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Water quality — Determination of total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TN_b), dissolved bound nitrogen (DN_b), total bound phosphorus (TP_b) and dissolved bound phosphorus (DP_b) after wet chemical catalysed ozone hydroxyl radical oxidation (COHR)

Qualité de l'eau — Détermination du carbone organique total (COT), du carbone organique dissous (COD), de l'azote total lié (TN_b), de l'azote dissous lié (DN_b), du phosphore total lié et du phosphore dissous lié (DP_b) après oxydation par l'ozone avec des radicaux hydroxyles et catalyseur en milieux aqueux (COHR)

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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*.

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), dissolved bound nitrogen (DN_b), total bound phosphorus (TP_b) and dissolved bound phosphorus (DP_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, the sum of inorganic and organic nitrogen, and the sum of inorganic and organic phosphorus. These parameters can be dissolved in water or bonded to dissolved or suspended matter under specified conditions. If the sample is not filtered the parameter is associated with suspended matter. This document does not give information on the nature of the substances.

Water quality — Determination of total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TN_b), dissolved bound nitrogen (DN_b), total bound phosphorus (TP_b) and dissolved bound phosphorus (DP_b) after wet chemical catalysed ozone hydroxyl radical oxidation (COHR)

WARNING — Persons using this document should be familiar with normal laboratory practices. This document does not purport to address all 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 essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

1 Scope

This document specifies a multi-parameter method for the determination of total organic carbon (TOC), total nitrogen (TN_b) and total phosphorus (TP) in drinking water, raw water, ground water, surface water, sea water, saline water, process water, domestic and industrial wastewater, after a chemical oxidation process. It is applicable to both dissolved and bound suspended materials.

The method allows for determination of TOC, TN and TP. The lower and upper working ranges for these parameters are dependent upon instrument conditions (for example sample volume, reaction chemistry amounts) and can be adjusted for a wider range. Typical measurement ranges are shown in Figures C.1 to C.3.

The analysis procedure is carried out instrumentally by a single oxidation process.

Dissolved nitrogen gas is not included in the TN_b measurement in this method. When present in the sample, elemental carbon, cyanate and thiocyanate will be included in the TOC result.

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 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 8245, *Water quality — Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*

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 http://www.electropedia.org/

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

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

3.4
purgeable organic carbon
POC
organic carbon present in water which can be purged under the conditions of this method

3.5
non purgeable organic carbon
NPOC
organic carbon present in water which is not purged

3.6
total nitrogen
TN
sum of organically and inorganically bound nitrogen present in water or suspended matter

3.7
total phosphorus
TP
sum of organically and inorganically bound phosphorus present in water and suspended matter measured under the conditions of this method

4 Principle

Wet chemical oxidation of the sample by hydroxyl radicals, and catalysed ozone for the measurement of TOC, TN_b, and TP_b.

Organic carbon (TOC) is oxidized to carbon dioxide (CO_2). For the determination of total organic carbon that includes purgeable organic carbon by difference, the procedure shall be as specified in Annex A. Detection is by nondispersive infrared (NDIR) spectrometry.

Detection is by photometric analysis in the ultraviolet wavelength range 200 nm to 220 nm. Detection is by colorimetric analysis using a photometer under the visible spectra between 380 nm and 470 nm wavelengths.

This document can be applied for the determination of TOC, TN_b and TP_b separately, or for simultaneous analysis, which consists of a non-dispersive infrared carbon dioxide analyser and a visible and UV photometer.

Quality control is necessary to verify the validity of the calibration function. Replicate determinations can be necessary, depending on the matrix. The method of standard addition can be used if matrix interferences are expected.

Inorganic carbon is removed by acidification and purging with a carrier gas (see 11.4).

Performance results from the interlaboratory trial is provided in Annex B. Supplemental single laboratory performance data is provided in Annex C.

5 Interferences

5.1 General

Depending on concentration and analysis range, interferences with the determination of TOC, TN_b and TP_b can arise from possible sample carry over effects. In some cases, replicate injections can be necessary. When carryover is suspected, insert a reagent blank in the analytical run, immediately after the suspect sample.

Interferences can arise from memory effects. Replicate injections maybe necessary (11.4.1).

Samples with high pH values, highly buffered samples and samples with high chloride content can cause interference.

Large suspended particles can lead to a loss of quality of the analytical result. If a homogenized sample containing suspended particles produces results (obtained from replicate measurements) which deviate by more than 10 %, an accurate TOC TN_b and TP_b result cannot be obtained on the sample.

Seek advice from the manufacturer to resolve these interferences. Particles in general can cause interference with sample injection. To mitigate particle interference, samples can be homogenized or filtered using filters and screen meshes. When the sample is filtered through a 0,45 µm membrane filter, the TOC result represents dissolved organic carbon (DOC) and dissolved TN_d and TP_d as specified in ISO 8245, results from samples analysed without filtration are reported as TOC, TN_b and TP_b.

