5310 TOTAL ORGANIC CARBON (TOC)*

5310 A. Introduction

1. General Discussion

The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. Some of these carbon compounds can be oxidized further by biological or chemical processes, and the biochemical oxygen demand (BOD), assimilable organic carbon (AOC), and chemical oxygen demand (COD) methods may be used to characterize these fractions. Total organic carbon (TOC) is a more convenient and direct expression of total organic content than either BOD, AOC, or COD, but does not provide the same kind of information. If a repeatable empirical relationship is established between TOC and BOD, AOC, or COD for a specific source water then TOC can be used to estimate the accompanying BOD, AOC, or COD. This relationship must be established independently for each set of matrix conditions, such as various points in a treatment process. Unlike BOD or COD, TOC is independent of the oxidation state of the organic matter and does not measure other organically bound elements, such as nitrogen and hydrogen, and inorganics that can contribute to the oxygen demand measured by BOD and COD. TOC measurement does not replace BOD, AOC, and COD testing.

Measurement of TOC is of vital importance to the operation of water treatment and waste treatment plants. Drinking water TOCs range from less than 100 μg/L to more than 25,000 μg/L. Wastewater may contain very high levels of organic compounds (TOC $>$100 mg/L). Some of these applications may include waters with substantial ionic impurities as well as organic matter.

In many applications, the presence of organic contaminants may degrade ion-exchange capacity, serve as a nutrient source for undesired biological growth, or be otherwise detrimental to the process for which the water is to be utilized. For drinking waters in particular, organic compounds may react with disinfectants to produce potentially toxic and carcinogenic compounds.

To determine the quantity of organically bound carbon, the organic molecules must be broken down and converted to a single molecular form that can be measured quantitatively. TOC methods utilize high temperature, catalysts, and oxygen, or lower temperatures ($<$100 °C) with ultraviolet irradiation, chemical oxidants, or combinations of these oxidants to convert organic carbon to carbon dioxide (CO_2). The CO_2 may be purged from the sample, dried, and transferred with a carrier gas to a nondispersive infrared analyzer or coulometric titrator. Alternatively, it may be separated from the sample liquid phase by a membrane selective to CO_2 into a high-purity water in which corresponding increase in conductivity is related to the CO_2 passing the membrane.

2. Fractions of Total Carbon

The methods and instruments used in measuring TOC analyze fractions of total carbon (TC) and measure TOC by two or more determinations. These fractions of total carbon are defined as: inorganic carbon—the carbonate, bicarbonate, and dissolved CO_2; total organic carbon (TOC)—all carbon atoms covalently bonded in organic molecules; dissolved organic carbon (DOC)—the fraction of TOC that passes through a 0.45-μm-pore-diam filter; suspended organic carbon—also referred to as particulate organic carbon, the fraction of TOC retained by a 0.45-μm filter; purgeable organic carbon—also referred to as volatile organic carbon, the fraction of TOC removed from an aqueous solution by gas stripping under specified conditions; and nonpurgeable organic carbon—the fraction of TOC not removed by gas stripping.

In most water samples, the inorganic carbon fraction is many times greater than the TOC fraction. Eliminating or compensating for inorganic carbon interferences requires determinations of both TC and inorganic carbon to measure TOC. Inorganic carbon interference can be eliminated by acidifying samples to pH 2 or less to convert inorganic carbon species to CO_2. Subsequent purging of the sample with a purified gas or vacuum degassing removes the CO_2 by volatilization. Sample purging also removes purgeable organic carbon so that the organic carbon measurement made after eliminating inorganic carbon interferences is actually a nonpurgeable organic carbon determination: determine purgeable organic carbon to measure TOC. In many surface and ground waters the purgeable organic carbon contribution to TOC is negligible. Therefore, in practice, the nonpurgeable organic carbon determination is substituted for TOC.

Alternatively, inorganic carbon interference may be compensated for by separately measuring total carbon (TC) and inorganic carbon. The difference between TC and inorganic carbon is TOC.

The purgeable fraction of TOC is a function of the specific conditions and equipment employed. Sample temperature and salinity, gas-flow rate, type of gas diffuser, purging-vessel dimensions, volume purged, and purging time affect the division of TOC into purgeable and nonpurgeable fractions. When separately measuring purgeable organic carbon and nonpurgeable organic carbon on the same sample, use identical conditions for purging during the purgeable organic carbon measurement as in purging to prepare the nonpurgeable organic carbon portion for analysis. Consider the conditions of purging when comparing purgeable organic carbon or nonpurgeable organic carbon data from different laboratories or different instruments.

