



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 D 5173; 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:

D 1129 Terminology Relating to Water²

D 1193 Specification for Reagent Water²

D 2777 Practice for 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 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents³

D 3864 Guide for Continual On-Line Monitoring Systems for Water Analysis²

D 4453 Practice for Handling of Ultra-Pure Water Samples²

D 4779 Test Method for Total, Organic, and Inorganic Carbon in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection³

D 4839 Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection³

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Guide D 3864.

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.

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 of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water.

Current edition approved Feb. 10, 1997. Published April 1997. Originally published as D 5173 – 91. Last previous edition D 5173 – 91 (1995).

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 11.02.

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.

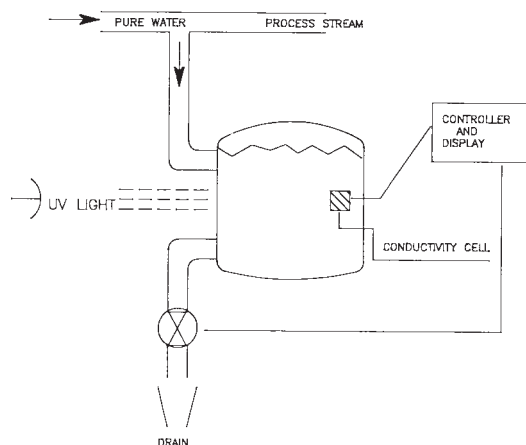
6.3 Particulates suspended in the water stream may cause blockage in the monitor over a period of time, and may also be hard to oxidize. If problems are anticipated, the water stream should be appropriately filtered upstream of the monitor. The parameter measured in the filtered water will be dissolved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

INTERMITTENT FLOW FOR HIGH PURITY WATER



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

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 D 1193, Type II. The carbon content of this water should be measured regularly by a suitably sensitive test method, such as Test Method D 4779. 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 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.

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.

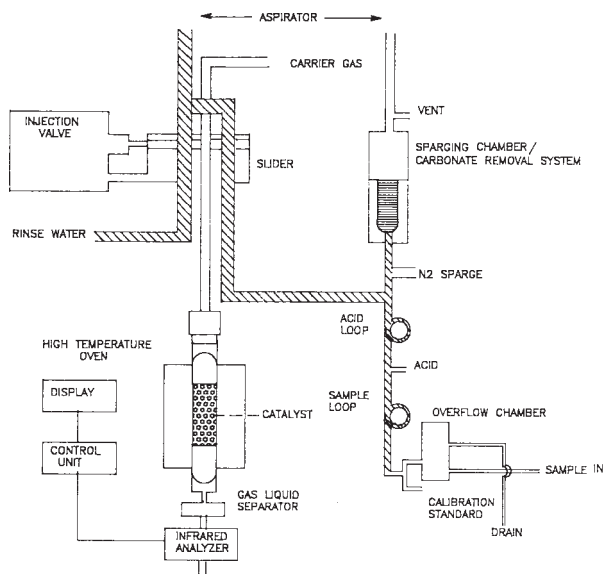


FIG. 2 High Temperature Unit

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.

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 D 3370, D 3694, and D 4453 address handling of water samples. While the most rigorous method of cleaning glassware is described below, Practice D 4453 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.

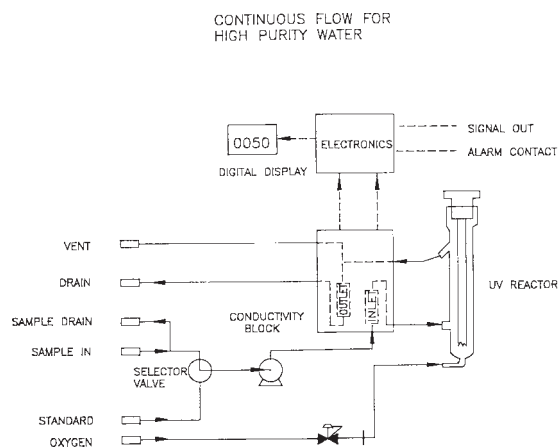
8.3.3 Put the closures loosely on the bottles while the latter are still warm. When the bottles have cooled to room temperature, tighten the closure.