If a homogenized sample containing large suspended material produces results (obtained from replicate measurements) which deviate by more than 10 % from each other, an accurate and precise TOC, TN_b, or TP_b result cannot be quantified.

5.2 TOC

Inorganic carbon (for example CO_2 or ions of carbonic acid) present in the sample can interfere with the determination of TOC or DOC. Inorganic carbon is removed by acidification and sparging prior to sample oxidation.

NOTE Purgeable organic carbon (POC) compounds, such as benzene, toluene, cyclohexane and chloroform, can partly escape during the acidification and sparging of the TIC. In the presence of these substances, the TOC concentration can be determined by applying the TC-TIC method (see Annex A).

Interference from chloride can occur at chloride concentrations greater than 3 %. If chloride interference is suspected, dilute the sample and re-analyse.

5.3 TN

Depending on sample matrix conditions, interferences may occur with the measurement of TN_b. If interferences are suspected, perform a suitable sample dilution, or by applying standard addition techniques.

Interference from chloride can occur at chloride concentrations greater than 3 %. If chloride interference is suspected, dilute the sample and re-analyse.

5.4 TP

Depending on sample matrix conditions, interferences can occur with the measurement of TP_b. If interferences are suspected, perform a suitable sample dilution, or by applying standard addition techniques.

Interference from chloride can occur at chloride concentrations greater than 3 %. If chloride interference is suspected, dilute the sample and re-analyse.

6 Reagents

Use only reagents of analytical grade.

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

NOTE There is no need to dry cellulose before usage.

Prepare concentrations and volumes of solutions as described in the manufacturers' instrument manuals. Alternatively, use commercially available stock solutions at the required concentration.

6.1 Water.

The contents of bound nitrogen, phosphorus, and carbon in water being used for the preparation of samples and solutions shall be sufficiently low to be negligible in comparison with the lowest TOC, TN_b and TP_b concentrations to be determined.

6.2 Sulfuric acid, H_2SO_4, ρ = 1,84 g/ml.

6.3 Manganese sulfate monohydrate, $MnSO_4 \cdot H_2O$, ≥99 %.

6.4 Sodium hydroxide, NaOH, ≥97 %.

6.5 Hydrochloric acid, w(HCl) = 37 %.

6.6 Ammonium heptamolybdate tetrahydrate, $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$, ≥99 %.

6.7 Ammonium metavanadate, NH_4VO_3, ≥99 %.

6.8 Potassium hydrogen phthalate, $(C_8H_5KO_4)$, ≥99,7 %.

6.9 Sodium nitrate, $NaNO_3$, ≥99 %.

6.10 Potassium dihydrogen phosphate, KH_2PO_4, ≥99 %.

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

6.12 Triethyl phosphate, $(C_2H_5)_3PO_4$.

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

7 Solution preparations

7.1 Blank solution

Use water (6.1) as the blank solution.

7.2 Sample oxidation solutions

7.2.1 Sulfuric acid TIC and catalyst solution

Prepare the sulfuric acid TIC and catalyst by slowly adding 49,9 ml of sulfuric acid (6.2) to 800 ml of water (6.1) in a 1 000 ml volumetric flask. Dilute to volume with water (6.1) and cool to room temperature. Add 0,04 g of manganese sulfate (6.3) to the sulfuric acid/water mixture. Determine the acid normality and adjust to (1,80 N ± 0,01N) H_2SO_4.

NOTE For higher sulfuric acid TIC and catalyst oxidation concentration, maintain an acid to base concentration (7.2.2) ratio of 3:2, keeping the amount of manganese sulfate at 0,04 g.

The range of sulfuric acid normality should be 1,8 N to 2,5 N.

7.2.2 Base oxidation solution

Prepare the sodium hydroxide solution by slowly adding 48 g of NaOH (6.4) to a 1 000 ml volumetric flask containing approximately 500 ml of water (6.1). Mix the solution until the NaOH has dissolved, then stopper the flask and allow the solution to come to room temperature. Bring solution to volume with water (6.1).

For higher sodium hydroxide concentrations, maintain an acid (7.2.1) to base concentration ratio of 3:2.

The range of sodium hydroxide molarity should be 1,2 M to 1,7 M.

7.2.3 TP solution

7.2.3.1 Prepare the hydrochloric acid reagent (solution A) by slowly adding 494 ml of concentrated HCl (6.5) to 500 ml of water (6.1) in a 1 000 ml volumetric flask. Mix gently and allow the solution to come to room temperature. Bring the solution to volume with water (6.1), then stopper the flask.

7.2.3.2 Prepare the ammonium heptamolybdate tetrahydrate reagent (solution B) by adding 25 g of ammonium heptamolybdate tetrahydrate (6.6) to 300 ml of water (6.1) in a 500 ml beaker. Stir to dissolve.

7.2.3.3 Prepare the ammonium metavanadate reagent (solution C) by adding 2,5 g of ammonium metavanadate (6.7) to 300 ml of water (6.1) in a 500 ml beaker. Dissolve by bringing the solution to a boil. Cool to room temperature.