3. Selection of Method

The high-temperature combustion method (B) is suitable for samples with higher levels of TOC that would require dilution for the various persulfate methods (5310C or D). Generally, it also will determine organic carbon from compounds that are chemically refractory and not determined by 5310C or D. High-temperature combustion may be desirable for samples containing

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high levels of suspended organic carbon, which may not be efficiently oxidized by persulfate and/or UV methods. Interlaboratory studies have shown biases on the order of 1 mg/L using older high-temperature instruments. With newer instruments, detection limits as low as 10 μg/L have been reported. Some high-temperature combustion instruments are not designed for levels below 1 mg/L. The high-temperature methods accumulate nonvolatile residues in the analyzer, whereas, in 5310C, residuals are drained from the analyzer. Section 5310C generally provides better sensitivity for lower-level (<1 mg/L) samples. Persulfate and/or UV oxidation are useful for TOC as low as 10 μg/L. Because the range of sensitivity of the methods overlaps, other factors may dictate method choice in the range of 1 mg/L to 50 mg/L. A method may be chosen on the basis of desired precision, ease of use, cost, etc. Section 5310D generally is equivalent to 5310C, but the equipment for 5310D is no longer manufactured.

To qualify a particular instrument for use, demonstrate that the single-user precision and bias given in each method can be reproduced. Also, preferably demonstrate the overall precision by conducting in-house studies with more than one operator.

Evaluate the selected method to ensure that data quality objectives are attained. Evaluate method detection level in a matrix as similar as possible to the unknowns as described in Section 1030C. Be aware that instrument blanks are handled in a variety of ways in TOC analyzers and that the true magnitude of the blank may not be readily apparent to the analyst. Some instruments "zero out" much of the blank by adjusting the zero on the detector. Others enter blank values in units such as mv responses rather than absolute concentrations, whereas other instruments accumulate the total blank in the system during a blank run. Carefully observe the variability of low-level measurements and check it any time reagents or instrument operations are changed. The following methods note that when a water blank is run there is a contribution to the observed blank value from the level of carbon in the blank water.

The methods show expected single-operator and multiple-laboratory precision. These equations are based on referenced interlaboratory studies that in some cases were performed on older equipment. The range of testing is important to observe because the error and bias generally will be some significant fraction of the low standard. Consult references to determine type of equipment and conditions of the interlaboratory study. Determine the performance of the instrument being used by analyzing waters with matrices similar to those of unknowns, using the procedures outlined in Section 1040B.

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5310 B. High-Temperature Combustion Method

1. General Discussion

The high-temperature combustion method has been used for a wide variety of samples, but its utility is dependent on particle size reduction because it uses small-orifice syringes.

a. Principle: The sample is homogenized and diluted as necessary and a microportion is injected into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide, platinum group metals, or barium chromate. The water is vaporized and the organic carbon is oxidized to CO_2 and H_2O. The CO_2 from oxidation of organic and inorganic carbon is transported in the carrier-gas streams and is measured by means of a nondispersive infrared analyzer, or titrated coulometrically.

Because total carbon is measured, inorganic carbon must be removed by acidification and sparging or measured separately and TOC obtained by difference.

Measure inorganic carbon by injecting the sample into a reaction chamber where it is acidified. Under acidic conditions, all inorganic carbon is converted to CO_2, which is transferred to the detector and measured. Under these conditions organic carbon is not oxidized and only inorganic carbon is measured.

Alternatively, convert inorganic carbonates to CO_2 with acid

and remove the CO_2 by purging before sample injection. The sample contains only the nonpurgeable organic carbon fraction of total carbon: a purgeable organic carbon determination also is necessary to measure TOC.

b. Interference: Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles also can be lost during sample blending, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection. Filtration, although necessary to eliminate particulate organic matter when only DOC is to be determined, can result in loss or gain of DOC, depending on the physical properties of the carbon-containing compounds and the adsorption or desorption of carbonaceous material on the filter. Check filters for their contribution to DOC by analyzing a filtered blank. Note that any contact with organic material may contaminate a sample. Avoid contaminated glassware, plastic containers, and rubber tubing. Analyze sample treatment, system, and reagent blanks.

