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Secretariat: DS

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

*Einführendes Element — Haupt-Element — Ergänzendes Element*

*Élément introductif — Élément central — Élément complémentaire*

ICS:

Descriptors:

# Contents

# Foreword

This document TC BT TF 151 WI 99024 has been prepared by Technical Committee CEN/TC BT TF 151 "Horizontal standards in the field of sludge, bio-waste and soil", the secretariat of which is held by DS.

This document is currently submitted to the CEN Enquiry.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex Z, which is an integral part of this document.

This standard is applicable and validated for several types of matrices. The table below indicates which ones.

| **Material** | **Validated for**<br><br>**(type of sample, e.g. municipal sludge, compost)** | **Reference:** |
|---|---|---|
| Sludge | Municipal sludge, North Rhine Westphalia | JRC report |
| Soil | Sludge amended soil, Barcelona | JRC report |
| Biowaste | Fresh compost, Vienna | JRC report |
| Waste | Filter cake, bottom ash, electro-plating sludge, dredged sludge, rubble | EN 13137 |

# Introduction

This European Standard is developed in the project 'Horizontal'. It is the result of a desk study of standards for determination of total organic carbon (17). The desk study aimed at evaluating the existing standards on determination of total organic carbon in sludge, soil, treated biowaste and neighbouring fields. After an evaluation study, in which e.g. the ruggedness of the method was studies, a European wide validation of the draft standard has taken place. The results of the desk studies as well as the evaluation and validation studies have been subject to discussions with all parties concerned in CEN. The standard is part of a modular horizontal approach in which the standard belongs to the analytical step.

Until now test methods determining properties of materials were often prepared in Technical Committees (TCs) working on specific products or specific sectors. In those test methods often steps as sampling, extraction, release or other processing, analyses, etc were included. In this approach it was necessary to develop, edit and validate similar procedural steps over and over again for every material or product. Consequently this has resulted in duplication of work. To avoid such duplication of work for parts of a testing procedure references to parts of test methods from other TCs were introduced. However the following problems are often encountered while using references in this way: 1) The referenced parts are often not edited in a way that they could easily be referred to, 2) the referenced parts are often not validated for the other type of material and 3) the updates of such test standards on products might lead to inadequate references.

In the growing amount of product and sector oriented test methods it was recognised that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements of the test procedure could be described in a way that can be used for all materials and products or for all materials and products with certain specifications.

Based on this hypothesis a horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in assessing a property and not the whole ” chain of measurement” (from sampling to analyses). A beneficial feature of this approach is that “modules” can be replaced by better ones without jeopardizing the standard “chain”.

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

The modules that relates to this standard are specified in section XX Normative references.

An overview of modules and the manner, in which modules are selected will be worked out later, at which time proper reference in this standard will be provided.

# 1 Scope

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

Coal and charcoal (elemental carbon) and inorganic carbon compounds except of carbonates will be determined as organic carbon when present in the sample.

(This standard based on EN 13137 may include waste samples (and is prepared for) – depending on appropriate decision in TC 292 WG 5)

# 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).

CSS99031 Sludge, treated biowaste, and soils in the landscape – Sampling – Framework for the preparation and application of a sampling plan

CSS99058 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 1: Guidance on selection and application of criteria for sampling under various conditions

CSS99057 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 2: Guidance on sampling techniques

CSS99032 Sludge, treated biowaste, and soils in the landscape – Sampling - Part 3: Guidance on sub-sampling in the field

CSS99059 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery

CSS99060 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 5: Guidance on the process of defining the sampling plan

CSS99035 Soil, sludge and treated biowaste – Pre-treatment for organic characterisation

CSS99022 Sludge, soil and treated biowaste – Determination of dry matter – Gravimetric method

ISO 10693, Soil quality – Determination of carbonate content – Volumetric method

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

ISO 6296, Petroleum products - Determination of water - Potentiometric Karl Fischer titration method

# 3 Terms and definitions

For the purposes of this European Standard, 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 elemental carbon according to this standard

**3.2**
**Total Inorganic Carbon (TIC)**
quantity of carbon that is liberated as carbon dioxide by acid treatment according to this standard

**3.3**
**Total Organic Carbon (TOC)**
quantity carbon that is converted into carbon dioxide by combustion according to this standard and which is not liberated as carbon dioxide by acid treatment according to this standard

# 4 Safety remarks

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 microorganisms 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. Using less sample material or covering the sample with inert material can reduce this risk.

# 5 Principle

## 5.1 General

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

## 5.2 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 un-dried sample or dried sample is converted to carbon dioxide by combustion in an oxygen-containing gas flow free of carbon dioxide. For soil dried samples are used. 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 ionisation 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. 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).

### 5.3 Method B (direct procedure)

In this procedure the carbonates present in the un-dried or dried 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 5.2 and indicates the TOC directly.

### 5.4 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. In samples with relatively high inorganic carbon contents method B is preferred.

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).

The quality of results of Method B is dependent on experience and practise, 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 performance of Method B.

## 6 Interferences and sources of errors

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

Depending the laboratory experience on samples with high carbonate contents 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.

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 sample 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.

Elementary carbon, determined separately, may be subtracted if required for the sample. If this is done this shall be reported by the laboratory.

## 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

Calcium carbonate, $CaCO_{3.}$

### 7.3 Sodium carbonate

Sodium carbonate $Na_2CO_3$, anhydrous.

### 7.4 Tetrasodium ethylenediamine tetraacetate-tetra-hydrate

$Na_4$-EDTA·$4H_20$ - $C_{10}H_{12}N_2O_8Na_4 \cdot 4H_2O$, heated at 80°C for two hours.

NOTE Other forms of $Na_4$-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 7.11 and7.12).

### 7.5 Potassium hydrogen phthalate

Potassium hydrogen phthalate, $C_8H_5O_4K$

### 7.6 Acetanilide

Acetanilide, $C_8H_9NO$.

### 7.7 Atropine

Atropine, $C_{17}H_{23}NO_{3.}$

### 7.8 Spectrographic graphite powder

Spectrographic graphite powder, C.

### 7.9 Sodium salicylate

Sodium salicylate, $C_7H_50_3Na$.

### 7.10 Aluminium oxide

Aluminium oxide, $Al_2O_3$, neutral, granular size < 200 µm, annealed at 600°C.

