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

Qualité de l'eau — Lignes directrices pour le dosage du carbone organique total (COT) et carbone organique dissous (COD)

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Contents

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 8245 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This second edition cancels and replaces the first edition (ISO 8245:1987) which has been technically revised.

Annexes A and B of this International Standard are for information only.

Introduction

It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably qualified staff.

Total organic carbon (TOC) is a measure of the carbon content of dissolved and undissolved organic matter present in water. It does not give information on the nature of the organic substance.

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

1 Scope

This International Standard gives guidance for the determination of total carbon (TC), total inorganic carbon (TIC) and total organic carbon (TOC) in drinking water, ground water, surface water, sea water and waste water. It also defines terms and specifies interferences, reagents, and sample pretreatment for water samples.

The method described in this International Standard applies to water samples containing organic carbon content ranging from 0,3 mg/l to 1000 mg/l. The lower limit concentration is only applicable in special cases, for example drinking water, measured by highly sensitive instruments. Higher concentrations may be determined after appropriate dilution.

This International Standard does not deal with the instrument-dependent specifications.

Purgeable organic substances, such as benzene, toluene, cyclohexane and chloroform, can also be determined using this method.

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

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, this publication do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*.

3 Terms and definitions

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

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

3.2
total inorganic carbon
TIC
sum of inorganic carbon present in water in the form of elemental carbon, total carbon dioxide, carbon monoxide, cyanide, cyanate and thiocyanate

NOTE TOC instruments most often measure TIC as CO_2 originating only from hydrogencarbonates and carbonates.

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

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

3.5
volatile organic carbon
VOC
purgeable organic carbon
POC
organic carbon present in water which can be purged under the conditions of this method

3.6
non-volatile organic carbon
NVOC
non-purgeable organic carbon
NPOC
organic carbon present in water which cannot be purged under the conditions of this method

4 Principle

Organic carbon (org. C) in water is oxidized to carbon dioxide by combustion, by the addition of an appropriate oxidant, by UV radiation or any other high-energy radiation.

The application of the ultraviolet method with only oxygen as an oxidant is restricted to low polluted waters, containing low concentrations of TOC.

NOTE In the presence of humic material, low TOC values may be obtained when UV radiation is used.

The carbon dioxide formed by oxidation is determined either directly or after reduction, for example to methane (CH_4).

The final determination of CO_2 is carried out by a number of different procedures, for example infrared spectrometry, titration (preferably in non-aqueous solution), thermal conductivity, conductimetry, coulometry, CO_2-sensitive sensors and flame ionization detection (used after reduction of CO_2 to methane, among others).

In addition to organic carbon, the water sample may contain carbon dioxide or ions of carbonic acid. Prior to the TOC determination, it is essential that this inorganic carbon be removed by purging the acidified sample with a gas which is free from CO_2 and organic compounds. Alternatively, both total carbon (TC) and total inorganic carbon (TIC) may be determined and the organic carbon content (TOC) may be calculated by subtracting the total inorganic carbon from the TC. This method is particularly suitable for samples in which the total inorganic carbon is less than the TOC.

Purgeable organic substances, such as benzene, toluene, cyclohexane and chloroform, may partly escape upon stripping. In the presence of these substances, the TOC concentration is determined separately or the differential method (TC – TIC = TOC) may be applied. By using the differential method, the value of the TOC should be higher than the TIC, or at least of similar size.

Inorganic carbon is removed by acidification and purging or is determined separately.

5 Reagents

Use only reagents of recognized analytical grade.

In this International Standard only those chemicals and gases which are used with the majority of TOC methods are listed. Reagents shall be used according to the manufacturer's instructions, and shall, if necessary, be pretreated.

5.1 Dilution water

The TOC of the water used for dilution and for preparation of the calibration standards shall be sufficiently low to be negligible in comparison with the lowest TOC concentration to be determined (see Table 1).

The choice of the method to pretreat water intended for dilution purposes depends on the concentration range of the sample under investigation as shown in Table 1.

NOTE For measurements of a TOC concentration $< 0,5$ mg/l, it is preferable to prepare water for blanks and calibration solutions immediately prior to analysis (see Table 1).

Table 1 — Dilution water specifications

TOC of sample mg/l	**Maximum acceptable TOC of dilution water** mg/l	**Dilution water: treatment method**
< 10	0,1* 0,3	UV treatment condensation
10 to 100	0,5	double distillation with $KMnO_4/K_2Cr_2O_7$
> 100	1	distillation
* Only for ultrapure water.		