Combustion temperatures above 950°C are required to decompose some carbonates. Systems that use lower temperatures must destroy carbonates by acidification. Elemental carbon may not be oxidized at lower temperatures but generally it is not present in water samples nor is it formed during combustion of dilute samples. The advantage of using lower temperatures (680°C) is that fusion of dissolved salts is minimized, resulting in lower blank values. Gases evolved from combustion, such as water, halide compounds, and nitrogen oxides, may interfere with the detection system. Consult manufacturers' recommendations regarding proper selection of scrubber materials and check for any matrix interferences.

The major limitation to high-temperature techniques is the magnitude and variability of the blank. Instrument manufacturers have developed new catalysts and procedures that yield lower blanks, resulting in lower detection levels.

c. Minimum detectable concentration: 1 mg C/L or less, depending on the instrument used. This can be achieved with most high-temperature combustion analyzers although instrument performance varies. The minimum detectable concentration may be reduced by concentrating the sample, or by increasing the portion taken for analysis.

d. Sampling and storage: If possible, rinse bottles with sample before filling and carry field blanks through sampling procedure to check for any contamination that may occur. Collect and store samples in glass bottles protected from sunlight and seal with TFE-backed septa. Before use, wash bottles with acid, seal with aluminum foil, and bake at 400°C for at least 1 h. Wash uncleaned TFE septa with detergent, rinse repeatedly with organic-free water, wrap in aluminum foil, and bake at 100°C for 1 h. Check performance of new or cleaned septa by running appropriate blanks. Preferably use thick silicone rubber-backed TFE septa with open ring caps to produce a positive seal. Less rigorous cleaning may be acceptable if the concentration range is relatively high. Check bottle blanks with each set of sample bottles to determine effectiveness or necessity of cleaning. Preserve samples that cannot be examined immediately by holding at 4°C with minimal exposure to light and atmosphere. Acidification with phosphoric or sulfuric acid to a pH $\leq$2 at the time of collection is especially desirable for unstable samples, and may be used on all samples: acid preservation, however, invalidates any inorganic carbon determination on the samples.

2. Apparatus

a. Total organic carbon analyzer, using combustion techniques.

b. Sampling, injection, and sample preparation accessories, as prescribed by instrument manufacturer.

c. Sample blender or homogenizer.

d. Magnetic stirrer and TFE-coated stirring bars.

e. Filtering apparatus and 0.45-μm-pore-diam filters. Preferably use HPLC syringe filters with no detectable TOC blank. Glass fiber or silver membrane filters also can be used. Rinse filters before use and monitor filter blanks.

3. Reagents

a. Reagent water: Prepare reagents, blanks, and standard solutions from reagent water with a TOC value less than 2 $\times$ the MDL (see Sections 1030 and 1080).

b. Acid: Phosphoric acid, H_3PO_4. Alternatively use sulfuric acid, H_2SO_4.

c. Organic carbon stock solution: Dissolve 2.1254 g anhydrous primary-standard-grade potassium biphthalate, $C_8H_5KO_4$, in carbon-free water and dilute to 1000 mL; 1.00 mL = 1.00 mg carbon. Prepare laboratory control standards using any other appropriate organic-carbon-containing compound of adequate purity, stability, and water solubility. Preserve by acidifying with H_3PO_4 or H_2SO_4 to pH $\leq$2, and store at 4°C.

d. Inorganic carbon stock solution: Dissolve 4.4122 g anhydrous sodium carbonate, Na_2CO_3, in water, add 3.497 g anhydrous sodium bicarbonate, $NaHCO_3$, and dilute to 1000 mL; 1.00 mL = 1.00 mg carbon. Alternatively, use any other inorganic carbonate compound of adequate purity, stability, and water solubility. Keep tightly stoppered. Do not acidify.

e. Carrier gas: Purified oxygen or air, CO_2-free and containing less than 1 ppm hydrocarbon (as methane).

f. Purging gas: Any gas free of CO_2 and hydrocarbons.

4. Procedure

a. Instrument operation: Follow manufacturer's instructions for analyzer assembly, testing, calibration, and operation. Adjust to optimum combustion temperature before using instrument; monitor temperature to insure stability.

b. Sample treatment: If a sample contains gross solids or insoluble matter, homogenize until satisfactory replication is obtained. Analyze a homogenizing blank consisting of reagent water carried through the homogenizing treatment.

