Water analysis
Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)
ISO-CEN EN  1484

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Introduction

It is absolutely essential that tests conducted according to this standard are 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 the water. It does not give information on the nature of the organic substance.

1. Scope
This European Standard gives guidance for the determination of organic carbon in drinking water, ground water,
surface water, sea water and waste water. It deals with definitions, interferences, reagents, and the same pretreatment of water samples with a content of organic carbon ranging from 0,3 mg/l to 1000 mg/l while the lower value is only applicable in special cases, for example drinking water, measured with instruments capable of measuring these low levels. Higher concentrations may be determined after appropriate dilution. This European Standard does not deal with the instrument-dependent aspects.

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 is removed by purging the acidified sample with a gas which is free from CO2 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 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.

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

NOTE: In presence of humic material low values may occur when UV-radiation is used.

2. Normative References
This European Standard incorporates by dated or undated reference provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated reference, subsequent amendment to or revisions of any of these publications apply to this European standard only when incorporated in it by amendment or revision. For updated reference the latest edition of the publication referred to applies-

EN ISO 5667-3 : 1995

3. Definitions
For the purposes of this European Standard the definitions apply:

3.1 Total Carbon (TC)
The sum of organically bound and inorganically bound carbon present in water, including elemental carbon.

3.2 Total inorganic carbon (TIC)
The sum of carbon present in water, consisting of elemental carbon, total carbon dioxide, carbon monoxide, cyanate, and thiocyanate. TOC instruments mostly register as TIC only the CO2 originating from hydrogen carbonates and carbonates.

3.3 Total organic carbon (TOC)
The sum of organically bound carbon present in water, bonded to dissolved or suspended matter. Cyanate, elemental carbon and thiocyanate will also be measured.

3.4 Dissolved organic carbon (DOC)
The sum of organically bound carbon present in water originating from compounds which will pass a membrane filter of pore size of 0,45 μm. Cyanate and thiocyanate are also measured.

3.5 Volatile organic carbon (VOC, POC)
Under the conditions of this method purgeable organic matter (POC).

3.6 Non volatile organic carbon (NVOC, NPOC)
Under the conditions of this method non-purgeable organic carbon (NPOC).

4. Principle
Oxidation of organic carbon (org. C) in water 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 gas as an oxidant is restricted to low polluted waters containing low concentrations of TOC. Inorganic carbon is removed by acidification and purging or is determined separately. The carbon dioxide formed by oxidation is determined either directly or after reduction, for example, to methane.
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, conductometry, coulometry, CO\(_2\)-sensitive sensors and flame ionization detection - used after reduction of the CO\(_2\), among others, to methane.

5. Reagents

5.1 General remarks

Use only reagents of recognized analytical grade.

In this European Standard only those chemicals and gasses are listed which are used with the majority of TOC methods. Reagents should be used according to the manufacturer’s instructions, and should be pretreated, if necessary.

The TOC of the water being used for dilution and for preparation of the calibration standards should be negligibly low, compared with the lowest TOC concentration to be determined.

The method for water treatment depends on the concentration range 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 the calibration solutions immediately prior to analysis (see table 1).

<table>
<thead>
<tr>
<th>TOC of the Sample (mg/l C)</th>
<th>Maximum acceptable TOC of the dilution water (mg/l C)</th>
<th>Example of water treatment methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 10</td>
<td>0,1*</td>
<td>UV treatment condensation</td>
</tr>
<tr>
<td></td>
<td>0,3</td>
<td></td>
</tr>
<tr>
<td>10 to 100</td>
<td>0,5</td>
<td>double distillation with KMnO4/K2Cr2O7</td>
</tr>
<tr>
<td>&gt; 100</td>
<td>1</td>
<td>Distillation</td>
</tr>
<tr>
<td>*only for ultrapure water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.2 Potassium hydrogen phthalate, stock solution, \(p\) (org. C) = 1 000 mg/l

Dissolve in a 1 000 ml one-mark volumetric flask 2,125 g of potassium hydrogen phthalate (C\(_8\)H\(_5\)KO\(_4\)) (dried for 1 h at a temperature between 105°C and 120°C) in 700 ml of water, and make up 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 hydrogen phthalate, standard solution, \(p\) (org.C) = 100 mg/l

Pipette 100 ml of the potassium hydrogen phthalate stock solution (5.2) into a 1 000 ml one-mark volumetric flask, and make up to volume with water.

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

5.4 Standard Solution for the determination of inorganic carbon, \(p\)\(\text{(inorg.C)}\) = 1 000 mg/l

Dissolve in a 1 000 ml one-mark volumetric flask 4,415 g of sodium carbonate (Na\(_2\)CO\(_3\)), dried for 1 h at (285±5)°C in approximately 500 ml of water.

