Designation: D 4779 – 93

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Method for Total, Organic, and Inorganic Carbon in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection [1]

This standard is issued under the fixed designation D 4779; 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), organic carbon (OC), and inorganic carbon (IC), in makeup water and high purity process water such as demineralizer effluent, condensate, and electronic grade rinse water. The tested concentration range is from 50 to 1000 µg of carbon per litre.

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

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

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 D-19 on Water[2]

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

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 *organic carbon (OC; frequently also TOC)*—carbon in the form of organic compounds.

3.2.3 *total carbon (TC)*—the sum of inorganic and organic carbon.

4. Summary of Test Method

4.1 For total carbon measurement, sample is injected into a gas-sparged reactor containing acidified potassium persulfate ($K_2S_2O_8$) or sodium persulfate ($Na_2S_2O_8$) solution; either elevated temperature or ultraviolet (UV) radiation is used to enhance the oxidation. Both inorganic and organic carbon compounds are converted into CO_2, which is swept, either directly or by trapping and thermal desorption, to a CO_2-specific linearized infrared detector. Output signal is measured as peak height or integrated area and results displayed as fractional milligrams of carbon per litre or equivalent. For direct organic carbon determination, the sample is acidified and sparged to remove inorganic carbon, prior to oxidation (purgeable organic compounds may be lost in this procedure). For inorganic carbon measurement, the CO_2 sparged off in the organic carbon step may be quantified, or the sample may be injected into the reactor with the UV source off so that organics are not oxidized.

4.2 Organic carbon may also be measured as the difference between“ total carbon'' and “inorganic carbon'' results.

5. Significance and Use

5.1 Accurate measurement of organic carbon in water at low and very low levels is of particular interest to the electronic, pharmaceutical, and steam power generation industries.

5.2 Elevated levels of organics in raw water tend to degrade ion exchange capacity. Elevated levels of organics in high purity water tend to encourage biological growth and, in some cases, are directly detrimental to the processes that require high purity water.

5.3 In the case of steam power generation, naturally occurring organics can degrade to CO_2 and low molecular weight organic acids which, in turn, are corrosive to the process equipment.

5.4 Inorganic carbon can also cause problems in a steam power system. CO_2 entering steam condensate that contains ammonia, reacts to form ammonium carbonate, which is not removed by the condenser air ejection system. If condensate polishers are operated beyond the ammonia break, continued operation on an ammonium cycle can result in selective exhaustion of the anion resin to the carbonate form, eluting silica, chloride, and sulfate into the condensate. The effect is immediately felt with powdered resin systems that have a very

---

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.11 on Standards for Water for Power Generation and Processes.

Current edition approved Sept. 15, 1993. Published November 1993. Originally published as D 4779 – 88. Last previous edition D 4779 – 88.

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

small inventory of anion resin.

6. Interferences and Limitations

6.1 If IC level is much higher than OC, the latter should be determined directly by acidifying the sample and sparging off IC before injection. Determination of OC by difference may introduce large error in such circumstances.

6.2 The process of removing IC by sparging may also remove some organic compounds, termed purgeable organic carbon (POC). The measurement done on the sparged sample will therefore be nonpurgeable organic carbon, and will not necessarily be equal to the OC figure arrived at by subtracting the IC measurement from the TC measurement. Users of this test method are responsible for determining whether the POC fraction is significant in their samples.

6.3 High-purity water is a very active scavenger of CO_2 and other impurities from air, syringes, bottles, pipes, etc. Stringent precautions must be taken to prevent sample contamination during collection, transportation, storage, and analysis.

6.4 *Method Accuracy*:

6.4.1 To produce accurate OC data, both method blank and recovery must be known.

6.4.1.1 *Method Blank*—The blank response of a method must be determined and subtracted from the sample response. This is especially true when making very low level measurements as in the case of high purity water applications. Some examples of contributors to method blank are: (1) the sample injection device used; (2) inlet septa; (3) chemical conversion method used; and (4) carrier gases, etc.

6.4.1.2 *Method Recovery*—To produce valid OC data, it must be assumed that all compounds are converted to a detectable species (that is, CO_2) with the same efficiency, independent of compound type or sample matrix. Since the conversion efficiency can be affected by many factors, it should be checked from time to time with selected compound types.