If inorganic carbon must be removed before analysis, transfer a representative portion (10 to 15 mL) to a 30-mL beaker, add acid to reduce pH to 2 or less, and purge with gas for 10 min. Inorganic carbon also may be removed by stirring the acidified sample in a beaker while directing a stream of purified gas into the beaker. Because volatile organic carbon will be lost during purging of the acidified solution, report organic carbon as total nonpurgeable organic carbon. Check efficiency of inorganic carbon removal for each sample matrix by splitting a sample into two portions and adding to one portion an inorganic carbon level similar to that of the

sample. The TOC values should agree; if they do not, adjust sample container, sample volume, pH, purge gas flow rate, and purge time to obtain complete removal of inorganic carbon.

If the available instrument provides for a separate determination of inorganic carbon (carbonate, bicarbonate, free CO_2) and total carbon, omit decarbonation and determine TOC by difference between TC and inorganic carbon.

If dissolved organic carbon is to be determined, filter sample through 0.45-μm-pore-diam filter; analyze a filtering blank.

c. Sample injection: Withdraw a portion of prepared sample using a syringe fitted with a blunt-tipped needle. Select sample volume according to manufacturer's direction. Stir samples containing particulates with a magnetic stirrer. Select needle size consistent with sample particulate size. Other sample injection techniques, such as sample loops, may be used. Inject samples and standards into analyzer according to manufacturer's directions and record response. Repeat injection until consecutive measurements are obtained that are reproducible to within $\pm 10\%$.

d. Preparation of standard curve: Prepare standard organic and inorganic carbon series by diluting stock solutions to cover the expected range in samples within the linear range of the instrument. Dilute samples higher than the linear range of the instrument in reagent water. Inject and record peak height or area of these standards and a dilution water blank. Plot carbon concentration in milligrams per liter against corrected peak height or area on rectangular coordinate paper. This is unnecessary for instruments provided with a digital readout of concentration.

With most TOC analyzers, it is not possible to determine separate blanks for reagent water, reagents, and the entire system. In addition, some TOC analyzers produce a variable and erratic blank that cannot be corrected reliably. In many laboratories, reagent water is the major contributor to the blank value. Correcting only the instrument response of standards (which contain reagent water + reagents + system blank) creates a positive error, while also correcting samples (which contain only reagents and system blank contributions) for the reagent water blank creates a negative error. Minimize errors by using reagent water and reagents low in carbon.

Inject samples and procedural blanks (consisting of reagent water taken through any pre-analysis steps—values are typically higher than those for reagent water) and determine sample organic carbon concentrations directly from the readout or measurements by comparing corrected instrument response to the calibration curve. Instruments with coulometric detectors do not require calibration curves. Regularly analyze laboratory control samples to confirm performance of the instrument (see Quality Control, below). These detectors accumulate the system blank; therefore, monitor system blank regularly.

5. Calculations

Calculate corrected instrument response of standards and samples by subtracting the reagent-water blank instrument response from that of the standard and sample. Prepare a standard curve of corrected instrument response vs. TOC concentration. Subtract procedural blank from each sample instrument response and compare to standard curve to determine carbon content. Apply appropriate dilution factor when necessary. Subtract inorganic carbon from total carbon when TOC is determined by difference.

NOTE: The reagent water blank may include an instrument contribution not dependent on reagent-water carbon, and a true response due to reagent-water carbon. When reagent-water carbon is a significant fraction of reagent-water blank, a negative error no larger than reagent-water blank is introduced in the sample values. If TOC analyzer design permits isolation of each of the contributions to the total blank, apply appropriate blank corrections to instrument response of standards (reagent blank, water blank, system blank) and sample (reagent blank and system blank).

6. Quality Control

The quality control practices considered to be an integral part of each method are summarized in Table 5020:I.

Determine instrument detection limit according to Section 1030.

After every tenth analysis, analyze a blank and a laboratory control sample prepared from a source of material other than the calibration standards, at a level similar to the analytical samples. Preferably prepare the laboratory control sample in a matrix similar to that of the samples. Alternatively, periodically make known additions to samples to ensure recovery from unknown matrices.

7. Precision

The difficulty of sampling particulate matter on unfiltered samples limits the precision of the method to approximately 5 to 10%.

