Designation: D 5997 – 96 (Reapproved 2000)

An American National Standard

Standard Test Method for On-Line Monitoring of Total Carbon, Inorganic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection[1]

This standard is issued under the fixed designation D 5997; 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 on-line determination of total carbon (TC), inorganic carbon (IC), and total organic carbon (TOC) in water in the range from 0.5 µg/L to 50 000 µg/L of carbon. Higher carbon levels may be determined by suitable on-line dilution. This 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 using calibration data. 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 can be described by a set of chemometric equations for the chemical equilibrium of CO_2, HCO_3^-, H^+, and OH^-, 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, the use of two measurement channels allows determination of IC 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 carbonate and various organic compounds. This test method is effective with both deionized water samples and samples of high ionic strength. 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 inlet system generally limits the maximum size of particles that can be introduced. Filtration may also be used to remove particles, however, this may result in removal of organic carbon if the particles contain organic carbon.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to 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 the Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water[2]

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

D 4519 Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity[2]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *inorganic carbon (IC), n*—carbon in the form of carbon dioxide, carbonate ion, or bicarbonate ion.

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

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

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

3.2.4 *total organic carbon (TOC), n*—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 between TC and IC. If IC is high relative to TOC, it is desirable to use a vacuum degassing unit to reduce the IC concentration to obtain meaningful TOC values by difference.

4.2 The basic steps of this test method are:

4.2.1 Conversion of remaining IC to CO_2 by action of acid,

4.2.2 Removal of IC, if desired, by vacuum degassing,

4.2.3 Split of flow into two streams to provide for separate IC and TC measurements,

4.2.4 Oxidation of TC to CO_2 by action of acid-persulfate aided by ultraviolet (UV) radiation in the TC channel,

4.2.5 Detection of CO_2 by passing each liquid stream over membranes that allow the specific passage of CO_2 to high-purity water where change in conductivity is measured, and

