Designation: D 5904 – 02

An American National Standard

Standard Test Method for Total Carbon, Inorganic Carbon, and Organic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection[1]

This standard is issued under the fixed designation D 5904; 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 in the range from 0.5 to 30 mg/L of carbon. Higher levels may be determined by sample dilution. The test method utilizes ultraviolet-persulfate oxidation of organic carbon, coupled with a CO_2 selective membrane to recover the CO_2 into deionized water. The change in conductivity of the deionized water is measured and related to carbon concentration in the oxidized sample. Inorganic carbon is determined in a similar manner without the requirement for oxidation. In both cases, the sample is acidified to facilitate CO_2 recovery through the membrane. The relationship between the conductivity measurement and carbon concentration is described by a set of chemometric equations for the chemical equilibrium of CO_2, HCO_3^-, H^+, and the relationship between the ionic concentrations and the conductivity. The chemometric model includes the temperature dependence of the equilibrium constants and the specific conductances.

1.2 This test method has the advantage of a very high sensitivity detector that allows very low detection levels on relatively small volumes of sample. Also, use of two measurement channels allows determination of CO_2 in the sample independently of organic carbon. Isolation of the conductivity detector from the sample by the CO_2 selective membrane results in a very stable calibration, with minimal interferences.

1.3 This test method was used successfully with reagent water spiked with sodium bicarbonate and various organic materials. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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

1.5 In addition to laboratory analyses, this test method may be applied to on line monitoring.

1.6 *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 Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 5810 Guide for Spiking Into Aqueous Samples[2]

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]

3. Terminology

3.1 *Definitions*—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 *potassium hydrogen phthalate (KHP)*—$KHC_8H_4O_4$.

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

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

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

4. Summary of Test Method

4.1 *Fundamentals*—Carbon can occur in water as inorganic and organic compounds. This test method can be used to make independent measurements of IC and TC and can also determine TOC as the difference of TC and IC. If IC is high relative

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

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

to TOC it is desirable to use a vacuum degassing unit to reduce the IC concentration as part of the measurement. Alternatively, the IC can be removed by acidifying and sparging the sample prior to injection into the instrument.

4.2 The basic steps of this test method are:

4.2.1 Removal of IC, if desired, by vacuum degassing;

4.2.2 Conversion of remaining inorganic carbon to CO_2 by action of acid in both channels and oxidation of total carbon to CO_2 by action of acid-persulfate, aided by ultraviolet (UV) radiation in the TC channel;

4.2.3 Detection of CO_2 that is swept out of the reactors by the liquid stream over membranes that allow the specific passage of CO_2 to high purity water where change in conductivity is measured; and

4.2.4 Conversion of the conductivity detector signal to a display of carbon concentration in parts per million (ppm = mg/L) or parts per billion (ppb = µg/L). The IC channel

TABLE 1 Blank Contribution and Inorganic Carbon (IC) Removal Efficiency of Vacuum Degassing Unit

Unit Number	µg/L[A] TOC Background	µg/L[A] IC Background	IC Level with 25 000µ g/L Input
1	3.2	8.2	55
2	3.2	22	61
3	2.4	8.0	105
4	4.2	13	89
5	2.8	13	30
6	3.0	8.0	70
7	4.8	8.9	67
8	4.7	8.3	63
9	4.6	11	62
10	4.7	2.9	72

[A]Values are the difference between before and after addition of the degasser to a high purity (<5 µg/L) water stream.

