Designation: D 6317 – 98 (Reapproved 2004)

Standard Test Method for Low Level Determination of 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 6317; 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 10 to 1000 µg/L of carbon. This method is for laboratory or grab sample applications and has been subjected to an interlaboratory study under the guidelines of D 2777. Test Method D 5997 can be used for on-line determinations. The test method utilizes persulfate or ultraviolet oxidation of organic carbon, or both 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 oxidation step. 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^-, and 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 resulting in linear response of the method over the stated range of TOC. See Test Method D 4519 for a discussion of the measurement of CO_2 by conductivity.

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 various organic materials. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 In addition to laboratory analyses, this test method may be adapted to on line monitoring. See Test Method D 5997.

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:* [2]

D 1129 Terminology Relating to Water

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

D 1193 Specification for Reagent Water

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

D 3370 Practices for Sampling Water from Closed Conduits

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

D 5997 Test Method for On-Line Monitoring of Total Carbon, Inorganic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection

D 4519 Test Method for Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity

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

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

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Withdrawn.

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

4. Summary of Test Method

4.1 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 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. The basic steps of the procedure are as follows:

(1) Removal of IC, if desired, by vacuum degassing;

(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 ultraviolet (UV) radiation in the TC channel. (Acid-persulfate can be added but is usually not required at TOC levels below 1 ppm).

(3) Detection of CO_2 that is swept out of the U.V. reactor and delay coil by the liquid stream and passed through membranes that allow the specific passage of CO_2 to high purity water where change in conductivity is measured and;

(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 reading is subtracted from the TC channel to give a TOC reading. A diagram of suitable apparatus is given in Fig. 1.

