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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

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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) 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.

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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.