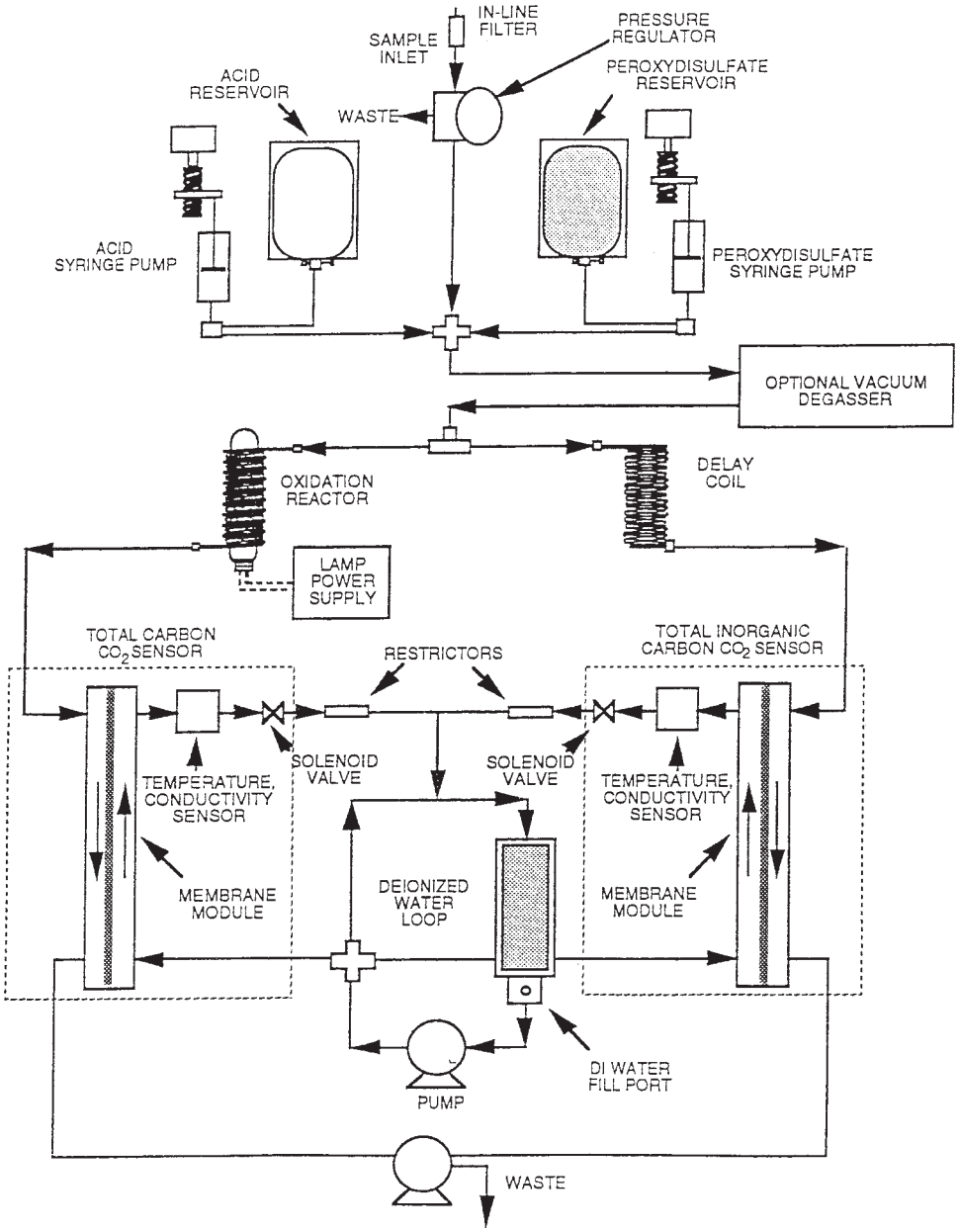


FIG. 1 Schematic Diagram of TOC Analyzer System

reading is subtracted from the TC channel to give a TOC reading. A diagram of suitable apparatus is given in Fig. 1. References **(1-5)**[4] provide additional information on this test method.

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 high purity and drinking water. 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.[5]

6. Interferences and Limitations

6.1 The oxidation of dissolved carbon to CO_2 is brought about at relatively low temperatures by the chemical action of reactive species produced by UV-irradiated persulfate ions. 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: by rerunning the sample under more vigorous reaction conditions; by analyzing the sample by an alternative method known to result in full recovery; or by spiking samples with known refractories and determining recovery.

