Designation: ~~D7573 – 18~~ D7573 – 18a

Standard Test Method for Total Carbon and Organic Carbon in Water by High Temperature Catalytic Combustion and Infrared Detection[1]

This standard is issued under the fixed designation D7573; 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), total organic carbon (TOC), dissolved organic carbon (DOC), and non-purgable organic carbon (NPOC) in drinking water, groundwater, surface water, wastewater, and seawater in the range from 0.5 mg/L to 50 mg/L. Concentrations of 50–4000 mg/L of carbon may be determined by automated injection of less sample volume or by sample dilution. Alternatively, use less sample volume and calibrate at higher concentrations..

1.2 The sample is injected into a tube heated at ≥680°C. The sample converts into a gaseous phase and forced through a layer of catalyst ensuring conversion of all carbon containing compounds to CO_2. A non-dispersive infrared (NDIR) detector measures the resulting CO_2.

1.3 For TOC and DOC analysis a portion of the sample is injected to determine TC or dissolved carbon (DC). A portion of the sample is then acidified and purged to remove the IC. The purged inorganic carbon is measured as TIC, or DIC. TOC or DOC is calculated by subtracting the inorganic fraction from the total carbon:

$$\mathrm{TOC} = \mathrm{TC} - \mathrm{IC} \tag{1}$$

1.4 For NPOC analysis a portion of sample is acidified and purged to remove IC. The purged sample is then injected to determine NPOC.

1.5 This test method is applicable to the matrices and concentrations validated in the inter-laboratory study. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices and different concentration ranges.

1.6 This test method is applicable only to carbonaceous matter in the sample that can be introduced into the reaction zone. The syringe needle or injector opening size generally limits the maximum size of particles that can be so introduced.

1.7 In addition to laboratory analyses, this test method may be applied to stream monitoring.

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 *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.*

1.10 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[3]
D1193 Specification for Reagent Water

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in 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.

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

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
D4448 Guide for Sampling Ground-Water Monitoring Wells
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6538 Guide for Sampling Wastewater With Automatic Samplers
D6759 Practice for Sampling Liquids Using Grab and Discrete Depth Samplers

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *dissolved organic carbon (DOC), n*—carbon determined on filtered samples.

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

~~3.2.2 *total organic carbon (TOC), n*—carbon in the form of organic compounds.~~

3.2.3 *non-purgable organic carbon (NPOC), n*—carbon measured in a sample after acidification and sparging to remove inorganic carbon.

~~3.2.4 *total carbon (TC), n*—the sum of IC and TOC.~~

~~3.2.5 *dissolved organic carbon (DOC), n*—carbon determined on filtered samples.~~

3.2.4 *purgable organic carbon (POC), n*—carbon that purges from acidified samples, also known as volatile organic compounds (VOC).

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

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

3.2.7 *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 an inorganic and organic compound. This test method can be used to make independent measurements of IC, NPOC, and TC, and can also determine OC by the difference of TC and IC. DOC is determined on samples that have been filtered through a 0.45-µm filter.

4.2 TOC and DOC procedures require that IC has been removed from the sample before it is analyzed for organic carbon content. The sample free of IC is injected into the TOC instrument where all carbon is converted to CO_2 and measured by the detector. Failure of the method to remove all IC prior to analysis for organic carbon will result in significant error. A diagram of suitable apparatus is given in Fig. 1.

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 pollutants in industrial wastewater. These measurements are also used in monitoring waste treatment processes.

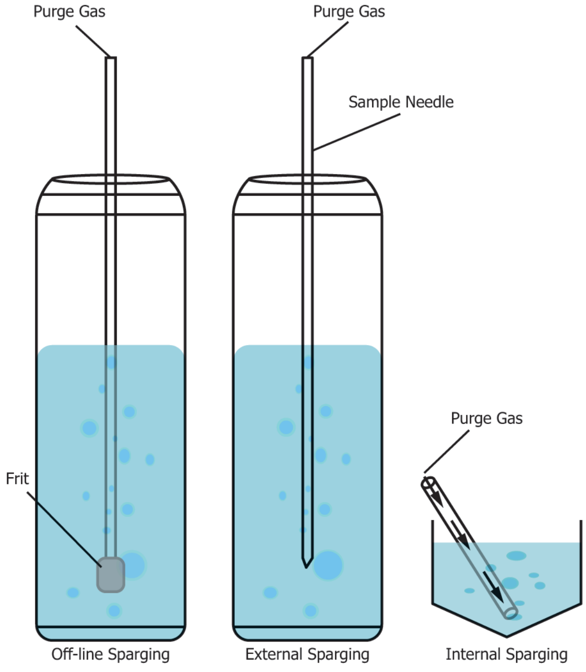

FIG. 1 TIC Removal

5.2 The relationship of TOC to other water quality parameters such as chemical oxygen demand (COD) and total oxygen demand (TOD) is described in the literature.[4]