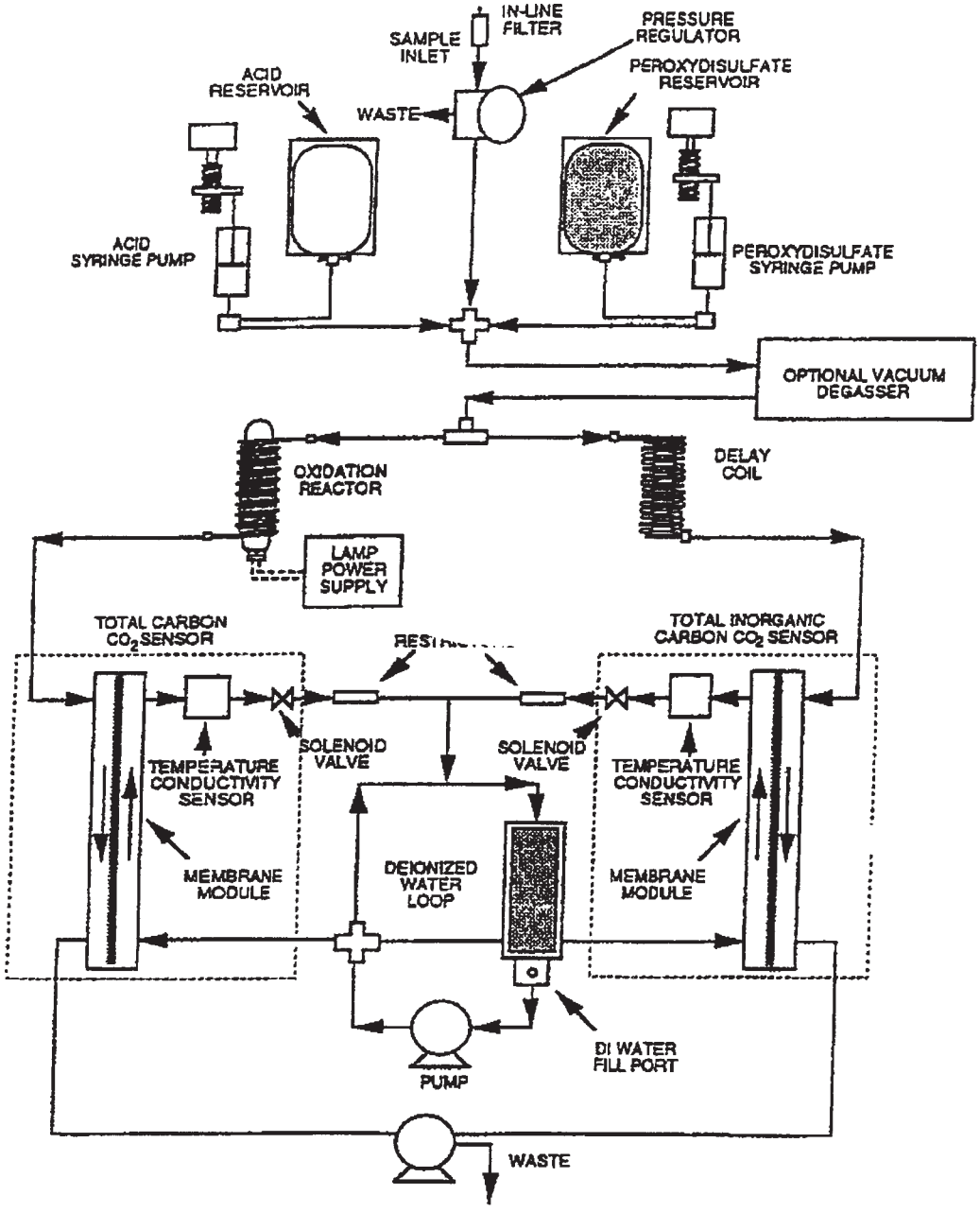

FIG. 1 Schematic Diagram of TOC Analyzer System

References **1-5**[4] provide additional information on the 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 impurities in high purity process water used in industries such as nuclear power, pharmaceutical, and electronics.

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 and water. 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 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 reference **(2)** 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. 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.

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. Table 1 provides typical IC removal performance and background levels of the vacuum degassing unit.

[4] The boldface numbers in parentheses refer to the list of references found at the end of this Test Method.

TABLE 1 Blank Contribution and IC. Removal Efficiency of Vacuum Degassing Unit.

Unit No.	µg/L[A] TOC background	µg/L[A] IC background	IC level with 25 000 µg/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.

6.5 Contamination of the sample with both CO_2 and organic carbon is a severe problem as lower levels of analyte are attempted. Throughout this method the analyst must be vigilant for all potential sources of contamination and must monitor blanks and adjust operations to prevent contamination.

7. Apparatus

7.1 *Apparatus for Carbon Determination*—A typical instrument consists of reagent and sample introduction mechanism, reaction vessel, detector, control system, and a display.[5] Fig. 1 shows a diagram of such an arrangement.

7.1.1 *Sampling Needle*— A double chambered needle capable of piercing the sample bottle septum and pulling sample from the bottom of the bottle is used. The second chamber vents the top of the bottle to prevent vacuum build up as the sample is withdrawn. Typically this needle is mounted on an autosampler to provide unattended analysis of several samples.

7.1.2 *I.C. Removal*— Vacuum degassing requires the manufacturer's module[5] which 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 provision for sparging the acidified sample 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.

7.1.3 *Reactor*—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 pas through the membrane into prepurified water for detection.

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

7.1.5 *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.

7.1.6 *Data Display*— The conductivity detector output is related to stored calibration data and then displayed as parts per million, (ppm = mg of carbon per litre) or parts per billion, (ppb = µg of carbon per L). 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

[5] Instruments manufactured and marketed by Sievers Instruments, Inc., 6185 Arapahoe Ave., Suite H1, Boulder, CO 80303 have been found satisfactory.

all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[6] 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 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. Continuous U.V. treatment of water with recycling through appropriate mixed bed ion exchange resins may be necessary to maintain an adequately low TOC reagent water.

