Hach Method 10267

Spectrophotometric Measurement of Total Organic Carbon (TOC) in Finished Drinking Water

Hach Company Method 10267
TNTplus 810/811

Revision 1.2
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Spectrophotometric Measurement of TOC in Finished Drinking Water

1.0 Scope and Application

1.1 This method is for the determination of total organic carbon (TOC) in finished drinking water.

1.2 The method is applicable in the range from 1.0 to 25.0 mg/L TOC. High TOC values can be determined by sample dilution.

1.3 This method is equally effective in performance and use to SM 5310-C and EPA 415.3 for the purposes of regulatory compliance reporting of TOC.

2.0 Summary of Method

2.1 The Hach TNTplus TOC chemistry follows acid persulfate digestion to oxidize TOC to carbon dioxide (CO_2). The generated CO_2 passes through a gas-permeable membrane into an indicator solution is measured spectrophotometrically. Inorganic carbon (IC) is removed from the sample prior to digestion by acidification and agitation.

2.2 The CO_2 produced from oxidation is detected and quantified using visible spectrum spectrophotometry at 435 nm.

3.0 Interferences

3.1 The items listed in the *Interfering substances* table have been individually checked up to the given concentrations and do not cause interference. The cumulative effects and influence of other ions have not been determined. Measurement results can be verified using sample dilutions or standard additions.

Interfering substance	Interference level (mg/L)
NH_4^+	200
Ca^+	2000 as $CaCO_3$
Cl^-	1000
Mg^+	2000 as $CaCO_3$
Inorganic Carbon	250 CO_3

4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst.

4.2 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

4.3 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of any chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in Sections 16.3 and 16.4.

5.0 Equipment

Note: *Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

5.1 Sampling equipment

5.1.1 Sample collection bottles – Collect samples in pre-cleaned glass bottles. Pre-cleaned bottles have been acid rinsed, sealed with foil, and baked at 400 °C for at least 1 hour.

6.0 Equipment for sample analysis

6.1 Hach Company DR 6000, DR 3900, DR 1900 spectrophotometer, or equivalent

6.2 Hach Company DRB200 reactor, or equivalent

6.3 Hach Company TOC X-5 shaker or equivalent

6.4 Equipment for standard preparation

6.4.1 Volumetric flask – Glass, 500-mL and 200-mL.

6.4.2 Volumetric pipette – Glass, assorted sizes.

7.0 Reagents and Standards

7.1 Organic-free water – Water in which TOC is below the detection limit of this method. Water prepared by passage of tap water through ion exchange and UV oxidation has been shown to be an acceptable source of reagent water.

7.2 Hach Company TNTplus TOC, Cat. No. TNT810 and TNT811.

7.3 Hach Company TOC Standard Solutions: 1000 mg/L as TOC (Cat. No. 2791505) or equivalent

7.4 Method detection limit (MDL) solution

7.4.1 If an MDL is required, prepare and measure 7 or more replicates of an MDL stock solution by diluting 3.0 mL of the 1000 mg/L standard spiking solution (Section 7.3) to 1000 mL. Final concentration = 3.0 mg/L TOC.

7.5 Initial precision and recovery (IPR) solution

7.5.1 Prepare and measure 4 or more replicates of an IPR stock solution by diluting 7.5 mL of the 1000 mg/L standard spiking solution (Section 7.3) to 500 mL. Final concentration = 15 mg/L TOC.

8.0 Sample Collection, Preservation and Storage

8.1 Samples should be collected in pre-cleaned glass bottles. Pre-cleaned bottles have been acid rinsed, sealed with foil, and baked at 400 °C for at least 1 hour. Protect samples from sunlight.

8.1.1 Rinse the sample bottle several times with sample. Fill the bottle completely full.

8.2 Analyze samples as soon as possible. If immediate analysis is not possible, preserve samples by cooling to <6 ^{o}C, and adjust the pH to < 2 with HCl, H_2SO_4, or H_3PO_4. Analyze the preserved within 28 days of preservation.