5.2 Potassium hydrogenphthalate stock solution, ρ(org. C) = 1 000 mg/l.

Dissolve 2,125 g of potassium hydrogenphthalate ($C_8H_5KO_4$) (dried for 1 h at a temperature between 105 °C and 120 °C) in a 1 000 ml one-mark volumetric flask filled with 700 ml of water (5.1), then dilute to volume with water.

The solution is stable for about 2 months if stored in a tightly stoppered bottle in a refrigerator.

5.3 Potassium hydrogenphthalate standard solution, ρ(org. C) = 100 mg/l.

Pipette 100 ml of the potassium hydrogenphthalate stock solution (5.2) into a 1 000 ml one-mark volumetric flask, and dilute to volume with water (5.1).

The solution is stable for about 1 week if stored in a tightly stoppered bottle in a refrigerator.

5.4 Standard solution for the determination of inorganic carbon, ρ(inorg. C) = 1 000 mg/l.

Dissolve 4,415 g of sodium carbonate (Na_2CO_3) [dried for 1 h at (285 ± 5)°C] in a 1 000 ml one-mark volumetric flask in approximately 500 ml of water (5.1).

Add 3,500 g of sodium hydrogencarbonate ($NaHCO_3$) (dried for 2 h over silica gel), and dilute to volume with water (5.1).

This solution is stable at room temperature for about 2 weeks.

5.5 Standard solution, to check the operational performance of the system.

NOTE 1 In the interlaboratory trial, copper phthalocyanine has been used for this purpose. A suitable test solution of copper phthalocyanine, ρ(org. C) = 100 mg/l, may be prepared as follows:

In a 1 000 ml volumetric flask, dissolve 0,256 g of copper phthalocyanine tetrasulfonic acid (tetrasodium salt) ($C_{32}H_{12}CuN_8O_{12}S_4Na_4$) in 700 ml of water, and dilute to volume with water (5.1).

The solution is stable for about 2 weeks.

WARNING — This reagent is toxic.

NOTE 2 Other stable titrimetric substances may replace reagents 5.2, 5.4 and 5.5.

5.6 Non-volatile acids, for expelling the carbon dioxide, such as phosphoric acid, $c(H_3PO_4)$ = 0,5 mol/l, or if necessary, more concentrated.

5.7 Gases, such as air, nitrogen, oxygen, free from carbon dioxide and organic impurities.

Use other gases in accordance with the instrument manufacturer's specifications.

6 Apparatus

Usual laboratory apparatus and the following.

6.1 Apparatus for the determination of organic carbon.

6.2 Homogenization device, for example a magnetic stirrer with adequate performance for the homogenization of dispersed matter, a suitable ultrasonic apparatus or a high speed stirrer.

7 Sampling and samples

7.1 Sampling

See also ISO 5667-3.

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.

Collect water samples in glass or polyethylene bottles, completely filled with the sample, and, if biological activity is suspected, acidify to pH 2 [for example with phosphoric acid (5.6)]. In some cases, loss of volatile substances may occur upon acidification of the sample with the loss of carbon dioxide. If volatile organic compounds are suspected, carry out the measurement without acidification and within 8 h of sampling. Otherwise, store the sample in a refrigerator at a temperature in the range of 2 °C to 5 °C, and analyse within 7 days. If this is not possible, the sample can be kept at –15 °C to –20 °C for several weeks.

7.2 Preparation of the water sample

If the sample is not homogeneous and it is not possible to obtain a representative sample, even after thorough shaking, use an appropriate apparatus (see 6.2) to homogenize the sample.

The homogeneity of the sample may be verified, for example, by separately analysing samples from the upper and lower layers of the bottle.

If only dissolved organic substances (DOC) are to be determined, filter the sample through a membrane filter, 0,45 µm pore size, which has previously been washed with hot water to completely remove adhering organic substances. Nevertheless, the carbon content of the filtrate shall be determined and taken into account.

8 Procedure

8.1 Calibration

Comparison methods (for example, IR detection) require calibration. In the case of absolute methods, for example acidimetry or coulometry, the calibration serves the purpose of verifying the analytical system.

Calibrate the instrument according to the manufacturer's instructions.

