



Standard Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection¹

This standard is issued under the fixed designation D 4839; 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), and total organic carbon (TOC) in water, wastewater, and seawater in the range from 0.1 mg/L to 4000 mg/L of carbon.

1.2 This test method was used successfully with reagent water spiked with sodium carbonate, acetic acid, and pyridine. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 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 limit the maximum size of particles that can be so introduced.

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

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 Steam²

D 1193 Specification for Reagent Water²

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²

D 3370 Practices for Sampling Water from Closed Conduits²

D 4129 Test Method for Total and Organic Carbon in Water by Oxidation and Coulometric Detection³

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data²

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)*—carbon in the form of carbon dioxide, carbonate ion, or bicarbonate ion.

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

3.2.3 *total carbon (TC)*—the sum of IC and OC.

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

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, TOC, and TC, and can also determine IC by the difference of TC and TOC, and TOC as the difference of TC and IC.

4.2 The essentials of this test method are: (a) removal of IC, if desired, by acidification of the sample and sparging by carbon-free gas; (b) conversion of remaining carbon to CO₂ by action of persulfate, aided either by elevated temperature or ultraviolet (UV) radiation; (c) detection of CO₂ that is swept out of the reactor by a gas stream; and (d) conversion of detector signal to a display of carbon concentration in mg/L. 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.

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 CO₂ is brought

¹ This test method is under the jurisdiction of ASTM Committee D-19 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 *Annual Book of ASTM Standards*, Vol 11.01.

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

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

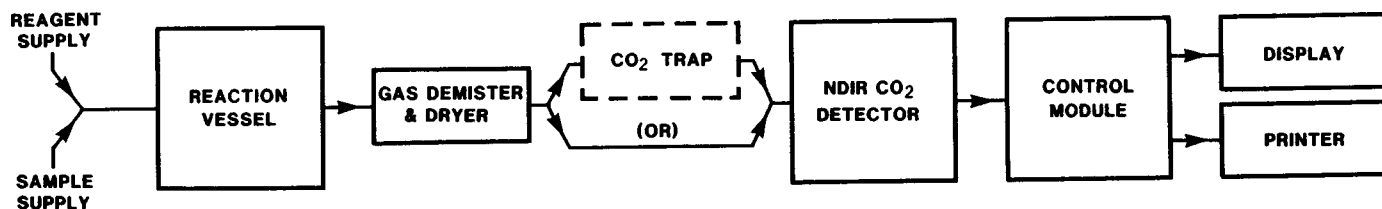


FIG. 1 Diagram of Apparatus

about at relatively low temperatures by the chemical action of reactive species produced by hot or UV-irradiated persulfate ions. Even if oxygen is used as the sparging gas, it makes a much lower contribution to oxidation than in high-temperature (combustive) systems. 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: (a) by monitoring reaction progress to verify that oxidation has been completed; (b) by rerunning the sample under more vigorous reaction conditions; (c) by analyzing the sample by an alternative method, such as Test Method D 4129, known to result in full recovery; or (d) by spiking samples with known refractories and determining recovery.

6.2 Chloride ion tends to interfere with oxidative reaction mechanisms in this test method, prolonging oxidation times and sometimes preventing full recovery. Follow manufacturer's instructions for dealing with this problem. See Appendix X1 for supporting data.

6.3 Homogenizing or sparging of a sample, or both, may cause loss of purgeable organic compounds, thus yielding a value lower than the true TOC level. (For this reason, such measurements are sometimes known as nonpurgeable organic carbon (NPOC)). The extent and significance of such losses must be evaluated on an individual basis. This may be done by comparing the TOC by difference (TC-IC) with the direct TOC figure, that is, that obtained from a sparged sample. The difference, if any, between these TOC figures represents purgeable organic carbon (POC) lost during sparging. Alternatively, direct measurement of POC can be made during sparging, using optional capabilities of the analyzer.

6.4 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.

7. Apparatus

7.1 *Homogenizing Apparatus*—A household blender is generally satisfactory for homogenizing immiscible phases in water.

7.2 *Sampling Devices*—Microlitre-to-millilitre syringes are typically required for this test method. Alternatives include manually operated or automatically operated sampling valves. 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 0.4 mm will be required for samples with particulate matter.

NOTE 1—See 6.1 concerning oxidation of particulate matter.

