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## Standard Test Method for Low Level Determination of Total Carbon, Inorganic Carbon and Organic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection<sup>1</sup>

This standard is issued under the fixed designation D6317; 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 in the range from 10 to 1000 µg/L of carbon. This method is for laboratory or grab sample applications and has been subjected to an interlaboratory study under the guidelines of [D2777](#). Test Method [D5997](#) can be used for on-line determinations. The test method utilizes persulfate or ultraviolet oxidation of organic carbon, or both coupled with a CO<sub>2</sub> selective membrane to recover the CO<sub>2</sub> into deionized water. The change in conductivity of the deionized water is measured and related to carbon concentration in the oxidized sample. Inorganic carbon is determined in a similar manner without the oxidation step. In both cases, the sample is acidified to facilitate CO<sub>2</sub> recovery through the membrane. The relationship between the conductivity measurement and carbon concentration is described by a set of chemometric equations for the chemical equilibrium of CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and H<sup>+</sup>, 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 CO<sub>2</sub> 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, use of two measurement channels allows determination of CO<sub>2</sub> in the sample independently of organic carbon. Isolation of the conductivity detector from the sample by the CO<sub>2</sub> selective membrane results in a very stable calibration, with minimal interferences.

1.3 This test method was used successfully with reagent water spiked with various organic materials. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 In addition to laboratory analyses, this test method may be adapted to on line monitoring. See Test Method [D5997](#).

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](#)

[D3370 Practices for Sampling Water from Closed Conduits](#)

[D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data \(Withdrawn 2002\)](#)<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.

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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](#).

**D5997** Test Method for On-Line Monitoring of Total Carbon, Inorganic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection

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

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

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

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

### 4. Summary of Test Method

4.1 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 of TC and IC. If IC is high relative to TOC it is desirable to use a vacuum degassing unit to reduce the IC concentration as part of the measurement. Alternatively, the IC can be removed by acidifying and sparging the sample prior to injection into the instrument. The basic steps of the procedure are as follows:

(1) Removal of IC, if desired, by vacuum degassing;

(2) Conversion of remaining inorganic carbon to CO<sub>2</sub> by action of acid in both channels and oxidation of total carbon to CO<sub>2</sub> by action of ultraviolet (UV) radiation in the TC channel. (Acid-persulfate can be added but is usually not required at TOC levels below 1 ppm).

(3) Detection of CO<sub>2</sub> that is swept out of the UV reactor and delay coil by the liquid stream and passed through membranes that allow the specific passage of CO<sub>2</sub> to high purity water where change in conductivity is measured and;

(4) Conversion of the conductivity detector signal to a display of carbon concentration in parts per million (ppm=mg/L) (ppm = mg/L) or parts per billion (ppb=µg/L). (ppb = µg/L). The IC channel reading is subtracted from the TC channel to give a TOC reading. A diagram of suitable apparatus is given in **Fig. 1**. References **1-5**<sup>4</sup> provide additional information on the 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 impurities in high purity process water used in industries such as nuclear power, pharmaceutical, and electronics.

### 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 and water. 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: by rerunning the sample under more vigorous reaction conditions or by spiking samples with known refractories and determining recovery.

6.2 Chloride ion above 250 mg/L tends to interfere with oxidative reaction mechanisms in this test method. Follow manufacturer's instructions for dealing with this problem. Other interferences have been investigated and found to be minimal under most conditions. Refer to the reference **(2)** 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. In this case the vacuum degassing unit on the instrument should be used to reduce the concentration of IC prior to measurement. Alternatively, the sample can be acidified and sparged prior to introduction into the instrument.

6.4 Use of the vacuum degassing unit or sparging the sample 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 application. **Table 1** provides typical IC removal performance and background levels of the vacuum degassing unit.

6.5 Contamination of the sample with both CO<sub>2</sub> and organic carbon is a severe problem as lower levels of analyte are attempted. Throughout this method, the analyst must be vigilant for all potential sources of contamination and must monitor blanks and adjust operations to prevent contamination.

