



Designation: D4839 – 03 (Reapproved 2017)

## Standard Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection<sup>1</sup>

This standard is issued under the fixed designation D4839; 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 determination of total carbon (TC), inorganic carbon (IC), and total organic carbon (TOC) in water, wastewater, and seawater in the range from 0.1 mg/L to 4000 mg/L of carbon.

1.2 This test method was used successfully with reagent water spiked with sodium carbonate, acetic acid, and pyridine. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 This test method is applicable only to carbonaceous matter in the sample that can be introduced into the reaction zone. The syringe needle or injector opening size generally limit the maximum size of particles that can be so introduced.

1.4 In addition to laboratory analyses, this test method may be applied to stream monitoring.

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

1.6 *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 determine the applicability of regulatory limitations prior to use.*

1.7 *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.*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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### 2. Referenced Documents

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

- D1129 Terminology Relating to Water
- D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)<sup>3</sup>
- D1193 Specification for Reagent Water
- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3370 Practices for Sampling Water from Closed Conduits
- D4129 Test Method for Total and Organic Carbon in Water by High Temperature Oxidation and by Coulometric Detection
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

### 3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

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

3.2.2 *refractory material, n*—that which cannot be oxidized completely under the test method conditions.

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

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

### 4. Summary of Test Method

4.1 *Fundamentals*—Carbon can occur in water as an inorganic and organic compound. This test method can be used to

<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> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

make independent measurements of IC, TOC, and TC, and can also determine IC by the difference of TC and TOC, and TOC as the difference of TC and IC.

4.2 The essentials of this test method are: (a) removal of IC, if desired, by acidification of the sample and sparging by carbon-free gas; (b) conversion of remaining carbon to CO<sub>2</sub> by action of persulfate, aided either by elevated temperature or ultraviolet (UV) radiation; (c) detection of CO<sub>2</sub> that is swept out of the reactor by a gas stream; and (d) conversion of detector signal to a display of carbon concentration in mg/L. A diagram of suitable apparatus is given in Fig. 1.

## 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.<sup>4</sup>

## 6. Interferences and Limitations

6.1 The oxidation of dissolved carbon to CO<sub>2</sub> is brought about at relatively low temperatures by the chemical action of reactive species produced by hot or UV-irradiated persulfate ions. Even if oxygen is used as the sparging gas, it makes a much lower contribution to oxidation than in high-temperature (combustive) systems. Not all suspended or refractory material may be oxidized under these conditions; analysts should take steps to determine what recovery is being obtained. This may be done by several methods: (a) by monitoring reaction progress to verify that oxidation has been completed; (b) by rerunning the sample under more vigorous reaction conditions; (c) by analyzing the sample by an alternative method, such as Test Method D4129, known to result in full recovery; or (d) by spiking samples with known refractories and determining recovery.

6.2 Chloride ion tends to interfere with oxidative reaction mechanisms in this test method, prolonging oxidation times and sometimes preventing full recovery. Follow manufacturer's instructions for dealing with this problem. See Appendix X1 for supporting data.

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 nonpurgeable organic carbon (NPOC)). The extent and significance of such losses must be evaluated on an individual basis. This may be done by comparing the TOC by difference (TC-IC) with the direct TOC figure, that is, that obtained from a sparged sample. The difference, if any, between these TOC figures represents purgeable organic carbon (POC) lost during sparging. Alternatively, direct measurement of POC can be made during sparging, using optional capabilities of the analyzer.

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.

## 7. Apparatus

7.1 *Homogenizing Apparatus*—A household blender is generally satisfactory for homogenizing immiscible phases in water.

7.2 *Sampling Devices*—Microlitre-to-millilitre syringes are typically required for this test method. Alternatives include manually operated or automatically operated sampling valves. Sampling devices with inside diameters as small as 0.15 mm may be used with samples containing little or no particulate matter. Larger inside dimensions such as 0.4 mm will be required for samples with particulate matter.

NOTE 1—See 6.1 concerning oxidation of particulate matter.

7.3 *Apparatus for Carbon Determination*—This instrument consists of reagent and sample introduction mechanism, a gas-sparged reaction vessel, a gas demister or dryer, or both, an optional CO<sub>2</sub> trap, a CO<sub>2</sub>-specific infrared detector, a control system, and a display. Fig. 1 shows a diagram of such an arrangement.

7.3.1 Sparging requires an inert vessel with a capacity of at least double the sample size with provision for sparging with 50 to 100 mL/min of carbon free gas. This procedure will remove essentially all IC in 2 to 10 min, depending on design.

7.3.2 *Oxidation*—The reaction assembly contains reagent and sample introduction devices, and a reactor vessel with sparging flow of carbon-free gas. The vessel may be heated by an external source, and may contain a UV lamp. The reaction vessel and sparging vessel (see 6.3) may be combined.

7.3.3 *Gas Conditioning*—The gas passing from the reactor is dried, and the CO<sub>2</sub> produced is either trapped and later

<sup>4</sup> Handbook for Monitoring Industrial Wastewater, Section 5.3, U.S. Environment Protection Agency, August 1973, pp. 5–12.

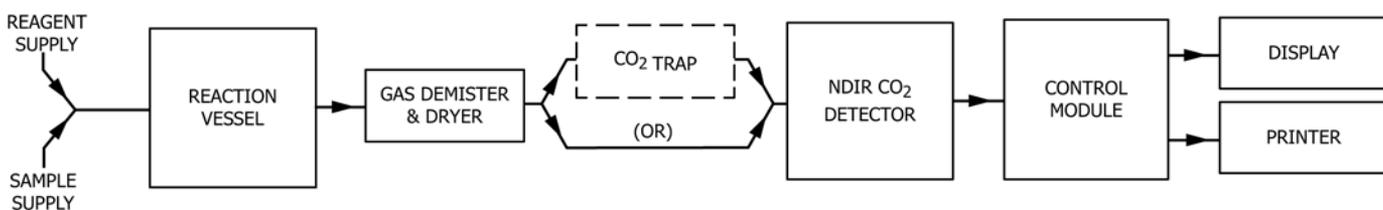


FIG. 1 Diagram of Apparatus