Interlaboratory studies of high-temperature combustion methods have been conducted in the range above 2 mg/L.[1] The resulting equation for single-operator precision on matrix water is:

$$S_o = 0.027x + 0.29$$

Overall precision is:

$$S_t = 0.044x + 1.49$$

where:

S_o = single-operator precision,
S_t = overall precision, and
x = TOC concentration, mg/L.

8. Reference

1. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1994. Standard Test Method for Total and Organic Carbon in Water by High Temperature Oxidation and by Coulometric Detection. D4129–88. Annual Book of ASTM Standards. American Soc. Testing & Materials, Philadelphia, Pa.

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5310 C. Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method

1. General Discussion

Many instruments utilizing persulfate oxidation of organic carbon are available. They depend either on heat or ultraviolet irradiation activation of the reagents. These oxidation methods provide rapid and precise measurement of trace levels of organic carbon in water.

a. Principle: Organic carbon is oxidized to carbon dioxide, CO_2, by persulfate in the presence of heat or ultraviolet light. The CO_2 produced may be purged from the sample, dried, and transferred with a carrier gas to a nondispersive infrared (NDIR) analyzer, or be coulometrically titrated, or be separated from the liquid stream by a membrane that allows the specific passage of CO_2 to high-purity water where a change in conductivity is measured and related to the CO_2 passing the membrane.

Some instruments utilize an ultraviolet lamp submerged in a continuously gas-purged reactor that is filled with a constant-feed persulfate solution. The samples are introduced serially into the reactor by an autosampler or they are injected manually. The CO_2 produced is sparged continuously from the solution and is carried in the gas stream to an infrared analyzer that is specifically tuned to the absorptive wavelength of CO_2. The instrument's microprocessor calculates the area of the peaks produced by the analyzer, compares them to the peak area of the calibration standard stored in its memory, and prints out a calculated organic carbon value in milligrams per liter.

Other UV-persulfate instruments use continuous-flow injection of the sample into the instrument. Removal of inorganic carbon by vacuum degassing is provided optionally. The sample is acidified and persulfate added. Sample flow is split; one channel passes to a delay coil while the other passes through the UV reactor. The CO_2 from each stream is separated from the sample stream by membranes selectively permeable to CO_2 that allow the CO_2 to pass into high-purity water where change in conductivity is measured. CO_2 from the non-UV-irradiated stream represents inorganic carbon. CO_2 from the irradiated stream represents TC. The instrument automatically converts the detector signals to unit of concentration (mg/L or μg/L). The TOC is calculated as the difference between the TC and inorganic carbon channels.

Heated-persulfate instruments utilize a digestion vessel heated to 95 to 100°C. Samples are added by direct injection, loop injection, line injection, or autosampler. After inorganic carbon is removed by acidification and sparging, a measured amount of persulfate solution is added to the sample. After an oxidation period, the resulting CO_2 is sparged from the solution and carried to an infrared analyzer specifically tuned to the absorptive wavelength of CO_2. The instrument's microprocessor converts the detector signal to organic carbon concentrations in mg/L based on stored calibration data.

b. Interferences: See 5310B.1*b*. Insufficient acidification will result in incomplete release of CO_2.

The intensity of the ultraviolet light reaching the sample matrix may be reduced by highly turbid samples or with aging of the ultraviolet source, resulting in sluggish or incomplete oxidation. Large organic particles or very large or complex organic molecules such as tannins, lignins, and humic acid may be oxidized slowly because persulfate oxidation is rate-limited. However, oxidation of many large biological molecules such as proteins and monoclonal antibodies proceeds rapidly. Because the efficiency of conversion of organic carbon to CO_2 may be affected by many factors, check efficiency of oxidation with selected model compounds representative of the compounds of interest in a matrix representative of the sample.

Some instruments give low results for certain difficult-to-oxidize compounds under certain conditions. The following compounds are difficult to oxidize, are sufficiently soluble in water, and can be mixed and measured accurately at trace levels: urea, nicotinic acid, pyridine, *n*-butanol, acetic acid, leucine, acetonitrile, octoxynol-9, tartaric acid, 1,10-phenanthroline, 1-glutonic acid, 2-propanol, and sodium dodecylbenzenesulfonate. Use these compounds as matrix additions to evaluate oxidation efficiency.

Persulfate oxidation of organic molecules is slowed in samples containing significant concentrations of chloride by the preferential oxidation of chloride; at concentrations above 0.05% chloride, oxidation of organic matter may be inhibited. To remove this interference add mercuric nitrate* to the persulfate solution in UV-persulfate instruments, or extend reaction time and/or increase amount of persulfate solution in heated-persulfate instruments.