6.2 Chloride ion above 250 mg/L tends to interfere with oxidative reaction mechanisms in this test method. Follow manufacturer's instructions for dealing with this problem. Other interferences have been investigated and found to be minimal under most conditions. Refer to the references for more information.

6.3 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. In this case the vacuum degassing unit on the instrument should be used to reduce the concentration of IC prior to measurement. Alternatively, the sample can be acidified and sparged prior to introduction into the instrument. Use of the vacuum degassing unit or sparging the sample may cause loss of volatile organic compounds, thus yielding a value lower than the true TOC level.

6.4 Use of the vacuum degassing unit or sparging the sample may cause loss of volatile organic compounds, thus yielding a value lower than the true TOC level. At low TOC levels, the degassing unit may introduce a measurable TOC and IC background. The user should characterize the background and performance of the degassing module for their application. A removal efficiency of 97 % of the inlet IC is considered satisfactory. Table 1 provides typical IC removal performance and background levels of the vacuum degassing unit.

7. Apparatus

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

7.2 *Apparatus for Carbon Determination*—A typical instrument consists of reagent and sample introduction mechanism, reaction vessel, detector, control system, and a display.[6] Fig. 1 shows a diagram of such an arrangement.

7.2.1 Vacuum degassing requires the manufacturer's module[6] that includes a vacuum pump and a hollow fiber membrane assembly. Use of this vacuum degasser will remove essentially all IC as part of the analysis. The membrane module consists of a tube and shell arrangement of microporous polypropylene hollow fibers. Sample flows along the inside of the fibers, while air is passed on the shell side-counterflow to the sample flow. The shell side pressure is reduced by means of a vacuum pump on the air outlet. The sample is acidified before introduction into the degasser to facilitate CO_2 transport through the hollow fibers. 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.

7.2.2 *Reaction*—The sample flow is split after the addition of reagents. Half of the flow passes to the delay coil while the other half passes into the oxidation reactor. The effluent from both streams passes over individual membranes that allow CO_2 to pass through the membrane into prepurified water for detection.

7.2.3 *Membrane*—The membrane is a CO_2 selective fluoropolymer that is hydrophobic and non-porous. Refer to the bibliography for additional details.

7.2.4 *Detector*—The CO_2 that has passed through the membrane into the purified water is measured by conductivity sensors. The temperature of the conductivity cell is also automatically monitored so the readings can be corrected for changes in temperature.

7.2.5 *Presentation of Results*—The conductivity detector output is related to stored calibration data and then displayed as parts per million, (ppm = milligrams of carbon per litre) or parts per billion, (ppb = micrograms of carbon per litre). Values are given for TC, IC, and TOC by difference.

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,[7] where such specifications are available. Other grades may be used,

[4] The boldface numbers given in parentheses refer to a list of references at the end of this standard.

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

[6] Instruments manufactured and marketed by Sievers Instruments, Inc., 2500 Central Ave., Suite H1, Boulder, CO 80301, have been found satisfactory.

[7] *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.

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 Type I or Type II in Specification D 1193. 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, 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). The carbon contribution of the reagent water should be determined and its effect 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.

8.3 *Persulfate Reagent (15 % w/v)*—Prepare ammonium persulfate to a concentration of 15 % w/v by dissolving 15 g of ammonium peroxydisulfate in water and diluting to 100 mL. Verify that it contains less than 2000 µg/L organic carbon contamination. Certification of reagent assay should be available. Reagents in prepackaged containers from the instrument manufacturer have been found to be acceptable.

8.4 *Acid Reagent (6M)*—Prepare acid solution to a concentration of 6M and verify that it contains less than 600 µg/L organic carbon contamination. Since halogens are potential interferences, use only sulfuric or phosphoric acid for reagents. Sulfuric acid is prepared by diluting 336 mL of 95 % reagent (sp gr 1.84) to 1 L with reagent water. Phosphoric acid is prepared by diluting 410 mL of 85 % reagent (sp gr 1.69) to 1 L with water. Certification of reagent assay should be available. Reagents in prepackaged containers from the instrument manufacturer have been found to be acceptable.

