



Designation: D5173 – 15 (Reapproved 2023)

## Standard Guide for On-Line Monitoring of Total Organic Carbon in Water by Oxidation and Detection of Resulting Carbon Dioxide<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This guide covers the selection, establishment, and application of monitoring systems for carbon and carbon compounds by on-line, 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 guide and other ASTM test methods. This guide covers carbon concentrations of 0.05  $\mu\text{g/L}$  to 50 000  $\text{mg/L}$ . Low end sensitivity and quantitative results may vary among instruments. This guide covers the on-line measurement techniques listed in Table 1. Additional laboratory test methods are available: Test Methods D4129, D4839, D5904, D6317, and D7573.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

1.4 *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.*

<sup>1</sup> This guide 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. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

- D1129 Terminology Relating to Water
- 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 Flowing Process Streams
- D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
- D3864 Guide for On-Line Monitoring Systems for Water Analysis
- D4129 Test Method for Total and Organic Carbon in Water by High Temperature Oxidation and by Coulometric Detection
- D4453 Practice for Handling of High Purity Water Samples
- D4839 Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection
- D5904 Test Method for Total Carbon, Inorganic Carbon, and Organic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection
- D5997 Test Method for On-Line Monitoring of Total Carbon, Inorganic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection
- D6317 Test Method for Low Level Determination of Total Carbon, Inorganic Carbon and Organic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection
- D7573 Test Method for Total Carbon and Organic Carbon in Water by High Temperature Catalytic Combustion and Infrared Detection

#### 2.2 Other Standards:

- EN1484 European Standard Water Analysis Guidelines for the Determination of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)<sup>3</sup>

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto: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> Available from European Committee for Standardization (CEN), Avenue Marnix 17, B-1000, Brussels, Belgium, <http://www.cen.eu>.

**TABLE 1 TOC Measurement Techniques and Typical Ranges**

TOC Measurement Technique	Typical Range <sup>A</sup>	Figure	ASTM Method
UV Light Oxidation/Conductivity Detection	0.1 µg/L to 2 mg/L	Fig. 1	...
Combustion Oxidation/IR Detection	4 µg/L to 20 000 mg/L	Fig. 2	...
UV Light Oxidation/Conductivity Detection—Continuous Flow	0.1 µg/L to 2 mg/L	Fig. 3	...
UV-Persulfate Oxidation/IR Detection—Continuous Flow	0.5 µg/L to 3 000 mg/L	Fig. 4	...
Catalyzed Ozone Hydroxyl Radical Oxidation/IR Detection	6 µg/L to 40 000mg/L	Fig. 5	...
Heated Persulfate Oxidation/IR Detection	0.05 mg/L to 250 mg/L	Fig. 6	...
UV Persulfate Oxidation/Membrane Conductivity Detection	0.5 µg/L to 50 mg/L	Fig. 7	D5997
Supercritical Oxidation/IR Detection	0.5 mg/L to 50 000 mg/L	Fig. 8	...

<sup>A</sup> Consult manufacturer for specific range of measurement.

### 3. Terminology

#### 3.1 Definitions:

3.1.1 For definitions of other terms used in this guide, refer to Terminology [D1129](#) and Guide [D3864](#).

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *electrical conductivity, n*—the reciprocal of the ac resistance in ohms measured between opposite faces of a centimetre cube of an aqueous solution at a specified temperature, measured in units of siemens/cm.

### 4. Summary of Guide

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. Some regulatory agencies require complete oxidation. This carbon dioxide is subsequently measured in the gas phase by a non-dispersive infrared detector, or is measured in solution by means of conductivity or membrane conductivity detection.

4.2 If there are suspended solids in the water stream, with some analyzers it is advisable to filter the solids out to prevent accumulation and possible blockage.

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 or compensated before analysis, the monitor will report total carbon.

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

4.5 Suspended elemental carbon may not be oxidized by low-temperature methods depending on several factors including analysis time, particle size and concentration, instrument design, etc.

### 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, life sciences, 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 power generation, naturally occurring organics can become degraded to CO<sub>2</sub> 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. Halogenated and sulfonated organics may not be detectable by conductivity but at boiler temperatures will release highly corrosive chlorides, sulfates, etc.

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 process water can help optimize treatment schemes. Measurement of organic carbon at discharge may contribute to regulatory compliance.

5.6 In life sciences, control of organic carbon is necessary to demonstrate compliance with regulatory limits for some types of waters.

