



Designation: D4129 – 05 (Reapproved 2020)

# Standard Test Method for Total and Organic Carbon in Water by High Temperature Oxidation and by Coulometric Detection<sup>1</sup>

This standard is issued under the fixed designation D4129; 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 and organic carbon in water and waste water, including brackish waters and brines in the range from 2 to 20 000 mg/L. This test method has the advantages of a wide range of concentration which may be determined without sample dilution and the provision for boat or capillary introduction of samples containing sediments and particulate matter where syringe injection is inappropriate.

1.2 This procedure is applicable only to that carbonaceous matter in the sample that can be introduced into the reaction zone. When syringe injection is used to introduce samples into the combustion zone, the syringe needle opening size limits the maximum size of particles that can be present in samples. Sludge and sediment samples must be homogenized prior to sampling with a micropipetor or other appropriate sampler and ladle introduction into the combustion zone is required.

1.3 The precision and bias information reported in this test method was obtained in collaborative testing that included waters of the following types: distilled, deionized, potable, natural, brine, municipal and industrial waste, and water derived from oil shale retorting. Since the precision and bias information reported may not apply to waters of all matrices, it is the user's responsibility to ensure the validity of this test method on samples of other matrices.

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

1.5 *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.* For specific precautionary statements, see 9.1 and 10.2.1.

<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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1.6 *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>

D513 Test Methods for Total and Dissolved Carbon Dioxide in Water

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D3370 Practices for Sampling Water from Flowing Process Streams

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data (Withdrawn 2002)<sup>3</sup>

D5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents (Withdrawn 2002)<sup>3</sup>

## 3. Terminology

3.1 *Definitions:*

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

## 4. Summary of Test Method

4.1 The sample is homogenized or diluted, or both, as necessary. If the sample does not contain suspended particles or high-salt level a 0.200-mL portion is injected into the reaction zone. For samples containing solids or high salt levels, portions are placed in combustion boats containing tungsten trioxide (WO<sub>3</sub>) or quartz capillaries and introduced into the

<sup>2</sup> 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.

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

reaction zone using a ladle. In the reaction zone the heat, oxidation catalyst and oxygen atmosphere convert carbonaceous matter to carbon dioxide (CO<sub>2</sub>). The oxygen gas stream sweeps the gaseous reaction products through a series of scrubbers for potentially interfering gases and then to the absorption/titration cell. The CO<sub>2</sub> is determined by automatic coulometric titration. Calibration by testing known carbon content standards is not required, however, standards are analyzed periodically to confirm proper operation.

4.2 Carbon dioxide is liberated from carbonates as well as from organic matter under the reaction conditions. Organic carbon is determined by difference between the total carbon and the inorganic carbon determined separately or by acidifying a portion of the sample to a pH of 2 or less and sparging with carbon dioxide-free gas to remove carbonates, bicarbonates, and dissolved carbon dioxide prior to total carbon determination. To determine organic carbon by difference the inorganic carbon is determined by acid release of carbon dioxide from a portion of the sample or other methods as given in Test Methods **D513**. For discussion of the limitations and guidelines for the use of the sparge technique, see **5.4** and the paper by Van Hall.<sup>4</sup>

4.3 Because of the various properties of carbon-containing compounds in water, any preliminary treatment of a sample prior to injection dictates a definition of the carbon measured. Filtration of the sample prior to injection will limit the carbon measured to dissolved carbonates and dissolved organic matter. Homogenizing permits determination of the carbon in insoluble carbonates and insoluble organic materials.

## 5. Significance and Use

5.1 This test method is necessary because of the need for rapid reliable tests for carbonaceous material in waters and sediments.

5.2 It is used for determining the concentration of organic carbon in water that comes from a variety of natural, domestic, and industrial sources. Typically, these measurements are used to monitor organic pollutants in domestic and industrial waste water.

5.3 When a sample is homogenized so that particulate, immiscible phases, and dissolved carbon from both organic and inorganic sources is determined, the measurement is called total carbon (TC). When inorganic carbon response is eliminated by removing the dissolved CO<sub>2</sub> prior to the analysis or the dissolved CO<sub>2</sub> concentration subtracted from the total carbon concentration, the measurement is called total organic carbon (TOC). When particulates and immiscible phases are removed prior to analysis the measurement is called dissolved carbon (DC), or dissolved organic carbon (DOC) if inorganic carbon response has been eliminated.

