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

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Foreword

This document is developed in the project 'Horizontal'. It is a result of a desk study on dry matter, loss on ignition and total organic carbon that aimed at describing horizontal standards to be used for sludge, soil and biowaste. After discussion with all parties concerned in CEN the standard will be developed further as a modular horizontal method and validated in the project 'Horizontal'.

Until now test methods determining properties of materials were often prepared in Technical Committees (TC's) working on specific products or specific sectors. 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 a test procedure and not the whole test procedure (from sampling to analyses).

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, together forming the basis for the test procedure.

This standard is a module for determination of total organic carbon. The other horizontal modules that will be available in due time are to be found in the informative annex [xxx], which contains a brief overview of the modules that are or will be worked out in the project 'Horizontal.'

The texts of chapters 1 to 13 are normative; annexes are informative, as stated in the top lines of the annexes.

Annex A of this European Standard is informative.

Introduction

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

1 Scope

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

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.

2 Normative references

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

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

ISO 8466-1, *Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function.*

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

EN XXXXX, *Chemical Analyses - Determination of dry matter and water content on a mass basis in sediment, sludge, soil, and waste - Gravimetric method.*

ISO 3696, *Water for analytical laboratory use – specification and test methods.*

3 Terms and definitions

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

3.1 total carbon (TC)

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

3.2 total inorganic carbon (TIC)

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

3.3 total organic carbon (TOC)

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

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

4 Principle

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

4.1 Method A (indirect procedure)

In this procedure the TOC is obtained by the difference between the results of the measurements of TC and TIC.

The total carbon (TC) present in the undried sample or previously dried sample is converted to carbon dioxide by combustion in an oxygen-containing gas flow free of carbon dioxide. To ensure complete combustion, catalysts and/or modifiers can be used. The released amount of carbon dioxide is measured by infrared spectrometry, gravimetry, coulometry, conductometry, thermal conductivity detection, flame ionization detection after reduction to methane, or other suitable techniques.

The TIC is determined separately from another sub-sample by means of acidification and purging of the released carbon dioxide. The carbon dioxide is measured by one of the techniques mentioned above.

4.2 Method B (direct procedure)

In this procedure the carbonates present in the undried sample 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 4.1 and indicates the TOC directly.

4.3 Applicability of Methods A or B

Methods A and B have the same applicability in the terms of TOC content and/or TIC to TOC ratio.

Method B may lead to incorrect results in following cases:

- the sample contains volatile substances that evaporate during the acidification (e.g. volatile hydrocarbons from sludge of oil separators);
- side reactions between the sample and the acid take place (e.g. decarboxylation, volatile reaction products).

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

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

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.

The procedures may lead to unreliable TOC results if the TIC to TOC ratio is very high (e.g. • 10).

Depending on the detection method used, different interferences may occur, for instance:

- the presence of cyanide can interfere with the coulometric detection of TIC by modifying the pH value (dissolution of HCN);
- high content of halogenated compounds may lead to an overestimation of TOC when coulometric detection is used; in some cases the classical silver or copper trap can be insufficient to absorb all halides.

6 Hazards

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

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

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

7 Reagents

7.1 General

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

Hygroscopic substances shall be stored in a desiccator.

7.2 Calcium carbonate, CaCO_3

7.3 Sodium carbonate, Na_2CO_3 , anhydrous

7.4 Tetrasodium ethylenediamine tetraacetate-tetra-hydrate, $\text{Na}_4\text{-EDTA}\cdot 4\text{H}_2\text{O}$,

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

NOTE Other forms of $\text{Na}_4\text{-EDTA}$ hydrates may be used if the water content is exactly known. Then the composition of the control mixtures has to be recalculated accordingly (see also 7.11 and 7.12).

7.5 Potassium hydrogen phthalate, $\text{C}_8\text{H}_5\text{O}_4\text{K}$

7.6 Acetanilide, $\text{C}_8\text{H}_9\text{NO}$

7.7 Atropine, $\text{C}_{17}\text{H}_{23}\text{NO}_3$

7.8 Spectrographic graphite powder, C

7.9 Sodium salicylate, $\text{C}_7\text{H}_5\text{O}_3\text{Na}$

7.10 Aluminium oxide, Al_2O_3 , neutral, granular size $< 200\ \mu\text{m}$, annealed at 600°C

7.11 Control mixture A: sodium carbonate (7.3), $\text{Na}_4\text{-EDTA}\cdot 4\text{H}_2\text{O}$ (7.4) and aluminium oxide (7.10) 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 $\text{Na}_4\text{-EDTA}\cdot 4\text{H}_2\text{O}$, 37,04 g of aluminium oxide).