### 6. Interferences

6.1 If inorganic carbon (dissolved CO<sub>2</sub> and ions in equilibrium with it) is present, it may lead to over-reporting of an organic carbon measurement unless it is compensated. Ion-exchange resins used for high purity water production typically remove CO<sub>2</sub> from the water, so this interferent is absent from such water unless the water stream comes in contact with the atmosphere prior to analysis. However, the ion-exchange resin can break down over time, producing a higher TOC carbon background, and must be monitored.

6.2 If electrical conductivity is used for the measurement of CO<sub>2</sub>, other conductive species in solution may cause over-reporting unless their background conductivity is measured and deducted or compensated. Background conductivity >2 µS/cm or pH >7 or both can cause loss of sensitivity to TOC. Observe instrument manufacturer specifications. A power plant sample with elevated pH and conductivity may be conditioned to be

within acceptable pH and conductivity ranges by continuously passing the sample through a cation exchange cartridge. The resulting TOC measurement will not include organic cations such as amines.

6.3 With electrical conductivity detection systems, halogen-, sulfur-, nitrogen- and phosphorus-containing organic compounds can result in interference with the TOC measurement. If problems are anticipated, the method of detection must be modified or the water itself must be treated to reduce the interfering background sufficiently to meet accuracy requirements.

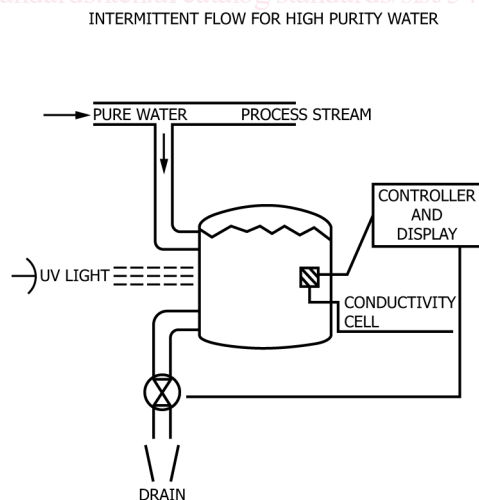
6.4 If particulates are suspended in the water stream, they may cause blockage in some analyzers over a period of time, and may also be hard to oxidize. If problems are anticipated, the water stream should be appropriately filtered upstream of the monitor and it must be recognized that results will not include solid organics. If the filter used is rated to 0.45 μm then the parameter measured will be dissolved organic carbon (DOC) as defined by EN1484.

6.5 Non-dispersive infrared detectors tuned to CO<sub>2</sub> absorbance are sensitive to water vapor, which may therefore give a positive interference unless the water vapor is removed.

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.

## 7. Apparatus

7.1 Figs. 1-8 show in block diagram form several designs of on-line total organic carbon (TOC) analyzers.



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 UV Light Oxidation with Conductivity Detection

## 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.<sup>4</sup> 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 water shall be understood to mean water meeting the quantitative requirements of Specification D1193, Type II. The carbon content of this water should be measured regularly by a suitably sensitive test method.

8.2.2 Water as free as possible of organics relative to the carbon levels being measured is required when establishing the test method blank.

8.3 Amber glass, HDPE, and TFE fluorocarbon bottles should be used to store water, organic-free water, and standard solutions. The bottles should be dedicated to their respective types of solution and should not interfere with the chosen measurement technique. Practices D3370, D3694, and D4453 address handling of water samples.

8.3.1 Clean bottles according to Practice D4453.

8.3.2 Follow the cleaning procedure before each re-use of the bottles.

8.4 *Gas Supply*—Use a gas free of CO<sub>2</sub> and organic matter, of purity specified by the equipment manufacturer.

### 8.5 Organic Carbon Solution, Standard:

8.5.1 Prepare high-concentration calibration standards (for example, 2000 mg/L carbon) using a water-soluble, stable compound. This stock solution can then be further diluted to a concentration suitable for the method used.

8.5.2 The compound used for calibration should be as similar as possible to the compound(s) expected to be present in the water to be analyzed.

8.5.3 Commercial standards are available from several sources in place of self-made standards. Verify that standards are certified and within their shelf life before using.