5.4 Homogenizing or sparging of a sample, or both, may cause loss of volatile organics, thus yielding a negative error. The extent and significance of such losses must be evaluated on

an individual basis. If significant quantities of volatile carbonaceous materials are present or may be present in samples organic carbon should be determined by the difference between the total carbon and the inorganic carbon concentrations. When organic carbon determined both by difference and by sparging agree it is acceptable to determine organic carbon by sparging for similar samples.

5.5 The relationship of TOC to other water quality parameters such as COD and BOD is described in the literature.<sup>5</sup>

## 6. Interferences

6.1 Any acidic or basic gas formed in the oxidation of the sample and not removed by the scrubbers will interfere with the test. Potentially interfering gases that are removed by the scrubbers include hydrogen sulfide (H<sub>2</sub>S), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen iodide (HI), sulfur dioxide (SO<sub>2</sub>), sulfur trioxide (SO<sub>3</sub>), free halogens, halogen oxides, and nitrogen oxides. Hydrogen fluoride (HF) may be removed by bubbling the gas stream through water in the water vapor condenser.

6.2 The capacity of the scrubbers for potentially interfering gases may vary with the type of samples being analyzed. If the scrubber capacity is exceeded it can be recognized by the titration continuing beyond the normal analysis time at a higher rate than the blank and high results for known carbon content standards as well as by appearance changes in the scrubbers. If the scrubber capacity is exceeded during an analysis the scrubbers should be replaced and the analysis repeated. Samples containing all concentrations of the potentially interfering species can be analyzed if the analyst uses great care to ensure that the scrubbers are and remain effective for his samples. The frequency of replacing the scrubbers will depend on the nature of the samples.

## 7. Apparatus

7.1 Apparatus for total carbon, organic carbon, and inorganic carbon determinations—combustion furnace with gas supply, gas purification train, flow control, acid reaction train, and carbon dioxide coulometer.<sup>6</sup> **Fig. 1** and **Fig. 2** show block diagrams of the apparatus.

7.2 *Sampling Devices*—A spring-loaded 0.200-mL syringe<sup>7</sup> (carbon analyzer syringe) having an all metal tip and a 50 mm long, 0.5-mm inside diameter needle with a square end is recommended for water samples containing little or no particulate matter.

7.3 *Homogenizing Apparatus*—A household blender with glass mixing chamber is generally satisfactory for homogenizing immiscible phases in water.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

<sup>5</sup> *Handbook for Monitoring Industrial Wastewater*, U.S. Environment Protection Agency, August 1973, pp. 5-10 to 5-12.

<sup>6</sup> Instruments marketed by Coulometrics, Inc., a subsidiary of UIC Inc., P.O. Box 563, Joliet, IL, 60434, or an equivalent, have been found satisfactory.

<sup>7</sup> Syringes manufactured by Hamilton Co., P.O. Box 10030, Reno, NV 89510, or an equivalent, have been found satisfactory for this purpose.

<sup>4</sup> Van Hall, C. E., Barth, D., and Stenger, V. A., "Elimination of Carbonates from Aqueous Solutions Prior to Organic Carbon Determinations," *Analytical Chemistry*, Vol 37, 1965, pp. 769-771.

