



Standard Test Method for On-Line Monitoring of Total Carbon, Inorganic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection¹

This standard is issued under the fixed designation D 5997; 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 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 CO_2 selective membrane to recover the 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 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 CO_2 , HCO_3^- , H^+ , and 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 D 4519 for a discussion of the measurement of 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 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 *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:

- D 1129 Terminology Relating to Water²
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits²
- D 1193 Specification for Reagent Water²
- D 2777 Practice for the Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water²
- D 3370 Practices for Sampling Water from Closed Conduits²
- D 4519 Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity²

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D 1129.

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.

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water. Current edition approved July 10, 1996. Published November 1996.

² Annual Book of ASTM Standards, Vol 11.01.

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 CO₂ 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 CO₂ by action of acid-persulfate aided by ultraviolet (UV) radiation in the TC channel,

4.2.5 Detection of CO₂ by passing each liquid stream over membranes that allow the specific passage of CO₂ 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

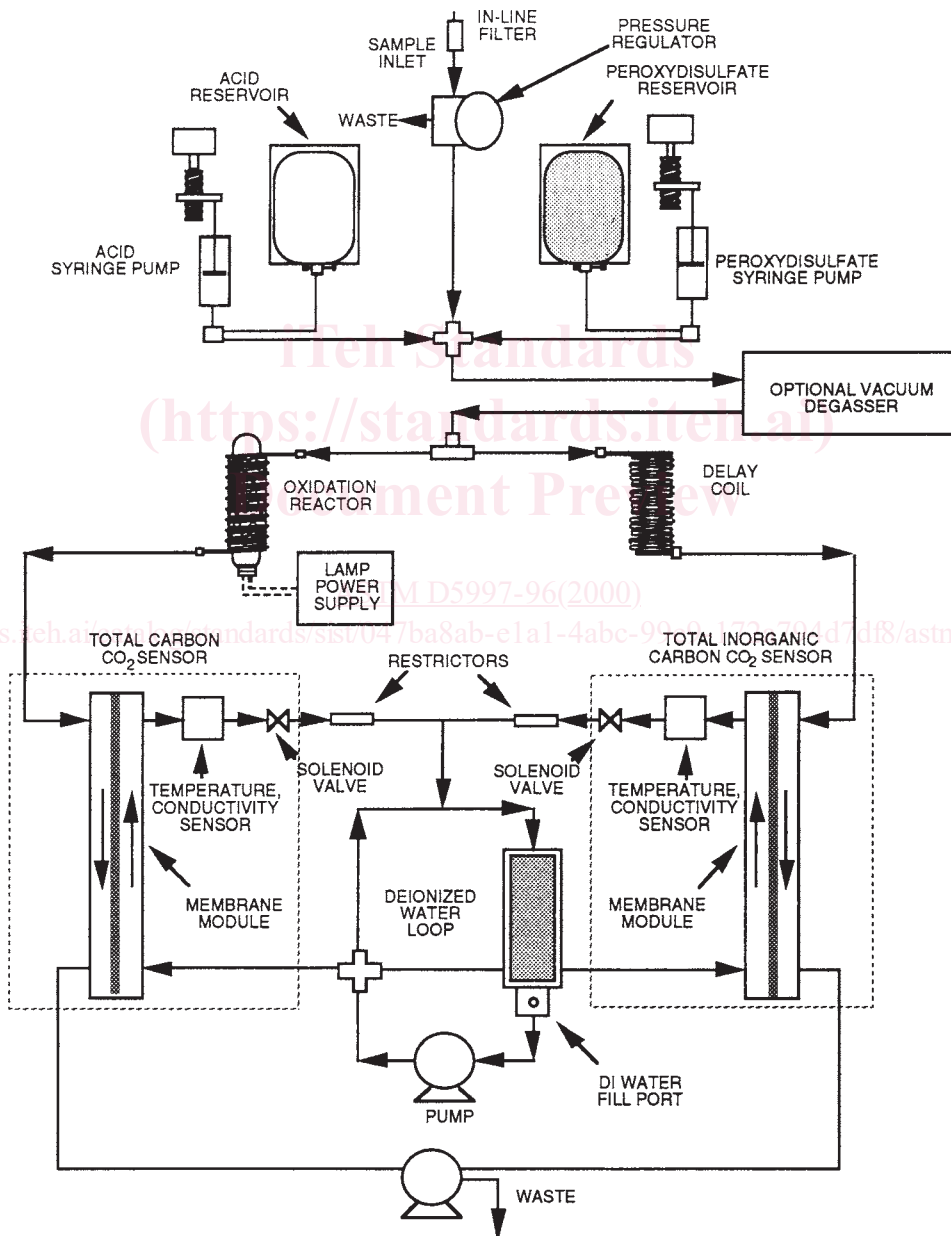


FIG. 1 Schematic Diagram of TOC Analyzer System

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 A1 for additional information regarding the significance of this test method.

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 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 A1 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. 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.

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.

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 CO₂ 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 CO₂ to pass through the membrane into prepurified water for detection.

7.1.3 *Detector*—The CO₂ 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 CO₂ selective fluoropolymer that is hydrophobic and non-porous. Refer to the bibliography in Annex A1 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

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

Unit No.	TOC Background, µg/L ^A	IC Background, µg/L ^A	IC Level with 25 000 µg/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

^A Values are the difference between, before, and after addition of the degasser to a high-purity (<5 µg/L) water stream.