7.2.3.4 While stirring, slowly add solution C (7.2.3.3) to 330 ml of solution A (7.2.3.1) in a 1 000 ml volumetric flask. Cool to room temperature.

7.2.3.5 Finally while stirring, slowly pour the content of solution B (7.2.3.2) into the volumetric flask that contains the mixture of solution A and solution C (7.2.3.4) and bring to volume with water (6.1).

7.2.4 TP hydrolysis solution

Prepare the hydrochloric acid solution by adding 249 ml of concentrated HCl (6.5) to an empty 1 000 ml volumetric flask. Slowly add 600 ml water (6.1) to the flask. Mix gently and allow the solution to come to room temperature. Bring the solution to volume with water (6.1), then stopper the flask.

7.3 Calibration stock solutions

7.3.1 Potassium hydrogen phthalate stock solution, ρ(C) = 1 000 mg/l.

Place 2,125 g of potassium hydrogen phthalate (6.8) 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 in a tightly stoppered glass bottle at (3 ± 2) °C.

7.3.2 Sodium nitrate stock solution, ρ(N) = 1 000 mg/l.

Place 6,07 g of $NaNO_3$ (6.9) in a 1 000 ml volumetric flask. Dissolve and dilute to volume with water (6.1).

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

7.3.3 Potassium dihydrogen phosphate stock solution, ρ(P) = 1 000 mg/l.

Prepare a 1 000 mg/l TP stock solution using potassium dihydrogen phosphate (KH_2PO_4). Place 4,43 g of KH_2PO_4 (6.10) in a 1 000 ml volumetric flask. Dissolve and dilute to volume with water (6.1).

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

7.4 Individual calibration standard solutions

7.4.1 TOC

Depending on the TOC or DOC concentration expected in the sample, use the potassium hydrogen phthalate stock solution (7.3.1) to prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible (see Annex C).

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 1 000 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 and 10,0 ml of the potassium hydrogen phthalate stock solution (7.3.1) 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 and 10 mg/l, respectively.

Prepare the calibration solutions on the day of use.

7.4.2 TN

Depending on the nitrogen concentration expected in the sample, use the sodium nitrate stock solution (7.3.2) to prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible (see Annex C).

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 1 000 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 and 10,0 ml of the sodium nitrogen stock solution (7.3.2) 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 and 10 mg/l, respectively.

Prepare the calibration solutions on the day of use.

7.4.3 TP

Depending on the phosphorus concentration expected in the sample, use the potassium dihydrogen phosphate stock solution (7.3.3) to prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible (see Annex C).

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

Pipette the following volumes into a series of 1 000 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 and 10,0 ml of the nitrogen stock solution (7.3.3) 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 and 10 mg/l, respectively.

Prepare the calibration solutions on the day of use.

7.4.4 Combined calibration standard solutions

Pipette the following volumes into a series of 1 000 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 and 10,0 ml of the potassium hydrogen phthalate, (7.3.1) sodium nitrate (7.3.2), potassium dihydrogen phosphate (7.3.3) stock standard solutions and dilute to volume with water (6.1).

The concentrations of the combined calibration standard 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 and 10 mg/l, respectively.

Prepare the calibration solutions on the day of use.

7.5 System check stock solutions

7.5.1 TOC and TN stock solution

Place 8,793 g of nicotinic acid (6.11) 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 when stored at (3 ± 2) °C.

7.5.2 TP stock solution

Place 5,881 g of triethyl phosphate (6.12) in a 1 000 ml volumetric flask. Dissolve and dilute to volume with water (6.1).

The solution contains 1 000 mg/l phosphorus (P).

The solution is stable for six months when stored in a tightly stoppered glass bottle at (3 ± 2) °C.

7.6 Particle processing control solution

7.6.1 Microcrystalline cellulose, $(C_6H_{10}O_5)_n$, , of particle size ranging from 0,02 mm to 0,1 mm.

Place 225 mg of cellulose (6.13) 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 solution with a magnetic stirrer until the suspension is homogeneous before use. Ultrasonic treatment should not be used because it reduces the particle size.

7.7 Gases

Use oxygen in accordance with the manufacturer's specifications.

8 Apparatus

8.1 Homogenization device, for the homogenization of dispersed matter, for example a suitable ultrasonic apparatus or a rotor/stator homogenizer (Clause 10), if needed.

NOTE Ultrasonic device is suitable for homogenization of samples but it is not suitable for homogenization of the cellulose test suspension (7.6.1) for particle processing control. Depending on the sample characteristics, a magnetic stirrer, or a high-speed stirrer, can also be used to homogenize the suspended matter.

8.2 TOC, TN, TP system.

Figure 1 describes the flow diagram examples of TOC, TN, TP systems and the typical apparatus components.

