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

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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*.

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, $\rho = 1{,}84$ g/ml.

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

6.4 Sodium hydroxide, NaOH, ≥97 %.

6.5 Hydrochloric acid, $w(\text{HCl}) = 37$ %.

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, $\rho(C) = 1\ 000$ 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, $\rho(N) = 1\ 000$ 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, $\rho(P) = 1\ 000$ mg/l.

Prepare a 1 000 mg/l TP stock solution using potassium dihydrogen phosphate ($K\ H_2PO_4$). Place 4,43 g of $K\ H_2PO_4$ (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.