### 7.11 Control mixture A

Control mixture A prepared from sodium carbonate (7.2), $Na_4$-EDTA·$4H_2O$ (7.4) and aluminium oxide (7.10) 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 $Na_4$-EDTA·$4H_2O$, 37,04 g of aluminium oxide).

### 7.12 Control mixture B

Control mixture B prepared from sodium salicylate (7.9), calcium carbonate (7.2), $Na_4$-EDTA·$4H_2O$ (7.4) and aluminium oxide (7.10) 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·$4H_2O$, 53,36 g of aluminium oxide).

### 7.13 Non-oxidizing mineral acid

Non-oxidizing mineral acid used for carbon dioxide expulsion, e.g. phosphoric acid $H_3P0_4$ (w = 85%)

Note  Due to possible corrosion by hydrochloric acid, phosphoric acid is preferred.

### 7.14 Synthetic air, nitrogen, oxygen or argon

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

## 8 Apparatus

a) Homogenisation device, for example mixers, stirrers, grinders, mills.

b) Analytical balance, accurate to at least 0,5 % of test portion weight.

c) Equipment for determination of carbon in solids, with accessories.

d) Purging unit for TIC determination, to Method A only.

e) Boats or crucibles, made of e.g. ceramics, silica glass, silver or platinum.

NOTE  Tin and nickel crucibles are not acid-resistant.

## 9 Sampling and sample pre-treatment

### 9.1 Sampling

Sampling are carried out in accordance with *CSS99031- 32 and 57 - 60*

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

### 9.2 Sample pre-treatment (to be uniformly coordinated with horizontal standard on pre-treatment)

Pre-treatment of the sample is carried out according to horizontal standard on pre-treatment CSS99035

The samples supplied for analysis should be as homogeneous as possible. For soils, dry samples shall be used. Depending on the nature and appearance of the sample different procedures can be used, for example:

f) Solid samples may be directly comminuted (avoiding heat) and reduced to a granular powder, preferable particle size less than 200 µm;

g) Moist or paste-like samples may be mixed with aluminium oxide (7.10) 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 (10.4 or 11.4).

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 homogenisation. For analysing liquid sludge, especially sewage sludge, freeze-drying may also be used. In case of soil air-drying may be applied. In these cases the test report has to contain a clause: "sample dried at 105 °C", "sample dried by freeze drying" (13d) respectively “samples air-dried”.

The determination of the water content (if needed) shall be performed on a separate sub sample.

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 CSS99022.

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-Fischermethod).

## 10 Procedure - Method A (Indirect method)

### 10.1 Determination

#### 10.1.1 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.

#### 10.1.2 Determination of the TC

The sample prepared according to 9.2 is weighed into a suitable vessel (boat or crucible made of e.g. ceramics, silica glass or platinum). To minimize carbon blank values the vessel may be pre-treated by heating (in a muffle-oven or the TC apparatus itself).

The sample is burned or decomposed in a flow of carrier gas containing oxygen (7.14).

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 1 500°C.

During the combustion of reactive samples, covering the sample with inert material, e.g. silica sand, may prevent detonation or fuming.

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.

#### 10.1.3 Determination of the TIC

The sample prepared according to 9.2 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 (7.13) 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 procedures in accordance with clause 4 and is expressed as carbon.

TIC may alternatively be determined by using ISO 10693.

## 10.2 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 (7.2), potassium hydrogen phthalate (7.5), acetanilide (7.6), atropine (7.7), spectrographic graphite powder (7.8). Sodium carbonate (7.3) and $Na_4$-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 shall be linear. Otherwise the working range must 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 after major changes of the equipment.

## 10.3 Control measurements

Control measurements shall be performed to check that the equipment is functioning correctly. They should be carried out regularly using the control mixture A (7.11) for the procedures according to 10.1.2. (TC) and 10.1.3 (TIC). Analysis of one concentration from the middle of the respective working range, possible repeated two or 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%.

The use of control charts for documentation of analytical quality is strongly recommended. When X-charts and r-charts are used, duplicate measurements of one control mixture sample 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:

<u>TC analysis</u>

— checking the homogeneity of the control mixture

- checking the calibration
- increasing the temperature during release of carbon dioxide
- using modifiers
- 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.

## 10.4 Calculation and expression of results

The TC and TIC mass contents of the samples prepared according to clause 9 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 Equation (1). In case of mixing the sample with aluminium oxide according to 9.2b) a dilution factor following Equation (2) has to be considered:

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

$$f = \frac{m_s + m_a}{m_s} \qquad (2)$$

where:

| | |
|---|---|
| $\varpi_{TOC}$ | is the TOC content as carbon in the original sample in grams per kilogram (g/kg); |
| $\varpi_{TC}$ | is the mean value of the TC content as carbon in the sample prepared according to 9.2 in grams per kilogram (g/kg); |
| $\varpi_{TIC}$ | is the mean value of the TIC content as carbon in the sample prepared according to 9.2 in grams per kilogram (g/kg); |
| $f$ | is the dilution factor resulting from the sample preparation of the original sample according to 9.2b); |
| $m_s$ | is the mass of the original sample (to be mixed with aluminium oxide according to 9.2b); |
| $m_a$ | is the mass of aluminium oxide according to 9.2b). |

The TOC value resulting from equation (1) is calculated on dry matter by Equation (3). For this purpose the water content determined separately according to 9.2 is used:

$$\varpi_{TOCdm} = \varpi_{TOC} \ x \frac{100}{100 - W} \qquad (3)$$

where:

| | |
|---|---|
| $\varpi_{TOCdm}$ | is the TOC content as carbon, calculated on dry matter basis in grams per kilogram (g/kg); |
| $\varpi_{TOC}$ | is the TOC content as carbon in the original sample in grams per kilogram (g/kg); |
| $W$ | is the water content of the original sample according to 9.2 as mass fraction in percent (%). |

The TOC content is reported as carbon on a dry matter basis. Following equation (3) results are obtained in g/kg. They can be converted into other units by using appropriate factors.

# 11 Procedure Method B (direct method)

## 11.1 Determination

### 11.1.1 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.

### 11.1.2 Removal of the inorganic carbon and determination of TOC

The sample prepared according to 9.2 is weighed into a suitable vessel (boat or crucible made of e.g. ceramics, silica glass or platinum). The vessel may be prepared by thermal treatment (in a muffle oven or the combustion apparatus itself) to minimize carbon blank values.