Add 3,500 g of sodium hydrogen carbonate (NaHCO\(_3\)) (dried for 2 h over silica gel), and make up to volume with water.

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

5.5 Substances, not readily oxidizable

A standard solution shall be used to check the operational performance of the system.

NOTE: In the interlaboratory trial, copper phthalocyanine has been used for this purpose. A suitable test solution of copper phthalocyanine, \(p\)(org.C) = 100 mg/l, may be prepared as follows: In a 1 000 ml volumetric flask 0,256 g of copper phthalocyanine-tetrasulfonic acid (tetrasodium salt) (C\(_{32}\)H\(_{12}\)CuN\(_8\)O\(_{12}\)S\(_4\)Na\(_4\)) are dissolved in 700 ml of water, and made up to volume with water. The solution is stable for about 2 weeks. WARNING: This reagent is toxic.
5.6 Further reagents
5.6.1 The reagents 5.2, 5.4 and 5.5 may be replaced by other reagents provided these are stable titrimetric substances.
5.6.2 Non volatile acids for expelling the carbon dioxide, such as phosphoric acid $c(H_3PO_4) = 0.5$ mol/l, if necessary, more concentrated.
5.7 Gases
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
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 EN 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 (5.6.2)). In some cases the result may be reduced by the loss of volatile substances during to the liberation of carbon dioxide, when the sample is acidified. 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 analyze within 7 days. If this is not possible, the sample can be kept at - 15° C to - 20°C for up to several weeks.
7.2 Preparation of the water sample
If, because of the inhomogeneity, the collection of a representative sample is not possible, even after thorough shaking, homogenize the sample, using for example, the apparatus as described in 6.2.
The homogeneity may be checked for example by analyzing a sample from the upper and the lower layer of the bottle.
If only dissolved organic substances (DOC) are to be determined, filter the sample through a membrane filter, pore size 0.45 m m, which has previously been washed with hot water to completely remove adhering organic substances. Nevertheless the carbon content of the filtrate has to 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 checking the analytical system.
Calibrate the instrument according to the manufacturer’s instructions.
Establish a calibration curve by analyzing potassium hydrogen phthalate standard solutions of adequate concentrations. For example for mass concentrations ranging from 10 mg/l to 100 mg/l proceed as follows:
Prepare a series of at least 5 calibration solutions from the potassium hydrogen phthalate stock solution (5.2), and make up to volume with water.
Analyze each solution and the blank solution (from the flask without added potassium hydrogen phthalate) in accordance with the manufacturer’s instructions.
Establish a calibration curve by plotting the mass concentrations of TOC, in milligrams per litre of carbon, 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 per litre of carbon.
In the case of the determination of TIC it is necessary to establish a calibration curve by analyzing calibration solutions made from solution (5.4).
In the case of the determination of TOC from the difference TC-TIC, it is necessary to establish a calibration curve by analyzing calibration solutions prepared from a known mixture of the standard solutions 5.3 and 5.4.

8.2 Control Procedures
Analyze the test solutions (either 5.2; or 5.3; or 5.5; or 5.6.1) 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 intra-laboratory quality criteria allow, then the following causes of error
should be investigated:
- Malfunction of the instrument (for example in the oxidation or detection system, leakages, faults in the temperature or the gas control);
- Changes in concentration in the test solution;
- Contamination of the measuring assembly.
Regularly check the entire measuring system according to the instructions of the manufacturer; also check the entire systems regularly 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. In the case of direct determination of the TOC, remove the total inorganic carbon (ensure that the pH is below 2) prior to analysis. 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 10 determinations) carry out appropriate control experiments at the intervals recommended by the manufacturer or specified by the laboratory.
After acidification, blow a stream of pure inert gas free from CO2 and organic impurities through the system (for approximately 5 min) in order to remove CO2.

9. Evaluation of results
9.1 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 the 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 CO2 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, calculated in mg/l, may also be obtained from the following equation:

\[ \frac{1 \cdot f \cdot v}{V_p} \]

Where:
- \( I \) is the instrument specific response;
- \( f \) is the calibration factor evaluated as in 8.1 in milligrams per litre of carbon;
- \( V \) is the volume of the diluted water sample, in millilitres;
- \( V_p \) is the sample volume being diluted to \( V \), in millilitres.

9.2 Expression of Results
The results are expressed in milligrams per litre of carbon. The way of expressing the results depends on the random error (precision) of the measurement. 2 or 3 significant figures are reported.
Examples:
- \( p(\text{TOC}) = 0.76 \text{ mg/l carbon} \)
- \( p(\text{TOC}) = 530 \text{ mg/l carbon} \)
- \( p(\text{TOC}) = 530 \text{ mg/l carbon} \)
Information on repeatability and reproducibility, as obtained from an interlaboratory experiment, is given in the annex.