6. Interferences and Limitations

6.1 The oxidation of dissolved carbon to CO_2 is brought about at high temperatures (680°C) in the presence of oxygen. A catalyst promotes the oxidation process and the resulting carbon dioxide is measured by a non-dispersive infrared detector (NDIR). Suspended and refractory materials are completely oxidized under these conditions.

6.2 Acid preservation can precipitate some compounds, such as humic acids, removing them from solution and causing erroneously low results.

6.3 Homogenizing or sparging of a sample, or both, may cause loss of purgable organic compounds, thus yielding a value lower than the true TOC level. (For this reason, such measurements are sometimes known as NPOC). The extent and significance of such losses must be evaluated on an individual basis. Comparison of the difference, if any, between NPOC and TOC by subtraction represents POC lost during sparging.

6.4 If POC is important then TOC must be measured by subtraction:

$$TOC = TC - TIC \tag{2}$$

6.5 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 ground water high in IC and low in TOC will give a poorer TOC value as (TC – IC) than by direct measurement as NPOC.

6.6 Samples containing high levels (>1 ppm) of surfactant may lose TOC by foaming.

6.7 Elemental carbon may not be completely combusted; however, it is not generally found in water samples. Elemental carbon does not form during the catalytic oxidation of water samples.

6.8 Inorganics dissolved in the sample are not volatilized into gas and remain on the catalyst or quartz shard surfaces. High amounts of solids eventually react with the quartz surfaces causing devitrification, or solidify in the catalyst bed decreasing flow rates. Limit sample volume injected to reduce the amount of soluble salts and to reduce cooling of the reaction chamber. Buildup of salts; reduction of flow rate, or large injection volumes could result in peak splitting.

6.9 Carbon in reagent water and reagent blanks can be reduced to a minimum, and consistent value, but cannot be completely eliminated. Analyzing low-level TOC (less than 1.0 mg/L) bears special consideration requiring that the same water used to set the baseline be used to prepare the calibration standards.

6.10 Atmospheric carbon dioxide absorbs into reagent water increasing its inorganic carbon content with time. The small levels of CO_2 absorbed into reagent water can cause considerable inaccuracies in low-level TIC analysis. For instance, a 40-millilitre vial of reagent water containing no detectable TIC was analyzed to contain 160 µg/LTIC after 1 hour of exposure to ambient air.

6.11 Trace organics in the atmosphere can be absorbed into reagent water increasing its organic carbon content with time. The small levels of organics absorbed into reagent water can cause considerable inaccuracies in low-level (<1 mg/L) TOC measurements.

7. Apparatus

NOTE 1—See also Fig. 2.

7.1 *Sampling Devices*—Manually operated or automatically operated sampling valves, or syringes are typically used with this method. Sampling devices with inside diameters as small as 0.15 mm may be used with samples containing little or no particulate matter. Larger inside dimensions, such as 0.2 mm, will be required for samples with particulate matter.

7.2 *Apparatus for Carbon Determination*—This instrument consists of reagent and sample introduction mechanism, a gas-sparged reaction vessel for TIC removal, the high temperature combustion chamber with catalyst, a gas demister or dryer and halogen trap, an optional CO_2 trap, a CO_2-specific infrared detector, a control system, and a display. Fig. 1 shows a diagram of such an arrangement.

7.2.1 Reaction vessel consists of TIC removal and the combustion chamber.

7.2.1.1 *TIC Removal*—Sparging requires an inert vessel with a capacity of at least double the sample size with provision for sparging with 50 to 200 mL/min of carbon-free gas. This procedure should remove essentially all IC in 2 to 10 min, depending on design and can be at room temperature or at elevated temperatures (≤70°C) to promote CO_2 removal. Verify that heated sparging does not remove >5 % of the NPOC. Fig. 1 illustrates three different options for TIC removal.

7.2.1.2 *Combustion Chamber*—A heated catalyst contained in a quartz tube, may contain quartz wool, quarts shards, or other items to protect the catalyst from dissolved salts to extend its life.