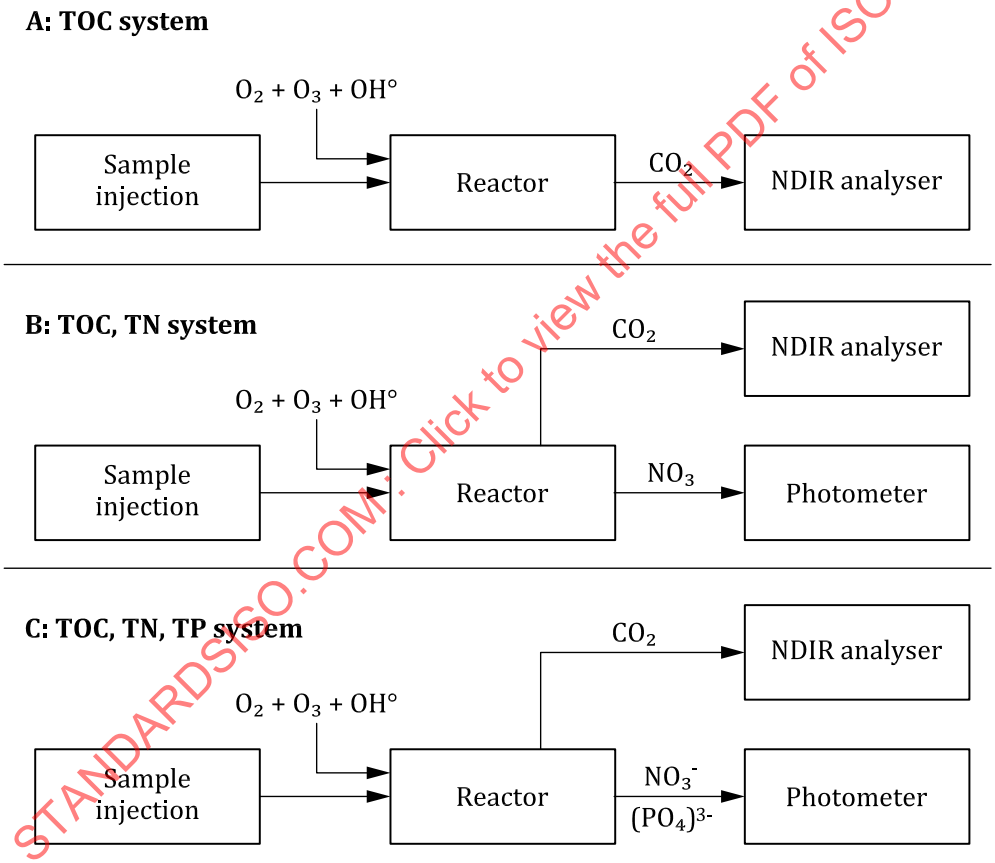

Figure 1 — Example of catalysed ozone hydroxyl radical oxidation systems for TOC (A), and for simultaneous determination of TOC, TN (B) and TOC, TN, TP (C)

9 Quality requirements for the analytical system

9.1 System check

Carry out system check determinations using at least two dilutions of the system check solution (7.5) 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 can be tolerated.

A minimum of two replicate injections shall be carried out. 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 should not differ by more than 1 mg/l.

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

9.2 Recovery and variation of replicate determinations for particle processing control for TOC, TN_b, and TP_b

A minimum of three independent replicate measurements of the cellulose test suspension (7.6) shall be carried out (11.4.2). 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, TN_b, and TP_b determinations.

Users applying instruments for the simultaneous determination of TOC, TN_b, and TP_b need to check particle processing only for carbon.

During the system response check, a minimum of three replicate analyses shall be carried out.

Determine the repeatability of the analysis results as specified in ISO 5725-2. The calculated repeatability coefficient of variation shall not exceed ±5 %.

10 Sampling and sample preparation

10.1 Sampling and sample injection

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. Collect samples in glass or polyethylene bottles. Avoid transferring the samples to another container, if possible.

For the determination of dissolved carbon dissolved nitrogen, or dissolved phosphorus, 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 (3 ± 2) °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 (6.5) 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 (Annex A).

Homogenize the sample for the determination of TOC, TN_b, and TP_b using an efficient device (8.1).

Treat the blank solution (6.1) and calibration solutions (7.4.1, 7.4.2, 7.4.3, or 7.4.4) in the same way as the sample solution.

11 Procedure

11.1 General

The analyser system shall fulfil the requirements described in Clause 9 for filtered samples and for homogenized samples containing particulate material.

Set up the analyser system (8.2) according to the instrument manufacturer's instructions. Once the analytical system is stable, analysis can begin.

11.2 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 7.4.1, 7.4.2, 7.4.3 or 7.4.4 and Clause 10.

Analyse the calibration solutions in accordance with Clause 11.

Confirm the validity of the data obtained in accordance with 9.1 and calculate the regression function as specified in ISO 8466-1.

11.3 Validity check of the calibration function

Carry out this check in accordance with 9.1.

NOTE The data obtained from the system check (9.1) can be used for this check.

Recalibrate, if necessary.

11.4 Measurement

11.4.1 General

Adjust the sample to ambient temperature before analysis.