With any organic carbon measurement, contamination during sample handling and treatment is a likely source of interference. This is especially true of trace analysis. Take extreme care in sampling, handling, and analysis of samples below 1 mg TOC/L.

c. Minimum detectable concentration: Concentration of 0.01 mg TOC/L can be measured by some instruments if scrupulous attention is given to minimizing sample contamination and method background. See Section 1030 for procedures to evaluate the MDL for a specific instrument. Use the high-temperature combustion method (B) for high concentrations of TOC or dilute the sample, ensuring that the dilution process does not contaminate the sample.

d. Sampling and storage: See 5310B.l*d*.

2. Apparatus

a. Total organic carbon analyzer utilizing persulfate oxidation principle.

*NOTE: If mercuric nitrate is used to complex the chloride, use an appropriate disposal method for the treated waste to prevent mercury contamination.

b. Sampling and injection accessories, as specified by the instrument manufacturer.

3. Reagents

a. Reagents listed in 5310B.3.

b. Persulfate solution: Different instrument manufacturers recommend different forms and concentrations of peroxydisulfate. Typical preparations are as follows:

1) *Sodium peroxydisulfate*, 10%: Dissolve 100 g reagent in water; bring volume to 1 L.

2) *Ammonium peroxydisulfate*, 15%: Dissolve 150 g reagent in water; bring volume to 1 L.

3) *Potassium peroxydisulfate*, 2%: Dissolve 20 g reagent in water; bring volume to 1 L.

Check blank values from reagents and, if values are high, purify reagent or use a higher-purity source.

4. Procedure

a. Instrument operation: Follow manufacturer's instructions for assembly, testing, calibration, and operation.

b. Sample preparation: If a sample contains gross particulates or insoluble matter, homogenize until a representative portion can be withdrawn through the syringe needle, autosampler tubing, or sample inlet system of continuous on-line monitor.

If dissolved organic carbon is to be determined, filter sample and a reagent water blank through 0.45-μm filter. HPLC syringe filters have been found to pass water without contamination. Glass fiber or silver membrane filters also can be used. Check filter blanks regularly.

To determine nonpurgeable organic carbon, transfer 15 to 30 mL sample to a flask or test tube and acidify to a pH of 2. Purge according to manufacturer's recommendations. In some instruments this is performed internally. Check efficiency of inorganic carbon removal for each sample matrix by splitting a sample into two portions; to one of the portions, add inorganic carbon to a level similar to that of the sample. The TOC values should agree. If the values do not agree, adjust conditions such as sample container, sample volume, pH, purge-gas flow rate, and purge time to obtain complete removal of inorganic carbon.

c. Sample injection: See 5310B.4*c*.

d. Standard curve preparation: Prepare an organic carbon standard series over the range of organic carbon concentrations in the samples. Run standards and blanks and record analyzer's response. Determine instrument response for each standard and blank. Unless carbon dioxide is trapped and desorbed, producing consistent peak heights, determinations based on peak height may be inadequate because of differences in the rate of oxidation of standards and samples. Correct instrument response of standards by subtracting reagent water blank and plot organic carbon concentration in milligrams per liter against corrected instrument response. For instruments providing a digital computation of concentration, this is not necessary. Be sure that the instrument's algorithm includes blank correction and linearity of response. Analyze standards having concentrations above and below those determined in the samples, preferably prepared in a similar matrix, to confirm proper instrument operation.

5. Calculation

See 5310B.5, or use instrument manufacturer's procedure.

6. Quality Control

See 5310B.6.

7. Precision and Bias

Interlaboratory studies of persulfate and/or UV with NDIR detection methods have been conducted in the range of 0.1 mg/L to 4000 mg/L of carbon.[1] The resulting equation for organic carbon, single-operator precision is:

$$S_o = 0.04x + 0.1$$

Overall precision is expressed as:

$$S_t = 0.08x + 0.1$$

where:

S_o = single-operator precision,
S_t = overall precision, and
x = TOC concentration, mg/L.

An interlaboratory study was conducted for the membrane conductivity method,† covering samples with 1 to 25 mg/L organic carbon concentrations. The resulting equation for single-operator precision is:

$$S_o = 0.012x - 0.022$$

Overall precision is expressed as:

$$S_t = 0.027x + 0.09$$

where terms are defined as above.

