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Water quality — Determination of total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TNb) and dissolved bound nitrogen (DNb) after high temperature catalytic oxidative combustion

Qualité de l'eau — Dosage du carbone organique total (COT), carbone organique dissous (COD), azote lié total (TNb) et azote lié dissous (DNb) après combustion catalytique oxydante à haute température

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 230, *Water analysis*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 20236:2018), which has been technically revised.

The main changes are as follows:

- the method to determine concentrations <1 mg/l of C and N has been expanded;
- the normative references have been updated;
- the method to apply single component standard calibration solutions e.g. based on as ammonium sulfate or potassium nitrate, has been expanded;
- Clause A.5 has been added in order to require referencing the difference methods with the results report.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TNb) and dissolved bound nitrogen (DNb) are an analytical convention, whose characteristic is a parameter used for water quality control purposes. These parameters represent the sum of organically bound carbon as well as the sum of inorganic and organic nitrogen (but not nitrogen gas), which can be dissolved in water or bonded to dissolved or suspended matter under specified conditions and, if the sample is not filtered, includes that associated with suspended matter. It does not give information on the nature of the substances. The abbreviations TOC, DOC, TNb, DNb, TC and TIC refer to values determined by the high temperature method.

Details of a validation interlaboratory trial with the performance data for TOC or DOC and TNb or DNb, all using the high temperature method in this document, are given in Annex B.

Water quality — Determination of total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TNb) and dissolved bound nitrogen (DNb) after high temperature catalytic oxidative combustion

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

1 Scope

This document specifies a method to determine the total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TNb) and dissolved bound nitrogen (DNb) in the form of free ammonia, ammonium, nitrite, nitrate and organic compounds capable of conversion to nitrogen oxides.

Cyanide, cyanate and particles of elemental carbon (soot), when present in the sample, can be determined together with the organic carbon.

Dissolved nitrogen gas (N_2) is not determined.

NOTE Generally, the method can be applied for the determination of total carbon (TC) and total inorganic carbon (TIC) – see Annex A.

The method is applicable to water samples (e.g. drinking water, raw water, ground water, surface water, sea water, waste water, leachates).

This document is applicable to determination of TOC and DOC ≥1 mg/l and TNb and DNb ≥1 mg/l. The upper working range is restricted by instrument-dependent conditions (e.g. injection volume). Higher concentrations can be determined after appropriate dilution of the sample. The determination of concentrations <1 mg/l is dependent on instrument conditions applying appropriate calibration.

For samples containing volatile organic compounds (e.g. industrial waste water), the application of the difference method can be considered – see Annex A.

The procedure is carried out by automated analysis.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods — Part 1: Linear calibration function*

3 Terms and definitions

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

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

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

3.1
total carbon
TC
sum of measured organically and inorganically bound carbon present in water, including elemental carbon

Note 1 to entry: The total carbon is defined as measured under the conditions of the method described in this document.

3.2
total inorganic carbon
TIC
sum of measured inorganic carbon present in water

Note 1 to entry: The total inorganic carbon is defined as measured under the conditions of the method described in this document.

Note 2 to entry: The total inorganic carbon is measured as CO_2 originating only from carbonates, hydrogen carbonates and dissolved carbon dioxide.

3.3
total organic carbon
TOC
sum of measured organically bound carbon present in water, bonded to dissolved or suspended matter, including cyanate, thiocyanate and elemental carbon

Note 1 to entry: The total organic carbon is defined as measured under the conditions of the method described in this document.

Note 2 to entry: Volatile organic carbon cannot be guaranteed to be determined by the method.

Note 3 to entry: Generally, total organic carbon includes organic compounds in water that cannot be purged under the conditions of this method, also known as non-purgeable organic carbon (NPOC).

3.4
dissolved organic carbon
DOC
sum of measured organically bound carbon present in water originating from compounds passing through a membrane filter of 0,45 µm pore size, including cyanate and thiocyanate

Note 1 to entry: The dissolved organic carbon is defined as measured under the conditions of the method described in this document.

3.5
total bound nitrogen
TNb
sum of measured organically bound and inorganically bound nitrogen present in water or suspended matter

Note 1 to entry: The total bound nitrogen is defined as measured under the conditions of the method described in this document.