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

7.13 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 possible diluted 1 : 1 is preferred.

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

8 Equipment

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

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

8.3 Equipment for determination of carbon in solids; with accessories

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

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

9 Sample storage

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.

10 Procedure Method A (indirect method)

10.1 Sample preparation

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

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

- a) Solid samples may be directly comminuted (avoiding heat) and reduced to a granular powder, preferable particle size less than 200 μm .
- b) Moist or paste-like samples may be mixed with aluminium oxide (7.10) 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 (10.6 or 11.6).

If samples contain - according to the accuracy of the method - negligible amounts of volatile compounds except water, the samples may be dried at 105°C before homogenization. For analysing liquid sludges, especially sewage sludge, freeze-drying may also be used. In 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".

10.2 Water content

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

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

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

10.3 Determination

10.3.1 General

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

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

The weight of the test portion should be as large as possible and shall be chosen so that the liberated quantity of carbon dioxide lies within the working range of the equipment/calibration.

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

10.3.2 Determination of the TC

The sample prepared according to 10.1 is weighed into a suitable vessel (boat or crucible made of e.g. ceramics, silica glass, platinum or tin). To minimize carbon blank values the vessel may be pretreated 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 1500°C.

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

The carbon dioxide released during the analysis is measured using one of the detection methods in accordance with clause 4 and is expressed as carbon.

10.3.3 Determination of the TIC

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

The system is closed gas-tight and flushed with carrier gas until no more carbon dioxide from ambient air is present. Then acid (7.13) 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.

10.4 Calibration

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

Examples of calibration substances suitable for TC are calcium carbonate (7.2), potassium hydrogen

phthalate (7.5), acetanilide (7.6), atropine (7.7), spectrographic graphite powder (7.8). Sodium carbonate (7.3) and Na₄-EDTA (7.4) as well as all compounds with EDTA-structure shall not be used for calibration as they are used as control substances.

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

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

The following procedure should be adopted during calibration:

Establish the preliminary working range.

- Measure a minimum of five (recommended ten) standard samples at least in triplicate. The
- Concentration of these standard samples shall be distributed evenly over the working range.
- Calculate mean values for each concentration.
- Carry out a linear regression analysis with the mean values and test the linearity of the calibration function using ISO 8466-1.

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

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

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

10.5 Control measurements

Control measurements shall be performed to check that the equipment is functioning correctly. They should be carried out each working day using the control mixture A (7.11) for the procedures according to 10.3.2 (TC) and 10.3.3 (TIC). Analysis of one concentration from the middle of the respective working range repeated three times is sufficient. For the TC and TIC the mean recovery has to be between 90% and 110% with a coefficient of variation • 5%.

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:

TC analysis

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

10.6 Evaluation

The TC and TIC mass contents of the samples prepared according to 10.1 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 TC and TIC results are reported as means of at least two measurements each. The respective difference of the two values should be • 10% of the mean. If this is not the case, at least one further determination is necessary; then the coefficient of variation should be • 10%. If this is not the case, the relevant coefficient of variation shall be reported together with the result.

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 10.1 b) a dilution factor following equation (2) has to be considered:

$$V_{TOC} = f(V_{TOC} - V_{TIC}) \quad (1)$$

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

where:

| | |
|-----------|---|
| V_{TOC} | is the TOC content as carbon in the original sample in grams per kilogram (g/kg); |
| V_{TC} | is the mean value of the TC content as carbon in the sample prepared according to 10.1 in grams per kilogram (g/kg); |
| V_{TIC} | is the mean value of the TIC content as carbon in the sample prepared according to 10.1 in grams per kilogram (g/kg); |
| f | is the dilution factor resulting from the sample preparation of the original sample according to 10.1b); |
| m_s | is the mass of the original sample (to be mixed with aluminium oxide according to 10.1 b); |
| m_a | is the mass of aluminium oxide according to 10.1b). |

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 10.2 is used:

$$V_{TOC_{dm}} = V_{TOC} \times \frac{100}{100 - W} \quad (3)$$

where:

| | |
|----------------|--|
| $V_{TOC_{dm}}$ | is the TOC content as carbon, calculated on dry matter basis in grams per kilogram (g/kg); |
|----------------|--|

V_{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 10.2 as mass fraction in percent (%)

The TOC content is usually determined on the undried sample, but it is always 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 Sample preparation

See 10.1.