4.2.6 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

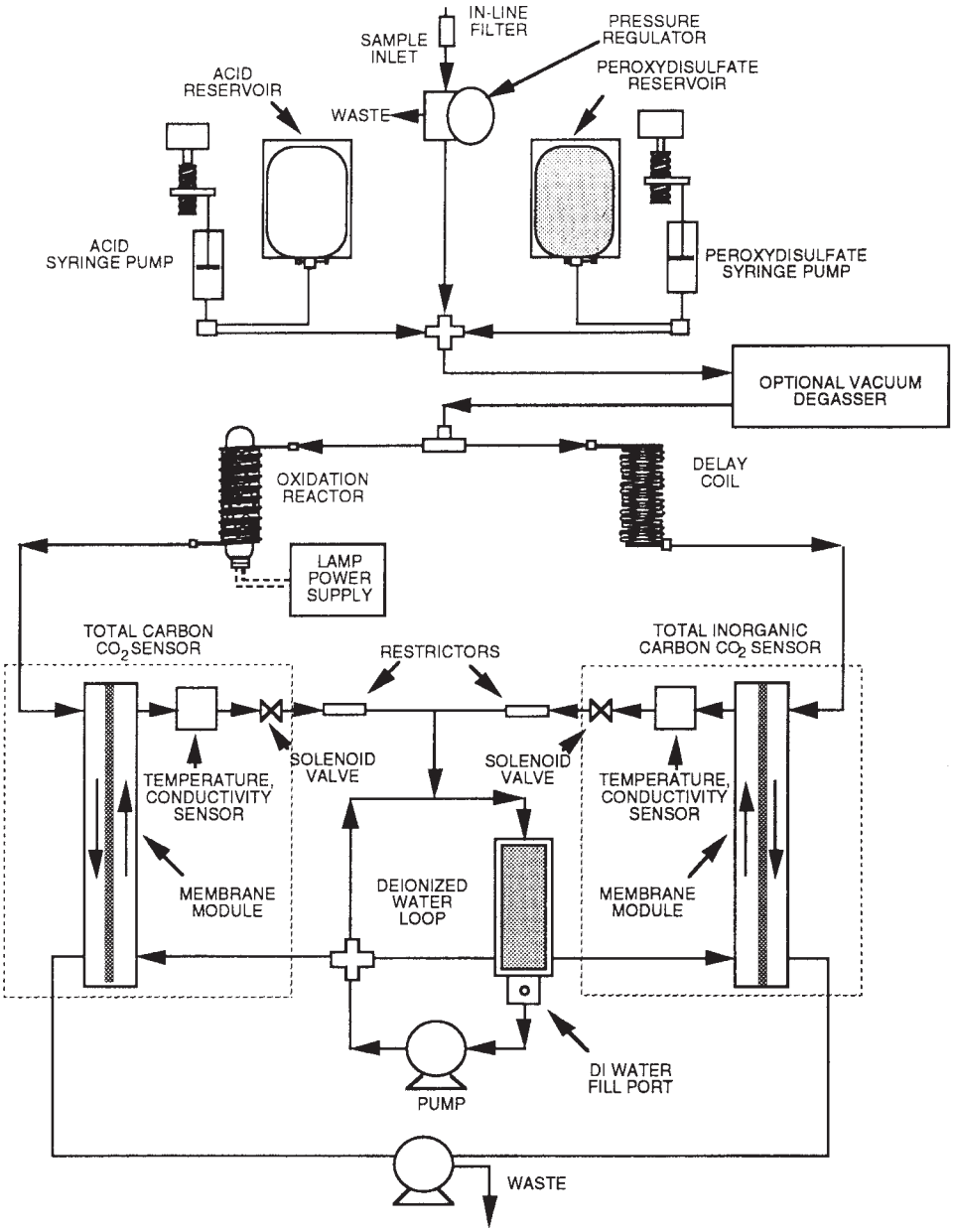


FIG. 1 Schematic Diagram of TOC Analyzer System

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

5. Significance and Use

5.1 This test method is useful for detecting and determining organic and inorganic carbon impurities in water from a variety of sources including industrial water, drinking water, and waste water.

5.2 Measurement of these impurities is of vital importance to the operation of various industries such as power, pharmaceutical, semiconductor, drinking water treatment, and waste treatment. Semiconductor and power applications require measurement of very low organic carbon levels (TOC < 1 µg/L). Applications in pharmaceutical industries range from USP purified water (TOC < 500 µg/L) to cleaning applications (500 µg/L < TOC < 50 000 µg/L). Drinking waters range from < 100 µg/L to 25 000 µg/L and higher. Some of these applications may include waters with substantial ionic impurities as well as organic matter.

5.3 Measurement of inorganic carbon as well as total organic carbon is highly important to some applications, such as in the power industry.

5.4 Continuous monitoring and observation of trends in these measurements are of interest in indicating the need for equipment adjustment or correction of water purification procedures.

5.5 Refer to Annex A1 for additional information regarding the significance of this test method.

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: (*1*) by rerunning the sample under more vigorous reaction conditions; (*2*) by analyzing the sample by an alternative method known to result in full recovery; or (*3*) by spiking samples with known refractories and determining recovery.

6.2 Interferences have been investigated and found to be minimal under most conditions. Chloride ions above 250 000 µg/L may cause low results. Follow the manufacturer's instructions for dealing with high-chloride interference. Other interferences have been investigated and found to be minimal under most conditions. The membrane is hydrophobic in nature and passes only gaseous materials. Potential interferences are nitrite, sulfide, and high levels of hypochlorite or iodine. Refer to Annex A1 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 water high in IC and low in TOC will give a less precise 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, or another method of inorganic carbon removal should be employed.

6.4 Use of the vacuum degassing unit or sparging the sample renders the IC reading meaningless and 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 applications. Table 1 provides typical IC removal performance and background levels of the vacuum degassing unit.

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. Fig. 1 shows a diagram of such an arrangement.

7.1.1 Vacuum degassing requires the manufacturer's module, 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.

7.1.2 *Reaction*—The sample flow is split after the addition of reagents. Half 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.

7.1.3 *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.

7.1.4 *Membrane*—The membrane is a CO_2 selective fluoropolymer that is hydrophobic and non-porous. Refer to the bibliography in Annex A1 for additional details.

7.1.5 *Internal Purified Water*—Water on the conductivity side of the membrane is purified by continual pumping through a mixed bed ion exchange resin as shown in Fig. 1. On power up, the instrument automatically delays for a period of at least

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

Unit No.	TOC Background, µg/L [A]	IC Background, µg/L [A]	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.

5 min to allow the water in the internal loop to be fully deionized. The mixed bed ion exchange resin has an expected life of several years. See 14.3 for details on monitoring the resin.

7.1.6 *Presentation of Results*—The conductivity detector output is related to stored calibration data and then displayed as parts per million (ppm = mg/L of carbon) or parts per billion (ppb = µg/L of carbon). Values are given for TC, IC, and TOC by difference. Data can be maintained on internal nonvolatile RAM, printer tape, or computer storage.