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[4] *Handbook for Monitoring Industrial Wastewater*, Section 5.3, U.S. Environment Protection Agency, August 1973, pp. 5–12.

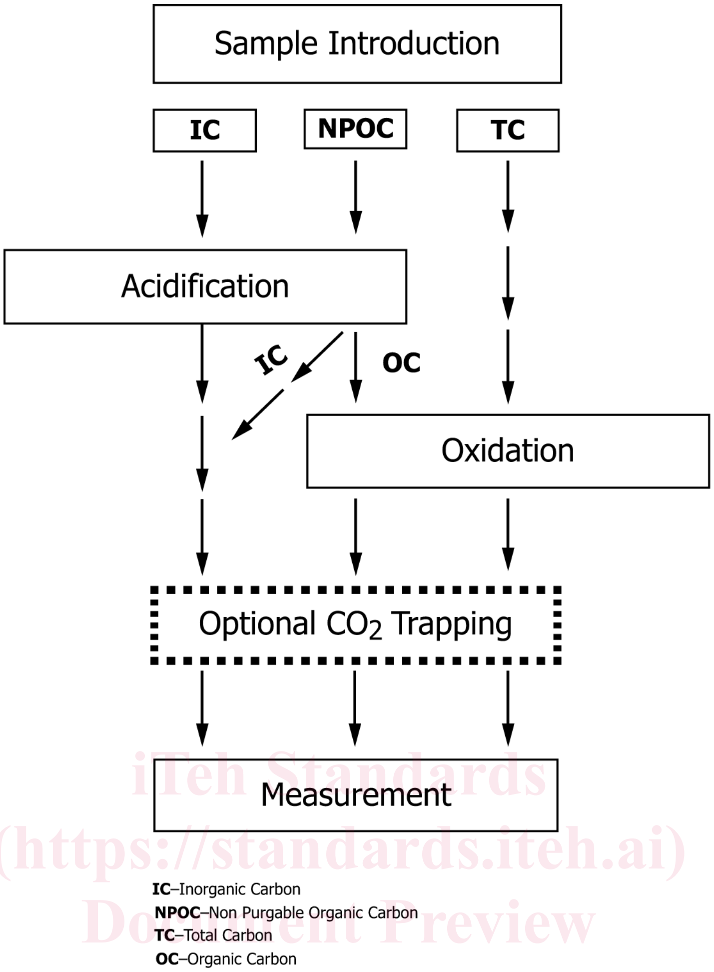

FIG. 2 Diagram of Apparatus

7.2.2 *Gas Conditioning*—The gas passing from the reactor is dried, and the CO_2 produced is either trapped and later released to the detector, or routed directly to the detector through a halogen-removing scrubber.

7.2.3 *Detector*—The CO_2 in the gas stream is detected by a CO_2-specific NDIR detector.

7.2.4 *Detector Response*—Integrated area unless CO_2 is collected and desorbed from a CO_2 specific trap. Area integration accurately quantifies carbon content in the event of split or overlapping peaks that result from furnace cooling or variable combustion rates of different organic molecules contained in a sample.

7.2.5 *Presentation of Results*—The NDIR detector output is related to stored calibration data and then displayed as milligrams of carbon per litre.

7.3 *Low TOC Sample Containers*—Analysis of TOC below 10 ppm requires the use of sample bottles and vials certified as low TOC. This avoids variable contribution of TOC and is especially important when analyzing TOC below 1 ppm.

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,[5] 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 Specification D1193, Type I or Type II. The indicated specification does not actually specify inorganic carbon or organic carbon levels but is recommended that NPOC be ≤ 0.05 mg/L. Higher 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

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[5] *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 *Annual 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.

significant, CO_2-free water may be prepared from reagent water by acidifying to pH 2, then sparging with fritted-glass sparger using CO_2-free gas (time will depend on volume and gas flow rate, and should be determined by test). Alternatively, if the carbon contribution of the reagent water is known accurately, its effect may be allowed for in preparation of standards and other solutions. CO_2-free water should be protected from atmospheric contamination. Glass containers are required for storage of water and standard solutions. It is recommended that the same reagent water be used in preparation of all standards and blanks per calibration.

8.3 *Acid*—Acid is used for sample preservation and TIC removal. Follow the manufacturers suggestions for acid and acid concentration used for TIC removal. Do not use nitric acid.