To remove the inorganic carbon prior to the determination of the TOC the sample is carefully treated with a small volume of non-oxidizing mineral acid (7.13). Add the acid very 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.

NOTE 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 – 25 mg of sample.

Allow at least 4 hours 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.

The sample is transferred to the combustion unit and heated carefully to remove the moisture. This may be realized by programming the temperature of the furnace or by inserting the sample slowly into the combustion unit. Then the sample is burnt in the carrier gas containing oxygen (7.14).

The combustion temperature has to 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 lies between 900°C and 1 500°C.

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

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

### 11.2 Calibration

The calibration for TOC has to be done in accordance with the calibration for TC (10.2). The selection of the calibration substances is analogous.

### 11.3 Control measurements

Control measurements should be carried out each working day using the control mixture B (7.12) for the procedure according to 11.1.2. Triple analysis of one point in the middle of the working range is sufficient. The mean recovery for the complete TOC procedure has to be between 90 % and 110 % with a coefficient of variation ≤ 10 %.

The use of control charts for documentation of analytical quality is strongly recommended. When X-charts and r-charts are used, duplicate measurements of one control mixture sample per batch is sufficient.

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

If the required recovery is not achieved, the following measures may be helpful:

<u>TOC analysis</u>

— 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.

<u>Removal of carbonates</u>

— decreasing the drying temperature of the acidified sample;

— decreasing the drying time of the acidified sample;

— omitting the drying step.

### 11.4 Calculation and expression of results

The TOC mass contents of the samples prepared according to 9.2 a) or b) 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 Equation (4). For this purpose the water content determined separately according to 9.2 and, if necessary, the dilution factor resulting from sample preparation is used.

$$\varpi_{TOCdm} = f \; x \, \varpi_{TOC} \; x \, \frac{100}{100 - W} \qquad (4)$$

where:

| | |
|---|---|
| $\varpi_{TOCdm}$ | is the TOC content as carbon, calculated on dry matter basis in grams per kilogram (g/kg); |
| $f$ | is the dilution factor resulting from the sample preparation of the original sample according to 9.2b) and in accordance with equation (2); |
| $\varpi_{TOC}$ | is the mean value of TOC content as carbon in the sample prepared according to 9.2 in grams per kilogram (g/kg); |
| $W$ | is the water content of the original sample according to 9.2 as mass fraction in percent (%). |

The TOC content is reported as carbon on a dry matter basis. Following equation (4) results are obtained in g/kg. They can be converted into other units by using appropriate factors.

## 12 Precision data

The performance characteristics of the method (Annex B) data have been evaluated. Table 1 gives the resulting typical values for repeatability and reproducibility limits as their observed ranges. The typical value is derived from the data in Table B.2 in Annex B by taking the median value and rounding the numbers.

**Table 1 — Typical values and observed ranges of the repeatability and reproducibility limits**

<table>
<tr><td colspan="3">The reproducibility limit provides a determination of the differences (positive and negative) that can be found (with a 95 % statistical confidence) between a single test result obtained by a laboratory using its own facilities and another test result obtained by another laboratory using its own facilities, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard and the two laboratory samples are obtained from the same primary field sample and prepared under identical procedures. Conversely, the repeatability limit refers to measurements obtained from the same laboratory, all other conditions being identical. The reproducibility limit and the repeatability limit do not cover sampling but cover all activities carried out on the laboratory sample including its preparation from the primary field sample.</td></tr>
<tr><td>Results of the validation of the determination of total organic carbon (TOC) by dry combustion in soil, sludge and treated biowaste</td><td>Typical value<br>%</td><td>Observed range<br>%</td></tr>
<tr><td>Repeatability limit, r</td><td>7</td><td>5 - 16</td></tr>
<tr><td>Reproducibility limit, R</td><td>16</td><td>12 - 27</td></tr>
</table>

NOTE 1. The above results refer to the difference that may be found between two test results performed on two laboratory samples obtained under the same conditions. In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the above typical reproducibility values and observed reproducibility ranges should be divided by √2 to obtain the corresponding typical dispersion limit and its observed range. In the example of TOC in Sludge 2 the result and its dispersion limit is221 ± 22 g/kg (2 * sR = 9.96 % of 221). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 199 g/kg and lower than 243 g/kg.

NOTE 2. The repeatability limit (r) and the reproducibility limit (R) as given in Table A.2 (Annex A) and in this table are indicative values of the attainable precision if the determination of total organic carbon (TOC) by dry combustion is performed in accordance with this standard [CSS99024].

NOTE 3. A limited number of materials and parameters were tested. Consequently, for other materials and parameters, performance characteristics may fall outside the limits as derived from the validation of the the determination of total organic carbon (TOC) by dry combustion in soil, sludge and treated biowaste.

NOTE 4 In particular for relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Table B.2 (Annex B) and this table.

## 13 Test report

The test report shall contain at least the following details:

a) reference to this European Standard and the Method used (A or B);

b) all necessary information on the full identification of the sample;

c) the result according to 10.4 or 11.4 respectively;

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

e) details of all procedural steps which deviate from this standard together with all circumstances that may have influenced the result.

# Annex A
(informative)

# Validation of dry combustion methods

## A.1 General

The performance data of method A and B given in Table 1 have been established in an European interlaboratory study on five samples of waste and sludge and one synthetic mixture carried out in 1999.

**Table 1 – Performance data (method A and B)**

| Sample | | $P$ | $N$ | $O$ (%) | $m$ (% $w_{dr}$) | $s_R$ (% $w_{dr}$) | $S_R$ (%) | $s_r$ (% $w_{dr}$) | $S_r$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| METHOD A | | | | | | | | | |
| S1 | synthetic mixture [1)] | 20 | 76 | 0 | 8,662 | 0,7614 | 8,79 | 0,1854 | 2,14 |
| S2 | filter cake | 20 | 76 | 1 | 7,798 | 1,4925 | 19,14 | 0,1716 | 2,20 |
| S3 | bottom ash | 19 | 73 | 5 | 3,631 | 0,5548 | 15,28 | 0,1205 | 3,32 |
| S4 | electro-plating sludge | 18 | 71 | 8 | 3,333 | 0,4029 | 12,09 | 0,1303 | 3,91 |
| S5 | dredged sludge | 19 | 71 | 0 | 7,559 | 1,8239 | 24,13 | 0,3409 | 4,51 |
| S6 | Rubble | 19 | 71 | 5 | 6,759 | 0,8408 | 12,44 | 0,2156 | 3,19 |
| METHOD B | | | | | | | | | |
| S1 | synthetic mixture [1)] | 10 | 40 | 20 | 8,332 | 0,4874 | 5,85 | 0,2316 | 2,78 |
| S2 | filter cake | 12 | 46 | 8 | 8,498 | 0,8354 | 9,83 | 0,2507 | 2,95 |
| S3 | bottom ash | 11 | 42 | 16 | 3,779 | 0,9905 | 26,21 | 0,1629 | 4,31 |
| S4 | electro-plating sludge | 10 | 40 | 20 | 3,413 | 0,4792 | 14,04 | 0,1782 | 5,22 |
| S5 | dredged sludge | 13 | 50 | 0 | 7,903 | 1 ,6588 | 20,99 | 0,4939 | 6,25 |
| S6 | Rubble | 11 | 43 | 12 | 6,327 | 1 ,6482 | 26,05 | 0,2461 | 3,89 |