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

8.4 *Gas Supply*—Use a gas free of CO₂ and organic matter, of a purity as specified by the equipment manufacturer. Oxygen is recommended.

8.5 *Organic Carbon Solution, Standard:*

8.5.1 Prepare high-concentration calibration standards (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. (See 8.5 of Test Method D 4779.)



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

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.

9. Hazards

9.1 Give full consideration to safe disposal of the analyzer’s spent samples and reagents (especially chromic acid), 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.

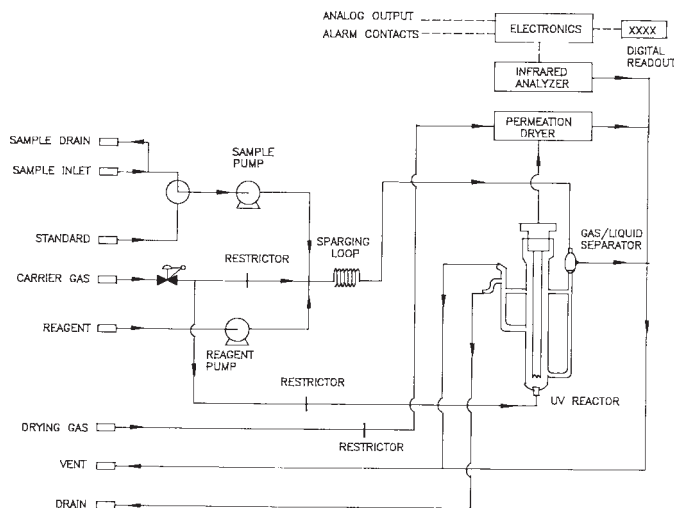
9.3.2 Fasten gas cylinders to a rigid structure.

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.

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 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

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 (that is, 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.

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.

10.6 Materials of construction that will be in contact with the sample should be such that will not react with the sample. Note that high-purity water monitoring may demand a minimum of organic polymers in the monitor, while certain process and waste streams may be highly corrosive and may therefore require inert polymers to be used.

10.7 Select the sampling point(s) so as to provide a representative and measurable sample as close as possible to the sample system and analyzer, and as outlined in Practices D 3370.

10.8 Select the sample transfer system, including pumps and transfer lines, so that the integrity of the sample is maintained from sampling point to analyzer, especially with respect to suspension of solids and biological growth.

10.9 Provide necessary sample conditioning equipment (for example, filters, diluters, homogenizers, stream splitters) that is consistent with the defined measurement objective.

10.10 Provide a means for introducing standard samples or withdrawing check samples immediately upstream of the analyzer.

10.11 Keep single- or multiple-sample streams that interface a single analyzer flowing all the time. Keep the manifold close to the analyzer to minimize cross-contamination.

10.12 Always keep sample lines as short as possible.

10.13 Provide appropriate protection of sample lines from extremely hot or freezing temperatures.

11. Calibration and Procedure

11.1 Establish a written calibration procedure and frequency consistent with the parameter being measured and the accuracy and reliability demanded by the measurement or control objectives.

11.1.1 Consult the analyzer supplier to determine the best calibration procedure to use with the specific analyzer in a particular application. This is particularly important when dealing with high-purity streams.

11.1.2 When required for regulatory compliance, use calibration procedures specified by the appropriate agency.

11.1.3 Refer to ASTM standards, where applicable, to determine appropriate calibration standards.

11.1.4 Provide calibration standards at concentrations and compositions as close as possible to those of the sample stream being analyzed. Note the need for scrupulously cleaned glassware. Low-level standards are particularly subject to change over time, and should be freshly made up as needed.

11.1.5 Before calibration, ensure that the sampling system and output instrumentation are functioning properly and that all preliminary adjustments to the analyzer required by the procedure have been made.