8.3 *Persulfate Reagent (15 % w/v)*—Prepare ammonium persulfate solution 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 (1000 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 g, so one L of 1 g/L of standard requires 1/0.471, or 2.12, 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 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 Samples must be collected in contamination free bottles sealed with a fluoropolymer lined septa. Specially cleaned (for TOC) 40 ml bottles are commercially available. The sample bottle should be rinsed several times with the sample, filled, and then tightly sealed.

9.3 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.

9.4 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 stringent measures must be taken to minimize contamination. Low level samples exposed to ambient air will generally increase in both inorganic and organic carbon. Sample container and all sampling devices must be clean and exposure of the sample to the atmosphere must be minimized. Blanks should be carried through all steps of the sampling and analysis procedure to check for contamination.

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 four (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 1000 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, allowing calibration at higher levels without loss of accuracy at low levels. See 14.1 for data regarding linearity of the response.

12. Procedure

12.1 The sample is introduced into the instrument by piercing the septum with a double chambered needle. The

[6] *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.

analyzer in either the grab sample or autosampler mode will pull sample out of the sample bottle, into the analyzer.

12.2 If inorganic carbon is to be removed by vacuum degassing, or if I. C. removal is unnecessary, 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) inject through the needle and sparge through the needle with an appropriate flow of gas. Use of the double chambered needle prevents contamination of the sample during sparging. Other configurations that prevent sample contamination are acceptable. Samples with high alkali content or buffer capacity may require larger amounts of acid. In such cases, incorporate this dilution into the calculation of results. 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.

12.3 Follow manufacturers' 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.

13.2 Blank correction should be applied to samples that have been prepared or diluted with reagent water. In the case of materials prepared in reagent water, the entire blank value obtained in the reagent water should be subtracted. In the case of dilution, the blank should be corrected for the dilution factor and subtracted from the obtained value.

14. Precision and Bias

14.1 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 shows instrument response for carbon versus carbon concentration over five orders of magnitude from 0.25 µg/L C to 25 000 µg/L C for two instruments calibrated at 25 000 µg/L C. As stated in Section 11, the user should confirm proper operation of the instrument by running check samples in the range of test samples.

14.2 An interlaboratory study was conducted to determine the precision and bias for the determination of Organic Carbon in water.[7] Standards prepared in reagent water were sent to twelve (12) laboratories for evaluation. One laboratory did not complete analysis of all samples. A second lab failed to get required recoveries (± 10 %) on the QC sample. The data from the other ten laboratories was used for this evaluation.