Establish a calibration curve by analysing potassium hydrogenphthalate standard solutions of adequate concentrations. For example, for mass concentrations ranging from 10 mg/l to 100 mg/l, prepare a series of at least five calibration solutions from the potassium hydrogenphthalate stock solution (5.2) as follows:

a) to prepare the calibration solutions, pipette into each of a series of 100 ml volumetric flasks for example 0 ml (blank), 1 ml, 2 ml, 3 ml, 5 ml, and 10 ml of the potassium hydrogenphthalate stock solution (5.2), and dilute to volume with water (5.1);

b) analyse each solution and the blank solution (from the flask without added potassium hydrogenphthalate) in accordance with the manufacturer's instructions;

c) establish a calibration curve by plotting the mass concentrations of TOC, in milligrams of carbon per litre, against the instrument-specific response units (I);

The reciprocal value of the slope of the resulting calibration line is the calibration factor f, in milligrams of carbon per litre.

In order to determine the TIC value, it is necessary to establish a calibration curve by analysing calibration solutions made from the solution described in 5.4.

In order to determine the TOC value from the difference TC – TIC, it is necessary to establish a calibration curve by analysing calibration solutions prepared from a known mixture of the standard solutions 5.3 and 5.4.

8.2 Control procedures

Analyse the test solutions (either 5.2, 5.3, 5.4 or 5.5; see note 2 in 5.5) with each series of samples in order to verify the accuracy of the results obtained by the method.

If the deviations found are higher than specified in within-laboratory quality criteria, investigate the following causes of error:

- malfunction of the instrument (for example in the oxidation or detection system, leakage, faults in the temperature or the gas control);
- change in concentration of the test solution;
- contamination of the measuring assembly.

Regularly verify the entire measuring system according to the instructions of the manufacturer and for the absence of leaks.

These control experiments are carried out in addition to the instrumental control as specified in the operating instructions provided by the instrument manufacturer.

8.3 Determination

Determine the TOC concentrations of the samples in accordance with the instrument manufacturer's instructions.

When TOC is determined directly, prior to analysis remove the total inorganic carbon by acidifying the sample to a pH below 2. Carefully minimize the loss of volatile organic substances.

The TOC concentration should be within the working range of the calibration. This can be achieved by diluting the sample.

Prior to each batch of TOC determinations (for example every 10 determinations), carry out appropriate control experiments at the intervals recommended by the manufacturer or as specified by the laboratory.

After acidification, blow a stream of pure inert gas, free from CO_2 and organic impurities, through the system (for approximately 5 min) in order to remove CO_2.

9 Expression of results

9.1 Method of calculation

Depending on the type of TOC instrument used, different kinds of readings may be obtained from which the TOC or DOC concentration of the analyzed sample is calculated. In case of discontinuous measurements, these values may be in terms of, for example, peak heights, peak areas or volume of the titrant required. Normally, peak areas are reported. Use peak heights only if they are proportional to the concentration.

In the case of quasi-continuous TOC or DOC measurements, the CO_2 concentration generated by the combustion of the organic matter is recorded, for example as a line on a strip chart recorder. The distance of this line from the zero line is proportional to the TOC concentration.

Calculate the mass concentration using the calibration curve (8.1).

The mass concentration of TOC or DOC, expressed in milligrams of carbon per litre, may also be obtained from the following equation:

$$\frac{I \cdot f \cdot V}{V_p} \tag{1}$$

where

I is the instrument specific response;

f is the calibration factor, in milligrams of carbon per litre, evaluated according to 8.1;

V is the volume, in millilitres, of the diluted water sample;

V_p is the sample volume, in millilitres, being diluted to V.

The results shall be expressed to two or three significant figures depending on the random error (precision) of the measurement.

EXAMPLES:

ρ(TOC) = 0,76 mg/l or

ρ(TOC) = 530 mg/l or

ρ(TOC) = $6{,}32 \times 10^3$ mg/l.

9.2 Precision

Information on repeatability and reproducibility, as obtained from an interlaboratory experiment, is given in annex A.

10 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) all details necessary for a complete identification of the sample tested;

c) details concerning the storage of the laboratory samples before analysis, including the time between sampling and analysis;

d) sample pretreatment (time for settlement, filtration);

e) the mass concentration of TOC and DOC respectively in the sample, in milligrams of carbon per litre;

f) details of any deviation from the procedure specified in this International Standard or any other circumstances that may have influenced the result.