8.5 *Organic Carbon, Standard Solution (2000 mg/L)*—Choose a water-soluble, stable reagent grade compound, such as benzoic acid or anhydrous potassium hydrogen phthalate ($KHC_8H_4O_4$). Calculate the weight of compound required to make 1 L of organic carbon standard solution; for example, $KHC_8H_4O_4$ = 0.471 g of carbon per gram, so 1 L of 2 g/L of standard requires 2/0.471, or 4.25, grams of KHP. Dissolve the required amount of standard in some CO_2-free water in a 1-L volumetric flask, add 1 mL of sulfuric acid, and dilute to volume. Dilutions of this stock solution containing 20 mg/L are to be used to calibrate and test performance of the carbon analyzer.

9. Sampling and Sample Preservation

9.1 Collect the sample in accordance with Specification D 1192 and Practices 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 the sample inlet tube or autosampler needle. Volatile organics may be lost.

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

9.5 For accurate measurements of samples containing <0.5 mg/L direct, on-line measurement should be used.

10. Instrument Operation

10.1 Follow the manufacturer's instructions for setting up the instrument and adjusting reagent flows. Ensure that the pH of the waste stream is below 4 in all cases. Additional acid is required if a vacuum degassing unit is used for IC removal. Follow manufacturer's instructions for reagent flows when using a degassing unit.

11. Calibration

11.1 Use appropriate dilutions of the standard solution of 2000 mg/L of carbon to check the instrument calibration.

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 Below 500 µg/L, contamination of reagents is a severe problem. Because of this it is recommended that the general calibration check of the instrument be carried out with standards above 500 µg/L. The response of the instrument is extremely linear that allows calibration at higher levels without loss of accuracy at low levels. See Section 15 for data regarding linearity of the response.

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 removed by vacuum degassing, no additional sample preparation is required. 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 CO_2 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.

12.3 Follow manufacturer's instructions for introducing the sample into the analyzer. The sample may be directly aspirated,

sampled from an auto sampler, or connected directly into a source for continuous on-line monitoring.

13. Calculation

13.1 Read carbon values directly from the digital display, printer, or computer connected to a suitable data interface on the instrument.

14. Quality Control

14.1 In order to be certain that analytical values obtained from using this test method are valid and accurate within the confidence limits of the test, the following quality control procedures must be followed when running this test.