After establishing the calibration function, inject the treated sample (Clause 10) into the analyser system and measure the samples as described in 11.1.

Determine the TOC, the TOC-TN, or the TOC-TN-TP concentrations of the samples in accordance with the instrument manufacturer's instructions.

Measure the samples and blank solution (6.1) carrying out at least two replicate injections. Calculate the mean. In accordance with 8.1 ensure two values are confirmed.

Repetition of the sample determination might be necessary.

11.4.2 Determination

11.4.2.1 General

When applying the simultaneous determination of TOC, TN_b, and TP_b, proceed in accordance 11.4.2.

The instrumental specifications for TOC, TN_b and TP_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 from the sample is below the lowest calibration standard establish a new calibration function that is representative of the initial sample measured concentration. The lowest calibration standard shall be no lower than the demonstrated LOQ of the method.

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

Measure the blank solution (7.1) in the same manner as samples.

11.4.2.2 TOC, TN_b, TP_b determination (direct method)

TOC, TOC-TN, and TOC-TN-TP is determined in the same manner. The sample is acidified to pH ≤2 using sulfuric acid reagent (7.2.1) purged with oxygen gas (7.7) and injected into the reactor.

The results are calculated in accordance with Clause 12.

11.4.2.3 Test for particle processing control

Analyses of samples containing solids, the homogenization and recovery of suspended sample components (particle processing capability of the instrument) shall be verified by using the cellulose test suspension (7.6.1) on each day of system operation.

Depending on the TOC concentration expected in the sample, use the cellulose test suspension (7.4.4) 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 (7.6.1) into a 100 ml volumetric flask and dilute to volume with water (6.1). Preparation of larger volumes are equivalently proportioned.

— The concentration of C in this solution is 10 mg/l.

— Prepare the solution 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 solution into the analyser. It is advisable to withdraw an aliquot while stirring the sample. If a laboratory autosampler is used, samples shall be stirred during sampling.

12 Evaluation

Calculate the mass concentration, ρ, in milligrams per litre in the sample using the mean values of the replicates (11.4.1) obtained as specified in ISO 8466-1, taking into account all of the dilution steps.

13 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

14 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 21793:2020;

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

c) expression of the results in accordance with Clause 13;

d) sample pretreatment, if relevant;

e) any deviation from this method;

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

Annex A
(normative)

Determination of total organic carbon that includes purgeable organic carbon by difference

A.1 General

Purgeable organic substances, such as benzene, toluene, cyclohexane and chloroform are inefficiently recovered from the requirements in Clauses 1 through 13. This occurs during the purging of the TIC prior to NPOC analysis.

If high levels of purgeable organic carbon is suspected in a sample, follow the procedures in A.2 through A.4.

A.2 TC determination (direct method)

Carry out a calibration in accordance with 11.2 using the TOC calibration solutions (7.4).

NOTE If preferred, the TC calibration can be carried out using TIC and TOC mixture standard solutions following the practices described in Clause 7.

When the calibration is complete, to measure the samples add base reagent and ozone to the sample reactor, then the sample in that order. Perform the oxidation reaction and measure the TC.

If the concentration of the TC is below the lower calibration standard of the calibration ranges, establish a separate calibration for the lower working range.

Calculate the TC concentrations in the sample using the mean result values of the replicates obtained as specified in ISO 8466-1.

Report the results with the required decimal points.

A.3 TIC determination (direct method)

Analyse a second sample as described in Clauses 1 through 13 and measure the TIC.

A.3.1 Reagents.

A.3.1.1 Sodium carbonate, Na_2CO_3.

A.3.1.2 Sodium hydrogen carbonate, $NaHCO_3$.

A.3.2 TIC stock standard solution, $\rho(C)$ = 1 000 mg/l.

Prepare a 1 000 mg/l TIC stock solution using sodium carbonate, (Na_2CO_3). Add 8,84 g of a 99,9 % mass fraction Na_2CO_3 into water (6.1). Add enough water to make the solution exactly 1 l. Mix well until all Na_2CO_3 is dissolved in water.

Alternatively, to prepare a 1 000 mg/l TIC stock solution using sodium hydrogen carbonate ($NaHCO_3$), add 7,04 g of a 99,5 % mass fraction $NaHCO_3$ into water (6.1). Add enough water to make the solution exactly 1 l. Mix well until all $NaHCO_3$ is dissolved in water.

The solution is stable for two months if stored in a tightly stoppered glass bottle at (3 ± 2) °C.

Depending on the TIC concentration expected in the sample, prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible. Prepare the calibration solutions on the day of use.

A.3.2.1 TIC standard solution, ρ(C) = 100 mg/l.

Pipette 100 ml of the TIC stock standard solution (A.2.2) 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.3.2.2 TIC calibration solutions

Depending on the TIC concentration expected in the sample, use the TIC standard solution (A.2.3) 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 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.2.3) 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.

