INTERNATIONAL STANDARD

ISO 20236

First edition
2018-09

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

Qualité de l'eau — Dosage du carbone organique total (COT), carbone organique (COD), azote lié total (TN_b) et azote lié dissous (DN_b) après combustion oxidatif catalytique à haute temperature

Reference number
ISO 20236:2018(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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*.

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 (TN_b) and dissolved bound nitrogen (DN_b) are an analytical convention, the respective result of which 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.

Details of an interlaboratory trial on the performance data for TOC or DOC and TN_b or DN_b are given in Annex B.

Water quality — Determination of total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TN_b) and dissolved bound nitrogen (DN_b) 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 for the determination of total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TN_b) and dissolved bound nitrogen (DN_b) in the form of free ammonia, ammonium, nitrite, nitrate and organic compounds capable of conversion to nitrogen oxides under the conditions described. The procedure is carried out instrumentally.

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).

The method allows a determination of TOC and DOC ≥ 1 mg/l and TN_b and DN_b ≥ 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.

For samples containing volatile organic compounds (e.g. industrial waste water), the difference method is used, see Annex A.

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

The method is not appropriate for the determination of volatile, or purgeable, organic carbon under the conditions described by this method.

Dissolved nitrogen gas (N_2) is not determined.

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 and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Terms and definitions

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

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

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

3.2
total inorganic carbon
TIC
sum of inorganic carbon present in water sample measured under the conditions of this method

Note 1 to entry: TIC is measured as CO_2 originating only from carbonates, hydrogen carbonates and dissolved carbon dioxide.

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

Note 1 to entry: Volatile organic carbon cannot be guaranteed to be determined by the method.

Note 2 to entry: Generally, TOC 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 organically bound carbon present in water originating from compounds passing through a membrane filter of 0,45 µm pore size, including cyanate and thiocyanate measured under the conditions of this method

3.5
total bound nitrogen
TN_b
sum of organically bound and inorganically bound nitrogen present in water or suspended matter measured under the conditions of this method

3.6
dissolved bound nitrogen
DN_b
sum of organically and inorganically bound nitrogen present in water originating from compounds passing through a 0,45 µm membrane filter measured under the conditions of this method

4 Principle

Thermal catalytic combustion of the sample containing organic carbon, and inorganic and organic nitrogen in an oxygen-containing atmosphere at ≥ 680 °C for TOC or DOC and ≥ 720 °C for TN_b or DN_b determinations.

The TOC or DOC determination is carried out in accordance with 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 verifications of different suppliers.

Oxidation of organic carbon (TOC, DOC) with oxygen or synthetic air to carbon dioxide. Detection by means of infrared spectrometry (IR). Combustion of inorganic and organic nitrogen with oxygen or synthetic air and conversion to nitric oxide.

Reaction with ozone giving electronically excited nitrogen oxides. Detection by means of chemiluminescence (CLD) (see Annex C for alternative detection).

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

Quality control is necessary to check the validity of the calibration function (see 10.3). Replicate determinations 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 TN_b or DN_b 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 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 replicate measurements that deviate by more than 10 %, an accurate TOC or TN_b result cannot be obtained on the sample.

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 the 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 the TC. This calculation leads to correct results only as long as carbon monoxide, cyanide, cyanate and thiocyanate are present with 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 TN_b or DN_b

High loads of dissolved or total organic carbon (DOC or TOC) can lead to poor recovery of TN_b or DN_b. Suspected problems can be identified by determining nitrogen before and after suitable dilution, or by using standard addition techniques.

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 in accordance with 10.2 and applying a nitrogen mixed standard solution II (6.9.3.4) can result in a negative TN_b bias for ammonium-N determinations (e.g. ammonium sulfate solution) and a positive bias for nitrate-N determinations (e.g. potassium nitrate solution).

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 TN_b and TOC, an appropriate mixture of the 1 000 mg/l TOC and TN_b stock solutions (6.8.2 and 6.9.3.3) for the preparation of standard and calibration 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 TN_b concentration to be determined.

6.2 Sulfuric acid, ρ = 1,84 g/ml.

6.3 Hydrochloric acid, ω(HCl) = 32 %.

6.4 Nicotinic acid, $C_6H_5NO_2$, > 99,5 %.

6.5 TOC and TN_b 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 Gases or synthetic air, free from impurities with influence of the determinant (e.g. carbon dioxide, organic carbon, nitrogen compounds).

Use gases in accordance with the manufacturer's specifications, for example oxygen, 99,7 % volume fraction.

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 five to ten 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 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 mg/l, 2 mg/l, 3 mg/l, 4 mg/l, 5 mg/l, 6 mg/l, 7 mg/l, 8 mg/l, 9 mg/l or 10 mg/l, respectively.