3.6
dissolved bound nitrogen
DNb
sum of measured organically and inorganically bound nitrogen present in water originating from compounds passing through a 0,45 µm membrane filter

Note 1 to entry: The dissolved bound nitrogen is defined as measured under the conditions of the method described in this document.

3.7
chemiluminescence
emission of light by an atom or molecule that is in an excited state as the result of a chemical reaction

4 Principle

Thermal catalytic combustion of organic carbon, and inorganic and organic nitrogen in an oxygen-containing atmosphere is done at ≥680 °C to determine TOC or DOC and at ≥720 °C to determine TNb or DNb.

The TOC or DOC determination is carried out according to the direct measurement method.

Prior to combustion, remove inorganic carbon by acidification and purging with a carrier gas (6.7).

NOTE Platinum and cerium(IV), for example, can be used as catalyst material for combustion. The catalyst serves to accelerate the oxidation process of carbon containing water constituents in excess of oxygen to produce the required carbon dioxide gas for the detection process. Depending on combustion temperature and temperatures in the combustion zone, different catalysts can be used, e.g. metals or metal oxides for temperatures ≥680 °C or sintered alumina for temperatures around 1 200 °C, according to specifications of different suppliers.

The oxidation of organic carbon (TOC and DOC) present in the sample to carbon dioxide is carried out with oxygen or synthetic air followed by the detection of the formed CO_2 by means of infrared (IR) spectrometry.

The combustion and conversion of inorganic and organic nitrogen present in the sample to nitric oxide is carried out with oxygen or synthetic air. The reaction with ozone gives electronically excited nitrogen oxides (NO). The detection of the formed NO is carried out by a chemiluminescence detector (CLD). See Annex C for alternative detection techniques.

This document can be applied for the determination of TOC or DOC and TNb or DNb separately or for simultaneous TOC or DOC and TNb or DNb determinations, for example connecting the IR detector with a chemiluminescence detector in series.

Quality control is necessary to check the validity of the calibration function (see 10.3). Repeating sample measurement can be necessary. The method of standard addition can be required if matrix interferences are expected (see 5.3 and 10.4.2.1).

5 Interferences

5.1 General

Interferences with the determination of TOC or DOC and TNb or DNb can arise from memory effects. Replicate injections are necessary (see 10.4.1).

Detergents, oils and fats can influence the surface tension of the sample, causing erroneous data. A dilution of the sample can reduce such risk.

Samples with extreme pH values, highly buffered samples and samples with high salt contents can cause interference. Seek advice from the instrument manufacturer to solve these interferences.

Suspended material can lead to a loss of quality of the analytical result. If a homogenized sample containing suspended material produces results obtained from injections of independent aliquots in different vials that deviate by more than 10 %, an accurate TOC or TNb result cannot be obtained on the sample (see Annex B).

5.2 TOC or DOC

Inorganic carbon (e.g. CO_2 or ions of carbonic acid) present in the sample interferes with the determination of TOC or DOC. Inorganic carbon is removed by acidification and purging with a gas that is free from CO_2 and organic compounds prior to TOC or DOC determination (see 10.4.2.2 and 10.4.2.3).

NOTE 1 Alternatively, the differential method determining the TC and TIC separately can be applied (see Annex A). The TOC can be calculated by subtracting TIC from TC. This calculation leads to correct results only as long as carbon monoxide, cyanide, cyanate and thiocyanate are present in negligible concentrations.

NOTE 2 Purgeable organic carbon substances, such as benzene, toluene, cyclohexane and chloroform, can partly escape upon stripping (see 10.4.2.2 and 10.4.2.3). In the presence of these substances, the TOC concentration can be determined separately, for example, by applying the differential method (see Annex A).

5.3 TNb or DNb

High loads of DOC or TOC can lead to poor recovery of TNb or DNb. Suspected problems can be identified by determining the nitrogen before and after suitable dilution, or by using standard addition techniques.

NOTE The phrase "high loads" cannot be quantified as it generally depends on, for example, sample matrix properties, equipment applied or working range chosen.