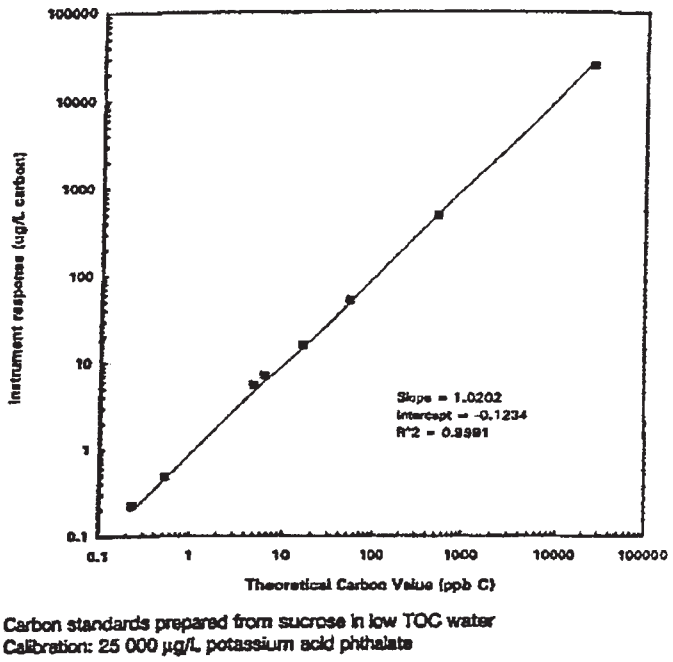

FIG. 2 Instrument Response Versus Carbon Concentration

14.2.1 Results of this collaborative study may not be typical of results for matrices other than those studied.

14.2.2 Ten samples (five pairs) were analyzed at each laboratory for Organic Carbon. The study samples included eight samples made from sucrose (NIST 170) and two samples made from benzoic acid (Baker 0076-001). The samples contained an IC background level of approximately 100 µg/L. In addition, blank and QC samples were sent with concentrations noted on the labels to ensure proper performance of the method. All participants used autosamplers that took ten consecutive aliquots of each sample vial. The first three were ignored to insure that the instrument was completely purged of the previous sample. The mean of the remaining seven values was used for all subsequent calculations. Each laboratories blank data was subjected to the outlier test and the average blank value for each laboratory was subtracted from each result. Table 2 summarizes blank values and deviations for each participant's study.

14.2.3 Data was evaluated as defined in D 2777–96 and summarized in Table 3. Labs 1 and 11 were eliminated as outliers by the ranking test. No individual outliers were found, so all data from the remaining eight laboratories was used for the evaluation. The last two rows of Table 3 show the standard deviations and relative standard deviations for seven replicates from a single sample container.

[7] Supporting data for the precision and bias statements have been filed at ASTM headquarters.

TABLE 2 Summary of Blank Values from Participating Laboratories

Lab No.	1	2	3	4	5	6	7	8	9	10	11	12
No. Retained values	5	5	3	5	5	5	4	5	5	5	5	5
Ave Blank µg/L	14.6	26.8	29.8	48.1	14.3	14.9	22.9	22.4	36.3	12.5	19.4	26.5
Overall Std Dev	0.8	7.0	8.8	4.0	2.5	5.4	2.3	3.1	10.2	2.5	2.5	4.7
% RSD	5.25	26.26	29.58	8.32	17.46	36.40	10.00	13.76	28.15	20.33	12.77	17.79

TABLE 3 Final Statistical Summary for Total Organic Carbon

Conc: (µg/L)	10	11	25	28	50	55	100	110	495	550
Number of Retained Values	8	8	8	8	8	8	8	8	8	8
True Concentration	10.0	11.0	25.0	28.0	50.0	55.0	100.0	110.0	495.0	550.0
Mean Recovery	8.53	6.04	20.58	23.14	49.19	51.13	96.70	103.08	482.45	541.33
% Recovery	85.25	54.89	82.30	82.63	98.38	92.95	96.70	93.70	97.46	98.42
Overall Std Dev (St)	4.45	3.62	3.92	2.17	4.77	2.57	6.51	4.39	17.40	21.75
Overall Std Dev, %	52.19	59.92	19.07	9.40	9.69	5.03	6.73	4.26	3.61	4.02
Number of Retained Pairs	8		8		8		8		8	
Single Std Dev (So)	5.28		1.87		2.00		3.46		3.59	
Analyst Relative deviation, %	72.47		8.54		4.00		3.47		0.70	
7 Replicate Runs Std. Dev	0.46	0.40	0.96	0.39	0.55	0.52	0.60	0.48	1.17	1.36
7 Replicate Runs Std Dev, %	1.41	1.39	1.62	0.82	0.58	0.68	0.50	0.37	0.25	0.26

14.2.4 The following equations are developed using an unweighted least squares regression of the data obtained in this study:

slope intercept (1)

$$XBAR = 0.9859(C) - 3.1485, (R^2 = 0.999)$$

$$S_t = 0.0325(C) + 2.4914, (R^2 = 0.9628)$$

$$S_o = 0.0007(C) + 3.1582, (R^2 = 0.0105)$$

where:

S_t = overall precision
S_o = single operator precision
C = concentration

14.2.5 Fig. 3 shows the regression fitted to relate overall standard deviations to concentration.

14.2.6 *Discussion*—The relatively high and variable blank values shown in Table 2 suggest that there is variable contamination between sample containers. This is further supported by the good single container precision for seven replicate runs from the same sample container as shown in the last two rows of Table 3. These data, showing much higher deviations between vials than within one vial, suggests that the variability and detection limits suggested by the study are limited by the cleanliness of the sample vials and sample preparation operations. The users of this method must carefully evaluate the cleanliness of their sample handling and preparation techniques.