A.4 Evaluation

Use the mass concentrations of TC and TIC, ρ, in milligrams per litre in sample using the mean value of the replicates [11.4.1] obtained as specified in ISO 8466-1.

Take into account all of the dilution steps.

Calculate the combined non-purgeable and purgeable organic carbon according to Formula (1):

$$TOC = TC - TIC \quad (1)$$

Annex B
(informative)

Performance data TOC/TN

B.1 General

An interlaboratory trial (ILT) was organized in 2017 in cooperation with AQS Baden-Wuerttemberg in Germany. Test facilities from Ireland, Mexico, Poland, Turkey and United States have participated. In parallel with the TOC/TN combustion ILT, samples from AQS were analysed by the above-mentioned test facilities. The type of instruments and the analytical conditions applied conformed to the quality parameters specified in the method.

The statistical data of results evaluated in accordance with ISO 5725-2 are presented in Tables B.1 and B.2.

Table B.1 — Performance data TOC

Analyte	Matrix	l	n	o	X	$\bar{\bar{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
				%	mg/l	mg/l	%	mg/l	%	mg/l	%
TOC direct	Synthetic	8	36	0,0	8,9	6,0	67,4	0,50	8,3	0,04	0,7
	Drinking water	8	36	0,0		5,35		0,77	14,4	0,47	8,7
	Surface water	8	36	0,0		7,64		0,40	5,2	0,22	2,9
	Wastewater 1	8	36	0,0		10,6		0,56	5,3	0,22	2,0
	Wastewater 2	8	36	0,0		19,28		0,90	4,7	0,19	1,0

l Number of laboratories after outlier rejection.

n Number of individual test results after outlier rejection.

o Percentage of outliers.

X Assigned value.

$\bar{\bar{x}}$ Overall mean of results (without outliers).

η Recovery rate.

s_R Reproducibility standard deviation.

$C_{V,R}$ Coefficient of variation of reproducibility.

s_r Repeatability standard deviation.

$C_{V,r}$ Coefficient of variation of repeatability.

NOTE All samples (except drinking water matrix) contained microcrystalline cellulose.

Table B.2 — Performance data TN_b

Analyte	Matrix	l	n	o %	X mg/l	$\bar{\bar{x}}$ mg/l	η %	s_R mg/l	$c_{V,R}$ %	s_r mg/l	$c_{V,r}$ %
TN direct	Synthetic[a]	6	33	8,3	3,3	2,7	81,8	0,42	15,3	0,06	2,2
	Drinking water[a]	7	33	8,3		4,1		0,44	10,8	0,09	2,2
	Surface water[a]	6	30	16,7		5,3		0,37	7,0	0,51	1,0
	Wastewater 1[a]	6	30	16,7		13,7		0,31	2,3	0,12	0,8
	Wastewater 2[a]	7	33	8,3		18,2		0,39	2,2	0,10	0,5

For an explanation of symbols, see Table B.1.

NOTE All samples (except drinking water matrix) contained microcrystalline cellulose.

[a] For these data sets the number of laboratories after outlier rejection was below eight due to the small number of participants applying the method. The estimates for reproducibility and repeatability standard deviation therefore have a higher uncertainty and should be used with care.

B.2 Performance data TP

The samples used in this ILT upon measurement were determined to not contain TP ≥ 1 mg/l. Therefore, a table of results is not provided. However, TP results from a separate single laboratory study are given in Tables C.9 to C.12.

Annex C
(informative)

Informative validation data, system check recovery and particle check recovery for TOC/TN/TP

Table C.1 — Supplemental TOC validation test data (NSAI – ANSI collaborative study)

Analyte	Matrix	l	n	o %	X mg/l	$\bar{x}$ mg/l	η %	s_r mg/l	$C_{V,r}$ %
TOC direct	Brewery treated wastewater	1	6	0		3,0		0,05	1,86
	Brewery treated wastewater low level spike	1	6	0	3,6	6,2	91,2	0,15	2,42
	Brewery treated wastewater medium level spike	1	6	0	49,98	52,9	99,9	0,08	0,16
	Brewery treated wastewater high level spike	1	6	0	90,0	92,7	99,6	0,08	0.1
	Pharmaceutical treated wastewater	1	6	0		2,4		0,12	5,00
	Pharmaceutical treated wastewater low level spike	1	6	0	3,09	6,5	93,9	0,09	1,38
	Pharmaceutical treated wastewater medium level spike	1	6	0	50,03	55,0	103	0,32	0.6
	Pharmaceutical treated wastewater high level spike	1	6	0	90,02	95,0	101	0,12	0,12

l Number of laboratories after outlier rejection.

n Number of individual test results after outlier rejection.

o Percentage of outliers.

X Assigned value.

$\bar{x}$ Overall mean of results (without outliers).

η Recovery rate.

s_r Repeatability standard deviation.

$C_{V,r}$ Coefficient of variation of repeatability.

NOTE Sample spikes were from potassium hydrogen phthalate for TOC.