[1)] = 9,1% (theoretical value)

$p$ Number of laboratories

$N$ Number of observed values

$O$ Percentage of outliers

$m$ General mean

$w_{dr}$ Dry matter

$s_R$ Estimate of the reproducibility standard deviation

$s_r$ Estimate of the repeatability standard deviation

$S_R$ Estimate of the relative reproducibility standard deviation

$S_r$ Estimate of the relative repeatability standard deviation

## A.2 Additional results of inter-laboratory tests

### A.2.1 Influence of temperature and modifiers on the decomposition of barium carbonate as an example for a refractory compound

**Table A.1 – Influence of temperature and modifiers on the decomposition of barium carbonate**

| - | - | 900°C | 1100°C | 1300°C |
|---|---|---|---|---|
| Modifier | Ratio $BaCO_3$:modifier | TC% | | |
| 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 |

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

### A.2.2 Influence of aluminium oxide or sodium sulphate used for sample preparation on the recovery of TOC

A real, moist sample (filter cake) was examined by several laboratories. The laboratories used aluminium oxide as well as sodium sulphate for sample preparation (see 9.2). 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 sulphate in a ratio 1:4 to 1:14, see Table A.2.

**Table A.2 - Influence of aluminium oxide or sodium sulphate used for sample preparation on the recovery of TOC**

| Laboratory identification | 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+ $Na_2SO_4$ |
| 1 | 11,7 | 12,8 | 11,3 | - | - | - | 11,4 | 12,3 | 11,0 |
| 2 | 11,8 | 11,9 | 11,0 | 11,5 | 11,6 | 10,9 | - | - | - |
| 3 | 11,6 | 11,9 | - | 11,4 | 11,6 | - | 11,7 | 11,7 | - |
| 4 | 12,0 | 12,1 | 11,6 | 11,8 | 11,8 | 11,5 | 12,0 | 11,3 | - |
| 5 | 11,1 | 11,6 | 11,4 | 10,8 | 11,5 | 11,4 | - | - | - |
| 6 | 11,9 | 12,0 | 10,6 | 11,6 | 11,8 | 10,5 | - | - | - |
| 7 | 12,9 | 13,8 | 10,7 | - | - | - | 9,7 | 12,7 | 5,8 |
| 8 | 11,8 | 11,7 | 10,7 | 11,7 | 11,4 | 10,6 | - | - | - |
| 9 | 11,6 | 11,1 | 10,6 | 11,5 | 11,0 | 10,6 | - | - | - |
| mean | 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 sulphate for sample preparation leads to

— high consumption of sodium sulphate 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.

### A.2.3 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 several laboratories, see Tables A.3 and A.4.

**Table A.3 – Method A: influence of TIC/TOC ratio on the recovery and the coefficient of variation**

| | | Laboratory identification | 1 | 2 | 3 | 4 | 5 | 6 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | ratio TIC:TOC | expected | found | | | | | | mean | recovery | coefficient of variation |
| TC measurements % | 5:5 | 10 | 9,9 | 10,0 | 9,7 | 9,9 | 9,7 | 9,94 | 9,85 | 98% | 1% |
| | 5:1 | 6 | 6,1 | 6,0 | 5,9 | 5,9 | 5,9 | 5,92 | 5,94 | 99% | 1% |
| | 5:0,5 | 5,5 | 5,4 | 5,5 | 5,5 | 5,5 | 5,5 | 5,43 | 5,45 | 99% | 0% |
| | 5:0,1 | 5,1 | 5,1 | 5,1 | 5,0 | 5,0 | 5,0 | 4,99 | 5,02 | 98% | 1% |
| TIC measurements % | 5:5 | 5 | 4,4 | 5,0 | 4,8 | 4,9 | 4,8 | 4,89 | 4,78 | 96% | 4% |
| | 5:1 | 5 | 4,8 | 5,0 | 4,9 | 4,9 | 4,9 | 4,88 | 4,90 | 98% | 1% |
| | 5:0,5 | 5 | 4,9 | 5,0 | 4,8 | 5,1 | 5,0 | 4,86 | 4,93 | 99% | 2% |
| | 5:0,1 | 5 | 4,9 | 5,0 | 4,8 | 4,9 | 4,9 | 4,90 | 4,89 | 98% | 1% |
| TOC results % | 5:5 | 5 | 5,5 | 5,0 | 4,9 | 5,0 | 4,9 | 5,05 | 5,06 | 101 % | 5% |
| | 5:1 | 1 | 1,2 | 1,0 | 1,0 | 1,0 | 1,0 | 1,04 | 1,05 | 105% | 9% |
| | 5:0,5 | 0,5 | 0,6 | 0,5 | 0,7 | 0,4 | 0,4 | 0,57 | 0,52 | 104% | 20% |
| | 5:0,1 | 0,1 | 0,1 | 0,1 | 0,2 | 0,0 | 0,2 | 0,08 | 0,11 | 112% | 51% |

**Table A.4 – Method B: influence of TIC/TOC ratio on the recovery and the coefficient of variation**

| | | laboratory identification | A | B | C | D | E | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ratio TIC:TOC | expected | found | | | | | mean | recovery | coefficient of variation |
| TOC measurements % | 5:5 | 5 | 5,3 | 5,1 | 5,0 | 4,5 | 4,5 | 4,91 | 98% | 7% |
| | 5:1 | 1 | 1,4 | 1,1 | 1,0 | 0,9 | 0,9 | 1,05 | 105% | 20% |
| | 5:0,5 | 0,5 | 0,6 | 0,5 | 0,5 | 0,9 | 0,4 | 0,57 | 114% | 32% |
| | 5:0,1 | 0,1 | 0,0 | 0,1 | 0,1 | 0,3 | 0,1 | 0,14 | 137% | 65% |

Up to a TIC to 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.

