimize carbon blank values.

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 (6.12). 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 acid to be added at a time is recommended, e.g. 12 increments of 50 µl non-oxidizing acid, diluted with water (1:10) per 10 mg to 25 mg of sample.

Allow at least 4 h for the complete removal of the carbon dioxide. Stirring of the sample may reduce time needed for oxidation.

If moistening with the acid is difficult, the sample may be dampened beforehand with as little water as possible.

The moisture may 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 (6.13).

The combustion temperature shall be high enough to convert the organic carbon completely to carbon dioxide. The use of modifiers e.g. tin, 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 may 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, gravimetry, coulometry, conductometry, thermal conductivity detection, flame ionisation detection after reduction to methane, or other suitable techniques, and is expressed as carbon.

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

10.2 Calibration

The calibration for TOC shall be done in accordance with the calibration for determination of TC (9.2). The same calibration substances can be used.

10.3 Control measurements

Control measurements should be carried out using control mixture B (6.11) for the procedure according to 10.1.2. 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 TOC 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.

Removal of carbonates:

- decreasing the drying temperature of the acidified sample;
- decreasing the drying time of the acidified sample;
- omitting the drying step.

10.4 Calculation and expression of results

The TOC mass contents of the samples prepared according to Clause 8 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 (4). For this purpose the water content determined separately and, if necessary, the dilution factor resulting from sample preparation is used (see Formula (2)).

$$m_{\mathrm{TOC,dm}} = f \times m_{\mathrm{TOC}} \times \frac{100}{100 - w} \qquad (4)$$

where

$m_{\mathrm{TOC,dm}}$	is the TOC content as carbon, calculated on dry matter basis expressed in grams per kilogram (g/kg);
m_{TOC}	is the TOC content as carbon in the sample expressed in grams per kilogram (g/kg);
w	is the water content of the sample as mass fraction expressed in percent (%);
f	is the dilution factor resulting from the sample preparation of the sample according to Clause 8 (see Formula (2)).

The TOC content is reported as carbon on a dry matter basis. According to Formula (4) results are obtained in grams per kilogram (g/kg), but other units may be used.

11 Precision

The performance characteristics of the method data have been evaluated (see Annex A and Annex C).

12 Test report

The test report shall contain at least the following information:

a) a reference to this European Standard (EN 15936);

b) complete identification of the sample;

c) the applied method (Method A or Method B);

d) information on applied pretreatment procedure;

e) information of determined and subtracted amount of elementary carbon, if relevant;

f) expression of results, according to 9.4 or 10.4 respectively;

g) any details not specified in this European Standard or which are optional, as well as any factor which may have affected the results.

Annex A
(informative)

Repeatability and reproducibility data

A.1 Materials used in the interlaboratory comparison study

An interlaboratory comparison of the determination of TOC in sludge, treated biowaste and soil was carried out with 25 to 29 European laboratories on six materials in 2008. Detailed information can be found in the final report on the interlaboratory comparison study mentioned in [6].

Another validation study on the determination of TOC in waste was carried out in 2005.

Table A.1 lists the types of materials tested in the study on soil, sludge and treated biowaste, Table A.2 lists the materials tested in the waste study.

Table A.1 — Materials tested in the interlaboratory comparison of the determination of TOC in sludge, treated biowaste and soil

Grain size	Sample	Material
Sludge (< 0,5 mm)	Sludge 1	Mix 1 of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany
	Sludge 2	Mix 2 of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany
Fine grained (< 2,0 mm)	Compost 1	Fresh compost from Vienna, Austria
	Compost 2	Compost from Germany
	Soil 4	Sludge amended soil from Hohenheim, Germany
	Soil 5	Agricultural soil from Reading, United Kingdom

Table A.2 — Materials tested in an interlaboratory comparison of the determination of TOC in waste

Grain size	Sample	Material
< 2,0 mm	Waste 1	Filter cake
< 2,0 mm	Waste 2	Bottom ash
< 2,0 mm	Waste 3	Electro Plating Sludge
< 2,0 mm	Waste 4	Dredged Sludge
< 2,0 mm	Waste 5	Rubble

A.2 Interlaboratory results

The statistical evaluation was conducted according to ISO 5725-2. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) were obtained (Table A.3 to A.5).