Table C.2 — Supplemental TOC validation test data (NSAI – ANSI collaborative study)

Analyte	Matrix	l	n	o %	X mg/l	$\bar{\bar{x}}$ mg/l	η %	s_r mg/l	$C_{V,r}$ %
TOC direct	Seawater (2,12 % chloride)	1	6	0		0,23[a]		0,05	21,7
	Seawater (2,12 % chloride) low level spike	1	6	0	3,12	3,5	104	0,04	1,14
	Seawater (2,12 % chloride) medium level spike	1	6	0	50,01	50,7	101	0,05	0,10
	Seawater (2,12 % chloride) high level spike	1	6	0	90,07	90,3	100	0,15	0,17
	Surface water #1	1	6	0		7,3		0,0	0,0
	Surface water #1 low level spike	1	6	0	3,03	10,2	103	0,05	0,49
	Surface water #1 medium level spike	1	6	0	50,11	55,4	97,2	0,33	0,60
	Surface water #1 high level spike	1	6	0	100,2	106	99,3	0,08	0,08
	Surface water #2	1	6	6		5,1		0,10	1,96
	Surface water #2 low level spike	1	6	0	3,03	7,8	94,0	0,04	0,51
	Surface water #2 medium level spike	1	6	0	55,0	53,3	88,5	0,23	0,43
	Surface water #2 high level spike	1	6	0	90,19	93,7	98,8	0,28	0,30

For an explanation of symbols, see Table C.1.

NOTE Sample spikes were from potassium hydrogen phthalate for TOC.

[a] Value below quantitation limit.

Table C.3 — Supplemental TOC validation test data (NSAI – ANSI collaborative study)

Analyte	Matrix	l	n	o %	X mg/l	$\bar{\bar{x}}$ mg/l	η %	s_r mg/l	$C_{V,r}$ %
TOC direct	Municipal wastewater #1final effluent	1	6	0		8,6		0,19	2,16
	Municipal wastewater #1 final effluent low level spike	1	6	0	2,07	11,4	103	0,00	0,00
	Municipal wastewater #1 final effluent medium level spike	1	6	0	50,24	58,7	100	0,31	0,53
	Municipal wastewater #1 final effluent high level spike	1	6	0	90,00	98,3	100	0,64	0,65
	Municipal wastewater #1 primary effluent	1	6	0		5,8		0,05	0,89
	Municipal wastewater #1 primary effluent low level spike	1	6	0	2,02	7,8	98,2	0,10	1,26
	Municipal wastewater #1 primary effluent medium level spike	1	6	0	49,99	56,2	101	0,10	0,18
	Municipal wastewater #1 primary effluent high level spike	1	6	0	90,00	94,8	98,9	0,16	0,17
	Municipal wastewater #2 final effluent	1	6	0		13,6		0,08	0,60
	Municipal wastewater #2 final effluent low level spike	1	6	0	3,02	16,6	99,3	0,05	0,31
	Municipal wastewater #2 final effluent medium level spike	1	6	0	50,00	63,9	103	0,06	0,10
	Municipal wastewater #2 final effluent high level spike	1	6	0	90,10	103	101	0,19	0,18

For an explanation of symbols, see Table C.1.

NOTE Sample spikes were from potassium hydrogen phthalate for TOC.

Table C.4 — Supplemental TOC validation test data (NSAI – ANSI collaborative study)

Analyte	Matrix	l	n	o %	X mg/l	$\bar{\bar{x}}$ mg/l	η %	s_r mg/l	$C_{V,r}$ %
TOC direct	Municipal waste-water #2 secondary effluent	1	6	0		12,5		0,08	0,65
	Municipal waste-water #2 secondary effluent low level spike	1	6	0	3,05	15,2	104	0,05	0,34
	Municipal wastewa-ter #2 secondary efflu-ent medium level spike	1	6	0	50,03	62,8	102	0,50	0,79
	Municipal waste-water #2 secondary effluent high level spike	1	6	0	100,18	111	99,6	0,51	0,46
	Drinking water	1	6	0		2,4		0,04	1,67
	Drinking water lower level spike	1	6	0	4,11	6,6	101	0,05	0,75
	Drinking water medium level spike	1	6	0	50,1	52,8	102	0,13	0,25
	Drinking water high level spike	1	6	0	90,1	92,5	101	0,21	0,23

For an explanation of symbols, see Table C.1.

NOTE Sample spikes were from potassium hydrogen phthalate for TOC.