Not all organic nitrogen compounds are quantitatively converted to nitrogen oxide by the combustion procedure described, and consequently to nitrogen dioxide by the reaction with ozone. Poor recoveries can occur with compounds containing either double- or triple-bonded nitrogen atoms. The use of a calibration function calculated according to 10.2 and applying a nitrogen mixed standard solution II (6.9.3.4) can result in a TNb bias for ammonium-N determinations (e.g. ammonium sulfate solution) and for nitrate-N determinations (e.g. potassium nitrate solution). In this case, a single standard (ammonium sulfate or potassium nitrate) can be used.

The use of sulfuric acid for sample preservation or acidification can lead to reduced TNb or DNb results when the calibration standards are not acidified in the same way as the samples.

6 Reagents

Use reagents of pro analysis grade, if available.

Dry all solid reagents for at least 1 h at (105 ± 5) °C. Store the dried solid in a desiccator before weighing.

NOTE It is not necessary to dry cellulose before usage.

Prepare alternative concentrations and volumes of solutions as described hereafter, if necessary. Alternatively, use commercially available stock solutions of the required concentration.

When applying the simultaneous determination of TNb and TOC, the stock solution (6.5) or an appropriate mixture of the 1 000 mg/l TOC and TNb stock solutions (6.5 or 6.8.2 with 6.9.3.1 or 6.9.3.2 or 6.9.3.3) for the preparation of standard, calibration and system check solutions can be used.

6.1 Water.

The contents of carbon and bound nitrogen in water used for the preparation of samples and solutions shall be sufficiently low to be negligible in comparison with the lowest TOC and TNb concentration to be determined.

6.2 **Sulfuric acid**, (H_2SO_4) $\rho = 1{,}84$ g/ml.

6.3 **Hydrochloric acid**, (HCl) $\omega = 30$ % to 32 %.

6.4 **Nicotinic acid**, ($C_6H_5NO_2$), >99,5 %.

6.5 TOC and TNb stock solution for system check.

Place 8,793 g of nicotinic acid (6.4) in a 1 000 ml volumetric flask. Dissolve and dilute to volume with water (6.1).

The solution contains 5 147 mg/l of carbon and 1 000 mg/l of nitrogen.

The solution is stable for six months if stored at (3 ± 2) °C.

6.6 Blank solution.

Fill a 100 ml volumetric flask with water (6.1).

6.7 Oxygen or synthetic air, free from impurities (e.g. carbon dioxide, organic carbon, nitrogen compounds) with influence of the determinant.

Use gases in accordance with the manufacturer's specifications, e.g. a volume fraction of oxygen of 99,7 %.

6.8 Reagents for the TOC or DOC determination.

6.8.1 Potassium hydrogen phthalate, $C_8H_5KO_4$.

6.8.2 Potassium hydrogen phthalate stock solution, $\rho(C) = 1\,000$ mg/l.

Place 2,125 g of potassium hydrogen phthalate (6.8.1) in a 1 000 ml volumetric flask. Dissolve and dilute to volume with water (6.1).

The solution is stable for six months if stored at (3 ± 2) °C.

6.8.3 Potassium hydrogen phthalate standard solution, $\rho(C) = 100$ mg/l.

Pipette 100 ml of the potassium hydrogen phthalate stock standard solution (6.8.2) into a 1 000 ml volumetric flask and dilute to volume with water (6.1).

The solution is stable for one month if stored at (3 ± 2) °C.

6.8.4 TOC and DOC calibration solutions.

Depending on the TOC or DOC concentration expected in the sample, use the potassium hydrogen phthalate standard solution (6.8.3) to prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible.

For example, proceed as follows for the range 1,0 mg/l C to 10,0 mg/l C.

Pipette the following volumes into a series of 100 ml volumetric flasks: 1,0 ml, 2,0 ml, 3,0 ml, 4,0 ml, 5,0 ml, 6,0 ml, 7,0 ml, 8,0 ml, 9,0 ml or 10,0 ml of the potassium hydrogen phthalate standard solution (6.8.3) and dilute to volume with water (6.1).

The concentrations of carbon in these calibration solutions are: 1,0 mg/l, 2,0 mg/l, 3,0 mg/l, 4,0 mg/l, 5,0 mg/l, 6,0 mg/l, 7,0 mg/l, 8,0 mg/l, 9,0 mg/l or 10,0 mg/l, respectively.

