

Standard Operating Procedure for the
Analysis of Dissolved and Total
Organic Carbon
CCAL 20A.3

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Table of Contents

1.0	Scope and Application	3
2.0	Summary of Method	3
3.0	Definitions	3
4.0	Interferences	4
5.0	Safety	4
6.0	Equipment and Supplies.....	5
7.0	Reagents and Standards	6
7.1	Preparation of Reagents	6
7.2	Preparation of Standards	6
8.0	Sample Handling and Storage.....	6
9.0	Quality Control	7
10.0	Calibration and Standardization	7
11.0	Procedure	8
11.1	Shimadzu TOC-VCSH Instrument Operating Parameters.....	8
11.2	Procedure	8
11.3	System Notes.....	8
11.3.1	Yearly preventative maintenance as suggested by the manufacturer is required for optimum performance.....	8
12.0	Data Analysis and Calculations	8
13.0	Method Performance	9
14.0	Pollution Prevention	9
15.0	Waste Management.....	9
16.0	References	10
17.0	Tables, Diagrams, Flowcharts, and Validation Data.....	10
18.0	Document Revision History.....	10

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1.0 Scope and Application

- 1.1 This method details the determination of Dissolved Organic Carbon and Total Organic Carbon in fresh waters by oxidative combustion and infrared analysis. This practical range of determination for this method as reported by the manufacturer is 0 – 25000 ug/L. The laboratory determined Method Detection Limit is 50 ug/L.

2.0 Summary of Method

- 2.1 Samples are acidified with hydrochloric acid and sparged with zero air to remove inorganic carbon. The sample is then injected into a heated reaction chamber packed with platinum catalyst. The water is vaporized and the organic carbon oxidized to carbon dioxide and water by catalytic combustion. The CO₂ formed is transported to the detector in a carrier gas stream and measured directly by an infrared detector. The amount of CO₂ is directly proportional to the concentration of carbonaceous material in the sample.

3.0 Definitions

- 3.1 DI water: Water that has been through a deionization system to produce water similar to ASTM Type I reagent with 16.7 Mohms resistivity (ASTM) (Reference 16.3).
- 3.2 Method Detection Limit (MDL): The minimum concentration of an analyte that can be measured and reported with 99% confidence, based on a one-sided 99% confidence interval (*t*-value at a significance level of 0.01 and *n-1* degrees of freedom) from at least seven repeated measurements of a low concentration standard measured within an analysis run.

$$\text{MDL} = ts$$

Where,

t = Student's t value at a significance level of 0.01 and $n-1$ degrees of freedom

s = standard deviation of at least seven repeated measurements of a low level standard

4.0 Interferences

- 4.1 This method is actually for analysis of NPOC (non-purgeable organic carbon) which refers to organic carbon present in a non-volatile form. In most literature for water analysis, the terms are used interchangeably because the amount of purgeable organic substances in natural waters is small. Because purgeable organic substances may be lost during sparging, true TOC may be determined by calculating the difference between TC and IC.
- 4.2 Any contact with organic material may contaminate a sample. Care must be taken in sample handling and storage to minimize exposure.
- 4.3 This procedure is applicable only to homogeneous samples which can be reproducibly injected by microliter syringe into the instrument; the inner diameter of the syringe and injection tubing limit the maximum particulate size that may be included with the sample aliquot.
- 4.4 Inorganic carbon is considered an interference in the analysis and must be removed or accounted for in the final calculation.
- 4.5 Removal of inorganic carbon by acidification and sparging may result in the loss of volatile organic substances.
- 4.6 Combustion temperatures above 950°C are required for decomposition of some carbonates. Acidification may aid decomposition. Elemental carbon is not oxidized at the lower temperature used in this method, but it is generally not present in fresh water samples.

5.0 Safety

- 5.1 The toxicity or carcinogenicity of each reagent has not been precisely determined; however, each chemical should be regarded as a potential health hazard. Exposure to these chemicals should be reduced to the

lowest possible level. Cautions are included for known extremely hazardous materials.

