



Designation: **D5997–96 (Reapproved 2009) D5997 – 15**

## Standard Test Method for On-Line Monitoring of Total Carbon, Inorganic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection<sup>1</sup>

This standard is issued under the fixed designation D5997; 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 on-line determination of total carbon (TC), inorganic carbon (IC), and total organic carbon (TOC) in water in the range from 0.5  $\mu\text{g/L}$  to 50 000  $\mu\text{g/L}$  of carbon. Higher carbon levels may be determined by suitable on-line dilution. This test method utilizes ultraviolet-persulfate oxidation of organic carbon coupled with a  $\text{CO}_2$  selective membrane to recover the  $\text{CO}_2$  into deionized water. The change in conductivity of the deionized water is measured and related to carbon concentration in the oxidized sample using calibration data. Inorganic carbon is determined in a similar manner without the requirement for oxidation. In both cases, the sample is acidified to facilitate  $\text{CO}_2$  recovery through the membrane. The relationship between the conductivity measurement and carbon concentration can be described by a set of chemometric equations for the chemical equilibrium of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{H}^+$ , and  $\text{OH}^-$ , and the relationship between the ionic concentrations and the conductivity. The chemometric model includes the temperature dependence of the equilibrium constants and the specific conductances resulting in linear response of the method over the stated range of TOC. See Test Method D4519 for a discussion of the measurement of  $\text{CO}_2$  by conductivity.

1.2 This test method has the advantage of a very high sensitivity detector that allows very low detection levels on relatively small volumes of sample. Also, the use of two measurement channels allows determination of IC in the sample independently of organic carbon. Isolation of the conductivity detector from the sample by the  $\text{CO}_2$  selective membrane results in a very stable calibration with minimal interferences.

1.3 This test method was used successfully with reagent water spiked with sodium carbonate and various organic compounds. This test method is effective with both deionized water samples and samples of high ionic strength. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 This test method is applicable only to carbonaceous matter in the sample that can be introduced into the reaction zone. The inlet system generally limits the maximum size of particles that can be introduced. Filtration may also be used to remove particles, however, this may result in removal of organic carbon if the particles contain organic carbon.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

### 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

<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.

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<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.

**D3370 Practices for Sampling Water from Closed Conduits**

**D4519 Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity**

### 3. Terminology

#### 3.1 Definitions:

3.1.1 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 *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 inorganic and organic compounds. This test method can be used to make independent measurements of IC and TC and can also determine TOC as the difference between TC and IC. If IC is high relative to TOC, it is desirable to use a vacuum degassing unit to reduce the IC concentration to obtain meaningful TOC values by difference.

4.2 The basic steps of this test method are:

4.2.1 Conversion of remaining IC to CO<sub>2</sub> by action of acid,

4.2.2 Removal of IC, if desired, by vacuum degassing,

4.2.3 Split of flow into two streams to provide for separate IC and TC measurements,

4.2.4 Oxidation of TC to CO<sub>2</sub> by action of acid-persulfate aided by ultraviolet (UV) radiation in the TC channel,

4.2.5 Detection of CO<sub>2</sub> by passing each liquid stream over membranes that allow the specific passage of CO<sub>2</sub> to high-purity water where change in conductivity is measured, and

4.2.6 Conversion of the conductivity detector signal to a display of carbon concentration in parts per million (ppm = mg/L) or parts per billion (ppb = µg/L). The IC channel reading is subtracted from the TC channel reading to give a TOC reading. A diagram of suitable apparatus is given in **Fig. 1**.

### 5. Significance and Use

5.1 This test method is useful for detecting and determining organic and inorganic carbon impurities in water from a variety of sources including industrial water, drinking water, and waste water.

5.2 Measurement of these impurities is of vital importance to the operation of various industries such as power, pharmaceutical, semiconductor, drinking water treatment, and waste treatment. Semiconductor and power applications require measurement of very low organic carbon levels (TOC < 1 µg/L). Applications in pharmaceutical industries range from USP purified water (TOC < 500 µg/L) to cleaning applications (500 µg/L < TOC < 50 000 µg/L). Drinking waters range from < 100 µg/L to 25 000 µg/L and higher. Some of these applications may include waters with substantial ionic impurities as well as organic matter.

5.3 Measurement of inorganic carbon as well as total organic carbon is highly important to some applications, such as in the power industry.

5.4 Continuous monitoring and observation of trends in these measurements are of interest in indicating the need for equipment adjustment or correction of water purification procedures.

5.5 Refer to **Annex A** the **Bibliography** section for additional information regarding the significance of this test method.

### 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 UV-irradiated persulfate ions. 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: (1) by rerunning the sample under more vigorous reaction conditions; (2) by analyzing the sample by an alternative method known to result in full recovery; or (3) by spiking samples with known refractories and determining recovery.