Prepare the calibration solutions on the day of use.

6.8.5 Hydrochloric acid TIC stripping solution, e.g. $c(HCl) = 3$ mol/l.

6.8.6 Cellulose $(C_6H_{10}O_5)_n$, microcrystalline of particle size ranging from 0,02 mm to 0,1 mm.

6.8.6.1 Cellulose test suspension for particle processing control, $\rho(C)$ = 100 mg/l.

Place 225 mg of cellulose (6.8.6) in a 1 000 ml volumetric flask, moist with water (6.1) and dilute to volume with water (6.1).

The mixture is stable for one month if stored at (3 ± 2) °C.

Homogenize the suspension with a magnetic stirrer until the suspension is homogeneous before use. Ultrasonic treatment shall not be used because it reduces the particle size.

NOTE It can be helpful to stir the suspension continuously.

6.9 Reagents for the TNb and DNb determination.

6.9.1 Ammonium sulfate, $(NH_4)_2SO_4$.

6.9.2 Potassium nitrate, KNO_3.

6.9.3 Nitrogen stock standard solutions for calibration.

6.9.3.1 Ammonium sulfate stock solution, $\rho(N)$ = 1 000 mg/l.

Place 4,717 g of ammonium sulfate (6.9.1) in a 1 000 ml volumetric flask. Dissolve in 500 ml of water (6.1) and dilute to volume with water (6.1).

The solution is stable for six months if stored at (3 ± 2) °C.

6.9.3.2 Potassium nitrate stock solution, $\rho(N)$ = 1 000 mg/l.

Place 7,219 g of potassium nitrate (6.9.2) in a 1 000 ml volumetric flask. Dissolve and dilute to volume with water (6.1).

The solution is stable for six months if stored at (3 ± 2) °C.

6.9.3.3 Nitrogen mixed standard solution I, $\rho(N)$ = 1 000 mg/l.

Mix equal volumes of the solutions 6.9.3.1 and 6.9.3.2 to produce a nitrogen mixed standard solution.

The solution is stable for one month if stored at (3 ± 2) °C.

6.9.3.4 Nitrogen standard solution II, $\rho(N)$ = 100 mg/l.

Pipette 100 ml of nitrogen mixed standard solution I (6.9.3.3) into a 1 000 ml volumetric flask and dilute to volume with water (6.1).

The solution is stable for one month if stored at (3 ± 2) °C.

6.9.4 TNb and DNb calibration solutions.

An example for appropriate mixed nitrogen calibration solutions is given as follows.

Depending on the nitrogen concentration expected in the sample, use the nitrogen standard solution II (6.9.3.4) to prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible.

For example, proceed as follows for the range 1,0 mg/l N to 10 mg/l N.

Pipette the following volumes into a series of 100 ml volumetric flasks: 1,0 ml, 2,0 ml, 3,0 ml, 4,0 ml, 5,0 ml, 6,0 ml, 7,0 ml, 8,0 ml, 9,0 ml or 10,0 ml of the nitrogen mixed standard solution II (6.9.3.4) and dilute to volume with water (6.1).

The concentrations of nitrogen in these calibration solutions are: 1,0 mg/l, 2,0 mg/l, 3,0 mg/l, 4,0 mg/l, 5,0 mg/l, 6,0 mg/l, 7,0 mg/l, 8,0 mg/l, 9,0 mg/l or 10,0 mg/l, respectively.

Prepare the calibration solutions on the day of use.

Alternatively, single component standard calibration solutions can be applied. Prepare appropriate concentrations of ammonium sulfate (6.9.3.1) or potassium nitrate (6.9.3.2) accordingly.

NOTE The application of a mixed calibration solution can cause losses in the TNb signal. In such cases, applying a single component calibration (e.g. NH_4-N calibration solutions) can avoid such effects.

7 Apparatus

The usual laboratory apparatus and, in particular, the following.

7.1 Homogenization and particle size reducing device, for the homogenization of dispersed matter, for example a suitable ultrasonic apparatus or a rotor-stator homogenizer (see Clause 9) ensuring a resulting particle size smaller than the sample injection device, to have dimensions of suspended solids lower than the aspirating needle/hydraulics, if necessary.