11.2 *Instrument Adjustment, Calibration, and Operation:*

11.2.1 Follow manufacturer's instructions for instrument warm-up, gas flows, and liquid flows.

11.2.2 For calibration, make various dilutions of a 2000 mg/L standard organic solution. Use dilutions as specified by manufacturer. Clean glassware used in preparation of standards scrupulously. Low-concentration standards are particularly subject to changes over time, due to contamination or decomposition, and need to be made fresh.

11.2.3 Calibration protocols may vary with equipment manufacturers. Calibrate the instrument as instructed by the manufacturer, and use standards to verify linearity within the specific range of interest for actual measurements. Plots of standard concentration versus instrument reading may be used for this purpose.

11.3 *Spot Sample Check:*

11.3.1 With the sample flow through the analyzer sampling line uniformly and the analyzer readout as close as possible to an equilibrium value, withdraw a sample from the inlet stream, as described in Practices D 3370.

11.3.2 Record time, sample number, date, and the corresponding analyzer readout and immediately analyze the sample, in duplicate, using Test Method D 4779 or D 4839, as appropriate.

11.3.3 Average the results of the duplicate analyses. Discard tests that fail to meet repeatability requirements.

11.3.4 Determine the analyzer calibration adjustment required so that results of analysis and the analyzer readout coincide. Adjust the analyzer with the analyzer controls accordingly.

11.3.5 Repeat this procedure until no further change is needed, consistent with the quality of data required.

11.4 *Multiple Standard Calibration:*

11.4.1 Prepare a series of calibration standards covering the range of measurements for the sample being analyzed, following instructions in the test method or in the analyzer supplier's instructions.

11.4.2 Check all operating conditions of the system in accordance with analyzer specifications and allow sufficient time for instrument equilibrium.

11.4.3 Introduce a calibration standard of a concentration level recommended by the instrument supplier into the analyzer using the recommended instrument operating procedure. Activate the readout equipment.

11.4.4 After sufficient sample has been allowed to flow through the analyzer, adjust the readout to conform to the desired value.

11.4.5 Repeat 11.4.3 for the remaining standards from the calibration series, recording the equilibrium readout value each time.

11.4.6 Plot a calibration curve of standard value versus readout response from the above data.

11.4.7 Discard any standard when any change of composition is detected.

11.5 *Laboratory Check Sample for Flow-Through System:*

11.5.1 Withdraw from the spot sampling line or otherwise obtain directly from the sample stream sufficient sample for calibration, representative of one concentration within the range of measurement of the analyzer (see Practices D 3370).

11.5.2 Analyze the sample for total organic carbon using a batch-type (laboratory) TOC analyzer and Test Method D 4779 or D 4839 as appropriate.

11.5.3 If necessary, prepare additional standards to cover the range of interest by dilution with reagent water or by "spiking" with known amounts of an appropriate standard.

11.5.4 Serially introduce the standards into the analyzer, using the recommended instrument operating procedures, and allow the analyzer readout to reach equilibrium.

11.5.5 Plot a calibration curve of concentration of parameter being determined versus readout response from the readout data.

11.6 After initial calibration with standard solutions or actual samples, as in 11.2 through 11.4, analyzer calibrations can be rechecked with secondary standards.

11.6.1 A solution containing material other than organic carbon, but producing the same analyzer output as that component, may be used in place of the standard solution.

11.6.2 An optical filter may be placed in the beam of a photometric analyzer to produce an output equivalent to that produced by the organic carbon in the water.

12. Calculation and Interpretation of Results


12.1 Each individual monitoring system determines the calculations necessary to perform on the output signal. Most analyses are recorded as direct readouts based on instrument calibration. However, in some cases, the measurement sensitivity range is involved and scale factors are necessary to determine the final results. This is usually a simple multiplication step.

13. Precision and Bias

13.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D 2777 since this test method is a continuous determination. This inability of Practice D 2777 procedures to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D 2777.

14. Keywords

14.1 dissolved carbon; electrolytic conductivity; elemental carbon; inorganic carbon; non-dispersive infrared detector; on-line monitoring system; organic carbon; persulfate solution; photometric analyzer; purgeable organics; reaction chamber; reagent; total carbon; total organic carbon; wastewater treatment

 **D 5173 – 97 (2001)**

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