6.4.2 As an aid to checking recovery, the following compounds are listed in decreasing order of oxidation rate by UV-promoted persulfate oxidation:

6.4.2.1 Potassium acid phthalate (KHP),
6.4.2.2 Urea,
6.4.2.3 Nicotinic acid,
6.4.2.4 Pyridine,
6.4.2.5 n-Butanol,
6.4.2.6 Acetic acid,
6.4.2.7 Leucine, and
6.4.2.8 Acetonitrile.

6.4.3 As an expedient for most applications, method validation can be checked using KHP, acetic acid, and acetonitrile in deionized water. Ideally, all solutions should give equivalent conversion efficiencies (for example, percent recovery).

6.5 As with other methods for TC, IC, OC, and other water quality parameters such as COD, this test method inherently entails limitations. For example, the relatively low temperature oxidation will not oxidize graphite or fines from an activated carbon bed. Certain dissolved organics in water may not fully oxidize in this test method, yielding an error. One such component known to produce low recovery is carbon tetrachloride. The users of this test method are encouraged to verify performance of the method on the compounds or sample types of interest in their application.

7. Apparatus

7.1 *Carbon Analyzer*[3]—A reagent and sample introduction mechanism, a gas-sparged reaction vessel, a gas demister or dryer, or both, a CO_2 trap (optional), a CO_2-specific infrared detector, a control system, and a display.

7.2 *Sparging Apparatus*—A glass vessel and supply of CO_2-free gas to be bubbled through a water sample to remove inorganic carbon as CO_2.

7.3 *Sample Injector*—An all-fluorocarbon sampling valve, such as used for sample introduction in liquid chromatography, may be used to introduce the sample.

7.4 Fig. 1 shows a diagrammatic presentation of an analyzer that has been found satisfactory for this purpose.

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 shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[4] 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 decreasing the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise stated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II. The OC of this water should be measured regularly and this value should be taken into consideration when preparing standards. It will typically be in the range of 0.2 mg/L or less. Organic-free water is desired for establishing the method blank when measuring OC below 1 mg of carbon per litre. Absolutely carbon free water may not be realistically obtainable and measurement of its carbon level, if any, may be beyond the scope of this test method. However, a working approximation of this goal is the solution contained in

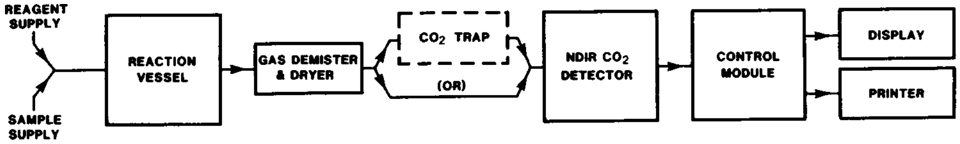

FIG. 1 Diagrammatic Presentation of an Analyzer

---

[3] Model DC-80 TOC analyzer marketed by Dohrmann and model 700 TOC analyzer marketed by OI Corp were used in the collaborative study.

[4] *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.

the reaction vessel of certain designs of instrument. Alternatively, water that has been acidified, mixed with persulfate to a final concentration of 2 % w/v, heated, or exposed to ultraviolet radiation, or both, and thoroughly sparged (see 9.3) may be used.

8.3 Amber glass bottles should be used to store reagent water, organic-free water, and also standard solutions. See Section 9 for preparation of bottles. It is preferable to dedicate bottles for these uses.

8.4 *Gas Supply*—Use a gas free of CO_2 and organic matter, of a purity as specified by the equipment manufacturer. Oxygen is recommended.

8.5 *Organic Carbon, Standard Solution*—Prepare a high-concentration standard using a water-soluble, stable reagent grade compound (see 6.4.2). This stock solution can then be further diluted to a concentration suitable for the method used. For example, to prepare a 2000 mg/L carbon standard of potassium hydrogen phthalate (KHP), note that KHP contains 0.471 g of carbon per gram, so 1 L of standard can be made by dissolving 2 divided by 0.471, or 4.25 g, of KHP in 1 L of water using a volumetric flask and reagent-grade water.