### A.2.4 Method A: recovery of TOC for the control mixture A (7.11)

A synthetic mixture of sodium carbonate, $Na_4EDTA\text{-}4H_20$ and aluminium oxide (TOC = TIC = 5%) was analysed by seven laboratories using method A. Results, see Table A.5.

**Table A.5 – Method A: recovery of TOC for the control mixture**

| Laboratory identification | TC % | Recovery % | TIC % | Recovery % | TOC % | Recovery % |
|---|---|---|---|---|---|---|
| 1 | 9,4 | 94 | 4,7 | 94 | 4,8 | 95 |
| 2 | 9,9 | 99 | 4,8 | 95 | 5,2 | 104 |
| 3 | 9,4 | 94 | 5,0 | 99 | 4,4 | 88 |
| 4 | 9,8 | 98 | 4,9 | 98 | 4,9 | 98 |
| 5 | 10,1 | 101 | 4,9 | 97 | 5,3 | 106 |
| 6 | 9,8 | 98 | 4,9 | 97 | 5,0 | 100 |
| 7 | 9,6 | 96 | 4,9 | 99 | 4,6 | 92 |
| 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.

### A.2.5 Method B: influence of the temperature during the removal of inorganic carbon on the recovery of TOC

The control mixture B (7.12) with an expected value of 6,66% was analysed by one laboratory using the procedure of method B (11.1.2).

**Table A.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 A.6.

# Annex B
(informative)

## Repeatability and reproducibility data

## B.1 Performance characteristics

### B.1.1 Objective of the interlaboratory comparison

In a European wide interlaboratory comparison study according to ISO 5725-2, the performance characteristics of the standard “Determination of total organic carbon (TOC) by dry combustion in soil, sludge and treated biowaste” were established.

### B.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of determination of total organic carbon (TOC) by dry combustion in soil, sludge and treated biowaste  was carried out with 15 European laboratories on 6 materials. The materials selected for the interlaboratory comparison were chosen to represent soil, sludge and biowaste as broad as possible, because the standard will find general application across different types of soil and soil related materials.  (detailed information can be found in the final report on the Interlaboratory comparison study mentioned in the Bibliography).

In the interlaboratory comparison study the following starting points were used:

- The laboratory samples were all taken from one large batch of the different materials according to the normal practice. The normal size reduction and the normal repeated mixing were carried out as needed to obtain representative laboratory samples from the large batch sample (ref JRC).
- The experimental plan was designed by project HORIZONTAL on the basis of each laboratory being given two laboratory samples of each material to be tested. This is in accordance with ISO 5725-2.

The materials examined cover all the grain size classes to which the the determination of total organic carbon (TOC) by dry combustion in soil, sludge and treated biowaste applies: very fine grained materials (like sludge: 0 µm to about 125 µm) and fine-grained materials (soil and compost: 0 mm to 4 mm).

Table B.1 provides a list of the types of materials chosen for testing and the selected components.

Table B.A.1 — Material types tested and components analysed in the interlaboratory comparison of the method for the determination of total organic carbon (TOC) by dry combustion in soil, sludge and treated biowaste.

| Grain size class | Sample code | Material type tested | Parameters/congeners |
|---|---|---|---|
| Sludge (<0.5 mm) | Sludge 1 | Mix 1 of municipal WWTP sludges from North Rhine Westphalia, Germany | TOC |
| | Sludge 2 | Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany | TOC |
| Fine grained (< 2 mm) | Compost 1 | Fresh compost from Vienna, Austria | TOC |
| | Compost 2 | Compost from Germany | TOC |
| | Soil 4 | A sludge amended soil from Hohenheim, Germany | TOC |
| | Soil 5 | An agricultural soil from Reading, UK | TOC |

### A.1.3 Interlaboratory comparison 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 B.2).

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by the same laboratory using its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The repeatability limit was calculated using the relationship : $r_{test} = f \cdot \sqrt{2} \cdot s_{r,test}$ with the critical range factor f = 2.

For instance, the repeatability limit around a measurement result of 200 g TOC/kg is ± 14.3 g TOC/kg (i.e ± 7 % of 200).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value f = 2 used in the factor $f \cdot \sqrt{2}$ corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value f = 2 corresponds to the usual value k = 2 of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). However it may be necessary to use a larger value for f in situation as described in clause 12.

The reproducibility, like repeatability is also determined as an interval around a measurement result (i.e. "reproducibility limit"). This interval corresponds to the maximum difference that can be expected (with a 95%

statistical confidence) between one test result and another test result obtained by another laboratory, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard by two different laboratories using their own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The reproducibility limit was calculated using the relationship: $R = f \cdot \sqrt{2} \cdot s_R$ with the critical range factor f = 2.

For instance, the reproducibility limit around a measurement result 200 g TOC/kg is ± 31.1 g TOC/kg (i.e. ± 16 % of 200).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value f = 2 used in the factor $f \cdot \sqrt{2}$ corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value f = 2 corresponds to the usual value k = 2 of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the dispersion limit is equal to $k \cdot s_R$ with the usual value k = 2, resulting in a dispersion limit lower than the reproducibility limit (i.e. a ratio of $\sqrt{2}$). However it may be necessary to use a larger value $f \cdot \sqrt{2}$ (or k) in situation as described in clause 12 .

In case of relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Tables B.2 (this means that the value chosen for the critical range factor f is larger than 2 as well as for the coverage factor k for dispersion). This is because the extreme results may have been obtained in accordance with the present standard and/or be caused by the variability within, or in between, the laboratory samples.