8. Reference

1. American Society for Testing and Materials. 1994. Standard Test Method for Total Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection. D4839-88. Annual Book of ASTM Standards. American Soc. Testing & Materials, Philadelphia, Pa.

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† Data may be obtained from *Standard Methods* technical information manager at *www.standardmethods.org/contact/*.

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5310 D. Wet-Oxidation Method

1. General Discussion

The wet-oxidation method is suitable for the analyses of water, water-suspended sediment mixtures, seawaters, brines, and wastewaters containing at least 0.1 mg nonpurgeable organic carbon/L. The method is not suitable for the determination of volatile organic constituents.

a. Principle: The sample is acidified, purged to remove inorganic carbon, and oxidized with persulfate in an autoclave at temperatures from 116 to 130°C. The resultant carbon dioxide (CO_2) is measured by nondispersive infrared spectrometry.

b. Interferences: See 5310B.1*b* and C.1.*b*

c. Minimum detectable concentrations: High concentrations of reducing agents may interfere. Concentration of 0.10 mg TOC/L can be measured if scrupulous attention is given to minimizing sample contamination and method background. Use the high-temperature combustion method (B) for high concentrations of TOC.

d. Sampling and storage: See 5310B.1*d*.

2. Apparatus

a. Ampules, precombusted, 10-mL, glass.
b. Ampule purging and sealing unit.
c. Autoclave.
d. Carbon analyzer.
e. Homogenizer.

3. Reagents

In addition to the reagents specified in 5310B.3*a*, *c*, *e*, and *f*, the following reagents are required:

a. Phosphoric acid solution, H_3PO_4, 1.2*N:* Add 83 mL H_3PO_4 (85%) to water and dilute to 1 L with water. Store in a tightly stoppered glass bottle.

b. Potassium persulfate, reagent-grade, granular. Avoid using finely divided forms.

4. Procedure

Follow manufacturer's instructions for instrument assembly, testing calibration, and operation. Add 0.5 mL 1.2*N* H_3PO_4, solution to precombusted ampules.

To analyze for dissolved organic carbon, follow the filtration procedure in 5310B. Homogenize sample to produce a uniform suspension. Rinse homogenizer with reagent water after each use. Pipet water sample (10.0 mL maximum) into an ampule. Adjust smaller volumes to 10 mL with reagent water. Prepare one reagent blank (10 mL reagent water plus acid and oxidant) for every 15 to 20 water samples. Prepare standards covering the range of 0.1 to 40 mg C/L by diluting the carbon standard solution. Immediately place filled ampules on purging and seating unit and purge them at rate of 60 mL/min for 6 min with purified oxygen. Add 0.2 g potassium persulfate using a dipper calibrated to deliver 0.2 g to the ampule. Seal samples according to the manufacturer's instructions. Place sealed samples, blanks, and a set of standards in ampule racks in an autoclave and digest 4 h at temperature between 116 and 130°C.

Set sensitivity range of carbon analyzer by adjusting the zero and span controls in accordance with the manufacturer's instructions. Break combusted ampules in the cutter assembly of the carbon analyzer, sweep CO_2 into the infrared cell with nitrogen gas, and record area of each CO_2 peak. **CAUTION: Because combusted ampules are under positive pressure, handle with care to prevent explosion**.

5. Calculations

Prepare an analytical standard curve by plotting peak area of each standard versus concentration (mg/L) of organic carbon standards. The relationship between peak area and carbon concentration is curvilinear. Define operating curves each day samples are analyzed.

Report nonpurgeable organic carbon concentration as follows: 0.1 mg/L to 0.9 mg/L, one significant figure; 1.0 mg/L and above, two significant figures.

6. Quality Control

See 5310B.6.

7. Precision and Bias

Multiple determinations of four different concentrations of aqueous potassium acid phthalate samples at 2.00, 5.00, 10.0,

and 40.0 mg C/L resulted in mean values of 2.2, 5.3, 9.9, and 38 mg/L and standard deviations of 0.13, 0.15, 0.11, and 1.4, respectively.

Precision also may be expressed in terms of percent relative standard deviation as follows:

Number of Replicates	Mean *mg/L*	Relative Standard Deviation %
9	2.2	5.9
10	5.3	2.8
10	9.9	1.1
10	38.0	3.7

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