



Designation: D8361 – 20

# Standard Test Method for Total Organic Carbon in Water by Two Stage Wet Chemical Catalyzed Hydroxyl Radical Oxidation with Infra-Red Detection of Resulting Carbon Dioxide<sup>1</sup>

This standard is issued under the fixed designation D8361; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the catalyzed hydroxyl radical oxidation system for the in-stream, online (Guide [D5173](#)) or laboratory analysis of total organic carbon, total carbon and total inorganic carbon in drinking water, wastewater, industrial process water, and effluent water. It is applicable to both dissolved and suspended materials. Suspended materials and particulates up to 2 mm in diameter can be analyzed.

1.2 This test method allows for determination of  $\text{TOC} \geq 1$  mg/L,  $\text{TC} \geq 1$  mg/L, and  $\text{TIC} \geq 1$  mg/L. The lower and upper working ranges are restricted by instrument-dependent conditions (for example, sample volume, amount of each reactant) and can be adjusted for a wider range.

1.3 This test method can be applied for the determination of total carbon (TC) and total inorganic carbon (TIC). Volatile or purgeable organic carbon (VOC, POC) can be determined separately by this test method (see [Annex A1](#)).

1.4 This test method allows the measurement of organic and inorganic carbon concentration samples, and samples containing dissolved chlorides up to seawater chloride concentrations.

1.5 The chemical oxidation process, applied in this test method, takes place at ambient pressure and temperature by using hydroxyl radicals. The advantage of catalytic hydroxyl radical oxidation is that it is free from seawater salinity interference.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and deter-*

*mine the applicability of regulatory limitations prior to use. For specific hazard statements, see Section 9.*

1.8 *ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)
- [D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents](#)
- [D4453 Practice for Handling of High Purity Water Samples](#)
- [D5173 Guide for On-Line Monitoring of Total Organic Carbon in Water by Oxidation and Detection of Resulting Carbon Dioxide](#)
- [D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

### 2.2 Other Standard:

- [EN 1484 Water analysis guidelines for the determination of total organic carbon and dissolved organic carbon<sup>3</sup>](#)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee [D19](#) on Water and is the direct responsibility of Subcommittee [D19.03](#) on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

Current edition approved Dec. 1, 2020. Published December 2020. DOI: 10.1520/D8361-20.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Water Analysis Guidelines for the Determination of Total Organic Carbon and Dissolved Organic Carbon, European Standard EN 1484, European Committee for Standardization, May 1997.

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology **D1129**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *dissolved organic carbon (DOC)*, *n*—carbon determined on filtered samples.

3.2.2 *inorganic carbon (IC)*, *n*—carbon in the form of carbon dioxide, carbonate ion, or bicarbonate ion.

3.2.3 *in-stream analysis*, *n*—analyte determination achieved by capturing the sample from the desired stream of fluid that can be part of a process or of a water body and delivering it into the measurement cell.

3.2.4 *limit of detection (LOD)*, *n*—the lowest concentration that can be determined to be statistically different from a blank with 99 % confidence. LOD's are matrix, method, and analyte specific.

3.2.5 *limit of quantification (LOQ)*, *n*—the level above which quantitative results may be obtained at a specified degree of confidence; mathematically equal to 10 x the std deviation of the results for a series of replicates used to determine a justifiable LOD

3.2.6 *non-purgeable organic carbon (NPOC)*, *n*—carbon measured in a sample after acidification and sparging to remove inorganic carbon.

3.2.7 *organic carbon (OC)*, *n*—carbon that is bound to hydrogen, oxygen, sulfur, nitrogen through either single, double or triple bonds.

3.2.8 *purgeable organic carbon (POC)*, *n*—carbon that purges from acidified samples, also known as volatile organic compounds (VOC).

3.2.9 *total carbon (TC)*, *n*—the sum of IC and TOC.

3.2.10 *total organic carbon (TOC)*, *n*—carbon in the form of organic compounds.

### 4. Summary of Test Method

4.1 Carbon can occur in water as an inorganic and organic compound. This test method can be used to make independent measurements of IC, NPOC, and TC, and can also determine OC by the difference of TC and IC. DOC is determined on samples that have been filtered through a 0.45- $\mu$ m filter **(1, 2)**.<sup>4</sup>

4.2 TOC and DOC procedures require that IC has been removed from the sample before it is analyzed for organic carbon content. The sample free of IC is injected into the TOC instrument where all carbon is converted to CO<sub>2</sub> and measured by the detector. Failure of this test method to remove/determine all IC prior to analysis for organic carbon will result in significant error.

