



Designation: D5173 – 97(Reapproved 2007)

Standard Test Method for On-Line Monitoring of Carbon Compounds in Water by Chemical Oxidation, by UV Light Oxidation, by Both, or by High Temperature Combustion Followed by Gas Phase NDIR or by Electrolytic Conductivity¹

This standard is issued under the fixed designation D5173; 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 selection, establishment, and application of monitoring systems for carbon and carbon compounds by continual sampling or continuous flow-through, automatic analysis, and recording or otherwise signaling of output data. The system chosen will depend on the purpose for which it is intended (for example, regulatory compliance, process monitoring, or to alert the user to adverse trends) and on the type of water to be monitored (low purity or high purity, with or without suspended particulates, purgeable organics, or inorganic carbon). If it is to be used for regulatory compliance, the test method published or referenced in the regulations should be used in conjunction with this test method and other ASTM test methods. The test method covers carbon concentrations of 10 $\mu\text{g/L}$ to 5000 mg/L.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *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.* For specific hazard statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*²

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

¹ 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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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.

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
D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
D3864 Guide for On-Line Monitoring Systems for Water Analysis
D4453 Practice for Handling of High Purity Water Samples
D4779 Test Method for Total, Organic, and Inorganic Carbon in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection (Withdrawn 2002)³
D4839 Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129 and Guide D3864.

4. Summary of Test Method

4.1 A representative sample of a water stream, or the water stream itself flows into a reaction chamber where all or some of the dissolved organic carbon is oxidized to carbon dioxide by either of two means: (1) a chemical oxidant, an energy source such as ultraviolet (UV) radiation, or both, or (2) high temperature combustion. This carbon dioxide is subsequently measured in the gas phase by a non-dispersive infrared detector, or is measured in solution by means of electrolytic conductivity. Interference may occur from the latter method if the water sample has a high conductivity.

4.2 If there are suspended solids in the water stream, it is advisable to filter them out to prevent accumulation and possible blockage in the analyzer. The instrument will then measure dissolved carbon plus any particulate carbon that passes the filter. This parameter is usually called dissolved carbon.

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

4.3 If there is inorganic carbon present in the water (in the form of carbonate, bicarbonate, or carbon dioxide), it will also be detected as carbon dioxide. If inorganic carbon is not removed before analysis, the monitor will report total carbon.

4.4 Inorganic carbon is removed from the water stream by acidifying and sparging the sample. This process may also remove purgeable organic compounds.

4.5 Suspended elemental carbon will not be oxidized by low-temperature methods.

5. Significance and Use

5.1 Accurate measurement of organic carbon in water at low and very low levels is of particular interest to the electronic, pharmaceutical, and steam power generation industries.

5.2 Elevated levels of organics in raw water tend to degrade ion exchange resin capacity. Elevated levels of organics in high purity water tend to support biological growth and, in some cases, are directly detrimental to the processes that require high purity water.

5.3 In the case of steam power generation, naturally occurring organics can become degraded to CO₂ and low molecular weight organic acids that, in turn, are corrosive to the process equipment. Their effect on conductivity may also cause water chemistry operating parameters to be exceeded, calling for plant shutdown.

5.4 In process water in other industries, organic carbon can signify in-leakage of substances through damaged piping and components, or an unacceptable level of product loss.

5.5 In wastewater treatment, organic carbon measurement of influent and in-process water can help adjust optimize treatment schemes. Measurement of organic carbon at discharge may contribute to regulatory compliance.

6. Interferences

6.1 If inorganic carbon (dissolved CO₂ and ions in equilibrium with it) is present, it will give a false positive to an organic carbon measurement. Ion exchange resins used for high purity water production typically strip CO₂ from the water, so this interferent is absent from such water unless the water stream comes in contact with the atmosphere prior to analysis.

6.2 If electrolytic conductivity is used for the measurement of CO₂, other conductive species in solution will cause a positive interference unless their background conductivity is measured and deducted.

6.3 Particulates suspended in the water stream may cause blockage in the monitor over a period of time, and may also be hard to oxidize. If problems are anticipated, the water stream should be appropriately filtered upstream of the monitor. The parameter measured in the filtered water will be dissolved organic carbon (DOC).

6.4 Non-dispersive infrared detectors tuned to CO₂ absorbance are also sensitive to water vapor, which may therefore give a positive interference unless removed.