## 9. Hazards

9.1 Give full consideration to safe disposal of the analyzer's spent samples and reagents and cleaning solutions.

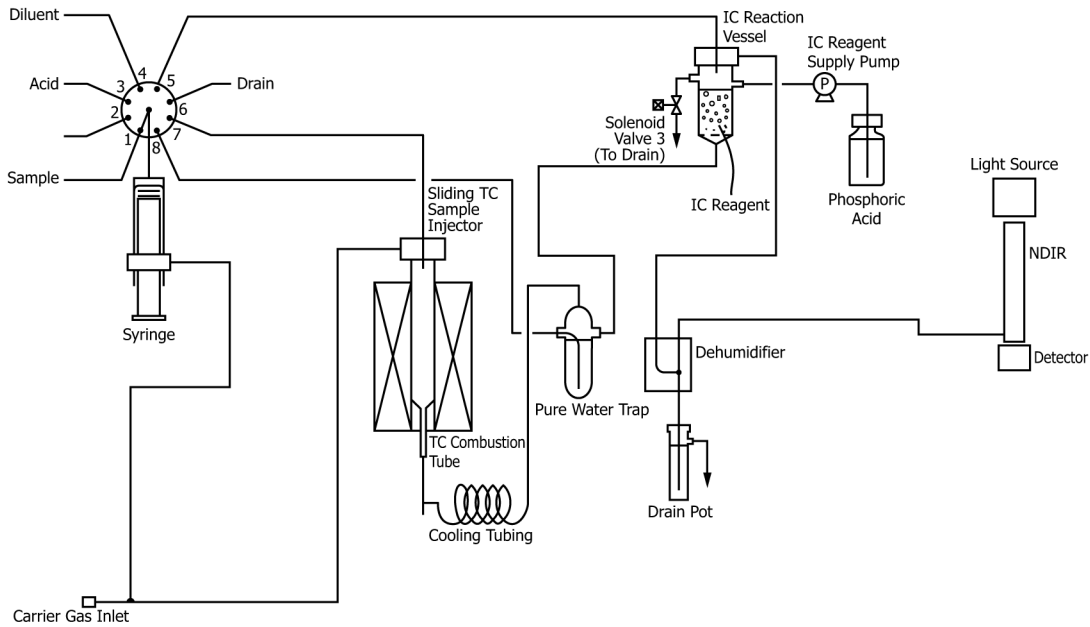
9.2 Provide pressure relief valves, if applicable, to protect both the analyzer and monitoring system.

9.3 Take precautions when using cylinders containing gases or liquids under pressure:

9.3.1 Gas cylinders must be handled by trained personnel only.

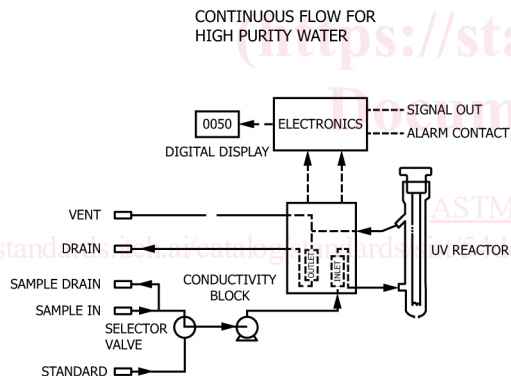
9.3.2 Fasten gas cylinders to a rigid structure.

<sup>4</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.



NOTE 1—The sample flows into a sample overflow chamber and out to drain. Periodically, 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 containing catalyst and heated at 680 °C to 900 °C. The organics in the sample are oxidized to carbon dioxide. The carrier gas flows continuously through the reaction chamber, carrying the CO<sub>2</sub> through a gas-liquid separator into the infrared analyzer. The concentration of CO<sub>2</sub> measured is directly correlated to the carbon concentration in the sample.

FIG. 2 Combustion Oxidation with IR Detection



NOTE 1—The water sample is pumped continuously to the first conductivity detector where the inlet conductivity is measured to establish the baseline. The sample then flows to the UV reaction chamber where the organics are oxidized, as described in the following equation:



As the organics oxidize, 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 UV Light Oxidation with Conductivity Detection—Continuous Flow for High-Purity Water

9.3.3 Take special safety precautions when using or storing combustible or toxic gases to ensure that the system is safe and free of leaks.

## 10. Technical Considerations

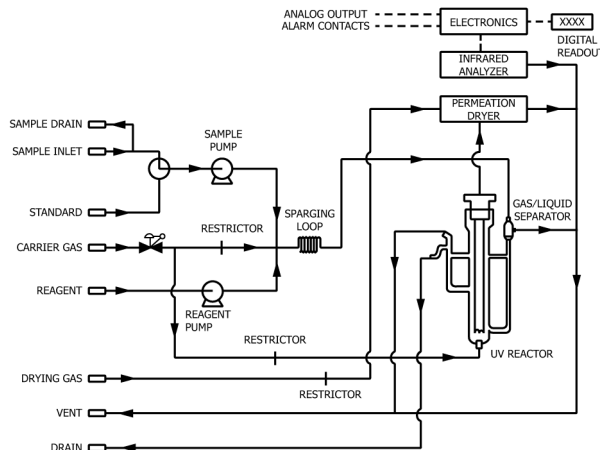
10.1 Carefully define the measurement objective for the monitoring system before specifying the apparatus. Consider such factors as the expected total level of carbon; whether significant inorganic carbon is likely to be present; whether there are significant levels of purgeable organic compounds in the stream; whether there are particulates in the water; how fast the system must respond to a change in carbon concentration in the stream; how accurate the result must be to meet internal and external requirements; and how readily the monitor’s calibration and performance can be checked.