5.2 The following chemicals have the potential to be highly toxic or hazardous. For detailed explanations, consult the MSDS.

5.2.1 Hydrochloric Acid

5.2.2 Sodium Carbonate

6.0 Equipment and Supplies

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.*

- 6.1 Shimadzu TOC-VCSH Analyzer
 - 6.1.1 Shimadzu ASI-V Autosampler
 - 6.1.2 Instrument Controller
 - 6.1.3 Data Collection Software
 - 6.1.4 High Sensitivity Catalyst
 - 6.1.5 CO₂ Absorber (soda lime)
- 6.2 “Ultra Zero Air” compressed air and regulator
- 6.3 40 mL borosilicate vials and septum caps
- 6.4 Laboratory glassware and pipettes
- 6.5 Balance
- 6.6 Safety glasses
- 6.7 Nitrile gloves
- 6.8 Lab coat or apron
- 6.9 Laboratory exhaust fume hood
- 6.10 High Density Polyethylene (HDPE) bottles
- 6.11 Muffle Furnace

7.0 Reagents and Standards

7.1 Preparation of Reagents

7.1.1 *2N Hydrochloric Acid*

Dilute one part concentrated hydrochloric acid with five parts DI water. A final concentration accuracy of $\pm 2\%$ is acceptable.

7.1.2 *pH 2 Hydrochloric Acid (system rinse)*

Dilute 5 mL of 2N HCl to 1 L with DI water.

7.2 Preparation of Standards

7.2.1 *Calibration Standards:*

Standards are prepared by dilution of a single element standard purchased from a vendor that provides traceability to NIST standards. Working standards for calibration are prepared at concentrations stated below.

Standard #	mg C/L
1	0.20
2	0.50
3	1.00
4	2.00
5	5.00

7.2.2 *Second Source Check Standard:*

Standard is prepared by dilution of a single element standard purchased from a vendor that provides traceability to NIST standards, this from a source other than that of the calibration standards. Check standard concentration should be mid-calibration range; currently 1.00 mg C/L.

8.0 Sample Handling and Storage

- 8.1 If required, unfiltered samples are filtered upon receipt through glass fiber (Whatman GF/F) filters into clean HDPE bottles and stored at 4°C in the dark until time of analysis. For samples less than 1-L in volume, a pre-ashed filter must be used. If samples must be held prior to analysis, they are stored frozen at -18°C.

9.0 Quality Control

- 9.1 Preparation of stock standards is recorded on worksheets and documented by weight of standard added to a given flask before dilution to volume with DI water. All records of certification are kept on file at CCAL Laboratory.
- 9.2 Blank: DI water run before and after the calibration, and after every check standard.
- 9.3 Second Source Check Standard: Run every ten samples to monitor drift and recovery.
- 9.4 Method Detection Limit (MDL): Established for each analyte. Based on a one-sided 99% confidence interval (t-value) from at least seven repeated measurements of a low concentration standard. The t-distribution value is multiplied by the standard deviation of the population (n-1) to obtain the MDL.
- 9.5 Analytical Duplicate: Separate analysis from the same sample aliquot. One per ten samples.
- 9.6 Standard recoveries are tracked over time to monitor overall performance.
- 9.7 Samples with concentration greater than the highest calibration standard are diluted and reanalyzed.
- 9.8 An atmospherically equilibrated bulk sample is analyzed once each analysis batch to monitor precision over time.

10.0 Calibration and Standardization

- 10.1 Balances: calibrated yearly by external vendor.
- 10.2 Pipette delivery checked by weight to within 1% of theoretical weight of aliquot volume.
- 10.3 The instrument is calibrated every analysis run. The r^2 value of each calibration curve should be greater than 0.999.
- 10.4 Check standard recovery must be within 10% of theoretical value.