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

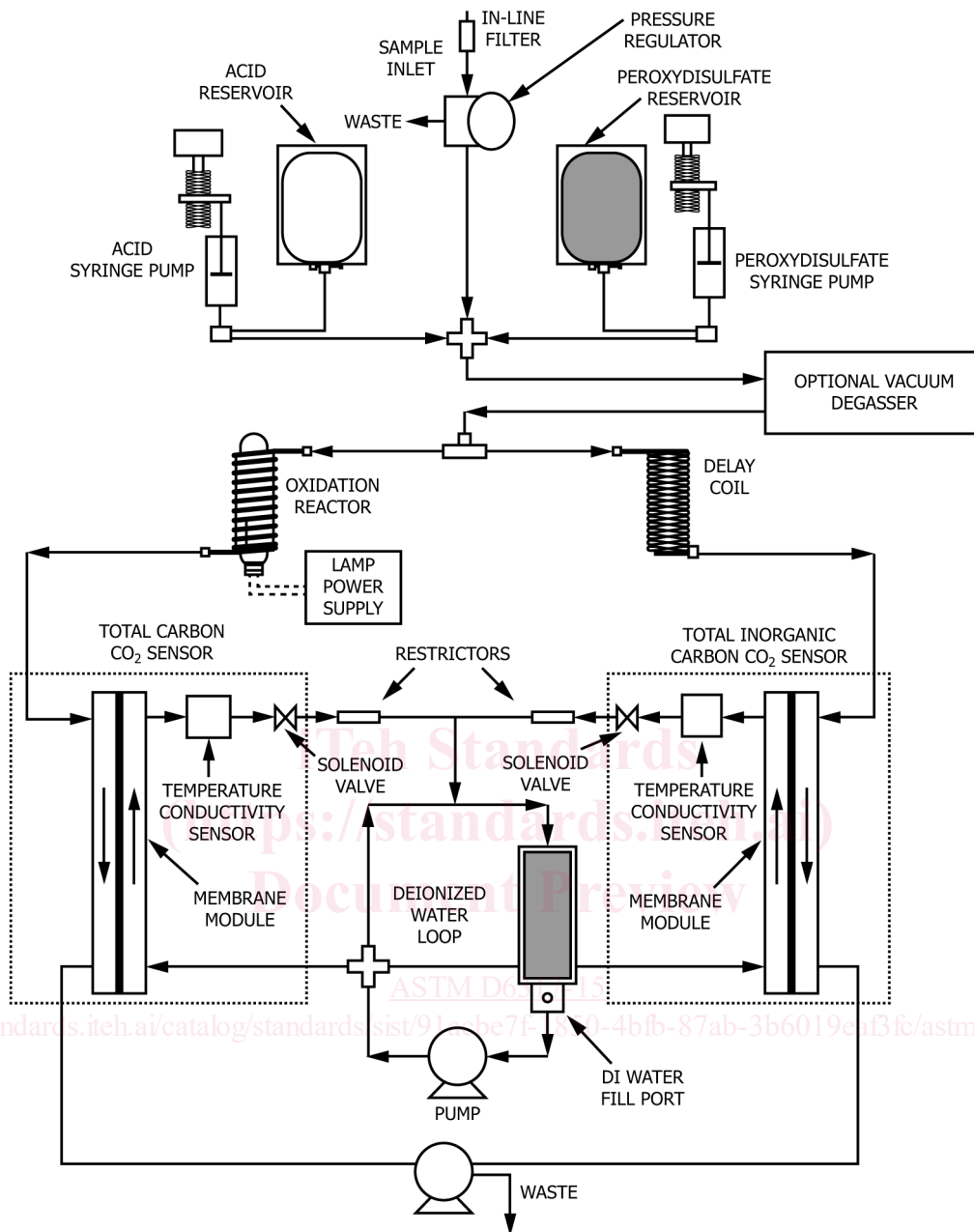


FIG. 1 Schematic Diagram of TOC Analyzer System

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

Unit No.	$\mu\text{g/L}^A$ TOC background	$\mu\text{g/L}^A$ IC background	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.

6.6 The membrane conductivity detection technique may experience positive interference in the presence of low molecular weight, reduced, inorganic acid species such as H<sub>2</sub>S or HNO<sub>2</sub>. 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.<sup>5</sup> Fig. 1 shows a diagram of such an arrangement.

7.1.1 *Sampling Needle*—A double chambered needle capable of piercing the sample bottle septum and pulling sample from the bottom of the bottle is used. The second chamber vents the top of the bottle to prevent vacuum build up as the sample is withdrawn. Typically this needle is mounted on an autosampler to provide unattended analysis of several samples.

7.1.2 *I.C./IC Removal*—Vacuum degassing requires the manufacturer's module<sup>5</sup> 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 CO<sub>2</sub> transport through the hollow fibers. Sparging requires an inert vessel with provision for sparging the acidified sample 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.

7.1.3 *Reactor*—The sample flow is split after the addition of reagents. Half of 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 CO<sub>2</sub> to pass through the membrane into prepurified water for detection.

7.1.4 *Membrane*—The membrane is a CO<sub>2</sub> selective fluoropolymer which is hydrophobic and non-porous. Refer to the bibliography for additional details.

7.1.5 *Detector*—The CO<sub>2</sub> 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.

7.1.6 *Data Display*—The conductivity detector output is related to stored calibration data and then displayed as parts per million, (ppm = mg of carbon per litre) or parts per billion, (ppb = µg of carbon per L-litre). Values are given for TC, IC, and TOC by difference.

## 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,<sup>6</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 Type I or Type II in Specification D1193. 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, CO<sub>2</sub>-free water may be prepared from reagent water by acidifying to pH 2, then sparging with fritted-glass sparger using CO<sub>2</sub>-free gas (time will depend on volume and gas flow rate, and should be determined by test). The carbon contribution of the reagent water should be determined and its effect allowed for in preparation of standards and other solutions. CO<sub>2</sub>-free water should be protected from atmospheric contamination. Glass containers are required for storage of water and standard solutions. Continuous UV treatment of water with recycling through appropriate mixed bed ion exchange resins may be necessary to maintain an adequately low TOC reagent water.

8.3 *Persulfate Reagent (15 % w/v)*—Prepare ammonium persulfate solution to a concentration of 15 % w/v by dissolving 15 g of ammonium peroxydisulfate in water and diluting to 100 mL. Verify that it contains less than 2000 µg/L organic carbon contamination. Certification of reagent assay should be available. Reagents in prepackaged containers from the instrument manufacturer have been found to be acceptable.

8.4 *Acid Reagent (6M) (6 M)*—Prepare acid solution to a concentration of 6M and verify that it contains less than 600 µg/L organic carbon contamination. Since halogens are potential interferences, use only sulfuric or phosphoric acid for reagents. Sulfuric acid is prepared by diluting 336 mL of 95 % reagent (sp gr 1.84) to 1 L with reagent water. Phosphoric acid is prepared by diluting

<sup>5</sup> Instruments manufactured and marketed by Sievers Instruments, Inc., 6185 Arapahoe Ave., Suite H1, Boulder, CO 80303 have been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

<sup>6</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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.