10.2 If the monitoring system is intended primarily to determine compliance with regulatory standards, the accuracy, precision, frequency of sampling, and response time may be dictated by the requirements of the regulations. A high degree of stability and on-line reliability is generally required. The analyzer response for a specific parameter must be referenced to a recognized or specified laboratory test method approved by the regulatory agency.

10.3 Monitoring systems intended to detect leaks and uncontrolled discharges (spills), for protection of treatment plants or receiving waters, require short sampling cycles and rapid response. Typically, these systems will activate alarms to alert operating personnel. Flow can then be diverted from normal channels until the upset has passed or has been corrected. Frequently, the monitoring system is used in some way to locate and identify the source of the spill.

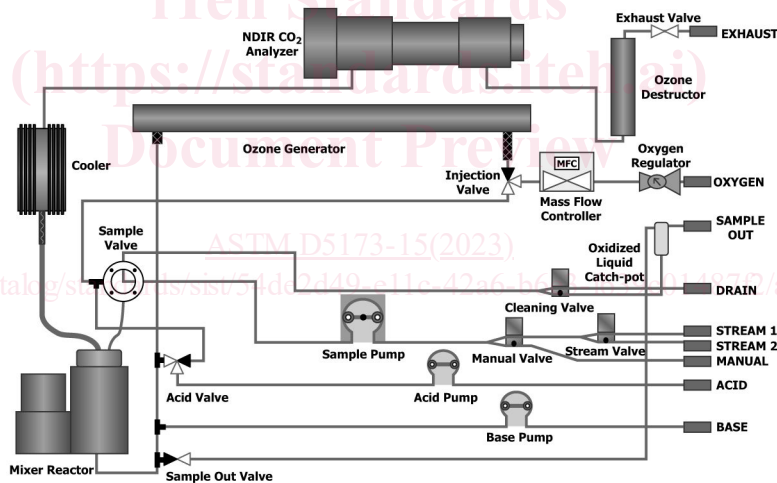


CONTINUOUS FLOW



NOTE 1—This TOC analysis unit uses ultraviolet-promoted persulfate oxidation combined with infrared detection to continuously 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 CO<sub>2</sub>. The acidified sample is then sparged with carrier gas (N<sub>2</sub> or O<sub>2</sub>) to remove the CO<sub>2</sub>. Passing through a liquid/gas separator, the CO<sub>2</sub> 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 CO<sub>2</sub>. The CO<sub>2</sub>-laden carrier gas is passed through a permeation dryer to remove moisture, and then through the NDIR detector, that measures the CO<sub>2</sub>. The electronics linearize and scale the IR detector signal to equate to milligrams/litre organics, displayed on the digital read-out.

FIG. 4 UV-Persulfate Oxidation with Infrared Detection—Continuous Flow



NOTE 1—A volume of unfiltered sample liquid is injected into the reactor. A base reagent is added and the sample is oxidized with hydroxyl radicals which are generated by exposing high pH reagents to ozone. The oxidation of organic compounds present in the sample takes place and both the primary compound “carbonates” and the secondary compound “oxalates” are formed. An acid reagent, which contains a catalyst, such as manganese, is added into the reactor and the carbonates are converted to carbon dioxide. Simultaneously, oxalates are broken down to carbon dioxide in the presence of the catalyst and ozone.

All carbon dioxide is sparged at pH near 1. Carbon dioxide gas is carried by the carrier gas through a cooler and measured using a non-dispersive infrared (NDIR) sensor. The result is displayed as TC (total carbon). The TC result represents the sum of TOC (which includes any volatile organics) and TIC (total inorganic carbon) present in the sample. The inorganic carbon present in the sample is sparged in the form of carbon dioxide gas by the addition of the acid reagent and is measured by the NDIR sensor. The result is displayed as TIC. The TOC result, including the volatiles, is then calculated from the difference between the TC and TIC measurements as:

$$TOC = TC - TIC$$

FIG. 5 Catalyzed Ozone Hydroxyl Radical Oxidation with Infrared Detection

10.4 Systems that monitor performance of process operations, such as waste treatment, may have varying degrees of sophistication and complexity, depending on the specific nature of the application.

10.5 Review all sample requirements with the equipment supplier. Be sure to define accurately all conditions of intended operation, the components in the sample and expected variations in the measured parameters.