11.2 Water content

See 10.2.

11.3 Determination

11.3.1 General

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

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

The weight of the test portion should be as large as possible and shall be chosen so that the liberated quantity of carbon dioxide lies within the working range of the equipment/calibration.

TOC measurements are made at least twice. The difference of the two values should be • 10% of the mean. If this is not the case, at least one further determination is necessary; the coefficient of variation should then be • 10%. If this is not the case, the coefficient of variation shall be reported together with the result.

11.3.2 Removal of the inorganic carbon and determination of TOC

The sample prepared according to 11.1 is weighed into a suitable vessel (boat or crucible made of e.g. ceramics, silica glass, platinum or tin). 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 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. 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).

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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 1500°C.

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

11.4 Calibration

The calibration for TOC has to be done in accordance with the calibration for TC (10.4). The selection of the calibration substances is analogous.

11.5 Control measurements

Control measurements should be carried out each working day using the control mixture B (7.12) for the procedure according to 11.3.2. 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:

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.

11.6 Evaluation

The TOC mass contents of the samples prepared according to 10.1 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 results are reported as a mean of at least two measurements. The difference of the two values should be • 10% of the mean. If this is not the case, at least one further determination is necessary; then the coefficient of variation should be • 10%. If this is not the case, the coefficient of variation shall be reported together with the result.

The TOC is calculated on dry matter basis by equation (4). For this purpose the water content determined separately according to 10.2 and, if necessary, the dilution factor resulting from sample preparation is used.

$$V_{TOCdm} = f \times V_{TOC} \times \frac{100}{100 - W} \quad (4)$$

where:

| | |
|-------------|--|
| V_{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 10.1b) and in accordance with equation (2); |
| V_{TOC} | is the mean value of TOC content as carbon in the sample prepared according to 10.1 in grams per kilogram (g/kg); |
| W | is the water content of the original sample according to 10.2 as mass fraction in percent (%). |

The TOC content is usually determined on the undried sample, but it is always 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 Performance characteristics

The performance data of method A and B given in Table 1 have been established in an European intercomparison 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 | | | | | | | | |

13 Test report

The test report shall contain at least the following details:

- c) reference to this European Standard and the Method used (A or B);
- d) all necessary information on the full identification of the sample;
- e) the result according to 10.6 or 11.6 respectively;
- f) details of all procedural steps which deviate from this standard together with all circumstances that may have influenced the result.

Annex A

(informative)

Additional results of inter-laboratory tests**A.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 |

Result:

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

A.2 Influence of aluminium oxide or sodium sulphate used for sample preparation on the recovery of TOe

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 10.1 and 11.1). 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 | | | | | |
|---------------------------|-----------------|--|---|--|---|-----------------|--|---|------|
| | original sample | sample+ Al ₂ O ₃ | sample+ Na ₂ SO ₄ | method A % | | | method B % | | |
| original sample | | | | sample+ Al ₂ O ₃ | sample+ Na ₂ SO ₄ | original sample | sample+ Al ₂ O ₃ | sample+ Na ₂ SO 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% | - |

Results:

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.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 Table A.3.1 and A.3.2.

Table A.3.1 - Method A: influence of TIC/TOC ratio on the recovery and the coefficient of variation

| | ratio TIC:TOC | Laboratory identification | 1 | 2 | 3 | 4 | 5 | 6 | | | |
|--------------------------|------------------|------------------------------|-------|------|-----|-----|-----|------|------|----------|-----------------------------|
| | | 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.3.2 - Method B: influence of TIC/TOC ratio on the recovery and the coefficient of variation

| | ratio TIC:TOC | laboratory identification | A | B | C | D | E | mean | recovery | coefficient of variation |
|--------------------------|------------------|------------------------------|-------|-----|-----|-----|-----|------|----------|-----------------------------|
| | | expected | found | | | | | | | |
| 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% |

Result:

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.4 Method A: recovery of TOE for the control mixture A (7.11)

A synthetic mixture of sodium carbonate, Na₄EDTA-4H₂O and aluminium oxide (TOC = TIC = 5%) was analysed by seven laboratories using method A. Results, see Table A.4.

Table A.4 - 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% | - |

Result: For method A the required recovery was generally achieved.

A.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 (11.3.2).

Table A.5 - 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 |

Result:

Temperatures higher than 40°C during the removal of inorganic carbon lead to poor recoveries of TOC, see Table A.5.