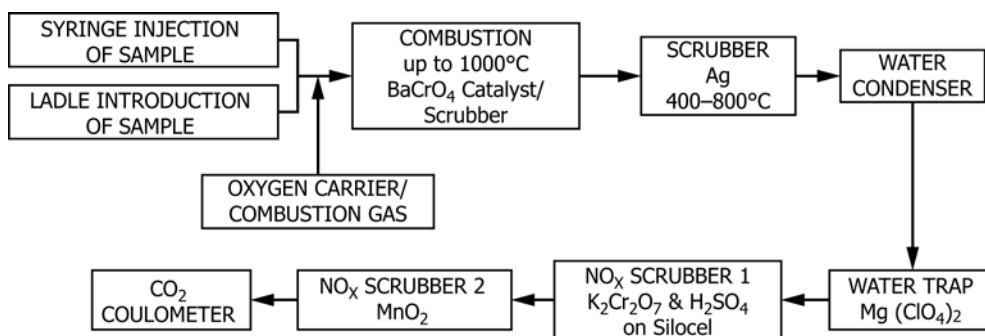


FIG. 1 Total Carbon and TOC Apparatus

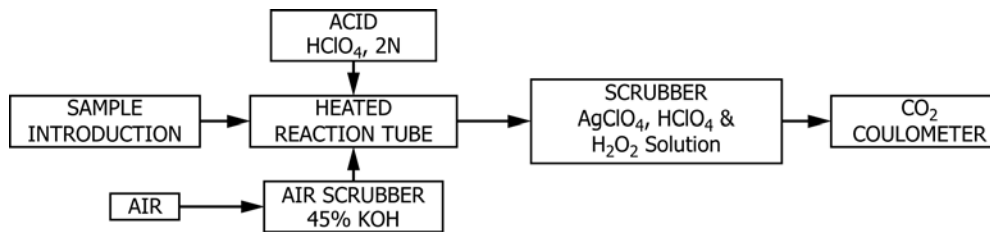


FIG. 2 CO<sub>2</sub> Evolution Apparatus

all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society.<sup>8</sup> Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to the Specification D1193, Type I. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the precision and bias of the test method. Type II water was specified at the time of round robin testing of this test method. If necessary, carbon dioxide-free water is to be prepared by boiling distilled water in a conical flask for 20 min. The boiled water is cooled in the flask stoppered with a one-hole rubber stopper fitted to a soda lime-Ascarite drying tube. For large (10 to 20 L) volumes of carbon dioxide-free water, the absorbed carbon dioxide may be removed by inserting a fritted-glass gas-dispersion tube to the bottom of the container and vigorously bubbling nitrogen through the water for at least 1 h. Carbon dioxide-free water may be stored if properly protected from atmospheric contamination.

NOTE 1—Glass containers are preferred for the storage of reagent water and most standard solutions. It is necessary to provide protection against changes in quality due to the absorption of gases or water vapor from the laboratory air. As volumes of fluid are withdrawn from the container, the replacement air should be passed through a drying tube filled with equal parts of 8 to 20-mesh soda lime, oxalic acid, and 4 to 8-mesh anhydrous calcium chloride, each product being separated from the other by a glass-wool plug.

<sup>8</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.

8.3 *Gas Supply*—Use oxygen of at least 99.6 % purity.

8.4 *Scrubber Tubes and Catalyst Packings* as well as instructions for their preparation are available from the equipment manufacturer.<sup>9</sup> Fig. 1 illustrates the flow diagram and names the reagents used.

8.5 *Carbon Dioxide Coulometer Reagents*—Cell solutions to absorb CO<sub>2</sub> from the gas stream and convert it to a titratable acid and permit 100 % efficient coulometric titration.<sup>9</sup>

8.6 *Acid*—Various acids may be used for acidification of samples. Hydrochloric acid is recommended. Phosphoric and sulfuric acids are suitable if they do not cause materials to precipitate from the sample. Nitric acid is not recommended because it may cause premature oxidation of organics in the sample.

8.7 *Organic Carbon Standard Solutions*—Although the method does not require sample standardization, proper operation of the instrument should be confirmed by injection of standards of similar composition and concentration to the unknown. Standards should be stable water soluble compounds such as KHP or benzoic acid of suitable purity.

## 9. Hazards

9.1 Injection of samples containing over 25 000 mg/L TOC or 0.5 mL water may cause explosion of the combustion tube.

## 10. Sampling

10.1 Collect the sample in accordance with Practices D3370 or other applicable ASTM method(s).

<sup>9</sup> Satisfactory reagents available from Coulometrics, Inc., a subsidiary of UIC Inc., P.O. Box 563, Joliet, IL, 60434 use ethanolamine to absorb CO<sub>2</sub> forming hydroxethylcarbamic acid that is titrated coulometrically using a color indicator for end-point detection.

## 10.2 Preservation:

10.2.1 To preserve samples for this analysis, store or ship samples in glass at or below 4°C. (**Caution**—Head space in the sample bottle or freezing the sample may contribute to the loss of volatile organics from some samples.)

10.3 For monitoring of waters containing solids or immiscible liquids of interest, use a mechanical homogenizer or ultrasonic disintegrator to homogenize samples.

10.4 For waste water streams where carbon concentrations are greater than the desired range of instrument operation, provide on-stream dilution of the sample if possible.

10.5 **A1.1** gives additional guidelines for preparing heavily contaminated water samples when using the sparge technique.

10.6 **A1.2** gives additional guidelines for samples containing solids and immiscible liquids.