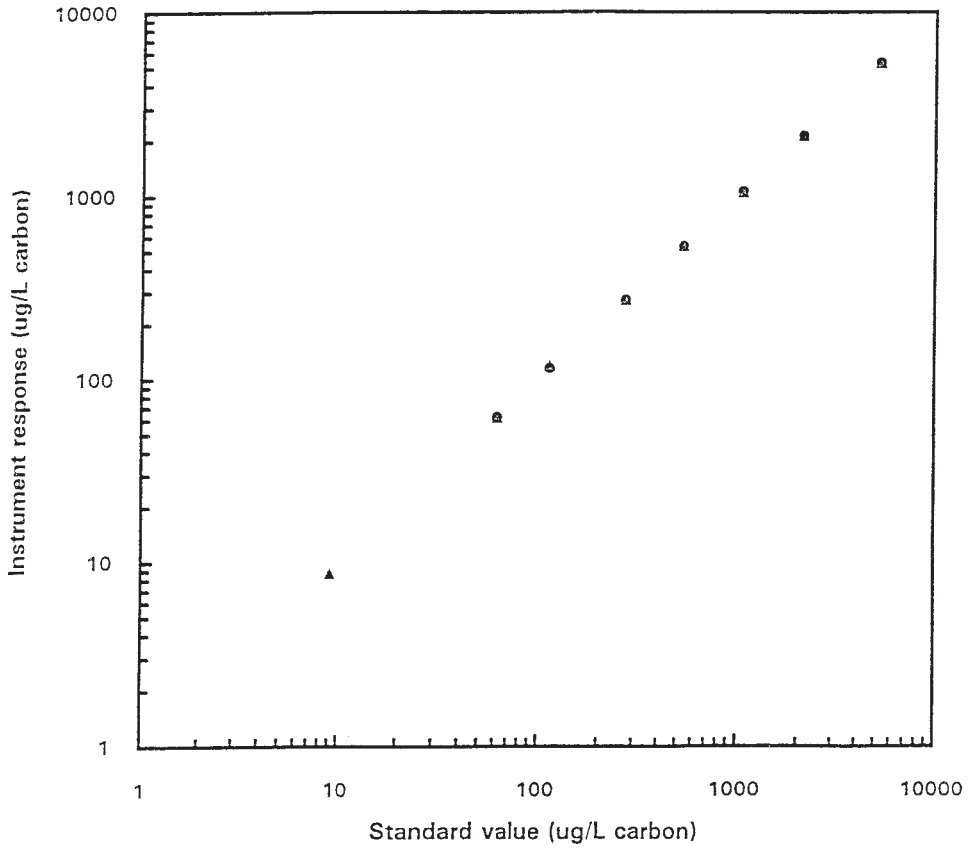
14.2 *Initial Demonstration of Laboratory Capability*—If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability. Analyze seven replicates of a standard solution prepared from a certified reference material containing a concentration of analyte similar to that expected in test samples and with the range of 1 to 30 mg/L. Each replicate must be taken through the complete analytical test method including any sample preservation steps. Calculate the mean and standard deviation of these values and compare to the acceptable ranges of precision and bias that may be calculated by the user using the precision and bias relationships listed in Section 15. This study should be repeated until the single operator precision and the mean values are within acceptable limits.

14.3 *Calibration Verification*—See Section 11.

14.4 Analyze a test method blank each time the test is run. Use low TOC reagent water in place of a sample and analyze as described in Section 12. The variability of blank values obtained must be less than that specified by the user after consideration of the precision and bias relationships near zero concentration.

14.5 In order to verify the quantitative value of the laboratory's calibration standard, analyze an independent reference material submitted as a regular sample (if practical) to the analyst periodically. The concentration of the reference material should be in the range of 1 to 30 mg/L. The value obtained must fall within the control limits specified by the outside source and the control limits used to evaluate the laboratory's routine calibration checks.

14.5.1 To insure that the test method is in control, analyze a laboratory control sample (LCS) at the beginning and end of the run. The LCS should be of similar concentration to the unknowns and be as representative of the unknowns as possible to adequately challenge the analytical system. If large numbers of samples are analyzed in a single day, analyze the LCS sample after every 20 samples. The LCS sample must be taken through all the steps of the procedure including sample preservation and preparation. The value obtained for the LCS



NOTE 1—Carbon standards prepared from sucrose in low TOC water. Calibration: 25 000 µg/L potassium acid phthlate.

FIG. 2 Instrument Response Versus Carbon Concentration

sample should be within control limits that may be calculated from the ST and x relationships in Section 15 as described in Practice D 5847.

14.5.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all samples in the batch must reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.6 To check for interferences in the specific matrix being tested, perform a recovery spike on at least one sample from each set of samples being analyzed by spiking a portion of the sample with a known concentration of TOC and taking it through the complete procedure. The spike concentration plus the background concentration of TOC must not exceed the upper limit of the method. However, the total concentration of analyte in the spiked sample must be greater than the lower level of quantitation. Calculate percent recovery of the spike (P) using the following formula:

$$P = 100\frac{[A(V_s + V) - BV_s]}{CV} \quad (1)$$

Where:

A = Concentration found in spiked sample,
B = Concentration found in unspiked sample,
C = Concentration of analyte in spiking solution,
V_s = Volume of sample used, and
V = Volume added with spike.

14.6.1 The percent recovery of the spike shall fall within 80-120%. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 1—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide 5810 for additional information.