7.3 *Apparatus for Carbon Determination*—This instrument consists of reagent and sample introduction mechanism, a gas-sparged reaction vessel, a gas demister or dryer, or both, an optional CO₂ trap, a CO₂-specific infrared detector, a control system, and a display. Fig. 1 shows a diagram of such an arrangement.

7.3.1 Sparging requires an inert vessel with a capacity of at least double the sample size with provision for sparging with 50 to 100 mL/min of carbon free gas. This procedure will remove essentially all IC in 2 to 10 min, depending on design.

7.3.2 *Oxidation*—The reaction assembly contains reagent and sample introduction devices, and a reactor vessel with sparging flow of carbon-free gas. The vessel may be heated by an external source, and may contain a UV lamp. The reaction vessel and sparging vessel (see 6.3.1) may be combined.

7.3.3 *Gas Conditioning*—The gas passing from the reactor is dried, and the CO₂ produced is either trapped and later released to the detector, or routed directly to the detector through a chlorine-removing scrubber.

7.3.4 *Detector*—The CO₂ in the gas stream is detected by a CO₂-specific nondispersive infrared (NDIR) detector.

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

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 D 1193, Type I or Type II. The indicated specification does not actually specify inorganic carbon or organic carbon levels. These 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 significant, CO₂-free water may be prepared from reagent water by acidifying to pH 2, then

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 *Anal. Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

sparging with fritted-glass sparger using CO₂-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. CO₂-free water should be protected from atmospheric contamination. Glass containers are required for storage of water and standard solutions.

8.3 Acid—Various concentrated acids may be used for acidification of samples and of the oxidizing reagent. Acids such as phosphoric (sp gr 1.69), nitric (sp gr 1.42), or sulfuric (sp gr 1.84) are suitable for most applications. Sulfuric acid should be used in the form of a 1 + 1 dilution, for safety reasons. Hydrochloric acid is not recommended.

8.4 Organic Carbon, Standard Solution (2000 mg/L)—Choose a water-soluble, stable reagent grade compound, such as benzoic acid or anhydrous potassium hydrogen phthalate (KHC₈H₄O₄). Calculate the weight of compound required to make 1 L of organic carbon standard solution; for example, KHC₈H₄O₄ = 0.471 g of carbon per gram, so one litre of 2 g/L of standard requires 2/0.471, or 4.25, grams of KHP. Dissolve the required amount of standard in some CO₂-free water in a 1-L volumetric flask, add 1 mL of acid, and dilute to volume. This stock solution, or dilutions of it, may be used to calibrate and test performance of the carbon analyzer.

8.5 Persulfate Solution—Prepare by dissolving the appropriate weight of potassium or sodium persulfate in 1 L of water, to produce the concentration specified by the instrument manufacturer. If specified, add 1 mL of phosphoric acid (sp gr 1.69) and mix well. Store in a cool, dark place. Recipes for this reagent solution may be modified by manufacturers to meet the needs of specific applications, for example, high chloride samples.

8.6 Gas Supply—A gas free of CO₂ and of organic matter is required. Use a purity as specified by the equipment manufacturer. The use of oxygen is preferred for the UV-persulfate method, and nitrogen or helium is preferred if a CO₂ trap is used between reactor and detector.

9. Sampling and Sample Preservation

9.1 Collect the sample in accordance with Specification D 1192 and Practice D 3370.

9.2 To preserve samples for this analysis, store samples in glass at 4°C. To aid preservation, acidify the samples to a pH of 2. It should be noted that acidification will enhance loss of inorganic carbon. If the purgeable 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.

9.3 For monitoring of waters containing solids or immiscible liquids that are to be injected into the reaction zone, use a mechanical homogenizer or ultrasonic disintegrator. Filtering or screening may be necessary after homogenization to reject particle sizes that are too large for injection. Volatile organics may be lost. See 6.3.

9.4 For wastewater streams where carbon concentrations are greater than the desired range of instrument operation, dilute the samples as necessary.

10. Instrument Operation

10.1 Follow the manufacturer's instructions for instrument warmup, gas flows, and liquid flows.

11. Calibration

11.1 Use the stock solution of 2000 mg/L of carbon, and various dilutions of it, for calibration.

NOTE 2—Dilutions should be made with CO₂-free water (see 8.2).

11.2 Calibration protocols may vary with equipment manufacturers. However, in general, calibrate the instrument in accordance with the manufacturer's instructions, and use standards to verify such calibration in the specific range of interest for actual measurements. Plots of standard concentration versus instrument reading may be used for calibration or to verify linearity of response.