Table B.A.2 — Results of the interlaboratory comparison studies of the Determination of total organic carbon (TOC) by dry combustion in soil, sludge and treated biowaste. All concentrations in g/kg.

| Matrix | Parameter | Mean | sr | sR | r | R | p | Outliers | Total number of data | No of LOD |
|---|---|---|---|---|---|---|---|---|---|---|
| Sludge 1 | TOC | 272 | 1.69% | 5.89% | 12.8 | 44.9 | 13 | 2 | 62 | 0 |
| Sludge 2 | TOC | 220 | 2.09% | 4.98% | 12.9 | 30.8 | 12 | 2 | 58 | 0 |
| Compost 1 | TOC | 246 | 2.46% | 4.33% | 16.9 | 29.9 | 13 | 2 | 58 | 0 |
| Compost 2 | TOC | 154 | 5.87% | 9.58% | 25.3 | 41.4 | 13 | 2 | 64 | 0 |
| Soil 4 | TOC | 16.4 | 2.64% | 5.23% | 1.21 | 2.40 | 12 | 3 | 62 | 0 |
| Soil 5 | TOC | 21.0 | 5.16% | 8.16% | 3.04 | 4.80 | 10 | 3 | 54 | 0 |

Abbreviations: sr Repeatability standard deviation; SR Reproducibility standard deviation; r Repeatability limit (comparing two measurements); R Reproducibility limit (comparing two measurements); p Number of labs.

# Annex C

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

**(This method is subject to validation by interlaboratory studies after which the status (as an integrated part of the standard) will be determined)**

## C.1 General

TOC determinations in solid samples such as soils and sediments can 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.

## C.2 Application range

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 (for example 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 must be stirred immediately prior to sampling by the analytical system. The analytical system must 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

The use of ultrapure water with a maximum TC content of 300 µg/L is required for the preparation and dilution of standard solutions as well as the hydrochloric acid used for the suspensions.

### C.4.2 Potassium hydrogen phthalate

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

### C.4.3 Hydrochloric acid

The suspensions are prepared in a 0.22 N hydrochloric acid solution. For the preparation of this solution, hydrochloric p.a. with a concentration of up to 37 % was used. Ultrapure water was used for the dilutions.

### C.4.4 Gases

Gases according to EN 1484.

Auxiliary gases such as carrier gas or sparging gas must 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 is required which includes 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

In principle, the instrument is calibrated according to the directions 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 ultrapure water. When available, the automatic dilution function of the analytical apparatus can be used to prepare the dilutions. For example: The standard solution contains 100 mg C/L. The dilution factors are 10, 5, 3, 2 and 1. This results in a dilution series with concentrations of 10,0, 20,0, 33,3, 50,0 and 100 mg C/L. A calibration line is established by plotting the TC mass concentrations, in milligrams per litre carbon, against the instrument-specific measuring value (I). The slope of this line corresponds to the instrument response factor and its reciprocal value is the calibration factor (f).

### C.6.2 Control experiments

Control experiments with respect to calibration are to be carried out according to EN 1484. In addition, the suitability of the instrument with regard to the suspension method should 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 mg (± 10 mg) of the dried and ground sample are weighed into a 300 mL Erlenmeyer flask, to which 200 mL of a 0,22 N hydrochloric acid solution (3.3) is subsequently added. If the sample consists mainly of carbonates (limestone), the amount of sample can be increased to a maximum of 2000 mg. In both cases, the volume percentage 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 17,000 rpm to 18,000 rpm. 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 as follows:

$$TOCs = \frac{Vsus * I * 100}{Es * f} [\%m/m]$$

$TOC_S$: organic carbon in the solid sample [% m/m]

I: instrument-specific measuring value [#]

$V_{SUS}$: volume of the suspension [L]

$E_S$: weight of the solid sample [mg]

f: calibration factor [# L / mg].

### C.7.2 Blank value

The TC blank values of the ultrapure water and the 0.22 N 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 % [m/m]. The calculation must take into account that ultra pure water is also used in the calibration. Therefore the following applies:

$$b = \frac{(b_{HCL} - b_{H_2O}) * V_{SUS} * 100}{Es} [\%m/m]$$

b: blank value with respect to the solid sample [% m/m]

$b_{HCL}$: blank value of the 0.22 N hydrochloric acid [mg/L]

$b_{H20}$: blank value of the ultrapure water.

The determination of the blank values $b_{H2O}$ and $b_{HCL}$ requires an analytical instrument with sufficient detection sensitivity for this concentration range (determination limit ≤ 200 µg/L).

## C.8 Method characteristics

**Table B.1 — Measurement of a certified reference material**

| **Reference material** | **NIST 1941b** |
|---|---|
| Target value (mass %) | 2,99 ± 0,24 |
| Number of in-house measurements | 50 (10 series of 5 injections) |
| Overall mean value (mass %) | 2,96 |
| Number of outliers (Grubbs) | 0 |
| Mean recovery (%) | 99,0 |
| Relative standard deviation: | |

| | |
|---|---|
| Within series (%)<br>Between series (%) | 5,6<br>4,1 |
| Overall standard deviation (%) | 4,6 |
| Extended measuring uncertainty (k = 2) | 24,1 % |

# Annex D
(informative)

# Validation document for the TOC suspension method

(according to document A0-2 in the German Standard Methods for the Examination of Water, Wastewater and Sludge)

## D.1 General information on development of the method

### D.1.1 Start and end date of the process

a) 08/2004 - 02/2006.

### D.1.2 Chairman and vice chairman

TEXT MISSING – UNLESS IT SHOULD BE A LISTING?

### D.1.3 Membership List

TEXT MISSING – UNLESS IT SHOULD BE A LISTING?

## D.2 Application area

### D.2.1 Parameters determined.

TOC.

### D.2.2 Area of operations

#### D.2.2.1 Tested matrices

a) Soils (sandy silt, topsoil, clay, shale).

b) Sediments (marine sediments, river sediments).

c) Suspended matter.

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

#### D.2.2.2 Tested and calibrated concentration range

0,1 - 20 % (m/m).

#### D.2.2.3 Further applications of the method

In principle, this method can be applied to TC and $TN_b$ in solids.

## D.3 Basic principles of the method

The TOC suspension method is a special sample preparation method for TOC determination in solid samples. The sample material is ground using an appropriate grinding method (for example ball mill) to a fine powder with particle size ≤ 130 µm, which is subsequently suspended in dilute hydrochloric acid.

Minimising of sedimentation of the suspension is very important. Sediment particles are effectively suspended using a homogeniser suitable for small particle sizes. The suspensions must be stirred immediately prior to sampling by the analytical system . The analytical system must be suitable with respect to samples containing particulate matter according to EN 1484.

Determination of organic carbon in 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. The following simplification can therefore be used: NPOC = TOC.