8.5.1 When preparing low-level standards, keep in mind the OC content of the reagent water used for dilutions (see Appendix X1).

8.6 *Phosphoric Acid* (H_3PO_4) (sp gr 1.69)—This compound may be used neat or diluted, as required by the manufacturer. Since it is added to the sample, the H_3PO_4 must be of the highest quality and must be handled carefully to minimize contamination.

8.7 *Persulfate Solution*—Prepare by dissolving an appropriate weight of $K_2S_2O_8$ or $Na_2S_2O_8$ in 1 L of water, to produce the concentration specified by the manufacturer. If specified, add 1 mL of H_3PO_4 (sp gr 1.69) and mix well. Store in a cool, dark location.

NOTE 1—Certain instruments may require carbon to be removed from acid and reagent as completely as possible. See the manufacturer's instructions.

9. Sample Handling

9.1 *Containers and Their Treatment*—Only amber glass bottles with TFE-fluorocarbon-lined bottle closures should be used. Clear glass bottles may be used if protected from sunlight. Where possible, bottles with volumes greater than 200 mL should be used, since small volumes (for example, 10 mL) are proportionately more susceptible to accidental contamination.

9.1.1 Clean sample bottles with chromic acid, rinse several times with water, and dry overnight at 400°C in a muffle furnace. If bottles are new, cleaning with laboratory detergent and rinsing with water may be sufficient, but blank values must be checked.

9.1.2 Rinse the TFE-fluorocarbon-linked closures several times with water, then allow them to soak in water overnight. Rinse these closures again with water before use.

9.1.3 Put the closures loosely on the bottles while the bottles are still warm. When the bottles have cooled to room temperature, tighten the closure.

9.1.4 Follow this cleaning procedure before each re-use of the bottles.

9.2 *Sampling and Preservation*—Collect the sample in accordance with Specification D 1192 and Practice D 3370.

9.2.1 It is recommended that any sample conditioning condensers, coolers, and associated fittings and valves used should be of either stainless steel or TFE-fluorocarbon and be maintained leak-free. When sampling steam condensate, the sample should be at less than 50°C and preferably near ambient temperature. Sampling points should never be in dead-ended portions of the high purity water systems.

9.2.2 Prior to taking a sample, flush the sample line using a continuous flow of high purity water. Sometimes several hours may be required, depending upon the length of the lines and flow rate permitted. Do not readjust flow rate before sampling.

9.2.3 When sampling, rinse and empty the bottle and the closure three times, fill the bottle from the bottom to overflowing and cap the bottle. If OC is to be measured instead of TC, it may be necessary to add H_3PO_4 to the sample bottle before the final fill-to-overflow, depending on the instrument used. Follow the manufacturer's instruction to bring the pH of the sample to about 2. Three drops of acid per 250 mL of sample is sufficient to acidify high purity water to a pH of 2 ± 1. Confirm this on a separate aliquot.

9.2.4 If the sample cannot be analyzed within 24 h of collection, it should be refrigerated at 4°C in an atmosphere free of organic vapors.

9.3 *Sparging to Remove Inorganic Carbon*—Since, by definition, low levels of carbon are to be expected in high-purity water, it is important to remove as much IC as possible before measuring OC. Use a high-efficiency fritted-glass sparger to admit 200 mL/min of carbon-free oxygen or nitrogen to the acidified sample in the original sample bottle. Fit the sparger and a coiled gas vent line into a bottle cap with TFE-fluorocarbon-backed liner. This cap should temporarily replace the original bottle cap when sparging is taking place. Continue sparging for at least 5 min. Take care to prevent cross-contamination during transfer of the sparger from one sample to another. Alternatively, such sparging may be done within the instrument.

9.4 *Analysis of Sample*—To minimize contamination, convey the sample to the reaction vessel through inert tubing, with volume determined by a sample loop filled and emptied by manual or automatic switching. It is important that the sample not be transferred to another container, or to a syringe.

9.4.1 Purge the head space in the sample bottle with pure gas as the sample is withdrawn to prevent contamination by laboratory air. This can most readily be accomplished if the sample pick-up tube, purge line, and gas vent line are all inserted into a bottle cap with TFE-fluorocarbon-backed liner that temporarily replaces the original bottle cap during sample analysis.