Table A.3 — Results of the interlaboratory comparison studies of the determination of total organic carbon (TOC) by dry combustion in sludge, treated biowaste and soil (Method A)

Matrix	l	n	n_o	$\bar{\bar{x}}$ g/kg	s_R g/kg	$C_{V,R}$ %	s_r g/kg	$C_{V,r}$ %
Sludge 1	15	62	2	272	16,0	5,89	4,6	1,69
Sludge 2	14	58	2	221	11,0	4,98	4,6	2,09
Compost 1	15	58	2	246	10,7	4,33	6,1	2,46
Compost 2	15	64	2	154	14,8	9,58	9,0	5,87
Soil 4	15	62	3	16,4	0,86	5,23	0,43	2,64
Soil 5	13	54	3	21,0	1,72	8,16	1,08	5,16

Explanation of symbols

l	number of participating laboratories
n	number of analytical results after outlier rejection
n_o	number of outliers
$\bar{\bar{x}}$	total mean of results (without outliers) (mass fraction)
s_R	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

Table A.4 — Results of the interlaboratory comparison studies of the determination of total organic carbon (TOC) by dry combustion in waste (Method A)

Matrix	l	n	o	$\bar{\bar{x}}$ %	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
Synthetic Mix	20	76	0	8,662	0,7614	8,79	0,1854	2,14
Waste 1	20	76	1	7,798	1,4925	19,14	0,1716	2,20
Waste 2	19	73	5	3,631	0,5548	15,28	0,1205	3,32
Waste 3	18	71	8	3,333	0,4029	12,09	0,1303	3,91
Waste 4	18	71	0	7,559	1,8239	24,13	0,3409	4,51
Waste 5	19	71	5	6,759	0,8408	12,44	0,2156	3,19

Explanation of symbols

l	number of participating laboratories
n	number of analytical results after outlier rejection
o	percentage of outliers
$\bar{\bar{x}}$	total mean of results (without outliers) (mass fraction)
s_R	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

Table A.5 — Results of the interlaboratory comparison studies of the determination of total organic carbon (TOC) by dry combustion in waste (Method B)

Matrix	l	n	o	$\bar{\bar{x}}$ %	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
Synthetic Mix	10	40	20	8,332	0,4874	5,85	0,2316	2,78
Waste 1	12	46	8	8,498	0,8354	9,83	0,2507	2,95
Waste 2	11	42	16	3,779	0,9905	26,21	0,1629	4,31
Waste 3	10	40	20	3,413	0,4792	14,04	0,1782	5,22
Waste 4	13	50	0	7,903	1,6588	20,99	0,4939	6,25
Waste 5	11	43	12	6,327	1,6482	26,05	0,2461	3,89
Explanation of symbols, see Table A.4.								

Annex B
(informative)

Factors influencing dry combustion methods

B.1 Influence of temperature and modifiers on the decomposition of barium carbonate as an example for a refractory compound

The use of modifiers may increase the recovery of TC for carbonates that originally decompose at higher temperatures, see Table B.1.

Table B.1 — Influence of temperature and modifiers on the decomposition of barium carbonate

Modifier	Ratio $BaCO_3$:modifier	TC %		
		900 °C	1 100 °C	1 300 °C
No modifier	-	< 0,1	< 0,1	5,8
Vanadium pentoxide	1:2	6,3	6,3	6,3
Tungsten oxide	1:2	< 0,1	6,0	6,3
Copper/tungsten	1:1:3	-	5,5	6,2
Tin	1:10	6,0	-	6,0

B.2 Influence of aluminium oxide or sodium sulfate used for sample preparation for the recovery of TOC

During a trial a real, moist sample (filter cake) was examined by nine laboratories. The laboratories used aluminium oxide as well as sodium sulfate for sample preparation. To get a granular powder, it was necessary to mix the moist or pasty sample with aluminium oxide in a ratio 1:3 or with sodium sulfate in a ratio 1:4 to 1:14, see Table B.2.