## 11. Calibration and Standardization

11.1 Set up the analyzer and fill coulometer cell in accordance with the manufacturer's specifications. Adjust the gas flow to 80 to 100 mL/min. Set the readout to milligrams per litre except when other than 0.200-mL samples are used in which case set the readout to micrograms.

11.2 Analyze samples of carbon dioxide-free water as instructed in Section 12 for samples to determine the instrument blank, *B*.

11.3 Calibration is not required, however, inject appropriate standard(s) prior to and following analysis of samples to confirm proper operation. The standard concentration(s) should be approximately that of the samples to be analyzed. If the recovery of standards is unacceptable the cause of poor results should be determined and corrected. Low results suggest a leak or exhausted combustion tube packing. High results suggest contamination of the samples or exhausted scrubber or combustion tube fillings.

## 12. Procedure

12.1 Condition each sample to bring the homogenous carbon content within range. Although analyses of samples containing up to 20 000 mg/L TOC is possible, dilution to TOC levels below 1000 is preferable if the sample contains salts or forms a precipitate upon acidification.

12.2 See 12.3, 12.4, and 12.5 for total carbon and TOC by sparging; 12.6 applies to carbonate carbon determinations when organic carbon is to be determined by difference.

12.3 *Syringe Injection of Samples*—Rinse the syringe several times with the solution to be analyzed, then fill to precise volume (0.200 mL). Wipe off the excess from the needle tip with soft paper tissue, taking care that no lint adheres to the needle. Insert the sample syringe into the injection port, inject the sample, and reset the coulometer to zero. Leave the syringe in the holder until the analysis is completed.

### 12.4 Ladle Introduction of Samples:

12.4.1 When a micropipet can be used with the sample, place 0.200 mL of the sample into a platinum boat or a capillary tube containing approximately 20 mg of WO<sub>3</sub>.

Position the boat (capillary) in the ladle and place the ladle in the cool portion of the combustion tube through the introduction port. After closing the introduction port, allow 60 s for the oxygen gas stream to sweep out air that entered then move the ladle into the furnace.

NOTE 2—The WO<sub>3</sub> is used to minimize potential difficulties caused by salts in samples. Use of the WO<sub>3</sub> will minimize the splattering of the sample which allows salts in the sample to degrade the combustion tube. The WO<sub>3</sub> also helps prevent salts from reacting with CO<sub>2</sub> forming carbonates which then decompose slowly lengthening the analysis time and increasing the instrument blank.

12.4.2 When a precise volume (0.200 mL) of the sample cannot be obtained, weigh the sample into the combustion boat or capillary tube and introduce it into the combustion zone as described in 12.4.1.

NOTE 3—When weighing samples the size of the sample may be increased. The carbon content must not exceed 4 mg or the water content exceed 0.4 mL.

NOTE 4—The density of the sample must be known to report the results if the result is to be given in mg/L when samples are weighed into combustion boats.

12.5 Consistent analysis times must be used for all samples and blanks. The time must be sufficient for all CO<sub>2</sub> to be swept from the combustion tube to the coulometer and titrated as evidenced by stable coulometer readings. The time required will depend upon the nature of the samples and is normally 3 to 7 min. High-level samples require longer analysis times than low level samples and may result in higher blank levels, especially if the samples are high in salts. If samples of a large concentration range are being analyzed care must be used when analyzing lower level samples following much higher level samples. Additional blanks must be run to confirm that the blank is reasonable and consistent.

12.6 Carbonate carbon may be determined using the methods given in Test Methods D513 or as instructed by equipment manufacturer.

## 13. Calculation

13.1 Read total carbon values of 0.200-mL samples directly from the digital display. Correct these values by subtracting the blank value, *B*, obtained with carbon dioxide-free water and correct for any dilutions made to obtain original sample values.

13.2 For organic carbon values of acidified and sparged 0.200-mL samples, read the values directly from the digital display. Correct these values by subtracting the blank value *B*, and correct for any dilutions in acidifying or other steps to obtain original sample values.

13.3 For organic carbon values determined by difference, the result is obtained as follows:

$$O = T - C$$

where:

*O* = organic carbon for original sample, mg/L

*T* = total carbon corrected for any blank and dilutions mg/L, and

*C* = carbonate carbon corrected for any blank and dilutions calculated in accordance with the instructions for the method used, mg/L.