9.4.2 Because of the low carbon levels expected, it is advisable to analyze any one sample at least three times and to average the results.

9.4.3 After the analysis of a particular sample, empty the bottle, rinse with high-purity water, add three drops of concentrated H_3PO_4, and refill with pure water and cap for storage until the next use.

10. Instrument Adjustment, Calibration, and Operation

10.1 Follow the manufacturer's instructions for instrument warmup, gas flows, and liquid flows.

10.2 For calibration, make various dilutions of the 2000 mg/L standard organic solution. Also, see the Appendix X1 regarding dilutions. Dilutions used should be as specified by the manufacturer.

NOTE 2—Glassware used in preparation of standards should be cleaned as scrupulously as that used for samples (see 9.1.1).

NOTE 3—Low-concentration standards are particularly subject to changes over time, due to contamination or decomposition, and should be made fresh as needed.

10.3 Calibration protocols may vary with equipment manufacturers. Calibrate the instrument as instructed by the manufacturer, and use standards to verify linearity within the specific range of interest for actual measurements. Plots of standard concentration versus instrument reading may be used for this purpose.

11. Procedure

11.1 For sample sparging and introduction, see 9.3.

11.1.1 To measure IC, inject sample into the analyzer and analyze under conditions preventing oxidation of organic compounds (for example, low temperature, absence of UV radiation, absence of chemical oxidizer).

11.1.2 To measure OC, inject appropriate volume of sparged sample into the analyzer, or, alternatively, set the analyzer to automatically remove IC.

11.1.3 To measure TC, inject appropriate volume of unsparged sample.

11.2 *Instrument Blank*—In accordance with the manufacturer's instructions, measure the blank by sampling the reaction vessel fluid. Make the measurement five times. Calculate the average and precision of the last three measurements. Deduct the average from the measured value for samples. Keep a record of the average over time as a means to monitor instrument performance.

12. Calculations

12.1 Read carbon concentrations directly from the instrument, and subtract instrument blank values if necessary.

13. Precision and Bias [5]

13.1 *Collaborative Test*—This test method was tested by sending four identical samples to each of twelve laboratories and asking them to measure TC and OC exactly in accordance with this test method. Nine laboratories returned data. One sample was of acidified laboratory deionized water that had been sparged while subjected to UV irradiation. The other three were of laboratory DI water spiked from 50 to 1000 µg/L TC, and 0 to 375 µg/L OC. The spiking chemicals used were sodium carbonate, acetic acid, and pyridine.

13.2 *Analysis of Data*—The returned data were divided into two groups according to oxidation method and independently tested for outlier laboratories and individual results in accordance with Practice D 2777. All results passed these tests. The *F* test at 95 % confidence level was then applied to the two sets of data to determine if there was a difference between the results of the two oxidation methods. None was found, so the results were pooled for further analysis. Outlier tests were repeated and again all laboratories and results passed.

13.3 *Precision*—Separate determinations of precision were made for TC and OC measurements. The results of weighted least-squares calculations were as follows:

$$\begin{array}{ll} TC & S_t = 0.02x + 43 \\ & S_o = 0.01x + 5 \\ OC & S_t = 0.18x + 26 \\ & S_o = 0.01x + 4 \end{array}$$

where:

x = average amount found, µg of carbon per litre,

S_t = overall precision, and

S_o = single-operator precision.

13.3.1 Fig. 2 shows a plot of the four precision determinations against the amount recovered. The linear regression fits are also shown in Fig. 2.

13.3.2 Single-operator precision is similar for both TC and OC.

13.3.3 Overall precision is markedly poorer for OC than for TC. This is probably attributable to the sparging step used to remove IC. Whether this is performed manually or automatically, the additional sample handling can introduce errors through different sparging conditions, or through contamination, or both.