11.3 Establish instrument blank according to the manufacturer's instructions.

12. Procedure

12.1 Mix or blend each sample thoroughly and carry out any necessary dilution to bring the carbon content within range of the instrument.

12.2 If inorganic carbon is to be measured directly, inject the sample into the analyzer under appropriate conditions.

12.3 If inorganic carbon is to be removed by sparging prior to sample introduction, acidify to approximately pH 2 with concentrated acid (if not already done) and sparge with an appropriate flow of gas. Samples with high alkali content or buffer capacity may require larger amounts of acid. In such cases, incorporate this dilution into the calculation. If incomplete sparging of CO₂ from IC is suspected, sparge and analyze the sample and then repeat the procedure until appropriate conditions are established. In difficult conditions, use of a fritted-glass sparger may help.

12.4 To measure TOC, inject an appropriate volume of the sample into the analyzer. If external sparging is required to remove IC, inject a sparged sample for the TOC measurement. See 6.3.

12.5 To measure TC, inject an appropriate volume of unsparged sample.

13. Calculation

13.1 Read carbon values directly from a digital display or printer, or both.

14. Precision and Bias ⁶

14.1 Collaborative Test—This test method was evaluated by sending seven identical sample to each of ten laboratories and asking them to measure TOC and TC exactly in accordance with this test method. Three of the ten laboratories did not make the TC measurement. One of the samples consisted of laboratory reagent water. The other six were of that water spiked to various levels with acetic acid, pyridine, and sodium carbonate. TC levels ranged from 0.6 to 2 000 mg/L, and TOC

⁶ Supporting data are available from ASTM Headquarters. Request RR: D-19-1130.

levels from 0.3 to 1 700 mg/L. An F test at 95 % confidence level showed no significant difference between the results of the five laboratories using UV-persulfate oxidation and those of the five laboratories using hot persulfate. Consequently, results were pooled for further analysis.

14.2 Removal of Outliers—Application of outlier tests specified in Practice D 2777 – 85 resulted in the elimination of one laboratory's TC and TOC results. In addition, three laboratories did not perform the TC analysis, so the effective number of laboratories was six for the TC measurement. Five of their individual results were later eliminated by outlier test. In the TOC determination, one additional laboratory failed the outlier test, leaving a total of eight. Three individual results were later eliminated.

14.3 Precision—Separate determinations of precision were made for TC and TOC measurements:

$$\text{For TC: } S_r = 0.03x + 0.3$$

$$S_o = 0.01x + 0.2$$

$$\text{For TOC: } S_r = 0.08x + 0.1$$

$$S_o = 0.04x + 0.1$$

where:

x = the recovered C concentration, mg/L,

S_r = overall precision, and

S_o = single-operator precision.

Fig. 2 shows a log-log plot of the overall and single-operator precision of all TC and TOC measurements not eliminated by outlier tests.

14.4 Bias—Fig. 3 plots “amount added” against “amount found,” with overall precision shown as an error bar. Bias significant at the 95 % level (student's t -test) is flagged. Water that was used as one of the samples is omitted, since no value equivalent to “amount added” is available. The contribution of the carbon in the water to the spiked samples was allowed for before analysis of bias. In general, bias is positive, with the

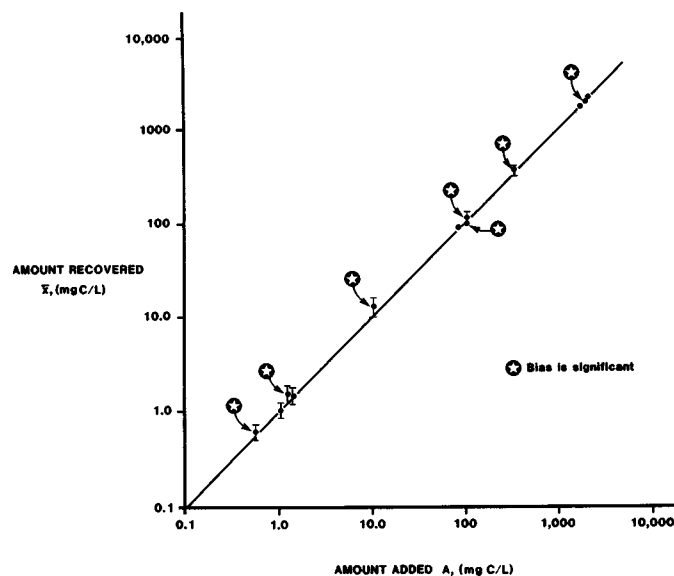


FIG. 3 Bias: Amount Added Versus Amount Recovered

values running from 1 % to 25 % of the amount added, with no particular pattern evident. Of the twelve bias measurements, ten were below 10 %. Users of this test method should make their own determination of bias.