8. Reagents and Materials

8.1 *Purity of Reagents*—Use reagent grade chemicals 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,[3] where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I or Type II. The indicated specification does not actually specify inorganic carbon or organic carbon levels. These levels can affect the results of this test method, especially at progressively lower levels of the carbon content in the samples to be measured. Where inorganic carbon in reagent water is significant, prepare CO_2-free water from reagent water by acidifying to pH 2 and sparge with fritted-glass sparger using CO_2-free gas (time will depend on volume and gas flow rate and should be determined by test). Determine the carbon contribution of the reagent water and allow for its effect in preparation of standards and other solutions. Protect CO_2-free water from atmospheric contamination. Glass containers are required for storage of water and standard solutions.

8.3 *Acid Reagent (6 M)*—Prepare acid solution to a concentration of 6 M 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. Prepare sulfuric acid by diluting 336 mL of 95 % reagent (sp gr 1.84) to 1 L with reagent water. Prepare phosphoric acid 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.

8.4 *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.

8.5 *Organic Carbon Solution Standard (2000 mg/L)*—Choose a water-soluble, stable reagent grade compound such as benzoic acid or anhydrous potassium hydrogen phthalate (KHP, $KHC_8H_4O_4$). 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 g of KHP. Dissolve the required amount of standard in some CO_2-free water in a 1-L volumetric flask, add 1 mL of concentrated H_2SO_4(sp gr 1.84), and dilute to volume. Dilutions of this stock solution containing 2 mg/L are to be used to calibrate and test performance of the carbon analyzer.

8.6 *Inorganic Carbon Solution Standard (2000 mg/L)*—Choose a water soluble, stable, reagent grade compound such as sodium carbonate (Na_2CO_3). Calculate the weight required to make 1 L of standard solution; for example, Na_2CO_3 = 0.113 g of carbon per g, so 1 L of 2 g/L of standard requiring 2/0.113 or 17.7 g of Na_2CO_3. Dissolve the required amount of standard in CO_2-free water in a 1 L volumetric flask. Keep this solution tightly sealed and do not add acid. Use dilutions of this stock solution containing 2 mg/L to calibrate and test performance of the carbon analyzer.

9. Sampling

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

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 and that no bubbles are present. Additional acid is required if a vacuum degassing unit is used for IC removal. Follow the 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 organic or inorganic 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 Contamination of reagents is a severe problem below 500 µg/L. 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 linear, which allows calibration at higher levels without loss of accuracy at low levels. See Section 15 for data regarding linearity of the response. Techniques such as use of an infusion pump to introduce standard solution into a stream of high-purity water may be used to reliably obtain TOC levels below 500 µg/L.

[3] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

12. Procedure

12.1 The analyzer has an internal pump that pulls the sample through the analyzer. Particulate matter that may cause clogging of the instrument plumbing should be removed with an in-line filter. A pressure regulator is used to reduce the pressure to near ambient. A flow is maintained with excess going to waste (or back into the process stream). Consult manufacturers' instructions for additional information.

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 Instrument calibration must be performed according to the manufacturer's schedule and instructions.

14.2 Instrument calibration and blank readings must be checked whenever reagents or UV lamps are changed. The calibration check should be carried out with a different calibration material and concentration than that used for the instrument calibration.

14.3 Resin quality should be checked at the same frequency as UV lamp replacement. In the on-line mode with the UV lamp off, measure low TOC water (<100 µg/L) that has been deionized to a resistivity of >18 Mohm-cm. If either the TC or IC channel measures >10 µg/L, the resin may need replacement.

14.4 The user should confirm that the unit is giving proper response using the sample matrix with compound types of interest and operating under the environmental extremes of interest.

15. Precision and Bias

15.1 Since this test method involves continuous sampling and measurement, Practice D 2777 is not applicable. As specified in the method, theoretically prepared standards can be used to check the calibration of the analyzer. When measuring levels below 500 µg/L, it is difficult to prevent contamination unless on-line sampling is used. Background water levels should be characterized and accounted for to prevent introduction of unacceptable bias. Accuracy of ±3 % (>15 µg/L) or ±0.5 µg/L (≤15 µg/L) and relative sample standard deviations of ±1 % (>15 µg/L) or ±0.2 µg/L (≤15 µg/L) are typical for TOC depending on the matrix (especially IC level) and sample level. Table 2 and Table 3 provide typical performance data at 500 and 25 000 µg/L C.

15.2 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. The limit of detection (LOD) for this test method was estimated by plotting the standard deviation for each of the three lowest concentrations against the analyzed concentration.[4] From this data the *y*-intercept is considered to be the best estimate of the precision at zero concentration (S_0). The S_0 value was determined to be 0.020 µg/L. The LOD is assigned as three times S_0 or 0.060 µg/L. This data supports the assigned limit of quantitations (LOQ) of 0.5 µg/L. Measurements of TOC were determined by introducing a known amount of standard directly into a continuous water sample using a metering pump or by preparing and analyzing flasks containing standards prepared using volumetric additions (see Table 4). The data was taken on several different days with each concentration level determined on a single day. For continuous flow data, the baseline level of TOC was measured before and after the standard addition, and the average baseline TOC values were subtracted from the measured TOC values. For analyses taken from flasks, the baseline was measured initially and then subtracted from the response. The number of repetitions of each sample analyzed in order to calculate the standard deviations is given in Table 4.