7. Apparatus

7.1 Figs. 1-4 show in block diagram form several designs of on-line total organic carbon (TOC) analyzers that have been successfully introduced.

8. Reagents and Materials

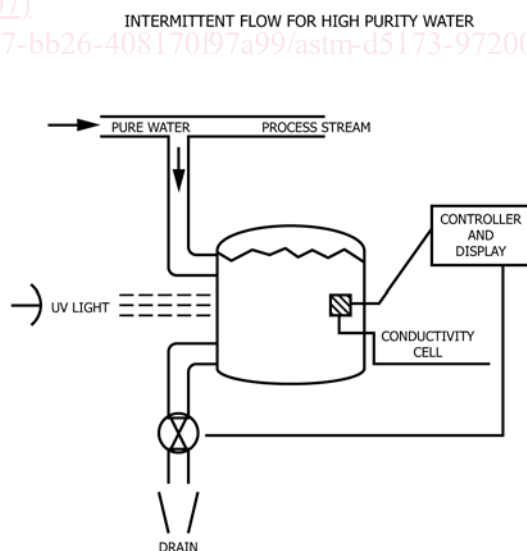
8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without decreasing the accuracy of the determinations.

8.2 *Purity of Water:*

8.2.1 Unless otherwise stated, references to reagent water shall be understood to mean that conforming to Specification D1193, Type II. The carbon content of this water should be measured regularly by a suitably sensitive test method, such as Test Method D4779. It will typically be less than 0.2 mg/L carbon.

8.2.2 Water as free as possible of organics is desirable when establishing the test method blank at carbon levels of less than 1 mg/L. Absolutely carbon-free water is not obtainable in ordinary circumstances. However, a working approximation to this goal is the solution contained in the reaction vessel of

⁴ *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.



NOTE 1—The unit employs available water system pressure to rinse the line and test chamber, followed by a downstream valve closure that isolates the sample. Subsequent irradiation with intense UV light breaks down organic compounds in the water, with the liberated carbon forming carbon dioxide in solution as carbonic acid. By monitoring the change in sample conductivity, corrected for temperature, the TOC concentration is calculated and displayed.

FIG. 1 Low Temperature Unit

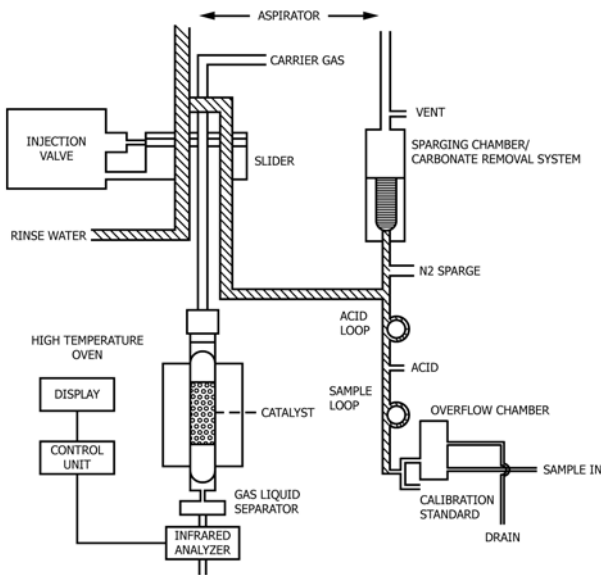
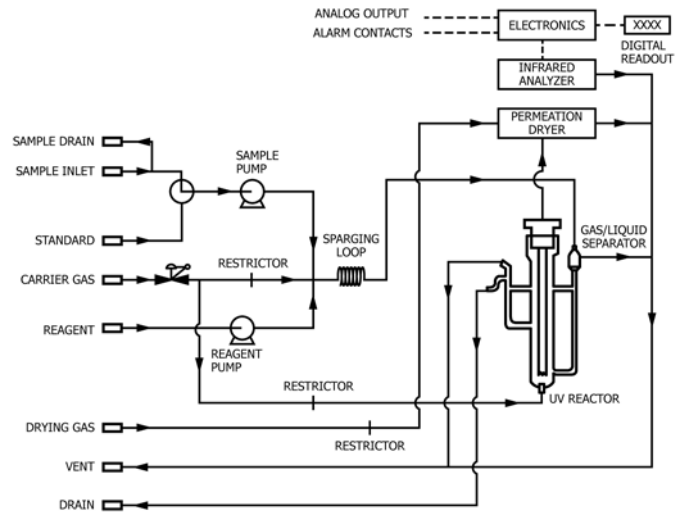