9.0 Quality Control

9.1 Each laboratory that uses this method is expected to operate a formal quality assurance program (16.1). The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analyses of laboratory prepared water standards as a test of continued performance to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Sections 9.2 and 9.3. The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery sample that the analysis system is in control.

9.1.2 Accompanying QC for the determination of TOC is required per analytical batch. An analytical batch is a set of samples processed during a contiguous 8-hour period. Each analytical batch must be accompanied by an ongoing precision and recovery sample (OPR), matrix spike sample (MS), and matrix spike duplicate sample (MSD) resulting in a minimum of four analyses (1 OPR, 1 sample, MS, and MSD).

9.2 Initial demonstration of laboratory capability.

9.2.1 To establish the ability to detect TOC the analyst shall determine the MDL using the apparatus, reagents, and standards that will be used in the practice of this method. An achieved MDL less than or equal to the MDL in Section 13.0 is recommended prior to the practice of this method.

9.2.2 Prepare and measure seven replicates of the MDL standard (Sect. 7.4) according to the procedure in Section 11.

9.2.3 Using the results of the set of seven analyses, compute the MDL using the following equation:

$$MDL = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}} \times 3.14$$

where:

n = Number of samples (7)
x = measured concentration of each sample

9.3 Initial precision and recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.3.1 Prepare and measure four samples of the IPR standard (Sect. 7.5) according to the procedure in Section 11.

9.3.2 Using the results of the set of four analyses, compute the average percent recovery (x) and the standard deviation of the percent recovery (s) for TOC. Use the following equation for calculation of the standard deviation of the percent recovery:

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

where:

n = Number of samples (4)
x = % recovery in each sample

9.3.2.1 Compare s and x with the corresponding limits for initial precision and recovery in Table 1 (Sect. 17). If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4 Ongoing precision and recovery (OPR) - To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the analyst shall perform the following operations:

9.4.1 Prepare a 15 mg/L recovery standard with each analytical batch as described in Sect. 7.5.1 and measure according to the procedure in Section 11. Calculate the percent recovery and compare this value with the limits for ongoing recovery in Table 2 (Sect. 17). If the percent recovery meets the acceptance criteria, system performance is acceptable. If the percent recovery falls outside the acceptance criteria, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4.1.1 Measure a field sample. After measuring the background concentration, spike the sample with a known concentration of TOC. The spike concentration should be 1-5 times the background concentration, but still within the reporting range of the method. Prepare a duplicate of this spiked sample.

9.4.1.2 Measure the spike duplicates and calculate the spike recovery for each sample and the relative percent difference (RPD) between the two results.

Use the following equation to calculate the spike recovery:

$$Spike\ Recovery = \frac{[Conc] - [Bkgd]}{[Sp]} \times 100$$

where:

[Conc] = the measured concentration of the spiked sample
[Bkgd] = the measured concentration of the un-spiked sample
[Sp] = the concentration of the spike

$$RPD = \frac{|Conc_1 - Conc_2|}{\left(\frac{Conc_1 + Conc_2}{2}\right)} \times 100$$

where:

$Conc_1$ = the concentration of the first spiked sample
$Conc_2$ = the concentration of the second spiked sample

9.4.1.3 Compare the spike recoveries and RPD with the corresponding limits in Table 2 (Sect. 17). If recoveries and RPD meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If recoveries or RPD fall outside the limits, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4.1.4 The laboratory should add results that pass to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Express the accuracy as a recovery interval from R - 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85% to 105%. Control charts are acceptable for evaluating process control, but under no circumstances can the control limits be widened beyond those established in the acceptance criteria defined in Section 13.

10.0 Calibration and Standardization

10.1 The Hach DR series spectrophotometers have a built-in calibration that is automatically used when the TNTplus TOC vial is inserted into the instrument. No further initial calibration is required. However, the instruments have the capability of developing a user-calibration. See manufacturer's manual for instructions.

10.2 Calibration Verification

10.2.1 To verify that the instrument is measuring TOC properly, analyze a 3.0 mg/L (Sect. 7.4) and 15.0 mg/L (Sect. 7.5) TOC standard. Results should be within 15 percent of the actual value. Perform this calibration verification daily while instrument is in use. If the calibration verification standard result is outside the limit, it is unacceptable. In this event, correct the problem, and repeat the test.