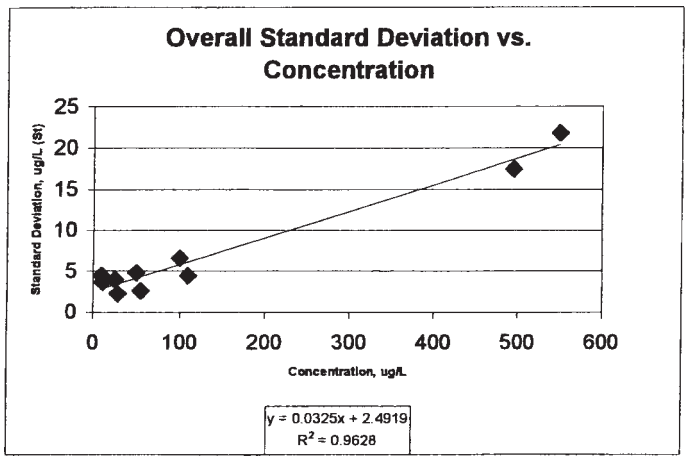

FIG. 3

15. Quality Control

15.1 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 should be followed when running the test.

15.1.1 *Analyst Performance Check*—If the analyst has not performed the test before or if he/she has never generated single operator precision, a precision and accuracy study must be performed to demonstrate analyst 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 10 to 550 µg/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 14. This study should be repeated until the single operator precision and the mean values are within acceptable limits.

15.1.2 *Calibration Verification*—See 11.1

15.1.3 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 the that specified by the user after consideration of the precision and bias relationships near zero concentration.

15.1.4 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 10 to 550 µg/L. The value obtained must fall within the control limits specified by the outside source or the control limits used to evaluate the laboratory's routine calibration checks.

15.1.5 To ensure that the test method is in control, analyze a quality control sample at the beginning and end of the run. If large numbers of samples are analyzed in a single day, analyze the QC sample after every 20 samples. The QC sample must be taken through all the steps of the procedure including sample preservation and preparation. The value obtained for the QC sample should be within $\bar{x} \pm 3S_T$ *control limits that may be calculated from the* S_T *and* $\bar{x}$ *relationships in 14.*

15.1.6 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:

$$P = 100\,\frac{[A(V_s + V) - BV_s]}{CV} \quad (2)$$

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

The percent recovery of the spike should fall within limits to be specified in advance by the user. If it does not, an interference may be present and the data for the set of samples must be qualified with a warning that the data are suspect or an alternate test method should be used.

15.1.7 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. Alternatively, accumulate data from duplicate analyses and develop a relationship between single operator precision and concentration within the laboratory.

16. Keywords

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

REFERENCES

(**1**) Godec, R. D., Kosenka, P.K., Hutte, R.S., "Method and Apparatus for the Determination of Dissolved Carbon in Water", U.S. Patent No. 5,132,094 (July 21, 1992).

(**2**) Godec, R., O'Neill, K., Hutte, R., "New Technology for TOC Analysis in Water", Ultrapure Water, Dec. 1992, 17-22.

(**3**) Deak-Phillips, A., Rathgraber, K., Hutte, R., "On-Line Application of a new TOC Analyzer in the Power Industry", *Proceedings of the 1993 Chemistry On-line Process Instrumentation Seminar*, Clearwater, FL.

(**4**) Barley, R., Hutte, R., O'Neill, K., "Application of TOC Monitoring in Semiconductor Manufacturing", Ultrapure Water, July/August 1994, 20-25.

(**5**) Bollinger, M. J., Craig, C. A., Godec, R., Kosenka, P., O'Niell, K, "A Novel Approach to Verifying TOC Instrument Accuracy," *Proceedings of the 16 th Annual Semiconductor Pure Water and Chemicals Conference*, March, 1997