14.7 To check the precision of sample analyses, analyze a sample in duplicate each day or shift the test is run. When large numbers of samples are being analyzed, analyze one out of every twenty samples in duplicate. Calculate the standard deviation of these replicate values and compare to the single operator precision found in the collaborative study using an F test. Refer to 6.4.4 of Practice D 5847 for information on applying the F test.

15. Precision and Bias [8]

15.1 Linearity of the response over the entire measurement range allows calibration at a single higher level concentration. This facilitates preparation of accurate standards minimizing the effect of contamination. Fig. 2 illustrates linear response from 50 to 5000 µg/L for an instrument calibrated at 25 000 µg/L. As stated in Section 11, the user should confirm proper operation of the instrument by running check samples in the range of test samples.

15.2 *Collaborative Test*—This method was evaluated at seven laboratories. Three labs used two different instrument models, and one lab used two different operators.

15.2.1 Four samples were analyzed at each laboratory in triplicate on three different days for total inorganic carbon (TIC), total carbon (TC) and total organic carbon (TOC). The study samples included a reagent blank (Type II water), two standards made from potassium acid phthalate and one standard made from fulvic acid, which also contained carbonate and chloride. The fulvic acid study sample was made to represent a naturally occurring, complex organic material combined with potentially interfering inorganic carbon and chloride. A description of the samples is as follows:

Study Sample	Concentration	Source
A	Reagent water	
B	1.25 mg/L TOC	5.0 mL stock/2 L
C	20.0 mg/L TIC	280.0 mg sodium bicarbonate + 40.210 mg
	10.0 mg/L TOC	fulvic acid standard
	250 mg/L chloride	(50.00 % C) + 824.1 mg sodium chloride/2 L
D	25.0 mg/L TOC	100.0 mL stock/2 L
Stock solution	500 mg/L TOC	531.8 mg KHP/L (NIST)

The KHP was obtained from the National Institute of Standards and Technology (NIST reference material 84j), the fulvic acid was obtained from the International Humic Substances Society (IHSS Suwannee Stream Standard Fulvic Acid) and the sodium carbonate and sodium chloride were ACS reagent grade materials.

15.2.2 *Analysis of Data*—The data were processed as specified in Practice D 2777. Two individual data points from one laboratory were rejected as outliers.

15.2.3 *Precision*—Separate determinations of precision were made for TC and TOC measurements. The results of weighted least-squares calculation were as follows:

$$TC\ S_t = .024x + .036$$

$$S_o = .007x + .006$$

$$TOC\ S_t = .027x + .090$$

$$S_o = .012x - .022$$

where:

x = average value found in mg C/L,
S_t = overall precision expressed in mg C/L, and
S_o = single-operator precision expressed in mg C/L.

Table 2 shows the determined S_o and S_t for the collaborative test.

15.2.4 *Bias*—Table 2 summarizes the observed bias for both TC and TOC measurements. The high TC bias on Sample C may be due to loss of CO_2 from the sodium bicarbonate standard.

[8] Supporting data are available from ASTM Headquarters. Request RR:D19-1156.

TABLE 2 Recovery and Precision of Known Amounts of Carbon in a Series of Prepared Standards

Method	Sample	Amount Added, mg/L	Amount Found, mg/L	±Bias	± Bias, %	Statistically Significant	S_o, mg/L	S_t, mg/L
TOC	B	1.25	1.22	0.03	3	Yes	0.0001	0.054
	C	10.0	9.67	0.33	3	Yes	0.050	0.61
	D	25.0	24.78	0.22	1	No	0.30	0.67
TC	B	1.25	1.22	0.03	2	No	0.0005	0.078
	C	30.1	27.83	2.27	7	Yes	0.042	0.55
	D	25.0	24.93	0.08	0	No	0.36	0.76

16. Keywords

16.1 carbon; carbon-dioxide; inorganic-carbon; low-temperature-oxidation; membrane-conductivity-detection; organic carbon; total carbon

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(**5**) Harrison, S., Gavlick, W., Ohlemeier, L., and Biwald, C., "The Use of Total Organic Carbon Analysis for Cleaner Residue Determination," *Pharmaceutical Technology*, December 1994.