4.3 This test method is used to monitor TOC from an aqueous sample. Ozone and base are added to a stream of water where hydroxyl radicals are formed. The hydroxyl radicals oxidize organic carbon to carbon dioxide and there is a

possibility to create oxalates. If any oxalates are formed, then they are further oxidized to CO<sub>2</sub> through acidification in the presence of ozone and catalyst.

4.3.1 In the first stage of the two-stage oxidation, the base reagent is added to the reaction vessel, and the sample is oxidized by hydroxyl radicals, which are generated by exposing high pH reagents to ozone. The oxidation process takes place at ambient conditions. The oxidation of organic compounds takes place and the primary compounds formed are “carbonates”, and depending on the organic constituents of the sample, the secondary compound “oxalates” can also be formed **(3, 4)**.

4.3.2 In the second stage of the two-stage oxidation an acid reagent, which contains a catalyst, is added into the reaction vessel and the carbonates are converted to carbon dioxide. Simultaneously, oxalates are broken down to carbon dioxide in the presence of the catalyst and ozone.

4.4 The quantification of TOC is achieved by measuring CO<sub>2</sub> over the oxidation time using non-dispersive infrared spectroscopy (NDIR) detection method.

### 5. Significance and Use

5.1 This test method is used for determination of the carbon content of water from a variety of natural, domestic, and industrial sources. In its most common form, this test method is used to measure organic carbon as a means of monitoring organic pollutants in industrial wastewater. These measurements are also used in monitoring waste treatment processes.

5.2 The relationship of TOC to other water quality parameters such as chemical oxygen demand (COD) and total oxygen demand (TOD) is described in the literature **(5)**.

### 6. Interference and Limitations

6.1 This test method is validated for chloride interference from seawater at a salinity of 2.1 %. For salinity greater than 2.1 % perform additional interference recovery test. No interference is expected below 30 % **(6)**.

6.2 Analyses of samples, which contain significant concentrations of VOC compounds, in a TIC and NPOC system, under-report the actual organic carbon concentrations. Preservation of sample by acidification needs to be avoided because it can lead to under-reporting of VOC values.

6.3 Homogenizing or sparging of a sample, or both, may cause loss of purgeable organic compounds, thus yielding a value lower than the true TOC level. (For this reason, such measurements are sometimes known as NPOC). The extent and significance of such losses must be evaluated on an individual basis. Comparison of the difference, if any, between NPOC and TOC by subtraction represents POC lost during sparging.

6.4 Note that error will be introduced when the method of difference is used to derive a relatively small level from two large levels. For example, a ground water high in IC and low in TOC will give a poorer TOC value as (TC – IC) than by direct measurement as NPOC.

6.5 Carbon in reagent water and reagent blanks can be reduced to a minimum, and consistent value, but cannot be

<sup>4</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

eliminated. Analyzing low-level TOC (less than 1.0 mg/L) bears special consideration requiring that the same water used to set the baseline be used to prepare the calibration standards.

6.6 Atmospheric carbon dioxide absorbs into reagent water increasing its inorganic carbon content with time. The small levels of CO<sub>2</sub> absorbed into reagent water can cause considerable inaccuracies in low-level TIC analysis.

6.7 Trace organics in the atmosphere can be absorbed into reagent water increasing its organic carbon content with time.

6.8 This test method measures TIC as the sum of dissolved carbon dioxide, carbonates and hydrogen carbonates. Cyanide, cyanate, and thiocyanate are reported as organic carbon and included in the NPOC, TC or TOC measurements depending on system configuration discussed in 4.2.

## 7. Apparatus

7.1 Fig. 1 shows the schematic block diagram of a TOC analyzer that is used in this standard. The system typically consists of sample and reagent introduction modules, a reaction vessel and NDIR analyzer. The sample is introduced into the reaction vessel and mixed with acid. This converts all the inorganic carbon into CO<sub>2</sub>, which is measured using a NDIR detector connected to the reaction vessel and used to calculate the TIC in the sample.

