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

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

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

The main changes are as follows:

— the method to determine concentrations <1 mg/l of C and N has been expanded;

— the normative references have been updated;

— the method to apply single component standard calibration solutions e.g. based on as ammonium sulfate or potassium nitrate, has been expanded;

— Clause A.5 Test report has been added in order to require referencing the difference methods with the results report.

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

Introduction

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

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

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

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

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

1 Scope

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

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

Dissolved nitrogen gas (N_2) is not determined.

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

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

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

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

The procedure is carried out by automated analysis.

2 Normative references

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

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

3 Terms and definitions

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

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

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

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

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

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

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

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

3.3
total organic carbon
TOC
sum of 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
TNb
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
DNb
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

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

4 Principle

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

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

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

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

Oxidation of organic carbon (TOC, DOC) present in the sample with oxygen or synthetic air to carbon dioxide followed by detection of the formed CO_2 by means of infrared (IR) spectrometry.

Inorganic and organic nitrogen present in the sample are combusted with oxygen or synthetic air and converted into to nitric oxide. The reaction with ozone yields electronically excited nitrogen oxides. The formed nitrogen monoxide (NO) is detected by means of chemiluminescence (CLD) See Annex C for alternative detection.

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

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

5 Interferences

5.1 General

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

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

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

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

5.2 TOC or DOC

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

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

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

5.3 TNb or DNb

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

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

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

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

6 Reagents

Use reagents of pro analysis grade, if available.

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

NOTE It is not necessary to dry cellulose before usage.

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

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

6.1 Water.

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

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

6.3 Hydrochloric acid, (HCl) ω = 30 % to 32 %.

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

6.5 TOC and TNb stock solution for system check.

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

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

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

6.6 Blank solution.

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