TABLE 2 Precision and Bias at 500 µg/L C

TOC Response, µg/L C
489.7
489.8
490.5
490.2
491.5
490.1
490.6
490.8
491.8
491.9
average = 490.7
error = 1.769 %
standard deviation = 0.162 %

NOTE 1— Sample: 499.5 µg/L C as sucrose in DI water
Calibration: 25.0×10^{3} µg/L C as potassium acid phthalate
25.0×10^{3} µg/L C as sodium carbonate
Zero: Low TOC (<5 µg/L C) DI water

TABLE 3 Precision and Bias at 25 000 µg/L C

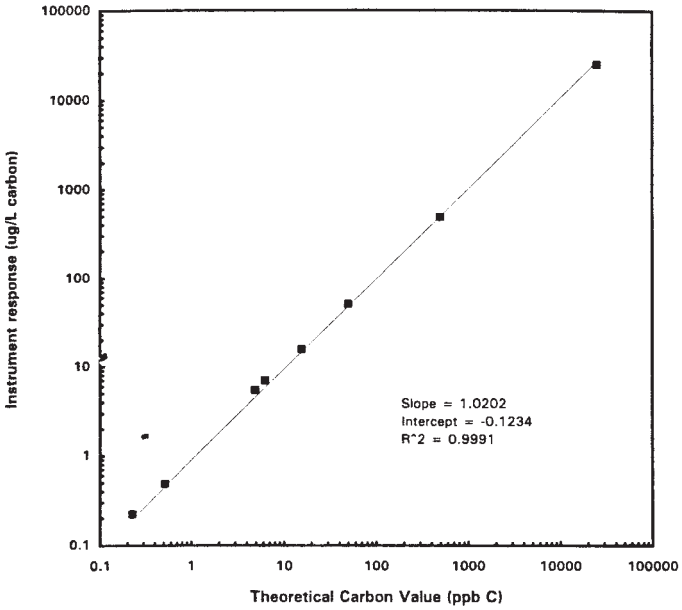
TOC Response, µg/L C
25 063
25 116
25 126
25 141
25 131
25 153
25 166
25 217
25 177
25 193
average = 25 148
error = −0.062 %
standard deviation = 0.172 %

NOTE 1— Sample: 499.5 µg/L C as sucrose in DI water
Calibration: 25.0×10^{3} µg/L C as potassium acid phthalate
25.0×10^{3} µg/L C as sodium carbonate
Zero: Low TOC (<5 µg/L C) DI water

16. Keywords

16.1 carbon; conductivity; inorganic carbon; membrane; on-line; total organic carbon

[4] Taylor, J. K., "Quality Assurance of Chemical Measurements," Louis Publisher, Chelsea, MI, 1987, pp. 78–82.



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

FIG. 2 Instrument Response Versus Carbon Concentration

TABLE 4 Detection Limit Study

Measurement Technique	Number of Repetitions (*n*)	Expected Value, µg/L	Mean Measured Response, µg/L	Standard Deviation, µ g/L
Grab from flask	10	25 159	25 143	43.3
Grab from flask	10	495.9	487.1	0.793
Grab from flask	10	50.00	50.89	0.279
Direct on-line	8	15.68	15.70	0.084
Direct on-line	9	6.359	6.996	0.091
Grab from flask	10	4.990	5.463	0.102
Direct on-line	10	0.519	0.488	0.037
Direct on-line	9	0.227	0.223	0.014

NOTE 1— Sample: Sucrose in water
Sample introduced by metering pump into continuous stream or as standard addition to flask
Calibration: 25.0×10^{3}µg/L C as potassium acid phthalate
25.0×10^{3}µg/L C as sodium carbonate

ANNEX

(Mandatory Information)

A1. BIBLIOGRAPHY

A1.1 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).

A1.2 Godec, R., O'Neill, K., Hutte, R., "New Technology for TOC Analysis in Water," *Ultrapure Water*, Dec. 1992, pp. 17–22.

A1.3 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.

A1.4 Barley, R., Hutte, R., O'Neill, K., "Application of TOC Monitoring in Semiconductor Manufacturing," *Ultrapure Water*, July/August 1994, pp. 20–25.