10. Test report
The test report shall contain the following information.
a) a reference to this European Standard;
b) all data required for a complete identification of the sample;
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 per litre;
f) details of any deviation from the procedure specified in this European Standard or any other circumstances that may have influenced the result.

### Annex A (informative)


### Annex B (informative)

Table B.1: Results of an interlaboratory trial on the TOC determination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal value</th>
<th>Total mean</th>
<th>Recovery</th>
<th>Reproducibility</th>
<th>Repeatability</th>
<th>Number of laboratories</th>
<th>Number of analytical results after elimination of outliers</th>
<th>Outliers of results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.3</td>
<td>2.99</td>
<td>129.9</td>
<td>0.687</td>
<td>23</td>
<td>0.19</td>
<td>6.3</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>18.5</td>
<td>19.2</td>
<td>103.9</td>
<td>1.23</td>
<td>6.4</td>
<td>0.38</td>
<td>2</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>139</td>
<td>115.9</td>
<td>12.4</td>
<td>8.9</td>
<td>2.8</td>
<td>2</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>307</td>
<td>13.9</td>
<td>4.5</td>
<td>3.8</td>
<td>1.2</td>
<td>54</td>
<td>244</td>
<td>20</td>
</tr>
</tbody>
</table>

Sample 1= Copper phthalocyaninetetrasulfonic acid, tetrasodium salt

Sample 2= Mixture of potassium hydrogen phthalate and Copper phthalocyanine tetrasulfonic acid, tetrasodium salt

Sample 3= Mixture of potassium hydrogen carbonate Potassium hydrogen phthalate and Copper phthalocyanine tetrasulfonic acid, tetrasodium salt

Sample 4= Industrial waste water, real sample, filtered
Note:

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 blank water).

The increased recovery rate in case of sample 3 is possibly caused by the very high TIC concentration. In similar cases, the statements from the instrument manufacturers concerning acid volume and stripping time are often non sufficient.

Annex C (informative)

Determination of samples containing particles

C.1 Additional conditions
The instrumental specifications for TOC measurement should at least be suitable for measuring particles of a size of 100 m (convention).
NOTE 1: In the interlaboratory trial (see table C.1), samples containing particles up to 100 m 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 as an example for samples containing suspended matter (see table C.1 results of the interlaboratory trial, Sample 1 b).

C.2 Suspension to test the particle processing capability
This suspension serves to check the homogenization and the recovery of incompletely dissolved sample components (particulate matter):
To prepare this suspension, 225 mg of cellulose, (C6H10O5)n, (particle size about 20 m to 100 m, concentration of the suspension test sample: 100 mg/l C) are placed into a 1 000 ml volumetric flask, moist with water, made up to volume with water, and stirred with a magnetic stirrer until the suspension is homogeneous. Ultrasonic treatment should not be used because it is necessary to stir each time before use.
Suspensions of equally well suited substances may also be used as standards, for example for the analysis of paper mill effluents.

C.3 Control of the homogenization and recovery of incompletely dissolved sample components (particle processing capability)
It is advisable with each batch of analyses of samples containing solids to check the homogenization and the recovery of suspended sample components (particle processing capability of the instrument) by using a test suspension (C.2). Withdrawal of an aliquot is to be made by stirring. If an autosampler is used, the aliquots in their vessels should be stirred. The mean value from a triple measurement should be between 90 mg/l and 100 mg/l, the repeatability variation coefficient should be < 10 %.
NOTE 1: For this test the particle size is important.
NOTE 2: An optimal homogenization without segregation of particles is provided, for example, by an oscillating stirrer.

C.4 Performance Data
Table C.1: Results of an interlaboratory trial on the TOC determination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal value</th>
<th>Total mean</th>
<th>Recovery</th>
<th>Reproducibility</th>
<th>Repeatability</th>
<th>Number of laboratories</th>
<th>Number of analytical results after elimination of outliers</th>
<th>Outliers of results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/l</td>
<td>mg/l</td>
<td>%</td>
<td>Standard deviation mg/l</td>
<td>Variation coefficient %</td>
<td>Standard deviation mg/l</td>
<td>Variation coefficient %</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>1 a</td>
<td>20</td>
<td>16.65</td>
<td>83.2</td>
<td>7.5</td>
<td>45.1</td>
<td>2</td>
<td>12.0</td>
<td></td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 b</td>
<td>20</td>
<td>0.53</td>
<td>2.7</td>
<td>0.4</td>
<td>75.0</td>
<td>0.15</td>
<td>27.3</td>
<td></td>
</tr>
</tbody>
</table>

**sample 1a=** Cellulose microcrystals (combustion determination)

**sample 1b=** Cellulose microcrystals (UV-oxidation)