NOTE An ultrasonic device is suitable for the homogenization of samples, but it is not suitable for the homogenization of the cellulose test suspension (6.8.6.1) for particle processing control.

7.2 High temperature combustion system, see Figure 1, conforming to the quality requirements given in Clause 8.

When measuring water samples containing particulate material, the instrument shall be capable of injecting the particulate material.

NOTE If using a system for simultaneous determination of TOC and TNb, the particle procession can be checked using the TOC cellulose test suspension (6.8.6.1). Chemicals for a suitable TNb test suspension were not available at the time of method development.

In general, the high temperature combustion system shall consist of the following components.

7.2.1 Sample injection device, for automated or manual operation.

The use of an autosampler shall include a device to homogenize samples (e.g. magnetic stirrer) before injection.

7.2.2 Reaction vessel for the combustion of TOC or DOC and to 720 °C for TNb or DNb compounds. It generally consists of an oven heatable to at least 680 °C for TOC or DOC and to 720 °C for TNb or DNb determinations.

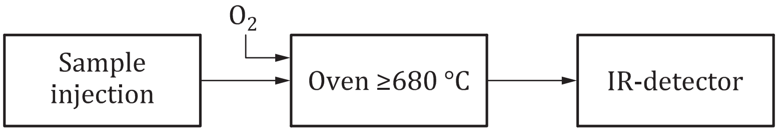
7.2.3 Detector.

7.2.3.1 IR detector for TOC or DOC determination.

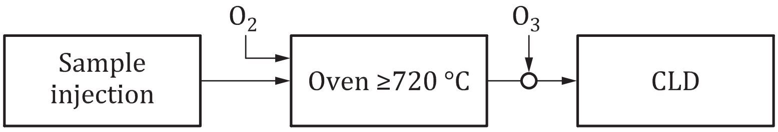
7.2.3.2 Chemiluminescence detector for TNb or DNb determination.

NOTE See Annex C for alternative detectors.

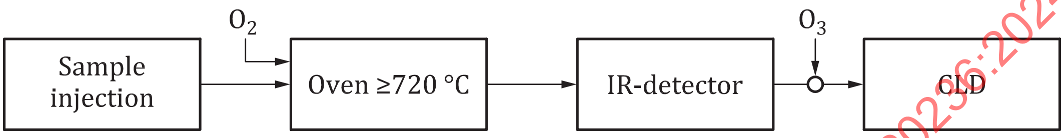
7.2.4 Recording device, e.g. PC with software for data acquisition and evaluation.



a) Device for separate TOC or DOC determination



b) Device for separate TNb or DNb determination



c) Device for simultaneous TOC and TNb, or DOC and DNb determinations

Figure 1 — Examples of high temperature combustion system configurations with a detector

8 Quality requirements for the analytical system

8.1 System check

The system check serves to identify significant deviations of calculated recoveries from known concentrations of measured standard solutions as well as unacceptable high variation coefficients. For example, the catalyst properties can become exhausted due to changes in the surface structure (e.g. precipitates) leading to reduced recoveries or increased variation coefficients.

System check determinations shall be carried out using an independent solution. Carry out system check determinations using at least two dilutions of the nicotinic acid standard solution (6.5) covering approximately 20 % to 80 % in the appropriate working range to identify any deviations of the response values obtained during the combustion stage. Deviations up to either ±10 % or ±1 mg/l, whichever is greater of the theoretical value, may be tolerated.

A minimum of two injections from one vial shall be carried out (see 10.4.1). The calculated deviation from the mean or the repeatability variation coefficient shall not exceed ±5 % or ±1 mg/l, whichever is greater. At concentrations of less than 10 mg/l, the individual values cannot differ more than 1 mg/l.

NOTE 1 Repeatability variation coefficient means the variation coefficient of replicate injections obtained with the same method on an identical sample.

NOTE 2 The equipment used usually calculates the repeatability automatically.

8.2 Particle processing control

This test is necessary for the determination of TOC and the simultaneous determination of TOC and TNb.

A minimum of three injections from one vial of the cellulose test suspension (6.8.6.1) shall be carried out (see 10.4.1). The mean value from a triple measurement shall not exceed ±10 % of the theoretical value. The repeatability variation coefficient shall be ≤10 % (see Annex B).