Table C.5 — Supplemental TN_b validation test data (NSAI – ANSI collaborative study)

Analyte	Matrix	l	n	o %	X mg/l	$\bar{\bar{x}}$ mg/l	η %	s_r mg/l	$C_{V,r}$ %
TN_b direct	Brewery treated wastewater	1	6	0		7,1		0,16	2,26
	Brewery treated wastewater low level spike	1	6	0	2,08	9,2	103	0,08	0,87
	Brewery treated wastewater medium level spike	1	6	0	5,03	12,2	102	0,08	0,66
	Brewery treated wastewater high level spike	1	6	0	15,03	14,6	105	0,06	0,41
	Pharmaceutical treated wastewater	1	6	0		11,9		0,59	4,96
	Pharmaceutical treated wastewater low level spike	1	6	0	3,03	12,8	105	0,0	0,0
	Pharmaceutical treated wastewater medium level spike	1	6	0	10,02	21,7	98,3	0,24	1,11
	Pharmaceutical treated wastewater high level spike	1	6	0	15,04	27,1	102	0,17	0,44
	Seawater (2,12 % chloride)	1	6	0		1,7		0,15	8,82
	Seawater (2,12 % chloride) low level spike	1	6	0	2,10	3,6	87,3	0,05	1,39
	Seawater (2,12 % chloride) medium level spike	1	6	0	10,02	11,7	101	0,05	0,44
	Seawater (2,12 % chloride) high level spike	1	6	0	15,05	16,4	97,2	0,05	0,30

For an explanation of symbols, see Table C.1.

NOTE Sample spikes were from sodium nitrate for TN.

Table C.6 — Supplemental TN_b validation test data (NSAI – ANSI collaborative study)

Analyte	Matrix	l	n	o %	X mg/l	$\bar{\bar{x}}$ mg/l	η %	s_r mg/l	$C_{V,r}$ %
TN_b direct	Surface water #1	1	6	0		1,5		0,05	3,33
	Surface water #1 low level spike	1	6	0	2,00	3,8	115	0,05	1,32
	Surface water #1 medium level spike	1	6	0	5,05	6,3	98,1	0,05	0,79
	Surface water #1 high level spike	1	6	0	17,0	17,6	96,0	0,05	0,28
	Surface water #2	1	1	0		1,3		0,05	0,85
	Surface water #2 low level spike	1	6	0	2,02	3,3	97,2	0,05	1,52
	Surface water #2 medium level spike	1	6	0	12,06	13,3	100	0,20	1,50
	Surface water #2 high level spike	1	6	0	15.05	16,0	98,3	0,05	0,31
	Municipal wastewater #1 final effluent	1	6	0		14,7		0,97	6,62
	Municipal wastewater #1 final effluent low level spike	1	6	0	2,06	14,8	96,3	0,04	0,28
	Municipal wastewater #1 final effluent medium level spike	1	6	0	10,14	24,9	107	0,12	0,47
	Municipal wastewater #1 final effluent high level spike	1	6	0	15,08	29,3	103	0,61	2,07

For an explanation of symbols, see Table C.1.

NOTE Sample spikes were from sodium nitrate for TN.

Table C.7 — Supplemental TN_b validation test data (NSAI – ANSI collaborative study)

Analyte	Matrix	l	n	o %	X mg/l	$\bar{\bar{x}}$ mg/l	η %	s_r mg/l	$C_{V,r}$ %
TN_b direct	Municipal wastewater #1 primary effluent	1	6	0		3,8		0,04	1,07
	Municipal wastewater #1 primary effluent low level spike	1	6	0	2,04	5,7	92,3	0,00	0,00
	Municipal wastewater #1 primary effluent medium level spike	1	6	0	5,03	8,3	88,8	0,04	0,49
	Municipal wastewater #1 primary effluent high level spike	1	6	0	15,03	17,7	92,9	0,10	0,55
	Municipal wastewater #2 final effluent	1	6	0		11,9		0,06	0,53
	Municipal wastewater #2 final effluent low level spike	1	6	0	2,02	14,0	106	0,08	0,58
	Municipal wastewater #2 final effluent medium level spike	1	6	0	5,05	16,3	103	0,10	0,65
	Municipal wastewater #2 final effluent high level spike	1	6	0	15,05	25,5	97,5	0,16	0,63
	Municipal wastewater #2 secondary effluent	1	6	0		12,2		0,10	0,81
	Municipal wastewater #2 secondary effluent low level spike	1	6	0	4,04	15,7	98,4	0,21	1,34
	Municipal wastewater #2 secondary effluent medium level spike	1	6	0	5,02	16,2	99,5	0,04	0,25
	Municipal wastewater #2 secondary effluent high level spike	1	6	0	17,04	28,3	103	0,12	0,43

For an explanation of symbols, see Table C.1.

NOTE Sample spikes were from sodium nitrate for TN.

Table C.8 — Supplemental TN_b validation test data (NSAI – ANSI collaborative study)

Analyte	Matrix	l	n	o	X	$\bar{\bar{x}}$	η	s_r	$C_{V,r}$
				%	mg/l	mg/l	%	mg/l	%
TN_b direct	Drinking water	1	6	0		1,0		0,04	4,00
	Drinking water lower level spike	1	6	0	3,21	4,3	103	0,18	4,19
	Drinking water medium level spike	1	6	0	5,03	6,0	95,2	0,06	1,00
	Drinking water high level spike	1	6	0	15,04	16,1	99,0	0,05	0,31

For an explanation of symbols, see Table C.1.

NOTE Sample spikes were from sodium nitrate for TN.