7.2 In the first stage of oxidation, the sample is mixed with a base along with oxygen and ozone which leads to the generation of hydroxyl radicals. Oxidation of the organic carbon generates CO<sub>2</sub>. In the second stage of oxidation the sample is mixed with acid and catalyst that completes the oxidation process and liberates CO<sub>2</sub>, which is again measured using a NDIR detector to determine the TOC.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals should be used in all analysis. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on

Analytical Reagents of the American Chemical Society.<sup>5</sup> The organic and inorganic carbon contamination inside the concentrated chemicals, which are used to prepare the reagents, should be as low as possible. Even though it is not recommended, other grades, such as technical grade reagents, may also be used, provided that the background contamination inside the reagents does not have any negative impact on the accuracy of the measurement.

8.2 *Purity of Water*—Unless otherwise stated, references to water shall be understood to mean water meeting the quantitative requirements of Specification D1193, Type I or Type II. This specification does not specify the maximum allowable inorganic and organic carbon contamination levels. Contamination in water may affect the accuracy of the measurements adversely. Glass containers are recommended for storage of water and standard solutions. Practices D3694 and D4453 address the handling of the water samples.

8.3 *Catalyzed Ozone Hydroxyl Radical Oxidation Reagents*—Prepare the reagents using Type I or Type II water. Fill approximately 70 % of the reagent containers with water.

8.3.1 *Acid Reagent (1.8 N)*—Prepare 1 L of 1.8 N Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) reagent. Gently add 90 g of 98 % pure H<sub>2</sub>SO<sub>4</sub> and mix the solution and bring to volume. Gently shake the container to mix the acid with the water. Add a quantity of manganese sulfate monohydrate (MnSO<sub>4</sub>·H<sub>2</sub>O) catalyst, to H<sub>2</sub>SO<sub>4</sub> reagent to achieve 40–80 mg/L MnSO<sub>4</sub>·H<sub>2</sub>O. For example, to make the 1 L H<sub>2</sub>SO<sub>4</sub> reagent containing 80 mg/L MnSO<sub>4</sub>·H<sub>2</sub>O, add 0.08 g of MnSO<sub>4</sub>·H<sub>2</sub>O into the solution.

8.3.2 *Base Reagent (1.2 N)*—Prepare the 1.2 N of sodium hydroxide solution by slowly adding 48 g of ≥97 % NaOH to a 1 000 mL volumetric flask containing approximately 500 mL

<sup>5</sup> ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

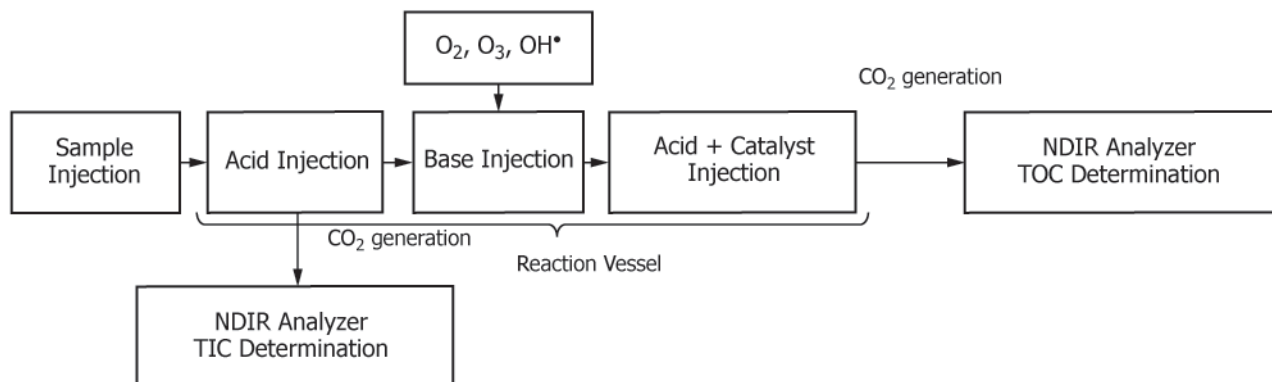


FIG. 1 Schematic Diagram of TOC Analyzer using the Catalyzed Ozone Hydroxyl Radical Oxidation

of water. 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.