11.0 Procedure

11.1 Instrument Setup – follow the instrument manufacturer's instructions for instrument setup.

11.2 Preparation

11.2.1 Low Range TNT 810: Pipet 2.0 or 2.5 mL of sample into the reagent vial, use volume as indicated in manufacturer's instructions.

11.2.2 High Range TNT 811: Pipet 1.0 mL of sample into the reagent vial.

11.3 Total Inorganic Carbon Removal

11.3.1 Place the uncapped reagent vial into the TOC-X5 shaker, raise the fan assembly, and turn the shaker on. The shaker will run for 5 min.

11.4 Reaction

11.4.1 Place the membrane cap on the indicator vial.

11.4.2 Invert the indicator vial and screw the other side of the membrane cap to the shaken reagent vial. Do not invert or shake the assembled vials.

11.4.3 Heat the reactor block to 100 °C.

11.4.4 Place the assembled vials into the reactor block, reagent vial down.

11.4.5 React for 120 minutes.

11.5 Analysis

11.5.1 Carefully remove the assembled vials from the reactor.

11.5.2 Invert the assembly so that the indicator vial is down.

11.5.3 Wipe the indicator vial and insert into the spectrophotometer. The instrument reads the barcode, then selects and performs the correct test. No zero is required. Results are reported in mg/L TOC.

12.0 Data Analysis and Calculations

12.1 TOC concentration is calculated automatically against internal instrument calibration.

13.0 Method Performance

Performance of the method was demonstrated in multi-lab studies comparing the method against EPA Reference Method SM 5310-C. The method was evaluated in a low ionic strength reference matrix as well as multiple geographically diverse finished drinking water samples obtained from both surface water and ground water sources.

Validation Results	Section	Limit
Method Detection Limit	9.2	0.33 mg/L TOC
Initial Recovery	9.3	103%
Initial Recovery Range	9.3	97.5% - 109%
Initial Precision 95%	9.3	0.03
Matrix Recovery	9.4.1	99.5%
Matrix Recovery Range	9.4.1	94.3 – 105%
Matrix Recovery Precision 95%	9.4.1	0.06

14.0 Pollution Prevention

14.1 Follow guidelines in Section 15.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect air, water, and land by minimizing and control all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 For further information on waste management, consult "The Waste Management manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

16.0 References

16.1 "Protocol for the Evaluation of Alternate Test Procedures for Organic and Inorganic Analytes in Drinking Water," USEPA, EPA-815-R-15-007, February 2015.

16.2 40 CFR 136, Appendix B.

16.3 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976)

16.4 "Safety in Academic Chemistry Laboratories," American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979.

16.5 "Water Analysis Handbook," Hach Company, 8th Edition, 2013.

17.0 Tables

17.1 Acceptance Criteria for Performance tests – The QC performance criteria for this method was performed with a Hach Company DR3900 Spectrophotometer and TNTplus 810 Reagent.

Table 1. Initial Precision and Recovery Acceptance Criteria

Parameter	Acceptance Criteria
Relative Standard Deviation	≤ 10%
Percent Recovery	90-110%

Table 2. Ongoing Precision and Recovery Acceptance Criteria

Parameter	Acceptance Criteria
Lab Fortified Blank Recovery	90-110%
Sample Matrix Spike Recovery	70-130%
Sample Matrix Spike RPD	≤ 10%

18.0 Glossary of Definitions and Purposes

The definitions and purposes are specified to this method but have been conformed to common usage as much as possible.

18.1 Units of weight and measure and their abbreviations

18.1.1 Symbols
°C: degrees Celsius

18.1.2 Alphabetical characters
mg/L: milligram per liter

18.2 Definitions, acronyms, and abbreviations

18.2.1 MDL: Method detection limit

18.2.2 IPR: Initial precision and recovery

18.2.3 OPR: On-going precision and recovery

18.2.4 MS: Matrix spike

18.2.5 MSD: Matrix spike duplicate

18.2.6 LIS: Low ionic strength, deionized water