FIG. 2 High Temperature Unit

NOTE 1—This unit is designed to continually measure TOC in a water sample. The sample flows into a sample overflow chamber and out to drain. Every 5.5 min, acid and sample are aspirated into the carbonate removal system. The inorganic carbon in the combined acid/sample is sparged with nitrogen gas. A fixed volume of sparged inorganic “carbon-free” sample is then injected into the reaction chamber heated at 900°C. The organics in the sample are oxidized to carbon dioxide. The carrier gas flows continuously through the reaction chamber, carrying the CO₂ through a gas-liquid separator into the infrared analyzer. The concentration of CO₂ measured is directly correlated to the carbon concentration in the sample.

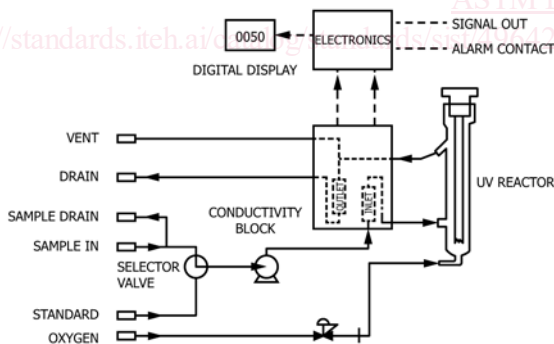
CONTINUOUS FLOW



NOTE 1—This TOC analysis unit uses ultraviolet-promoted persulfate oxidation combined with infrared detection to continually determine the concentration of organics in water. Sample flows continuously into the analyzer through a sample bypass, either by means of process pressure, or an optional sample pump. A side stream for analysis is continuously pumped at a constant rate and acidified with a sodium persulfate/phosphoric acid solution, that reacts with any inorganic carbon to form CO₂. The acidified sample is then sparged with carrier gas (N₂ or O₂) to remove the CO₂. Passing through a liquid/gas separator, the CO₂ is vented, and the liquid flows to the reaction chamber, where it is exposed to ultraviolet light. The UV radiation catalyzes the persulfate oxidation of the remaining organic carbon to CO₂. The CO₂-laden carrier gas is passed through a permeation dryer to remove moisture, and then through the NDIR detector, that measures the CO₂. The electronics linearize and scale the IR detector signal to equate to milligrams/litre organics, displayed on the digital read-out.

FIG. 4 Low Temperature UV-Persulfate Unit—Continuous Flow

CONTINUOUS FLOW FOR HIGH PURITY WATER



NOTE 1—Operation—The water sample is pumped continuously to the conductivity block where the inlet conductivity is measured to establish the baseline. The sample then flows to the UV reaction chamber where the organics are oxidized to form organic acids, as described in the following formula:



As the organics oxidize to organic acids, the conductivity of the sample increases. Next, the sample flows through the outlet conductivity detector, and then to drain. The electronics continuously compare the temperature-corrected conductivity readings from the inlet and outlet detectors, and derive the organic content of the sample in micrograms/litre that is shown on a digital display.

FIG. 3 Low Temperature Unit—Continuous Flow for High-Purity Water

carbon analyzers that UV-irradiate and sparge an acidified persulfate solution. Alternatively, water that has been acidified, mixed with persulfate to a final concentration of 2 % w/v, heated or exposed to ultraviolet radiation, or both, for at least an hour, then thoroughly sparged, may be used.

8.3 Amber glass bottles should be used to store reagent water, organic-free water, and standard solutions. The bottles should be dedicated to their respective types of solution. Practices D3370, D3694, and D4453 address handling of water samples. While the most rigorous method of cleaning glassware is described below, Practice D4453 has alternative procedures not involving Cr(VI).

8.3.1 Clean bottles with chromic acid, rinse several times with water, and dry overnight at 400°C in a muffle furnace.

8.3.2 Rinse the TFE-fluorocarbon-lined closures several times with water, then allow to soak in water overnight. Rinse these closures again with water before use.

8.3.3 Put the closures loosely on the bottles while the latter are still warm. When the bottles have cooled to room temperature, tighten the closure.

8.3.4 Follow the cleaning procedure in 8.3.1 through 8.3.3 before each re-use of the bottles.