11.0 Procedure

11.1 Shimadzu TOC-VCSH Instrument Operating Parameters

Compressed Air Pressure:	
Supply pressure @ tank regulator	600 kPa
Carrier Gas Pressure	200 kPa
Carrier Gas Flow Rate	150 mL/min
Sample Volume	500 uL
Acid Addition	1.5 % v/v 2N HCl
Analysis	NPOC
Calibration Method	Linear Regression
Catalyst	High Sensitivity
Spurge Time	4 minutes
Washes	2
Combustion Temperature	680°C

11.2 Procedure

- 11.2.1 Stabilize system with pH ~2 HCl (sets of 10 repeated measurements). Monitor peak profile for consistency.
- 11.2.2 Follow manufacturer's instructions for analysis. Refer to instrument manual.
- 11.2.3 After use, sample vials and septum are rinsed well with DI water and soaked overnight in 0.5 N HCl, rinsed well again and soaked overnight in DI water and air dried. In addition, the vials are baked at 550°C for three hours, cooled, and stored in a seal container until use.

11.3 System Notes

- 11.3.1 Yearly preventative maintenance as suggested by the manufacturer is required for optimum performance.
- 11.3.2 Catalytic tube must be maintained and replaced as needed.

12.0 Data Analysis and Calculations

- 12.1 A standard curve is prepared in Excel by plotting standard response against known concentration. Sample response is compared to the standard curve to determine concentration.
- 12.2 All raw data is copied into a template for calibration and sample concentration determination. Organic carbon in DI water must be corrected for in determination of sample concentration. The calibration

curve is shifted to pass through zero and the sample concentration determined from this corrected curve.

- 12.3 Samples with concentration greater than the highest calibration standard are diluted and reanalyzed.

13.0 Method Performance

- 13.1 This method was validated through inter-laboratory studies. The CCAL Water Analysis Laboratory participates in the National Water Research Institute's (NWRI) Environment Canada Proficiency Testing (PT) Program.

14.0 Pollution Prevention

- 14.1 The chemicals used in this method pose little threat to the environment when properly managed.
- 14.2 All standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of disposable waste.
- 14.3 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

15.0 Waste Management

- 15.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, and to protect the environment by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is 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 Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington DC, 20036.

16.0 References

- 16.1 Standard Methods For The Examination of Water and Wastewater, Method 5310 B; Total Organic Carbon (TOC), High-Temperature Combustion Method. American Public Health Association. 21st Edition, 2005.
- 16.2 Code of Federal Regulations. Protection of Environment. Section 40, Appendix B to Part 136. Definition and procedure for the determination of the method detection limit. Revision 1.11. Revised July 1, 1990. Office of the Federal Register, National Archives and Records.
- 16.3 ASTM. American Society for Testing and Materials. Standard Specifications for Reagent Water. D1193-77 (Reapproved 1983). Annual Book of ASTM Standards, Vol. 11.01. ASTM: Philadelphia, PA, 1991.
- 16.4 Shimadzu TOC-V CPH/CPN & TOC-Control V Software User's Manual. Shimadzu Corporation; Analytical & Measuring Instruments Division; Kyoto, Japan.
- 16.5 EPA Method 415.1, Editorial Revision 1974. "Organic Carbon, Total (Combustion or Oxidation)", US Environmental Protection Agency; Washington DC.
- 16.6 US EPA, November 2004, Revision 1. "Total Organic Carbon", Method 9060A, SW-846, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

- 17.1 NA

18.0 Document Revision History

Original Document: June 2006

Version: 20A.0

Edit Date: May 2009

New Version: 20A.1

Section 1.1: replaced manufacturer's detection limit with laboratory determined detection limit

Section 5.2: correct chemicals with potential

Section 6.11: add Muffle Furnace to Equipment List

Section 7.1.2: add system rinse reagent to Reagent Preparation

Section 9.8: add sample check standard used to monitor precision

Edit Date: February 2010

New Version: 20A.2

Address Update

Section 13.1: add Environment Canada Proficiency Testing Program participation.

Edit Date: March 2015

New Version: 20A.3

Section 6.2: add Ultra Zero Air requirement

Section 8.1: add pre-ashed filter requirement for sample volumes <1-L

General editing