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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Total Organic Carbon in Water[1]

This standard is issued under the fixed designation D 2579; 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.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

ε[1] NOTE—The title was corrected, and editorial corrections were made throughout, in March 1994.

1. Scope

1.1 This test method covers the determination of total organic carbon in water and wastewater, including brackish waters and brines.

NOTE 1—Test Methods D 4129, D 4779, and D 4839 may also be used to measure carbon in water.

1.2 This procedure is applicable only to that carbonaceous matter in the sample that can be injected into the reaction zone. The syringe needle and injector opening size limit the maximum size of particles that can be injected into the reaction zone. Sludge and sediment samples should be suspended in water prior to sampling with a micropipet, where applicable.

1.3 In addition to laboratory analyses, these procedures may be applied to stream monitoring.

1.4 This test method is applicable to determining total organic carbon in water in the range from 2 to 200 mg/L.[2]

1.5 It is the user's responsibility to ensure the validity of this test method on water of untested matrices.

1.6 *This standard does not purport to address all of the safety problems, 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 a specific hazard statement, see Note A3.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 513 Test Methods for Total and Dissolved Carbon Dioxide in Water[3]

D 1129 Terminology Relating to Water[3]

D 1192 Specification for Equipment for Sampling Water and Steam[3]

D 1193 Specification for Reagent Water[3]

D 3370 Practices for Sampling Water[3]

D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents[4]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[3]

D 4129 Test Method for Total and Organic Carbon in Water by Oxidation and Coulometric Detection[4]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]

D 4779 Test Method for Total, Organic, and Inorganic Carbon in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection[4]

D 4839 Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

4. Summary of Test Method

4.1 The water sample is homogenized or diluted, or both, as necessary. A micro portion is injected into a heated, catalyzed reaction zone in which the carbonaceous matter is converted to carbon dioxide. A flowing gas stream carries the gaseous reaction products through a detector which measures the carbon dioxide content of the gas stream. The detector output is graphically displayed by a recorder. The height of the peak is proportional to the carbon content of the sample. The proportionality is quantitated by a calibration curve prepared from known carbon content standards.

4.2 Since carbon dioxide is liberated from carbonates as well as from organic matter under the total carbon test conditions, carbonate carbon alone is determined by an injection into a separate reaction zone in which the temperature is too low to convert the organic matter to carbon dioxide. The organic carbon can thus be determined by difference. Alternately, the sample may be acidified to a pH of 2 or less and sparged with a carbon dioxide-free gas to remove carbonates and bicarbonates. The remaining solution can then be analyzed

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] Adapted from investigations at the Dow Chemical Co. and Union Carbide Corp.

[3] *Annual Book of ASTM Standards,* Vol 11.01.

[4] *Annual Book of ASTM Standards,* Vol 11.02.

for total carbon and thus organic carbon can be determined by virtue of acidification and sparging. See Annex A1.

4.3 Because of the various properties of carbon-containing compounds in water, any preliminary treatment of a sample prior to injection dictates a definition of the carbon measured. Filtration of the sample prior to injection will limit the carbon measured to soluble carbonates and soluble organic matter. Homogenizing permits determination of the carbon in insoluble carbonates and insoluble organic liquids and solids also. See Annex A2.

5. Significance and Use

5.1 This test method is used for determining the concentration of organic carbon in water that comes from a variety of natural, domestic, and industrial sources. Typically, these measurements are used to monitor and control organic pollutants in industrial wastewater. These measurements are also used to monitor and control domestic and industrial waste treatment processes.

5.2 When a sample is homogenized so that particulate and dissolved carbon from both organic and inorganic sources is determined, the measurement is called total carbon (TC). When inorganic carbon response is eliminated by one of the techniques prescribed in this test method, the measurement is called total organic carbon (TOC). When particulates are removed prior to analysis the measurement is called dissolved carbon (DC), or dissolved organic carbon (DOC) if inorganic carbon response has been eliminated.

5.3 Homogenizing or sparging of a sample, or both, may cause loss of volatile organics, thus yielding a negative error. The extent and significance of such losses must be evaluated on an individual basis.

5.4 The relationship of TOC to other water quality parameters such as COD and TOD is described in the literature.[5]

6. Apparatus

6.1 *Apparatus for Total and Carbonate Carbon Determination*[6]—A single- or dual-furnace unit, with gas supply, purification train, flow controls, nondispersive-type infrared stream analyzer set for carbon dioxide, and recorders.