6.2 Interferences have been investigated and found to be minimal under most conditions. Chloride ions above 250 000 µg/L may cause low results. Follow the manufacturer's instructions for dealing with high-chloride interference. Other interferences have been investigated and found to be minimal under most conditions. The membrane is hydrophobic in nature and passes only gaseous materials. Potential interferences are nitrite, sulfide, and high levels of hypochlorite or iodine. Refer to **Annex A** the **Bibliography** section for more information.

6.3 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 water high in IC and low in TOC will give a less precise TOC value as (TC-IC) than by direct measurement.

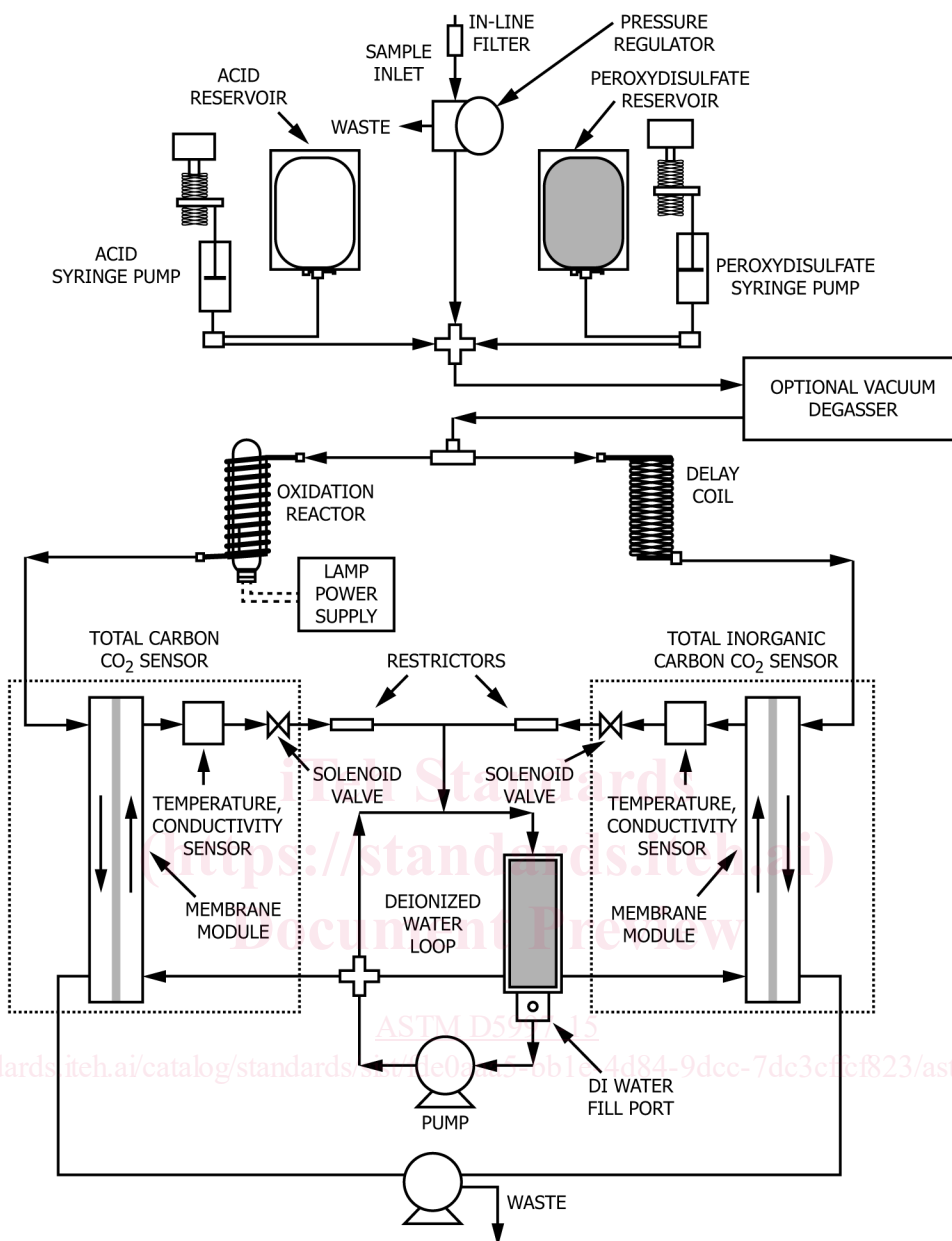


FIG. 1 Schematic Diagram of TOC Analyzer System

In this case the vacuum degassing unit on the instrument should be used to reduce the concentration of IC prior to measurement, or another method of inorganic carbon removal should be employed.