8.4 *Oxygen*—The carrier gas used in the catalyzed ozone hydroxyl radical oxidation method is oxygen. Oxygen shall be free of carbon dioxide, carbon monoxide, nitrogen, hydrocarbons and water. Typical oxygen purity supplied by an oxygen concentrator is 93 % ( $\pm 3$  %) with balance gas argon.

8.5 *TOC Standard Solution (1000 mg/L)*—Use non-volatile, soluble, stable, reagent grade and concentrated (typically greater than 99 % pure), organic carbon compounds to prepare the TOC standard solution. Potassium hydrogen phthalate (KHP) is typically used as standard. Gravimetrically weigh the corresponding mass of the organic compound required to prepare the 1000 mg/L TOC standard stock solution. For instance, weigh 2.13 g of 99.9 % pure KHP in a 1 L container and bring it up to volume. Apply standard dilution procedures to prepare standard solutions with concentrations less than 1000 mg/L. Standard solutions less than 5mg/L concentration should be prepared with multiple step dilutions for increased accuracy on the theoretical concentration levels.

**9. Hazards**

9.1 Take general electrical and chemical safety precautions when working with the TOC analyzer using this test method.

9.2 Take the same precautions required for any high pressure or compressed gas system when working with the oxygen gas. If oxygen cylinders are used, they must be labeled clearly for identification, well secured for storage and transport, and transferred safely using appropriate equipment such as carts and hand trucks. The use of extensive adaptors and couplers in the oxygen lines must be avoided. Do not allow oxygen to come in direct contact with grease, oil, fat, and other combustible materials. If oxygen concentrator is used, install the concentrator in a well-ventilated area and take necessary

precautions to prevent any fire hazard. Comply with all local and national regulations when working with oxygen.

9.3 Refer to manufacturer’s manuals for the details of the safety precautions.

**10. Calibration**

10.1 Calibrate the analyzer in accordance with the manufacturer’s instructions.

10.2 Prepare the preferred concentration TOC standard solution as described in 8.5 and if necessary, dilute the standard solution as required.

10.3 Connect the standard solution to the inlet port of the analyzer and begin the calibration or verification process using a TOC standard solution at the specific analysis range.

10.4 Connect the standard solution to the inlet port of the analyzer and begin the calibration or verification process using a TOC standard solution at the specific analysis range.

10.5 Fig. 2 shows an example of average TOC responses from a calibrated analyzer versus the known concentration TOC standard solutions at an analysis range from 1.1 to 250 mg/L carbon. This example calibration plot is built using the data shown in Table 1. The linear response of this example system is illustrated with a trend line and a linear equation including the coefficient of determination ( $R^2$ ) value on Fig. 2.