6.2 *Sample Syringe*—A microlitre syringe of suitable volume having an all-metal tip and a 50-mm long, 0.12-mm inside diameter needle with a square end tip is recommended.[7] If desired, automatic injection devices may be used.

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

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references by water shall be understood to mean reagent water conforming to Specification D 1193, Type II. Where specified, carbon dioxide-free water is to be prepared by boiling distilled water in a conical flask for 20 min. The boiled water is cooled in the flask that is stoppered with a one-hole rubber stopper fitted to a soda lime-Ascarite drying tube. For larger (10 to 20 L) volumes of carbon dioxide-free water, the absorbed carbon dioxide may be removed by inserting a fritted-glass gas-dispersion tube to the bottom of the container and bubbling nitrogen through the water for at least 1 h. Carbon dioxide-free water may be stored if properly protected from atmospheric contamination.

NOTE 2—Glass containers are preferred for the storage of reagent water and most standard solutions. It is necessary, however, to provide protection against changes in quality due to the absorption of gases or water vapor from the laboratory air. As volumes of fluid are withdrawn from the container, the replacement air should be passed through a drying tube filled with equal parts of 8 to 20-mesh soda lime, oxalic acid, and 4 to 8-mesh anhydrous calcium chloride, each product being separated from the other by a glass wool plug.

7.3 *Carbonate Carbon Solution, Standard* (1 mL = 1 mg C)—Dissolve 4.417 g of anhydrous sodium carbonate (Na_2CO_3) and 3.500 g of anhydrous sodium bicarbonate ($NaHCO_3$) in carbon dioxide-free water and dilute to 1 L in a volumetric flask (Note 2).

7.4 *Gas Supply*—Use gas supply recommended by the equipment manufacturer.

7.5 *Organic Carbon Solution, Standard* (1 mL = 1 mg C)—Choose a water-soluble, stable reagent grade compound, such as anhydrous potassium acid phthalate ($KHC_8H_4O_4$) (Note 3). Calculate the weight of compound required to make 1 L of organic carbon standard solution, for example:

$$KHC_8H_4O_4/8\ C = 204/96 = 2.125\ g\ KHC_8H_4O_4$$

Weigh this amount and transfer to a 1-litre volumetric flask. Dissolve in carbon dioxide-free water and dilute to volume (Note 3).

NOTE 3—Although potassium acid phthalate is a convenient primary standard, any other organic compound of sufficient purity, stability, and water solubility can be used. Similarly 1 mg C/mL is a convenient standard solution concentration for most analysis, but other carbon concentrations may be used, if desired.

7.6 *Reaction Tubes and Catalyst Packings*—Reaction tubes and catalyst packings are available from the equipment manufacturers. If desired, the catalyst packings can be made in the laboratory by following the manufacturer's directions.

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[5] *Handbook for Monitoring Industrial Wastewater*, U.S. Environmental Protection Agency, August 1973, pp. 5–10 to 5–12.

[6] Analyzers manufactured by the following companies were used in the collaborative test program: Beckman Instruments, 2500 Harbor Blvd., Fullerton, CA 92634; OI Corp., P.O. Box 2980, College Station, TX 77841; Union Carbide Corp., P.O. Box 8361, S. Charleston, WV 25303.

[7] Syringes manufactured by the Hamilton Co., P.O. Box 10030, Reno, NV 89510, have been found satisfactory.

[8] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

8. Sampling and Sample Preservation

8.1 Collect the sample in accordance with the applicable ASTM Standard as follows: Specification D 1192 and Practices D 3370 and D 3694.

8.2 If total carbon is to be reported, fill the container completely and refrigerate at 4°C.

8.3 For samples containing free carbon dioxide or those that have been acidified, allow headspace in the container before refrigerating, and loosen the cap before adjusting the sample to ambient room temperature.

8.4 For monitoring of waters containing solids or immiscible liquids that are to be injected into the reaction zone, employ a mechanical homogenizer or ultrasonic disintegrator in a continuous flow cell. Practice filtration or screening after homogenization to reject particle sizes too large for injection if necessary.

8.5 For wastewater streams where carbon concentrations are greater than the desired range of instrument operation, provide on-stream dilution of the sample.

9. Instrument Adjustment

9.1 Turn on the analyzer, in accordance with the manufacturer's specifications. Allow a warm-up time of at least 2 h for attainment of stable operation; in daily use the analyzer can be left on continuously. Adjust the gas flow rate to 80 to 100 mL/min. Adjust either the recorder or amplifier gain, or both, so that the midrange carbon standard gives a peak height of approximately half the recorder scale. At this setting the noise level should be minimum for the range, normally less than 0.5 % of full scale. If the noise level is higher, the analyzer or the recorder may require servicing, or a higher concentration range should be used.