13.3.4 In general, overall precision is much poorer than single-operator precision. Various instrumental and operational factors can contribute to this, in addition to those in 13.3.3. Because of the difficulty of making up accurate calibration standards at very low concentrations, most instruments in the study were probably calibrated at well above the levels of carbon actually in the samples. Consequently, variations in linearity from detector to detector would be particularly pronounced. Treatment of instrument blank will also contribute to interlaboratory discrepancies. Finally, variation will almost certainly be introduced through unavoidable, though slight, contamination during preparation, shipping, and handling of samples. Note that the validation study samples were shipped ready-to-analyze rather than as concentrated samples for dilution at the analysis site.

13.4 *Bias*—Fig. 3 shows bias in the form of amount added plotted against amount recovered. In the TC measurement, the three spiked samples showed relatively similar positive biases of from 92 to 125 µg of carbon per litre, after allowance for the measured TC level of the reagent water. These values were from one to four times the S_t for the sample. This bias was probably due to absorption of atmospheric CO_2 during the preparation and bottling of the samples.

13.4.1 The OC bias was lower than S_t for each of the three spiked samples, after allowance for the measured OC content of the water. This fact supports the contention that the samples were subject only to CO_2 contamination during the artificial process of spiking, and that additional organic carbon was not picked up.

---

[5] Supporting data are available from ASTM Headquarters. Request RR: D-19-1135.