Table B.2 — Influence of aluminium oxide or sodium sulfate used for sample preparation on the recovery of TOC

Statistical parameter	TC %			TOC %					
				Method A			Method B		
	Original sample	Sample + Al_2O_3	Sample + Na_2SO_4	Original sample	Sample + Al_2O_3	Sample + Na_2SO_4	Original sample	Sample + Al_2O_3	Sample + Na_2SO_4
Mean of 9 laboratories	11,8	12,1	11,0	11,5	11,5	10,9	11,2	12,0	8,4
Standard deviation	0,48	0,78	0,40	0,33	0,28	0,44	1,03	0,62	-
Coefficient of variation	4 %	6 %	4 %	3 %	2 %	4 %	9 %	5 %	-

The use of sodium sulfate for sample preparation leads to:

- high consumption of sodium sulfate necessary to get a granular powder;
- a higher limit of determination;
- problems in the use of quartz combustion tubes;
- generally reduced results compared with those from the original untreated sample.

The use of aluminium oxide for sample preparation leads to similar results compared with those from the original untreated samples and does not show the disadvantages cited above.

B.3 Influence of TIC:TOC ratio on the recovery and the coefficient of variation

Synthetic mixtures containing different ratios of calcium carbonate, glucose and aluminium oxide (TIC to TOC ratios 1:1 to 50:1) were examined by six laboratories (see Tables B.3 and B.4).

Table B.3 — Method A: influence of TIC:TOC ratio on the recovery and the coefficient of variation

	Ratio TIC:TOC	Expected	Mean	Recovery %	Coefficient of variation %
TC measurements %	5:5	10	9,85	98	1
	5:1	6	5,94	99	1
	5:0,5	5,5	5,45	99	0
	5:0,1	5,1	5,02	98	1
TIC measurements %	5:5	5	4,78	96	4
	5:1	5	4,90	98	1
	5:0,5	5	4,93	99	2
	5:0,1	5	4,89	98	1
TOC results %	5:5	5	5,06	101	5
	5:1	1	1,05	105	9
	5:0,5	0,5	0,52	104	20
	5:0,1	0,1	0,11	112	51

Table B.4 — Method B: influence of TIC:TOC ratio on the recovery and the coefficient of variation

	Ratio TIC:TOC	Expected	Mean	Recovery %	Coefficient of variation %
TOC measurements %	5:5	5	4,91	98	7
	5:1	1	1,05	105	20
	5:0,5	0,5	0,57	114	32
	5:0,1	0,1	0,14	137	65

Up to a TIC:TOC ratio of 10:1 good recoveries and coefficients of variation were obtained for both methods (A and B). Within this limit there is no significant difference between the two methods.

B.4 Method A: Recovery of TOC for control mixture A

A synthetic mixture of sodium carbonate, $Na_4EDTA \cdot 4\ H_2O$ and aluminium oxide (TOC = TIC = 5 %) was analysed by seven laboratories using Method A. Results, see Table B.5.

Table B.5 — Method A: Recovery of TOC for the control mixture

Statistical parameter	**TC** %	**Recovery** %	**TIC** %	**Recovery** %	**TOC** %	**Recovery** %
Expected	10	-	5	-	5	-
Mean	9,71	97	4,84	97	4,87	97
Standard deviation	0,28		0,10		0,31	
Coefficient of variation	3	-	2	-	6	-

For Method A the required recovery was generally achieved.

B.5 Method B: Influence of the temperature during the removal of inorganic carbon on the recovery of TOC

Control mixture B with an expected value of 6,66 % TOC was analysed by one laboratory using Method B.

Table B.6 — Method B: Influence of temperature during the removal of inorganic carbon on the recovery of TOC

Temperature °C	**TOC** %	**Recovery** %
20	6,6	99
30	6,5	98
40	6,3	94
50	5,3	80
70	4,1	62

Temperatures higher than 40°C during the removal of inorganic carbon lead to poor recoveries of TOC, see Table B.6.

Annex C
(informative)

Determination of total organic carbon (TOC) in solid samples using the suspension method

C.1 General

TOC determinations in solid samples such as soils and sediments may alternatively be carried out in suspensions. These suspensions are, in terms of analytical sample preparation, comparable to wastewater samples containing particulate matter. TOC determination is carried out after quantitative oxidation to CO_2 according to EN 1484.

The procedure is added as informative Annex, because during the assessment of the results of the interlaboratory trial systematically lower results of about 10 % compared to the normative Method A were obtained. Therefore the method can only be used for orientation.