## D.4 Interferences

a) Insufficient grinding, i.e. to attain particle sizes < 130 µm, can potentially lead to poor reproducibility.

b) Inclusions of, for instance, vitreous elemental carbon as well as carbonates. Fly ashes show significant differences in comparison with measuring methods for solids and suspensions.

## D.5 Reagents, test organisms, instruments

### D.5.1 Blank values

The ultra pure water used for dilution and the hydrochloric acid (p.a.) generate blank values. With respect to the solid sample, the blank value lies between 0.02 and 0.06 % carbon (m/m), provided that the instruments used are clean.

### D.5.2 Requirements with respect to purity of reagents

32 % hydrochloric acid p.a., ultra pure water (carbon content < 300 µg/L), potassium hydrogen phthalate p.a.

### D.5.3 Availability of reagents, standards and reference materials

a) Certified reference material NIST 1941b (marine sediment), NIST, Gaithersburg, MD 20899-1070, USA

b) Reference material QTM068MS (marine sediment), QUASIMEME, Wageningen, the Netherlands

### D.5.4 Stability of reagents

See information and instructions in the EN Standards listed in the Bibliography.

### D.5.5 Test organisms

No test organisms were used.

### D.5.6 Chromatographic separation phases

No separation phases were used.

### D.5.7 Instruments

The detection sensitivity of the analytical instruments must be sufficiently high in order to measure the blank value. Determination limit: TC < 200 µg C/L.

### D.5.8 Occupational safety and environmental protection/pollution control

See information and instructions in the DIN Standards listed in the Bibliography.

## D.6 Sampling and sample preparation

### D.6.1 Sampling

See information and instructions in the EN standards listed in the Bibliography.

### D.6.2 Sample stability and sample preservation

See information and instructions in the EN Standards listed in the Bibliography.

### D.6.3 Occupational safety and environmental protection

See information and instructions in the EN Standards listed in the Bibliography.

## D.7 Implementation

### D.7.1 Sample preparation enrichment conditions

200 mg (± 10 mg) of the dried and ground sample are weighed into a 300 mL Erlenmeyer, to which 200 mL of a 0,22 N hydrochloric acid solution is subsequently added. If the sample consists mainly of carbonates (limestone), the amount of sample can be increased to a maximum of 2000 mg. In both cases, the volume percentage 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 17,000 rpm to 18,000 rpm. A suspension is formed.

### D.7.2 Sample measurement, measuring instrument parameters

After purging with an inert gas, the NPOC and TOC in the suspension is determined as mean value from 4 single injections and subsequently calculated with reference to the original solid sample. The suspension has been stirred during purging and immediately prior to withdrawing of an aliquot of the sample. Apart from this, the guidelines of the instrument manufacturer are standard.

## D.8 Determination of the method characteristics

### D.8.1 Variances in homogeneity

a) Data are available (F-test, PW = 1,17, KW = 18,51).

### D.8.2 Linearity testing

a) F-test according to Mandel.

b) Optimal regression model: linear (PW = 4,05 KW = 21,19).

### D.8.3 Type of calibration

a) Linear regression.

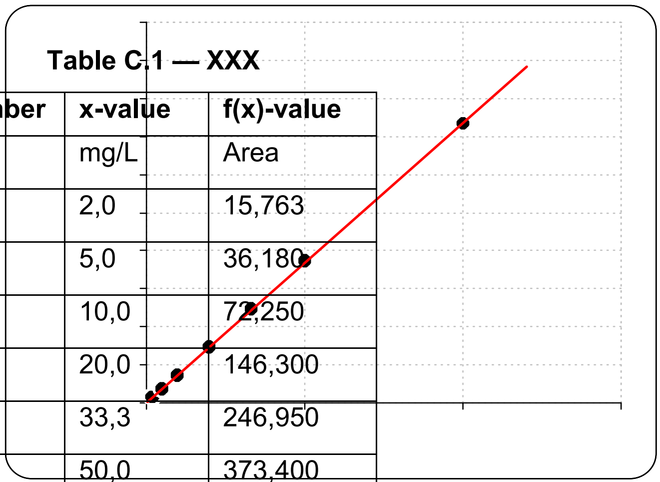
### D.8.4 Calibration standards

a) Potassium hydrogen phthalate p.a. 100 mg/L as stock solution.

### D.8.5 Calibration data and functions

**Table C.1 — XXX**

| Number | x-value | f(x)-value |
|---|---|---|
| | mg/L | Area |
| 1 | 2,0 | 15,763 |
| 2 | 5,0 | 36,180 |
| 3 | 10,0 | 72,250 |
| 4 | 20,0 | 146,300 |
| 5 | 33,3 | 246,950 |
| 6 | 50,0 | 373,400 |
| 7 | 100,0 | 734,150 |



a) Residues are normally distributed (R/s test, 99 %, PW = 2,89, KW = 2,26 – 3,33).

b) Residues do not show a trend (Neumann test, 99 %, PW = 2,03, KW = 0,61).

c) Residual standard deviation: 2,748.

d) Standard deviation of the method: 0,373.

e) f(x)-value = 7,36 * x-value + 0,475.

f) R = 0,9999, N = 7.

### D.8.6 Detection, quantification and determination limit (according to DIN 32645)

**Table C2 — XXX**

| | | |
|---|---|---|
| Detection limit | 1,1 mg/L | 0,1 % |
| Quantification limit | 2,2 mg/ L | 0,2 % |
| Determination limit | 3,9 mg/ L | 0,4 % |

Alternatively, calibrations were carried out in other concentration ranges with a possible determination limit of <100 µg C/L, corresponding to < 0,1 % (calibration range up to 1000 µg C/L).

### D.8.7 Recalibration

See information and instructions in the EN Standards listed in the Bibliopgrahy.

## D.9 Testing for trueness (accuracy of the mean)

### D.9.1 Reference material

See information in Clause 5.

### D.9.2 Standard addition method for the matrices

No standard addition method was deployed.

### D.9.3 Recovery rates

a) Reference material NIST 1941b: 99,0 % for N = 50 measurements.

b) Reference material QTM068MS: 97,6 % for N = 30 measurements.