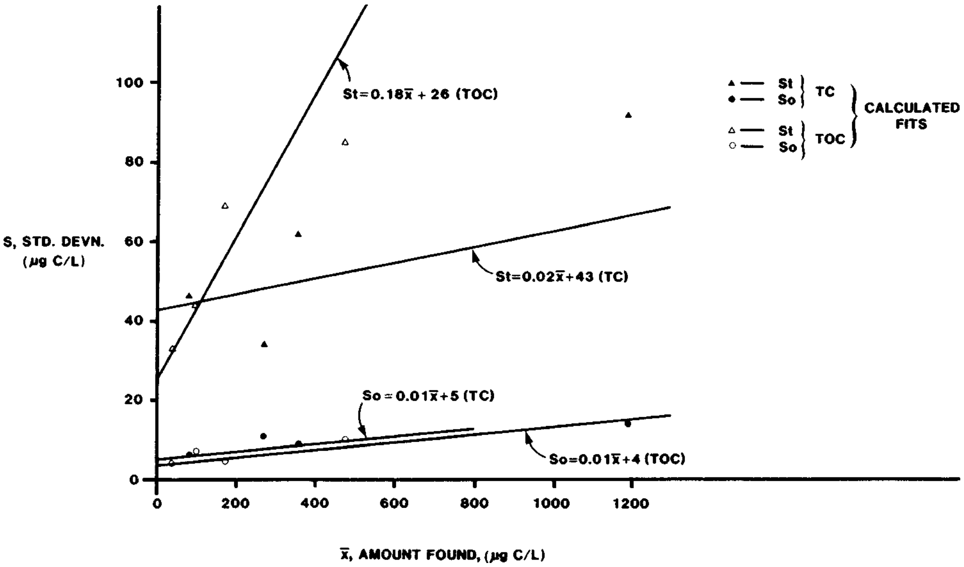

FIG. 2 Precision versus Amount Found

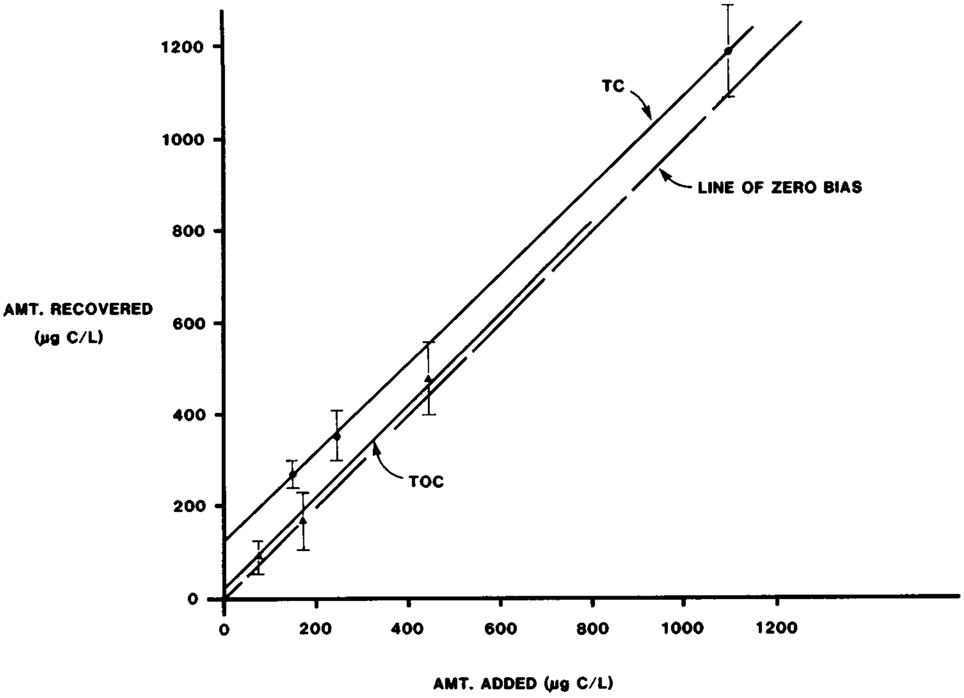

FIG. 3 Bias

13.5 *Matrix Effects*—All participants were asked to analyze a high-purity water of choice, then to use it to dilute the remainder of one of the samples provided, and finally to analyze that diluted sample. The waters taken were all nominally of high purity, yet varied from 7 to 370 µg of carbon per litre in TC content. Recovery of a nominal 119 µg of carbon per litre of added TC varied from 54 to 279 µg of carbon per litre. Similar highly variable results were found for OC measurement. No conclusions can be drawn about matrix effects on recovery, partly because of the poor data, and partly because the matrix was of essentially the same nature as the reagent water used in the test samples. Instead, it can be concluded that there was substantial contamination during the process of dilution and analysis, in addition to errors from sources mentioned in 13.3.4.

13.6 *Conclusion*—The interlaboratory study indicates that this test method can provide unbiased OC results down to the limit of the applicable range. TC figures, however, may be subject to positive bias from CO_2 in entrained air. Single-operator precision is generally adequate, but many factors combine to make interlaboratory comparisons difficult. Laboratories desiring to use this test method should be aware of the possibility of poor reproducibility and should refine techniques to minimize this problem.

14. Keywords

14.1 carbon; high purity water; ion exchange; organic compound; process water

APPENDIX

(Nonmandatory Information)

X1. COMPENSATION FOR CARBON CONTENT OF WATER WHEN PREPARING CALIBRATION STANDARDS

X1.1 Although it is possible to prepare water with a low level of carbon (less than 100 µg/L) by such procedures as acidification, irradiation, or treatment with a chemical oxidant, followed by sparging or boiling, it is impossible to remove all carbon. Consequently, when preparing low-level standards, the level of carbon in the water must be allowed for. The following procedure uses a 10 mg of carbon per litre standard as an example. Observe cautions regarding contamination mentioned in this test method.

X1.1.1 Prepare a 10.0 mg carbon per litre standard by drawing 1.00 mL of 2000 mg of carbon per litre carbon standard solution into two separate 200-mL volumetric flasks using a Mohr measuring pipet and making up to the mark with water. Calibrate the analyzer at 10.0 mg of carbon per litre using one solution, while reserving the other.

X1.1.2 After careful flushing of the injection equipment and lines, analyze replicate injections of the reagent water for TC. Determine and subtract a system blank as instructed by the manufacturer.

X1.1.3 Calculate the volume of water to be added to the reserved standard to bring its concentration down to 10.0 mg of carbon per litre as follows:

$$\text{volumeto be added, mL,} = 20x + 2x^2$$

where x is the average TC level in the water in milligrams per litre.

X1.1.4 Add this volume to the 200-mL volumetric flask using a Mohr measuring pipet and mix well.

X1.1.5 Recalibrate the instrument at 10.0 mg of carbon per litre using this test method.

X1.1.6 Redetermine the TC content of the water, readjust the standard, and repeat this procedure until no significant change is found in the TC value of the water.

X1.2 An alternative procedure is to add aliquots of carbon to the water over a range from 0 to 2.00 mg of carbon per litre, determine TC, and extrapolate to zero-added. The intercept will then be the TC concentration in the water.