C.2 Range of application

This annex describes the determination of TOC in solid samples in the range of 0,1 % to 20 %. The measuring range can, in principle, be extended downwards or upwards. This is conditional upon calibration of the corresponding measuring ranges, taking into consideration the sensitivity of the analytical system, sample dilution as well as blank values. The following matrices were successfully analysed using the suspension method:

a) soils (sandy silt, topsoil, clay, shale);

b) sediments (marine sediments, river sediments);

c) suspended sediments;

d) raw and secondary materials in cement production (limestone, raw meal, fine dust, paper fibres, oil shale, dry sludges, cement powder).

C.3 Basic principle of the method

The TOC suspension method is a special sample preparation procedure for TOC determination in solid samples. The sample material is ground to a fine powder using an appropriate method (e.g. ball mill), with particle size ≤ 130 µm which is subsequently suspended in diluted hydrochloric acid. It is very important to minimise sedimentation of the suspension. Particles are effectively reduced and suspended using a homogeniser suitable for small particle sizes. The suspensions shall be stirred immediately prior to sampling by the analytical system. The analytical system shall be suitable with respect to samples containing particulate matter according to EN 1484.

The determination of organic carbon in the suspensions is carried out using the NPOC method (Non-Purgeable Organic Carbon). The samples are suspended directly in hydrochloric acid in order to convert the inorganic carbon compounds (TIC) into CO_2. Using an inert gas, the CO_2 is subsequently purged from the sample. After drying, the sample no longer contains volatile compounds. Therefore the following simplification can be used: NPOC = TOC.

C.4 Reagents

C.4.1 Water used for dilution

Ultrapure water with a maximum TC content of 300 µg/l for the preparation and dilution of standard solutions and hydrochloric acid used for the suspensions.

C.4.2 Potassium hydrogen phthalate, $C_8H_5O_4K$.

Potassium hydrogen phthalate p.a. for the preparation of stock and standard solutions according to EN 1484.

C.4.3 Hydrochloric acid, HCl.

The suspensions are prepared in a 0,22 mol/l hydrochloric acid solution. For the preparation of this solution, use hydrochloric acid with a concentration of up to 37 %. For dilutions use ultrapure water .

C.4.4 Gases

Gases according to EN 1484.

Auxiliary gases such as carrier gas or sparging gas shall be virtually free from CO, CO_2 or hydrocarbons.

C.5 Apparatus

C.5.1 General. Laboratory apparatus according to EN 1484. 300 ml Erlenmeyer flask especially suited for sample preparation.

C.5.2 Homogenisation. A high-velocity homogeniser including a precision tool capable of reducing particles to sizes ≤ 15 µm, as well as a magnetic stirrer unit. The latter can also be part of the analytical apparatus.

C.6 Implementation

C.6.1 Calibration

Calibrate the instrument according to the instructions of the manufacturer. A calibration curve is obtained, where the TC (Total Carbon) is established using potassium hydrogen phthalate standard solution of suitable concentration. In order to be applicable to a wide concentration range, several calibration curves may be necessary. A calibration curve corresponds to a dilution series of at least 5 concentration levels. A potassium hydrogen phthalate standard solution is diluted with appropriate volumes of ultra pure water. When available, the automatic dilution function of the analytical apparatus can be used to prepare the dilutions. For example: The carbon content of the standard solution is 100 mg/l. The dilution factors are 10, 5, 3, 2 and 1. This results in a dilution series with carbon concentrations of 10,0 mg/l, 20,0 mg/l, 33,3 mg/l, 50,0 mg/l and 100 mg/l. A calibration line is established by plotting the TC mass concentrations, in milligrams per litre carbon, against the instrument-specific measuring value. The slope of this line corresponds to the instrument response factor and its reciprocal value is the calibration factor.

C.6.2 Control experiments

Control experiments with respect to calibration shall be carried out according to EN 1484. In addition, the suitability of the instrument with regard to the suspension method shall be thoroughly tested using reference materials. Suitable reference materials are:

- Certified reference material NIST 1941b (sediment), NIST, USA;
- PT sample QTM068MS (sediment), QUASIMEME, The Netherlands.