Annex A
(informative)

Results of an interlaboratory trial for TOC determination

Table A.1

Sample	**Nominal value TOC** mg/l	**Total mean TOC** mg/l	**Recovery** %	**Reproducibility**		**Repeatability**		**Number of laboratories**	**Number of analytical results after elimination of outliers**	**Outliers of results**
				Standard deviation mg/l	Variation coefficient %	Standard deviation mg/l	Variation coefficient %			
1	2,3	2,99	129,9	0,687	23	0,19	6,3	55	259	13
2	18,5	19,2	103,9	1,23	6,4	0,38	2	56	260	9
3	120	139	115,9	12,4	8,9	2,8	2	54	236	16
4		307		13,9	4,5	3,8	1,2	54	244	20

Sample 1: Copper phthalocyanine tetrasulfonic acid, tetrasodium salt.

Sample 2: Mixture of potassium hydrogenphthalate and copper phthalocyanine tetrasulfonic acid, tetrasodium salt.

Sample 3: Mixture of potassium hydrogencarbonate, potassium hydrogenphthalate and copper phthalocyanine tetrasulfonic acid, tetrasodium salt.

Sample 4: Industrial waste water, real sample, filtered.

NOTE 1 The reason for the recovery rate of 130 % as stated for sample 1 (sample with low TOC concentration) is possibly due to systematic errors (non-consideration or only partial consideration of the TOC concentration of the water blank).

NOTE 2 The increased recovery rate in the case of sample 3 is possibly caused by the very high TIC concentration. In similar cases, statements from the instrument manufacturers concerning acid volume and stripping time are often not sufficient.

Annex B

(informative)

TOC determination for samples containing particles

B.1 Additional conditions

The instrumental specifications for TOC measurement should at least be suitable for measuring particle sizes of 100 µm (convention).

NOTE 1 In the interlaboratory trial (see Table B.1), samples containing particles up to 100 µm have been measured.

NOTE 2 If the TOC determination of the sample containing particles does not lead to reproducible results, even after intensive homogenization, the sample may be filtered and the TOC of the filtrate and the residue may be determined separately.

Systems based on oxidation using UV are not suitable for the determination of microcellulose, an example of samples containing suspended matter [see B.4, Table B.1, sample 1 b)].

B.2 Test suspension for particle processing control

This test suspension serves to verify the homogenization and recovery of incompletely dissolved sample components (particulate matter).

To prepare this suspension, place 225 mg of cellulose, $(C_6H_{10}O_5)_n$, (particle size ranging from 20 µm to 100 µm, carbon concentration of the suspension test sample: 100 mg/l) in a 1 000 ml volumetric flask, moist with water. Dilute to volume with water and stir with a magnetic stirrer until the suspension is homogeneous. Ultrasonic treatment should not be used because it reduces the particle size. The mixture is stable in the refrigerator for about 2 weeks, but it is necessary to stir each time before use.

Suspensions of equally well-suited substances may also be used as test suspensions, for example for the analysis of paper-mill effluents.

B.3 Testing for homogenization and recovery of incompletely dissolved sample components (particle processing control)

It is advisable that for each series of analyses of samples containing solids, the homogenization and recovery of suspended sample components (particle processing capability of the instrument) be verified by using a test suspension (B.2). Withdrawal of an aliquot is to be made while stirring. If an autosampler is used, samples should be continuously stirred during analysis. The mean value from a triple measurement should be between 90 mg/l and 110 mg/l, the repeatability variation coefficient should be < 10 %.

NOTE 1 For this test, particle size is important.

NOTE 2 Optimal homogenization without particle segregation is provided, for example, by an oscillating stirrer.

B.4 Performance data

See Table B.1.

Table B.1 — Results of an interlaboratory trial for TOC determination

Sample	Nominal value TOC mg/l	Total mean TOC mg/l	Recovery %	Reproducibility		Repeatability		Number of laboratories	Number of analytical results after elimination of outliers	Outliers of results
				Standard deviation mg/l	Variation coefficient %	Standard deviation mg/l	Variation coefficient %			
1 a	20	16,65	83,2	7,5	45,1	2	12,0	32	149	0
1 b	20	0,53	2,7	0,4	75,0	0,15	27,3	15	56	10
Sample 1 a: Cellulose microcrystals (combustion determination).										
Sample 1 b: Cellulose microcrystals (UV oxidation).										

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