### D.9.4 Comparison with results of other analytical procedures

Measurements of different types of soil

1 = Suspension, 2 = SSM

| | | | | |
|---|---|---|---|---|
| Mean 1 | 0.6% | 0.7% | 1.2% | 1.7% |
| Mean 2 | 0.4% | 0.8% | 1.4% | 2.0% |
| sd 1 | 0.001 | 0.000 | 0.001 | 0.001 |
| sd 2 | 0.003 | 0.001 | 0.001 | 0.0004 |
| N1 | 5 | 4 | 5 | 5 |
| N2 | 5 | 5 | 5 | 5 |
| t | 1.233 | 1.364 | 2.304 | 2.004 |
| t(f,P=95%) | 2.306 | 2.365 | 2.306 | 2.306 |
| t(f,P=99%) | 3.355 | 3.499 | 3.355 | 3.355 |

## D.10 Precision testing

### D.10.1 Type of samples used

Reference materials, see Clause 5.

### D.10.2 Statistical evaluation

**Table C3 — XXX**

| | |
|---|---|
| **Reference material 1** | **NIST 1941b** |
| Target value (mass %) | 2,99 ± 0,24 |
| Number of in-house measurements | 50 (10 series of 5 injections) |
| Time frame | April to August 2005 |
| Overall mean value (mass %) | 2,96 |
| Number of outliers (Grubbs) | 0 |
| Mean recovery (%) | 99,0 |
| Relative standard deviations:<br>Within series (%)<br>Between series (%) | <br>5,6<br>4,1 |
| Overall standard deviation (%) | 4,6 |
| **Reference material 2** | **QTM068MS** |
| Target value (mass %) | 2,23 |
| Total error (%) | ± 0,33 |
| Number of measurements | 30 (6 series of each 5 injections) |
| Time frame | May to June 2005 |
| Overall mean value (mass %) | 2,15 |
| Number of outliers (Grubbs) | 0 |
| Mean recovery (%) | 97,6 |
| Relative standard deviations:<br>Within series (%)<br>Between series (%) | <br>5,3<br>8,9 |
| Overall standard deviation (%) | 7,5 |

## D.11 Robustness, stability

See Clause 4.

## D.12 Characteristic method data from round robin tests

### D.12.1 General

Three laboratories participated in the following tests on the TOC suspension method:

a) ISE (International Soil Analytical Exchange, WEPAL, Wageningen University, Wageningen, NL).

b) SETOC (International Sediment Exchange for Tests on Organic Contaminants, WEPAL, Wageningen University, Wageningen, NL).

### D.12.2 Time frame of the round robin tests

a) Time frame: October - December 2005; number of participating laboratories: 32

b) Time frame: October - December 2005; number of participating laboratories: 17

### D.12.3 Parameters analysed as described in Clause 2

a) TOC (mg/kg).

### D.12.4 Reference materials used as described in Clause 5

a) 100 g soil samples 1 - 4 (2 x sandy soil, 2 x clay)

b) 100 g sediment samples 1 - 4 (3 x sediment, 1 x clay)

### D.12.5 Matrices studied

See C.12.3.

### D.12.6 Concentration ranges studied

| | TOC-values [mg/kg] | | | Z-Scores | | |
|---|---|---|---|---|---|---|
| Sample | Lab 1 | Lab 2 | Lab 3 | Lab 1 | Lab 2 | Lab 3 |
| SETOC-1 | 101 | 101 | 101.0 | -0.56 | -0.56 | -0.56 |
| SETOC-2 | 41.9 | 43.8 | 41.3 | -0.31 | 0.16 | -0.46 |
| SETOC-3 | 44.0 | 46.5 | 42.4 | 0.38 | 2.04 | -0.68 |
| SETOC-4 | 57.9 | 56.6 | 56.9 | -0.23 | -0.82 | -0.69 |
| ISE-1 | 13.9 | 16.3 | 15.2 | -0.43 | 1.78 | 0.77 |
| ISE-2 | 18.3 | 17.8 | 19.6 | 0.52 | 0.03 | 1.78 |
| ISE-3 | 56.8 | 54.5 | 56.1 | -1.15 | -2.93 | -1.69 |
| ISE-4 | 46.3 | 46.0 | 49.9 | -2.84 | -3.01 | -0.80 |

| Sample | Median | MAD | N | Mean | sR | rel sR |
|---|---|---|---|---|---|---|
| SETOC-1 | 104 | 3.00 | 13 | 103 | 4.40 | 4.2 |
| SETOC-2 | 43.8 | 1.90 | 15 | 43.2 | 4.09 | 9.5 |
| SETOC-3 | 43.7 | 0.83 | 12 | 43.4 | 1.51 | 3.5 |
| SETOC-4 | 58.1 | 1.50 | 13 | 58.4 | 2.21 | 3.8 |
| ISE-1 | 14.2 | 0.70 | 29 | 14.4 | 1.09 | 7.6 |
| ISE-2 | 17.8 | 0.60 | 26 | 17.8 | 1.03 | 5.8 |
| ISE-3 | 58.2 | 0.80 | 24 | 58.3 | 1.29 | 2.2 |
| ISE-4 | 51.3 | 1.21 | 26 | 51.3 | 1.76 | 3.4 |

MAD = Median of absolute deviation

sR = Reproducibility

rel sR = Relative reproducibility

### D.12.7 Outlier rate

a) No information from the PT provider.

### D.12.8 Relative repeatability

a) No information from the PT provider

### D.12.9 Relative reproducibility

a) For relative reproducibility (rel sR) see 12.5

### D.12.10 Comparison of results obtained by other analytical procedures

See C.9.4.

## D.13 Measurement uncertainty

### D.13.1 Type of the investigation

Multiple measurements of certified reference materials in C.5.3.

### D.13.2 Typical result regarding specification of the matrix and concentration levels

U(y) = 12,3 % - 20,9 %.

The measurement uncertainty indicated is an expanded uncertainty (coverage factor k = 2, confidence level 95 %) calculated for sediments in the concentration range 2 % to 4 %.

## D.14 Evaluation

### D.14.1 Identification criteria

See information and instructions in the EN Standards listed in the Bibliography.

### D.14.2 Calculation and specification of the results

See information and instructions in the EN Standards listed in the Bibliography.

# Bibliography

[1] EN 1484, *(DEV H3) Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*

[2] EN 13137, *Characterisation of waste – determination of total organic carbon (TOC) in waste, sludges and sediments*

[3] Servos U, Gluschke M, Kramer T: Der TOC in Sedimenten und Böden – Fortschritte in der Analytik. Wasser, Luft und Boden (wlb), 10/2005, 46 – 49