



Designation: D4839 – 03 (Reapproved 2024)

Standard Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection¹

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 (ϵ) 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.*

2. Referenced Documents

- 2.1 *ASTM Standards:*²
- D1129 Terminology Relating to Water
 - D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)³
 - 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 Flowing Process Streams
 - 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.

¹ 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 For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

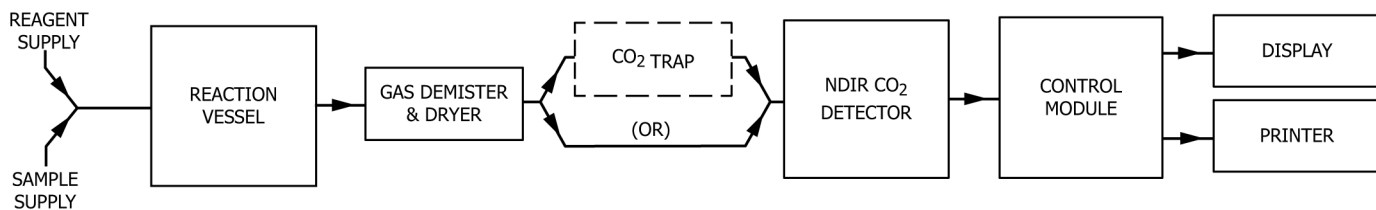


FIG. 1 Diagram of Apparatus

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 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 CO₂ by action of persulfate, aided either by elevated temperature or ultraviolet (UV) radiation; (c) detection of CO₂ 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.⁴

6. Interferences and Limitations

6.1 The oxidation of dissolved carbon to CO₂ 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 manufactur-

er'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 CO₂ trap, a CO₂-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 mL/min to 100 mL/min of carbon free gas. This procedure will remove essentially all IC in 2 min 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.

⁴ Handbook for Monitoring Industrial Wastewater, Section 5.3, U.S. Environmental Protection Agency, August 1973, pp. 5–12.

7.3.3 Gas Conditioning—The gas passing from the reactor is dried, and the CO₂ produced is either trapped and later released to the detector, or routed directly to the detector through a chlorine-removing scrubber.

7.3.4 Detector—The CO₂ in the gas stream is detected by a CO₂-specific nondispersive infrared (NDIR) detector.

7.3.5 Presentation of Results—The NDIR detector output is related to stored calibration data and then displayed as milligrams of carbon per litre.

8. Reagents and Materials

8.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,⁵ where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

8.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification **D1193**, Type I or Type II. The indicated specification does not actually specify inorganic carbon or organic carbon levels. These levels can affect the results of this test method, especially at progressively lower levels of the carbon content in the samples to be measured. Where inorganic carbon in reagent water is significant, CO₂-free water may be prepared from reagent water by acidifying to pH 2, then sparging with fritted-glass sparger using CO₂-free gas (time will depend on volume and gas flow rate, and should be determined by test). Alternatively, if the carbon contribution of the reagent water is known accurately, its effect may be allowed for in preparation of standards and other solutions. CO₂-free water should be protected from atmospheric contamination. Glass containers are required for storage of water and standard solutions.

8.3 Acid—Various concentrated acids may be used for acidification of samples and of the oxidizing reagent. Acids such as phosphoric (sp gr 1.69), nitric (sp gr 1.42), or sulfuric (sp gr 1.84) are suitable for most applications. Sulfuric acid should be used in the form of a 1 + 1 dilution, for safety reasons. Hydrochloric acid is not recommended.

8.4 Organic Carbon, Standard Solution (2000 mg/L)—Choose a water-soluble, stable reagent grade compound, such as benzoic acid or anhydrous potassium hydrogen phthalate (KHC₈H₄O₄). Calculate the weight of compound required to make 1 L of organic carbon standard solution; for example, KHC₈H₄O₄ = 0.471 g of carbon per gram, so one litre of 2 g/L of standard requires 2/0.471, or 4.25, grams of KHP. Dissolve the required amount of standard in some CO₂-free water in a 1 L volumetric flask, add 1 mL of acid, and dilute to volume.

⁵ *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

This stock solution, or dilutions of it, may be used to calibrate and test performance of the carbon analyzer.

8.5 Persulfate Solution—Prepare by dissolving the appropriate weight of potassium or sodium persulfate in 1 L of water, to produce the concentration specified by the instrument manufacturer. If specified, add 1 mL of phosphoric acid (sp gr 1.69) and mix well. Store in a cool, dark place. Recipes for this reagent solution may be modified by manufacturers to meet the needs of specific applications, for example, high chloride samples.

8.6 Gas Supply—A gas free of CO₂ and of organic matter is required. Use a purity as specified by the equipment manufacturer. The use of oxygen is preferred for the UV-persulfate method, and nitrogen or helium is preferred if a CO₂ trap is used between reactor and detector.

9. Sampling and Sample Preservation

9.1 Collect the sample in accordance with Guide **D1192** and Practices **D3370**.

9.2 To preserve samples for this analysis, store samples in glass at 4 °C. To aid preservation, acidify the samples to a pH of 2. It should be noted that acidification will enhance loss of inorganic carbon. If the purgeable organic fraction is important, fill the sample bottles to overflowing with a minimum of turbulence and cap them using a fluoropolymer-lined cap, without headspace.

9.3 For monitoring of waters containing solids or immiscible liquids that are to be injected into the reaction zone, use a mechanical homogenizer or ultrasonic disintegrator. Filtering or screening may be necessary after homogenization to reject particle sizes that are too large for injection. Volatile organics may be lost. See **6.3**.

9.4 For wastewater streams where carbon concentrations are greater than the desired range of instrument operation, dilute the samples as necessary.

10. Instrument Operation

10.1 Follow the manufacturer's instructions for instrument warm-up, gas flows, and liquid flows.

11. Calibration

11.1 Use the stock solution of 2000 mg/L of carbon, and various dilutions of it, for calibration.

NOTE 2—Dilutions should be made with CO₂-free water (see **8.2**).

11.2 Calibration protocols may vary with equipment manufacturers. However, in general, calibrate the instrument in accordance with the manufacturer's instructions, and use standards to verify such calibration in the specific range of interest for actual measurements. Plots of standard concentration versus instrument reading may be used for calibration or to verify linearity of response.

11.3 Establish instrument blank according to the manufacturer's instructions.