6.4 Use of the vacuum degassing unit or sparging the sample renders the IC reading meaningless and may cause loss of volatile organic compounds, thus yielding a value lower than the true TOC level. At low TOC levels, the degassing unit may introduce a measurable TOC and IC background. The user should characterize the background and performance of the degassing module for their applications. **Table 1** provides typical IC removal performance and background levels of the vacuum degassing unit.

6.5 The membrane conductivity detection technique may experience positive interference in the presence of low molecular weight, reduced, inorganic acid species such as  $H_2S$  or  $HNO_2$ . Such interferences can be eliminated by oxidation or removal of the gas.

## 7. Apparatus

7.1 *Apparatus for Carbon Determination*—A typical instrument consists of reagent and sample introduction mechanism, reaction vessel, detector, control system, and a display. **Fig. 1** shows a diagram of such an arrangement.

**TABLE 1 Blank Contribution and IC Removal Efficiency of Vacuum Degassing Unit**

Unit No.	TOC Background, $\mu\text{g/L}^A$	IC Background, $\mu\text{g/L}^A$	IC Level with 25 000 $\mu\text{g/L}$ Input
1	3.2	8.2	55
2	3.2	22	61
3	2.4	8.0	105
4	4.2	13	89
5	2.8	13	30
6	3.0	8.0	70
7	4.8	8.9	67
8	4.7	8.3	63
9	4.6	11	62
10	4.7	2.9	72

<sup>A</sup> Values are the difference between, before, and after addition of the degasser to a high-purity (<5  $\mu\text{g/L}$ ) water stream.

7.1.1 Vacuum degassing requires the manufacturer's module, which includes a vacuum pump and a hollow fiber membrane assembly. Use of this vacuum degasser will remove essentially all IC as part of the analysis. The membrane module consists of a tube and shell arrangement of microporous polypropylene hollow fibers. Sample flows along the inside of the fibers while air is passed on the shell side, counterflow to the sample flow. The shell side pressure is reduced by means of a vacuum pump on the air outlet. The sample is acidified before introduction into the degasser to facilitate  $\text{CO}_2$  transport through the hollow fibers.

7.1.2 *Reaction*—The sample flow is split after the addition of reagents. Half the flow passes to the delay coil while the other half passes into the oxidation reactor. The effluent from both streams passes over individual membranes that allow  $\text{CO}_2$  to pass through the membrane into prepurified water for detection.

7.1.3 *Detector*—The  $\text{CO}_2$  that has passed through the membrane into the purified water is measured by conductivity sensors. The temperature of the conductivity cell is also automatically monitored so the readings can be corrected for changes in temperature.

7.1.4 *Membrane*—The membrane is a  $\text{CO}_2$  selective fluoropolymer that is hydrophobic and non-porous. Refer to the bibliography in Bibliography section Annex A for additional details.

7.1.5 *Internal Purified Water*—Water on the conductivity side of the membrane is purified by continual pumping through a mixed bed ion exchange resin as shown in Fig. 1. On power up, the instrument automatically delays for a period of at least 5 min to allow the water in the internal loop to be fully deionized. The mixed bed ion exchange resin has an expected life of several years. See 14.3 for details on monitoring the resin.

7.1.6 *Presentation of Results*—The conductivity detector output is related to stored calibration data and then displayed as parts per million ( $\text{ppm} = \text{mg/L}$  of carbon) or parts per billion ( $\text{ppb} = \mu\text{g/L}$  of carbon). Values are given for TC, IC, and TOC by difference. Data can be maintained on internal nonvolatile RAM, printer tape, or computer storage.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Use reagent grade chemicals 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,<sup>4</sup> 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, prepare  $\text{CO}_2$ -free water from reagent water by acidifying to pH 2 and sparge with fritted-glass sparger using  $\text{CO}_2$ -free gas (time will depend on volume and gas flow rate and should be determined by test). Determine the carbon contribution of the reagent water and allow for its effect in preparation of standards and other solutions. Protect  $\text{CO}_2$ -free water from atmospheric contamination. Glass containers are required for storage of water and standard solutions.

8.3 *Acid Reagent (6 M)*—Prepare acid solution to a concentration of 6 M and verify that it contains less than 600  $\mu\text{g/L}$  organic carbon contamination. Since halogens are potential interferences, use only sulfuric or phosphoric acid for reagents. Prepare sulfuric acid by diluting 336 mL of 95 % reagent (sp gr 1.84) to 1 L with reagent water. Prepare phosphoric acid by diluting 410 mL of 85 % reagent (sp gr 1.69) to 1 L with water. Certification of reagent assay should be available. Reagents in prepackaged containers from the instrument manufacturer have been found to be acceptable.

<sup>4</sup> *Reagent Chemicals, American Chemical Society Specifications*, 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.