8.4 *Organic Carbon, Stock Calibration Standard Solution (1000 mg/L)*—Weigh 2.128 grams of anhydrous potassium hydrogen phthalate ($KHC_8H_4O_4$) previously dried for two hours at 120ºC and quantitatively transfer to a 1000-millilitre volumetric flask containing about 500 millilitres of reagent water. Stir to dissolve and add 1 millilitre of concentrated hydrochloric acid (HCl), dilute to the mark with reagent water and mix. Transfer to an amber glass reagent bottle and cap for storage. This stock solution, or dilutions of it, is used to calibrate and test performance of the carbon analyzer.

8.5 *Organic Carbon, Stock Calibration Verification Solution (1000 mg/L)*—Weigh 2.377 grams of sucrose (C_{12} $H_{22}O_{11}$) and quantitatively transfer to a 1000-millilitre volumetric flask containing about 500 millilitres of reagent water. Stir to dissolve and add 1 millilitre of concentrated hydrochloric acid (HCl), dilute to the mark with reagent water and mix. Transfer to an amber glass reagent bottle and cap for storage. This solution, or dilutions of it, is used to verify calibration accuracy and test performance of the carbon analyzer.

8.6 *Inorganic Carbon, Stock Calibration Standard Solution (1000 mg/L)*—Weigh 8.826 grams of anhydrous sodium carbonate (Na_2CO_3) previously dried at 120ºC for two hours and transfer to a 1000-millilitre volumetric flask containing about 500 millilitres of reagent water. Mix to dissolve, dilute to the mark, and mix.

8.7 *Inorganic Carbon, IC Test Solution (Alkalinity 834 mg* $CaCO_3$*/L)*—Dilute 10 millilitres of the inorganic carbon stock solution (Section 8.6) to 100 millilitres with reagent water. Use this solution to verify IC removal.

8.8 *Calibration Solutions*—TC, IC

8.8.1 *Organic Carbon Calibration Solutions*—At least 4 calibration concentrations and a calibration blank (CB) are used to prepare an initial calibration curve. Standards are prepared to cover the concentration of interest from the organic carbon stock calibration solution. Calibration standards are prepared in reagent water and preserved to pH <2 with concentrated HCl. Filtration of these standards for determination of dissolved organic carbon is unnecessary. These standards may be used for TC and NPOC calibrations. For NPOC the standards are sparged, just like samples, to remove the IC fraction. The calibration blank (CB) is a 0.0 mg C/L standard that contains the carbon contributed to the calibration standards by the reagent water. The CB is stored and treated the same as the calibration standards. These standards, if stored in the dark, are stable for about 30 days and may be used to recalibrate the instrument within the 30-day period. The CB stored with and prepared from the same reagent water as the calibration standards must be used as the blank when recalibrating the instrument. See Table 1 for calibration standard preparation.

8.8.2 *Inorganic Carbon Calibration Solutions*—At least 4 calibration concentrations and a CB are used to prepare an initial calibration curve. For best results, do not prepare inorganic carbon and organic carbon standards as mixed solutions. (These standards are not necessary for NPOC). See Table 1 for examples of calibration standard preparation.

8.9 *Gas Supply*—High-purity oxygen free of CO_2 and of organic matter is required. Use gas purity as specified by the equipment manufacturer. The use of oxygen is preferred.

9. Sampling and Sample Preservation

9.1 Collect the sample in accordance with Guides D1192, D4448, and D6538 and Practices D3370 and D6759.

9.2 To preserve samples for this analysis, store samples in low TOC glass at 2–6°C. To aid preservation, acidify the samples to a pH ≤2 with HCL, or the acid specified by the instrument manufacturer. It should be noted that acidification enhances loss of inorganic carbon. If the purgable organic fraction is important, fill the sample bottles to overflowing with a minimum of turbulence and cap them using a fluoropolymer-lined cap, without headspace. The sample must be analyzed within 28 days of collection.

TABLE 1 Preparation of Calibration Curve Standards for Organic Carbon and Inorganic Carbon

Cal Level	Concentration of Stock (mg/L)	Volume of Stock (mL)	Final Volume of Calibration Standard (mL)	Final Concentration of Calibrations Standard (mg/L)
Calibration Blank (CB)	- - -	0.0	1000	0.0
1	1000	0.5	1000	0.5
2	1000	1.0	1000	1.0
3	1000	10.0	1000	10.0
4	1000	25.0	1000	25.0
5	1000	50.0	1000	50.0
6	1000	100	1000	100
7	1000	200	1000	200