Prepare the calibration solutions on the day of use.

6.8.5 Hydrochloric acid TIC stripping solution, c(HCl) = e.g. 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 should not be used because it reduces the particle size.

6.9 Reagents for the TN_b and DN_b determination.

6.9.1 Ammonium sulfate, $(NH_4)_2SO_4$.

6.9.2 Potassium nitrate, KNO_3.

6.9.3 Nitrogen stock standard solutions.

6.9.3.1 Ammonium sulfate stock solution, ρ(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, ρ(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, ρ(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, ρ(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 TN_b and DN_b calibration solutions.

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

For example, proceed as follows for the range 1,0 mg/l 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 mg/l, 2 mg/l, 3 mg/l, 4 mg/l, 5 mg/l, 6 mg/l, 7 mg/l, 8 mg/l, 9 mg/l or 10 mg/l, respectively.

Prepare the calibration solutions on the day of use.

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), if needed.

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 Users applying a system for the simultaneous determination of TOC and TN_b can check for particle procession using the TOC cellulose test suspension (6.8.6.1). No recommendation can be given for a suitable TN_b test suspension.

In general, it 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 keep heterogeneous samples in a homogenous state (e.g. magnetic stirrer) before injection.

7.2.2 Reaction vessel

Oven, heatable to at least to 680 °C for TOC or DOC and to 720 °C for TN_b or DN_b determinations.

7.2.3 Detector.

7.2.3.1 IR detector for TOC or DOC.

7.2.3.2 Chemiluminescence detector (CLD) for TN_b or DN_b.

NOTE See Annex C for alternative detectors.

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

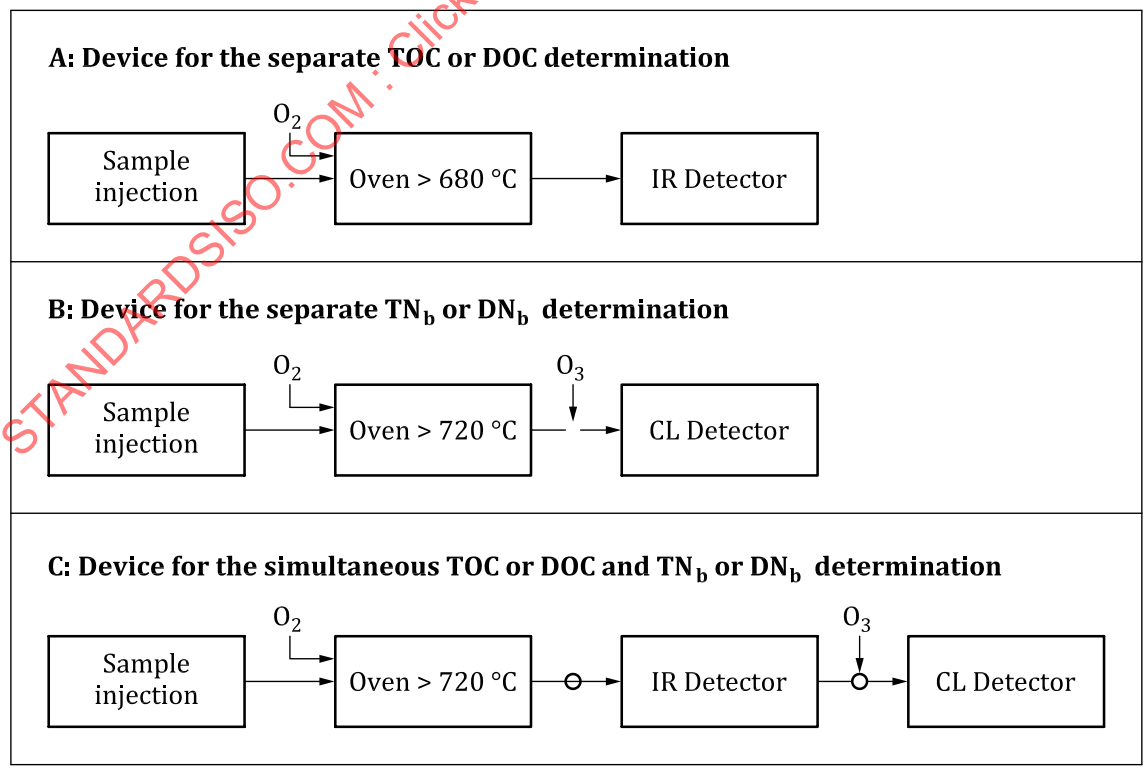

Figure 1 — Examples for high temperature combustion system configurations with detectors for the determination of A: TOC or DOC, B: DN_b or TN_b and C: TOC or DOC and DN_b and TN_b

8 Quality requirements for the analytical system

8.1 System check

Carry out system check determinations using at least two dilutions of the system check 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 ±5 % and or ±1 mg/l, whichever is greater of the theoretical value, may be tolerated.