**11. Procedure**

11.1 Follow the manufacturer’s instructions to install and set-up for sample analysis.

**12. Calculation and Analysis Data**

12.1 Read carbon values directly from a digital display, printer, or both devices.

12.2 Do not use automatic outlier removal procedures supplied with most software packages.

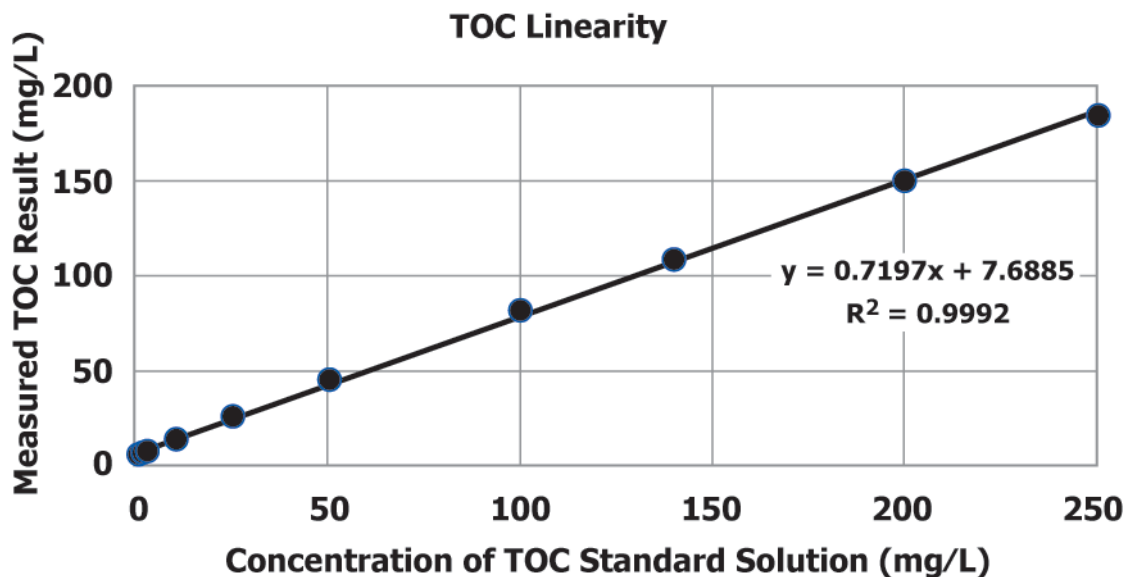


FIG. 2 Measured TOC Results versus the Concentration of TOC Standard Solutions

**TABLE 1 Preparation of Calibration Curve Standards for Organic Carbon**

Cal Level	Concentration of Stock (mg/L)	Volume of the Stock (mL)	Final Volume of the Calibration Std. (mL)	Final Concentration of Calibrations Standard (mg/L)
Calibration Blank	0	0	2000	0
1	2000	1.1	2000	1.1
2	2000	2.0	2000	2.0
3	2000	3.0	2000	3.0
4	2000	10	2000	10
5	2000	25	2000	25
6	2000	50	2000	50
7	2000	100	2000	100
8	2000	140	2000	140
9	2000	200	2000	200
10	2000	250	2000	250

### 13. Precision and Bias

13.1 The typical accuracy of TOC measurement in the catalyzed Hydroxyl radical oxidation TOC analyzer is  $\pm 2\%$  of reading or  $\pm 1$  mg/L, whichever is greater, at an analysis range from 1 to 250 mg/L. [Table 2](#) shows the typical performance data of this test method. The concentrations of the standard solutions, tabulated in [Table 2](#) are selected at the 5, 25, 50, 75, and 95 % of the full scale of the analysis range used. A minimum of six measurements are carried out at each theoretical concentration point.

13.2 The limit of detection (LOD), limit of quantitation (LOQ), method detection limit (MDL), and method limit (ML) values for this method are determined by analyzing a blank over several days of on-line analysis in accordance with the *Standard Methods for the Examination of Water and Wastewater* (7). [Table 3](#) summarizes the LOD, LOQ, MDL, and ML of catalyzed hydroxyl radical oxidation method and other related parameters.

### 14. Quality Control

14.1 When the reagents are replaced or replenished, the analyzer must be calibrated or verified with a reagent blank sample, a level of standard aligned with the manufacturer's specified range of the intended application.

14.2 Factors such as the sample injection volume, reagent injections, carbon dioxide analyzer range, etc. determine the overall accuracy of the system.

14.3 In addition to the precision and bias data discussed in [14.1](#), the LOD, LOQ, MDL, and ML values discussed in [13.2](#) are useful parameters which can be determined for each specific analysis range.

14.4 The calibration verification is performed using a standard solution that is aligned to the concentration range in the matrices being tested. If the verification value measured is less than or equal to 10 % (8) of the verification standard concentration, then complete the steps described in [14.5](#).

14.5 Complete below steps to carry out quality control procedures:

14.5.1 Connect the verification standard solution to the system.

14.5.2 Program the frequency of the verification cycle as in accordance with manufacturer's recommendations.

14.5.3 Run the verification cycle as in accordance with application and user requirements.

14.5.4 Verify system response as in accordance with Practice [D5847](#).

**TABLE 2 Precision and Bias of TOC Measurements**

NOTE 1—The sample used is potassium hydrogen phthalate standard solutions.

Concentration of the TOC Standard Solution, mg/L	Average Measured Result, mg/L TOC	Absolute Mean Error, %	Relative Standard Deviation, %
1.1	1.0	0.05	17.4
2.0	2.2	0.05	6.9
3.0	3.2	0.04	4.1
10	10	0.03	0.8
25	26	0.02	0.3
50	51	0.03	0.2
100	101	0.08	0.2
140	141	0.08	0.2
200	200	0.19	0.3
250	249	0.05	0.1