If the instrument fails the particle processing control test, the instrument is not appropriate for particle containing samples.

If using a system for simultaneous determination of TOC and TNb, the particle procession can be checked using the TOC cellulose test suspension (6.8.6.1) for the determination of TOC or the simultaneous determination of TOC and TNb need to check particle processing only for carbon.

NOTE A recommendation for an appropriate reagent to check particle processing for nitrogen cannot be given.

9 Sampling and sample preparation

When sampling, ensure that the samples being collected are representative (particularly in the presence of undissolved substances), and take care not to contaminate the samples with organic substances.

Use clean polyethene or glass bottles for sampling.

For the determination of dissolved carbon or dissolved bound nitrogen, filter the sample through a 0,45 µm membrane filter at the sampling site before applying any other preparation step. The absence of contamination coming from the filter shall be checked regularly.

Transport the sample at (5 ± 3) °C. Store the sample at (3 ± 2) °C in the dark and analyse it within 48 h.

Alternatively, stabilize the sample by the addition of sulfuric acid (6.2) or hydrochloric acid (6.3) to achieve a pH-value of ≤2, store it at (3 ± 2) °C in the dark and analyse it within 8 d. Do not acidify the sample when the difference method is applied (see Annex A).

NOTE 1 The use of sulfuric acid as a stabilizer can cause precipitation of sulfate on the catalyst. Information can be obtained from the catalyst supplier.

NOTE 2 The use of sulfuric acid for sample preservation can lead to reduced TNb or DNb results if sulfuric acid is not added to the calibration standards.

In some cases, the loss of volatile substances can occur upon acidification of the sample with the stripping of carbon dioxide. If volatile organic compounds are suspected, carry out the TNb or DNb measurement without acidification and the TOC or DOC measurement in accordance with Annex A within 8 h of sampling.

Otherwise, store the acidified sample in polyethene bottles at (−18 ± 3) °C and analyse it within three months. Take into account the possible formation of irreversible and inhomogeneous precipitation (e.g. proteins) when adjusting the sample to ambient temperature.

Homogenize the sample and, if necessary, reduce the particle size with an efficient device (7.1) for the determination of TOC and TNb.

Prepare and measure the blank solution (6.6) and calibration solutions (6.8.4 and 6.9.4) in the same way as the sample solution.

10 Procedure

10.1 General

The analyser system shall fulfil the requirements described in Clause 8 for filtered samples and for homogenized samples containing particulate material.

Set up the high temperature combustion system (7.2) in accordance with the instrument manufacturer's instructions. Once the analytical system is stable, analysis can begin.

Perform the calibration as described in 10.2. Use the calibration function to determine the concentration of TOC or DOC and/or TNb or DNb in the sample.

Prepare and measure the blank solution (6.6), quality control samples (6.5) and calibration solutions (6.8 and 6.9) in the same way as the sample solution.

10.2 Calibration

When the analytical system is first started up, and at intervals afterwards, establish a calibration function in accordance with ISO 8466-1 for the measurement as follows.

Prepare the calibration solutions as described in 6.8, 6.9 and Clause 9.

Analyse the calibration solutions in accordance with Clause 10.

10.3 Validity check of the calibration function

Confirm the validity of the data obtained in accordance with 8.1 and calculate the regression function in accordance with ISO 8466-1.

Carry out this check in accordance with 8.1.

NOTE The data obtained from the system check (see 8.1) can be used for this check.

Recalibrate, if necessary.

10.4 Measurement

10.4.1 General

Adjust the sample to ambient temperature before analysis.

After establishing the calibration function, inject the treated sample (see Clause 9) into the analyser system and measure the samples as described in 10.1.

Determine the TOC or DOC and/or TNb or DNb concentrations of the samples in accordance with the instrument manufacturer's instructions.

Measure the samples and the blank solution (6.6) carrying out at least two injections from the same vial. Calculate the mean. At least two values shall be confirmed in accordance with 8.1.

Repeat the sample measurement, if necessary.

10.4.2 Determination

10.4.2.1 General

When applying the determination of TOC and TNb, proceed in accordance with 10.4.2.2 and 10.4.2.4.