A minimum of two replicate injections shall be carried out (see 10.4.1). The calculated 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 may not differ more than 1 mg/l.

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

NOTE 2 The equipment used usually calculates the repeatability automatically.

8.2 Recovery and variation of replicate determinations for particle processing control for TOC and TN_b

A minimum of three independent replicate measurements 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 %.

If the instrument fails the particle processing control test, the instrument is not appropriate for TOC or TN_b determinations.

Users applying instruments for the simultaneous determination of TOC or DOC and DN_b or TN_b need to check particle processing only for carbon.

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 nitrogen, filter the sample through a 0,45 µm membrane filter on 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.

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 TN_b or DN_b 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 °C ± 3) °C and analyse it within one month. 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 TN_b.

Treat 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 analyser 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 TN_b or DN_b in the sample.

Treat the blank solution (6.6) and calibration solutions (6.8.4 and 6.9.4) 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 (see ISO 8466-1) for the measurement as follows.

Prepare the calibration solutions as described in 6.8.4, 6.9.4 and Clause 9.

Analyse the calibration solutions in accordance with Clause 10.

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

10.3 Validity check of the calibration function

Carry out this check in accordance with 8.1.

NOTE 1 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 TN_b or DN_b 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 replicate injections. Calculate the mean. At least two values should be confirmed in accordance with 8.1.

Repetition of the sample determination might be necessary.

10.4.2 Determination

10.4.2.1 General

When applying the simultaneous determination of TOC and TN_b proceed in accordance with 10.4.2.2 and 10.4.2.4.

The instrumental specifications for TOC and TN_b measurement shall be suitable for measuring samples containing particles.

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 expected, dilute the sample, if possible, or use the method of standard addition to confirm the results.

Analyse a control solution after each series of 10 samples. Recovery of the checked concentration shall be within ±5 % 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 sample pH to ≤ 2 using hydrochloric acid (6.8.5) or sulfuric acid (6.2). Purge the sample in order to remove inorganic carbon from the sample.

Inject the DOC sample into the analyser.

Calculate the DOC results in accordance with Clause 11.

10.4.2.4 TN_b determination

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

Calculate the TN_b results in accordance with Clause 11.

10.4.2.5 DN_b determination

Inject the 0,45 µm membrane filtered sample into the analyser for the determination of DN_b.

Calculate the DN_b results in accordance with Clause 11.

10.4.2.6 Test 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 should 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 mg/l. The repeatability variation coefficient shall be ≤ 10 %.

NOTE 1 For this test, particle size is important.

NOTE 2 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 as specified in ISO 8466-1.

Take into account all of the dilution steps.

12 Expression of results

Results shall be reported to a maximum of two significant figures.

EXAMPLE

TOC (C)	12 mg/l
TN_b (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 20236:2018;

b) identity of the water sample;

c) all information necessary for the complete identification of the sample;

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

e) sample pretreatment, if relevant;

f) any deviation from this method;

g) report of all circumstances that could have affected the results.

Annex A
(normative)

Determination of TOC and TIC applying the difference method

A.1 General

The requirements of Clauses 1 to 13 remain valid for the TC and TIC determination.

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 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. The order of the TIC and TC measurements does not influence the results. 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.

From both single results the TOC is then calculated by difference (TOC = TC – TIC).

The difference method is especially suitable for samples in which the TOC concentration is not substantially lower than the TIC concentration, since this method necessarily can lead to large inaccuracies, as TIC > TOC.

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, $\rho(C)$ = 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 five to ten 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 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 mg/l, 2 mg/l, 3 mg/l, 4 mg/l, 5 mg/l, 6 mg/l, 7 mg/l, 8 mg/l, 9 mg/l or 10 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 the TIC

Calculate the TIC mass concentration, ρ, in milligrams per litre in the sample using the mean signal values of the replicates (see 10.4.1) obtained as specified in 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)

Apply the system check procedure in accordance with Clause 8.

Apply the TOC calibration (see 10.2).

Inject the sample into the TOC device of the analyser in accordance with Clause 10.

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

When applying the simultaneous determination of TC and TIC, in accordance with the instrument manufacturer's instructions, use an appropriate mixture of the 1 000 mg/l TOC and TIC stock solutions (6.8.2 and A.2.1.3) for the preparation of standard and calibration solution of TC and TIC, distributed over the expected working range as evenly as possible.

A.4 Evaluation of the TC

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

Take into account all of the dilution steps.

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

A.5 Evaluation of the TOC

Calculate the TOC concentration using the TIC (A.3) and TC (A.4) results in accordance with Formula (A.1):

$$TOC = TC - TIC \tag{A.1}$$