C.6.3 Determination

(200 ± 10) mg of the dried and ground sample are weighed into a 300 ml Erlenmeyer flask, to which 200 ml of a 0,22 mol/l hydrochloric acid solution (C.4.3) is subsequently added. If the sample consists mainly of carbonates (e.g. limestone), the amount of sample may be increased to a maximum of 2 000 mg. In both cases, the volume fraction of the solid is considered to be negligible. The volume of the suspension is therefore 200 ml. This entire sample volume is subsequently homogenised over 3 min using a high-velocity homogeniser (precision tool!) at rotation speeds of 17 000 min^{-1} to 18 000 min^{-1}. A suspension is formed. After purging with an inert gas, the NPOC and TOC in the suspension is determined as mean value from a minimum of 4 single injections and subsequently calculated with reference to the original solid sample. The suspension is stirred during purging and immediately prior to sampling.

C.7 Evaluation of the results

C.7.1 General

The mass percentage of organic carbon in the solid sample is calculated using Formula (C.1):

$$\text{TOC}_\text{s} = \frac{V_\text{sus} \times i \times 100}{m_\text{s} \times f} \tag{C.1}$$

where

TOC_s	organic carbon in the solid sample expressed in percent (%) mass fraction;
i	instrument-specific measuring value;
V_sus	volume of the suspension expressed in litres (l);
m_s	mass of the solid sample expressed in milligrams (mg);
f	calibration factor expressed in litres per milligram (l/mg).

C.7.2 Blank value

The TC blank values of the ultra pure water and the 0,22 mol/l hydrochloric acid may not exceed 0,3 mg/l and 0,6 mg/l respectively. With respect to the solid samples, the blank value is therefore < 0,06 % (mass fraction). The calculation shall take into account that ultra pure water is also used in the calibration. Therefore, Formula (C.2) applies:

$$b = \frac{\left(b_\text{HCl} - b_\text{H2O}\right) \times V_\text{sus} \times 100}{m_\text{s}} \tag{C.2}$$

where

b	blank value with respect to the solid sample expressed in percent (%) mass fraction;
b_HCl	blank value of the 0,22 mol/l hydrochloric acid expressed in milligrams per litre (mg/l);
$b_{\text{H}_2\text{O}}$	blank value of the ultra pure water expressed in milligrams per litre (mg/l).

The determination of the blank values b_{H_2O} and b_{HCl} requires an analytical instrument with sufficient detection sensitivity for this concentration range (determination limit ≤ 200 µg/l).

C.8 Method performance data

In 2011 a validation study on the suspension method was carried out in which 16 laboratories participated with the suspension method and 10 laboratories used Method A as "reference method". For the results see Table C.1. The mean value of Method A has been taken as reference value for the suspension method.

Table C.1 — Results of the validation study of the determination of total organic carbon (TOC) by the suspension method

Matrix	l	n	n_o	$\bar{\bar{x}}$ g/kg	s_R g/kg	$C_{V,R}$ %	s_r g/kg	$C_{V,r}$ %
Suspension method								
Soil 1	16	79	0	40,4	9,4	23,3	3,1	7,7
Soil 2	15	73	1	2	0,9	45	0,4	20
Soil 3	15	74	1	53,1	6,3	11,9	4,2	7,9
Sediment 1	16	79	0	16,2	4,3	26,5	2,4	14,8
Sediment 2	16	79	0	53,4	16,4	30,7	2,2	4,1
Sewage sludge 1	15	74	1	236	28	11,9	13,1	5,6
Sewage sludge 2	15	74	1	220	24,4	11,1	13,6	6,2
Foundry sand	15	74	1	137	18,4	13,4	9,2	6,7
Method A (reference method)								
Soil 1	10	44	0	44,7	5,4	12	2	4,4
Soil 2	8	33	0	1,9	1	56,2	0,2	8,7
Soil 3	9	40	1	60,3	6,7	11,1	2,6	4,3
Sediment 1	10	45	0	21,3	4,7	21,9	2,3	10,8
Sediment 2	8	35	2	63,5	4,8	7,5	1,9	2,9
Sewage sludge 1	6	28	4	252	5,5	2,2	3,6	1,5
Sewage sludge 2	8	37	2	226	16,3	7,2	4	1,8

Explanation of symbols

l	number of participating laboratories
n	number of analytical results after outlier rejection
n_o	number of outliers
$\bar{\bar{x}}$	total mean of results (without outliers) (mass fraction)
s_R	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

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