The instrumental specifications for TOC and TNb measurement shall be suitable for measuring samples containing particles. The use of an autosampler shall include a device to homogenize samples (e.g. magnetic stirrer) before injection.

If the calculated concentration of the analyte in the sample exceeds the calibration range, dilute the sample and re-analyse it.

If the calculated concentration of the analyte in the sample is below the lower calibration standard of the calibration range, establish a separate calibration function for the lower working range, if necessary.

If matrix interferences are suspected, dilute the sample, if possible, or use the method of standard addition to confirm the results.

Analyse a control solution at the beginning and at the end of each batch and after every 20th sample. The recovery of the checked concentration shall be within ±10 % or ±1 mg/l, whichever is greater.

Measure the blank solution (6.6) in the same manner.

10.4.2.2 TOC determination (direct method)

Acidify the homogenized sample to pH ≤ 2 using hydrochloric acid (6.8.5) or sulfuric acid (6.2). Stir and purge the sample in order to remove inorganic carbon from the sample.

NOTE It is not necessary to stir drinking water samples.

Inject the TOC sample into the analyser.

Calculate the TOC results in accordance with Clause 11.

10.4.2.3 DOC determination (direct method)

Acidify the filtered sample to pH ≤ 2 using hydrochloric acid (6.8.5) or sulfuric acid (6.2). Purge the sample to remove inorganic carbon from the sample.

Inject the 0,45 µm membrane filtered (see Clause 9) sample into the analyser.

Calculate the DOC results in accordance with Clause 11.

10.4.2.4 TNb determination

Inject the homogenized sample into the analyser for the determination of TNb.

Calculate the TNb results in accordance with Clause 11.

10.4.2.5 DNb determination

Inject the 0,45 µm membrane filtered sample (see Clause 9) into the analyser for the determination of DNb.

Calculate the DNb results in accordance with Clause 11.

10.4.2.6 Testing for particle processing control

For analyses of samples containing solids, the homogenization and recovery of suspended sample components (particle processing capability of the instrument) shall be verified using the cellulose test suspension (6.8.6.1) on each day of system operation.

Depending on the TOC concentration expected in the sample, use the cellulose test suspension (6.8.6.1) to prepare a control suspension. For example, proceed as follows for a 10 mg/l C solution.

- Stir the suspension with a magnetic stirrer until the suspension is homogeneous.
- Ultrasonic treatment shall not be used because it reduces the particle size.
- Pipette 10 ml of the homogenized cellulose test suspension (6.8.6.1) into a 100 ml volumetric flask and dilute to volume with water (6.1).
- The concentration of C in this solution is 10 mg/l.
- Prepare the suspension on the day of use. It is advisable to pipette the aliquot during the homogenizing of the suspension by stirring the suspension with a magnetic stirrer.
- Inject at least two samples of the control suspension into the analyser. It is advisable to withdraw an aliquot while stirring the sample. If an autosampler is used, samples shall be stirred during sampling. The mean value from a triple measurement shall be between 9,0 mg/l and 11,0 mg/l. The repeatability variation coefficient shall be ≤10 %. For this test, particle size is important.

NOTE Optimal homogenization without particle segregation can be provided, for example, by an oscillating stirrer.

11 Evaluation

Calculate the mass concentration, ρ, in milligrams per litre in the sample using the mean values of the replicates (see 10.4.1) obtained in accordance with ISO 8466-1.

Take into account all of the dilution steps.

12 Expression of results

The analysis results obtained when applying this document are subject to a measurement uncertainty that is to be considered in the interpretation of the results.

The results shall be reported in milligrams per litre to a maximum of two significant figures.

EXAMPLE	TOC (C)	12 mg/l
	TNb (N)	3,2 mg/l

13 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this document, i.e. ISO 20236:2024;

b) the identity of the sample;

c) the expression of the results in accordance with Clause 12;

d) any deviation from this method;

e) all circumstances that can have affected the results;

f) the date of the test.

Annex A
(normative)

Determination of TOC applying the difference method

A.1 General

The general information of Clauses 1 to 3 and the requirements of Clauses 4 to 13 remain valid for the TOC determination applying the difference method.

The results according to this procedure cannot be ensured to be equivalent to those of the direct method.

In contrast to the direct determination of TOC or DOC (see 10.4.2.2 and 10.4.2.3), the difference method always requires two measurements (see A.2.3 and Clause A.3).