9.2 Immediately prior to carrying out calibrations or analyses, inject several portions of an appropriate standard into the reaction tube, until constant readings are obtained.

10. Calibration

10.1 Prepare a series of at least four carbon standard solution concentrations across the desired range by pipetting appropriate aliquots of the organic carbon or carbonate carbon solution, or both, into 100-mL volumetric flask. Dilute to volume with carbon dioxide-free water and mix.

10.2 *Manual Injection*—Rinse the syringe several times with the solution to be analyzed, fill, and adjust the precise volume. Wipe off the excess with soft paper tissue, taking care that no lint adheres to the needle. Insert the sample syringe, and inject the sample into the reaction tube with a single, rapid movement of the index finger. Leave the syringe in the holder until the flow rate returns to normal. Run duplicate determinations on each solution and on a water blank.

10.3 *Automatic Injection*—Successively introduce each standard until readings agree within ±1 %.

10.4 Direct the gas flow from the appropriate reaction tube to the analyzer. Check the gas flow rate (80 to 100 mL/min) and allow the baseline to become stabilized. Successively inject each standard and a water blank into the tube. Read the height of the corresponding recorder peaks. Repeat until peak heights are duplicated. Between injections allow the recorder pen to return to its baseline.

10.5 Repeat 10.2 through 10.4 for the other standard and reaction tube, if required.

10.6 Prepare standard curves by plotting milligram per litre of carbon versus respective peak height on rectangular coordinate graph paper for each parameter required (TC, IC, or TOC) by the specific analyzer used.

11. Procedure

11.1 Condition each sample to bring the homogeneous carbon content within range.

11.2 Following the technique described in 10.2, 10.3, and 10.4, inject samples successively into the appropriate tube and read the corresponding peak heights. From the appropriate calibration curve and each peak height observed, read the corresponding carbon concentration in milligram per litre.

11.3 Dilute the sample as required if carbon concentration is too high; or adjust the instruments to a higher concentration range, in accordance with the manufacturer's recommendations, up to the limit of the detection system.

12. Calculation

12.1 Calculate the total, carbonate, and organic carbon content of the sample in milligrams per litre as follows:

$$T = \text{avg } T \times A$$

where:
T = total carbon, mg/L, and
A = dilution factor.

$$C = \text{avg } C \times A$$

where:
C = carbonate carbon, mg/L.

$$O = T - C$$

where:
O = organic carbon, mg/L.

13. Precision and Bias

13.1 Precision and bias were determined by collaborative testing using three different instrument designs and by six different laboratories. Inorganic carbon was accounted for either by sparging or by difference. The matrix waters included tap water, lake water, and industrial effluent water. Each laboratory spiked known amounts of TOC into reagent water and a matrix water of its choice, and performed triplicate analyses of each spike level. The results of this testing are summarized in Table 1. For other matrices these data may not apply.

13.2 The precision of the test method as calculated by least squares analysis x_i, s_t, and s_o over the concentration range tested as follows:

$$\begin{aligned} \text{Reagent Water} \quad S_o &= 0.18x + 0.83 \\ S_t &= 0.045x + 1.09 \\ \text{Matrix Water} \quad S_o &= 0.027x + 0.29 \\ S_t &= 0.044x + 0.1.49 \end{aligned}$$

where:
x = concentration of TOC, mg/L.

14. Quality Assurance and Quality Control

14.1 Before this test method is applied to the analysis of

TABLE 1 Recoveries of Known Amounts of TOC[A]

Amount Added, mg/L	Amount Found, mg/L	n	s_t	s_o	Bias	%Bias	Statistical Significance, 95 % CL
			Reagent Water				
3.5	2.79	15	1.46	0.68	−0.7	−20.3	no
50	54.9	18	4.84	2.18	+ 4.9	+ 9.8	yes
105	108	18	3.38	2.71	+ 3	+ 2.86	yes
190	199	18	11.1	4.42	+ 9	+ 4.74	yes
			Matrix Water				
3.5	2.2	18	2.26	0.81	−1.3	−37.1	yes
50	53.4	17	4.08	2.23	+ 3.4	+ 6.8	yes
105	106	18	4.46	1.32	+ 1	+ 0.95	no
190	197	18	11.1	6.34	+ 7	+ 3.68	yes

[A] Supporting data are available from ASTM Headquarters. Request RR:D19 – 68.

samples of unknown TOC concentration, the analyst must establish quality control by procedures recommended in Practice D 4210 and Guide D 3856.