14.5 Matrix Effects—Participants were asked to measure the TC and TOC levels in a water sample of their choice, and then to spike the sample with one of the study samples and to measure the sample again. The chosen samples were: sink waste; DI water with KHP; soil solution; tap water with added IC; plant waste stream; synthetic sewage, and anion resin brine wash. TC recoveries averaged 86 % (range from 74 % to 92 %), and TOC, 82 % (from 47 % to 92 %). The negative bias, versus the positive bias noted in 14.4, can reflect incomplete oxidation of spiking compounds in the presence of other organics, errors introduced by sample handling, or other effects. In any event, no one matrix was studied in sufficient depth to provide an answer. Users of this test method should conduct their own experiments to determine recovery in their particular circumstances.

14.6 The quality assurance (QA)/quality control (QC) portion of this test method has not been completely established at this time. It is the intent of Subcommittee D19.06 that procedures be incorporated into this test method that require a minimum level of QC. These procedures will require, at minimum, a method startup check and ongoing performance checks. The analysts performing this test method will be required to measure their performance against the performance level achieved by the laboratories that participated in the ASTM round-robin study done on this test method. These formal QC procedures will be incorporated at such time as they have been officially accepted by the Society. See Practice D 4210.

15. Keywords

15.1 carbon; carbon dioxide; low temperature oxidation; organic carbon; total carbon

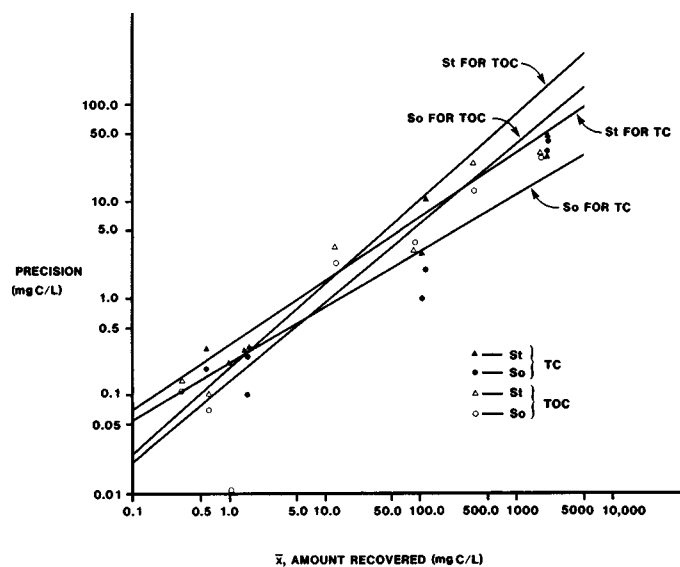


FIG. 2 Precision Versus Amount Recovered

APPENDIX

(Nonmandatory Information)

X1. RECOVERIES OF VARIOUS COMPOUNDS FROM CHLORIDE-CONTAINING SOLUTIONS WITH UV-PERSULFATE OXIDATION

X1.1 *Conditions*—Inject into the instrument 200 μL of solution, containing 100 ppm of carbon in the form of the compound indicated plus 1.8 % of chloride ion. Take results at the completion of oxidation or after 8 min, whichever occurs first. (See Table X1.1Table X1.2.)

TABLE X1.1 Percent Recovery

Analyte	No Mercuric Reagent	With Mercuric Reagent
Potassium hydrogen phthalate	90.5	101.2
Urea	101.1	...
Methanol	96.6	99.3
Nicotinic acid	91.0	97.9
Pyridine	88.6	98.0
Proline	86.0	92.2
<i>n</i> -Butanol	74.3	96.2
Acetic acid	66.5	101.3
Leucine	64.7	96.6
Acetonitrile	5.0	88.0

TABLE X1.2 Recoveries of Potassium Hydrogen Phthalate from Chloride-Containing Solutions Using Hot Persulfate Oxidation

ppm of Carbon	Recovery
200	99.4 %
800	92.0 %

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