Transfer an aliquot of the sample into the TIC reactor of the analyser device. Carbonates and hydrogen carbonates react in an acid medium to CO_2 and will be transferred to the IR detector by means of carrier gas passed through and detected as TIC. In a further step, all of the carbon (TC) is determined by injecting another aliquot of the sample into the reactor. In this case, both organic and inorganic carbon compounds are converted to carbon dioxide.

To avoid possible carry over effects, the TIC measurement should be done first.

From both single results, the TOC is then calculated by the difference method (TOC is equal to TC minus TIC, see Clause A.4).

When using the differential method, the value of the TOC should be higher than the TIC, or at least of similar concentration.

The difference method is especially suitable for samples in which purgeable organic substances, such as benzene, toluene, cyclohexane and chloroform, are suspected, which may partly escape upon stripping.

In order to determine the TIC value, it is necessary to establish a calibration curve by analysing calibration solutions made from the TIC standard solution (see A.2.1.4).

A.2 TIC determination (difference method)

A.2.1 Reagents

A.2.1.1 Sodium carbonate, Na_2CO_3.

A.2.1.2 Sodium hydrogen carbonate, $NaHCO_3$.

A.2.1.3 TIC stock standard solution, $\rho(C) = 1\ 000$ mg/l.

Place 4,415 g of sodium carbonate (A.2.1.1), dried for 1 h at (285 ± 5) °C, in a 1 000 ml volumetric flask and add 3,500 g of sodium hydrogen carbonate (A.2.1.2) dried for 2 h over silica gel. Dissolve in water (6.1) and dilute to volume with water.

Store the solution in a polyethene or a glass bottle. The solution is stable for several months if stored at (3 ± 2) °C.

A.2.1.4 TIC standard solution, ρ(C) = 100 mg/l.

Pipette 100 ml of the TIC stock standard solution (A.2.1.3) into a 1 000 ml volumetric flask and dilute to volume with water (6.1).

Store the solution in a polyethene or a glass bottle. The solution is stable for several months if stored at (3 ± 2) °C.

A.2.1.5 TIC calibration solutions.

Depending on the TIC concentration expected in the sample, use the TIC standard solution (A.2.1.4) to prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible.

For example, proceed as follows for the range of 1,0 mg/l C to 10,0 mg/l C.

Pipette the following volumes into a series of 100 ml volumetric flasks: 1,0 ml, 2,0 ml, 3,0 ml, 4,0 ml, 5,0 ml, 6,0 ml, 7,0 ml, 8,0 ml, 9,0 ml or 10,0 ml of the TIC standard solution (A.2.1.4) and dilute to volume with water (6.1).

The concentrations of carbon in these calibration solutions are: 1,0 mg/l, 2,0 mg/l, 3,0 mg/l, 4,0 mg/l, 5,0 mg/l, 6,0 mg/l, 7,0 mg/l, 8,0 mg/l, 9,0 mg/l or 10,0 mg/l, respectively.

Prepare the calibration solutions on the day of use.

A.2.2 Sampling

See Clause 9 and the following.

Use glass bottles for sampling.

Sample bottles shall be completely filled. Avoid transferring the samples to another container, if possible.

NOTE Any remaining air between bottle stopper and sample or the transfer of samples to another container can influence the TIC concentration.

The sample should be analysed on the day of sampling. If storage is required, refrigerate samples to approximately (3 ± 2) °C and analyse within 48 h.

A.2.3 TIC determination

Carry out a calibration in accordance with 10.2 using the TIC calibration solutions (A.2.1.5).

Analyse the sample applying the TIC device of the analyser in accordance with Clause 10.

Use the data obtained to calculate the analytical result for TIC.

A.2.4 Evaluation of TIC

Calculate the TIC mass concentration, ρ, in milligrams per litre in the sample using the mean signal values of the injections from one vial (see 10.4.1) obtained in accordance with ISO 8466-1.

Take into account all of the dilution steps.

Use the data obtained to calculate the analytical result for TIC.

A.3 TC determination (difference method)

A.3.1 Operation

Apply the system check procedure in accordance with Clause 9.

Apply the TOC calibration (see 10.2).