14.2 A duplicate sample and known standard must be analyzed each day that an analysis is performed. The duplicate and standard shall meet the limits as established by the control chart before a determination is considered satisfactory.

14.3 A blank and a spiked sample shall be analyzed each day that an analysis is performed. Spiking shall be in accordance with that outlined in the *Accuracy Check Using Recovery of Spikes* section of Guide D 3856. The blank shall be low enough that it will not unduly influence the data.

14.4 One sample must be analyzed in duplicate with each group of 10 or less samples. The results must meet the criteria established in Section 13 of this test method before the data for that batch or set of 10 samples is acceptable (Note 4).

14.5 Other QA/QC portions of this test method have not been completely established at this time. Analysts performing this test method will be required to measure their performance against the performance level achieved by the interlaboratory studies of this test method.

14.6 It is the intention of the Subcommittee D19.06 to incorporate formal QA/QC procedures into this test method at such time as they have passed the consensus process and have been officially accepted by the Society.

NOTE 4—The purpose of duplicate analyses is to ensure the analytical process is in control. The analyst must evaluate out of control responses for duplicates as either caused by out of control analytical processes or due to heterogeneous samples where duplication of results are difficult and do not reflect an out of control analytical process.

15. Keywords

15.1 infrared; organic carbon; oxidation; total carbon

ANNEXES

(Mandatory Information)

A1. CARBONATE CARBON

A1.1 Some models of the apparatus have only the total carbon reaction tube and are capable of determining only total carbon. Analysts having such apparatus may determine carbonate carbon separately by Test Method D 513 or other consensus standard method and correct the total carbon result to obtain organic carbon. Alternatively, carbon dioxide may be eliminated before the total carbon analysis, by either of the procedures described in the literature.[9] Then the combustion analysis represents organic carbon directly, although there may be a loss of volatile organics if the purging technique is employed.

[9] Van Hall, C. E., Barth, D., and Stenger, V. A., "Elimination of Carbonates from Aqueous Solutions Prior to Organic Carbon Determinations," *Analytical Chemistry,* Vol. 37, 1965, pp. 769–771.

A2. SAMPLE CONDITIONING FOR SUSPENDED SOLIDS AND IMMISCIBLE LIQUIDS

A2.1 If the sample is relatively homogeneous, no conditioning will be required except for possible dilution and mixing.

A2.2 Samples containing solids of no interest should be filtered prior to analysis. Sedimentation or centrifugation may also be employed for solids removal if desired.

A2.3 For laboratory analysis of samples containing immiscible liquid or solid phases of interest, homogenize the sample in a household-type blender or an ultrasonic disintegrator. Reproducibility of results will indicate when homogenization of the sample is complete.

A2.4 For on-stream analysis of samples containing immiscible liquid or solid phases of interest, the samples may be homogenized by means of an ultrasonic disintegrator or a Waring-type blender installed in a continuous flow cell. Samples would be taken downstream from the homogenizer.

A3. PACKING

A3.1 *Packing for Total Carbon Tube*[6]—Treat 15 g of long-fiber asbestos in a porcelain dish with a solution of 20 g of cobalt nitrate in 50 mL of water. Evaporate to dryness on a steam bath or hot plate. Place the dish in a cool muffle furnace, gradually heat up to 950°C, and hold there for 1 h. Cool the dish and contents and break up any large lumps. Add about 1 g to the combustion tube in small amounts, to provide a loose wad 40 to 60 mm in length near the exit end of the tube (Note A3.1).

NOTE A3.1—**Warning:** Caution should be exercised preparing this packing due to the hazardous nature of asbestos. Manufacturers have developed new materials that can be used.

A3.2 *Packing for Carbonate Tube*[6]—Place a small wad of quartz wool or asbestos near the exit end of the carbonate evolution tube. From the entrance end add 6 to 12-mesh quartz chips, allowing these to collect against the wad to a length of 100 mm. Pour an excess of 85 % phosphoric acid into the tube while holding it vertically, and allow the excess to drain out.

A3.3 *Packing for Total Carbon Tube*[6]—Place a small asbestos plug about 160 mm from the effluent end of a 400-mm long, 1.6-mm outside diameter Hastalloy tube. Pack with 100 mm of palladium wire crimped into about 2-mm cubes.

A3.4 *Packing for Carbonate Tube*[6]—Place a small asbestos plug about 160 mm from the effluent end of a 400-mm long, 160-mm outside diameter Hastalloy tube. Pack with 190 mm of 30 to 40-mesh sodium tetraphosphate.