Standard Operating Procedure for the Analysis of Dissolved Inorganic Carbon

CCAL 21A.1

Cooperative Chemical Analytical Laboratory
College of Forestry
Oregon State University
321 Richardson Hall
Corvallis, Oregon

Prepared by Kathryn Motter
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1.0 Scope and Application

1.1 This method details the determination of Dissolved Inorganic Carbon in fresh waters by acidification and sparging followed by infrared analysis. The 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 phosphoric acid and sparged with zero air to convert inorganic carbon to volatilized carbon dioxide. The CO_2 formed is transported to the detector in a carrier gas stream and measured directly by an infrared detector. The measured CO_2 consists of carbon derived from carbonates, hydrogen carbonates and dissolved carbon dioxide 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 Atmospheric contact must be limited to minimize carbon dioxide outgassing or uptake.

4.2 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.

4.4 Purgeable organic carbon that may be volatized during the sparging process is considered interference in the analysis.

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 Phosphoric Acid
  5.2.2 Hydrochloric Acid
  5.2.3 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 with IC Reaction Vessel

6.1.1 Shimadzu ASI-V Autosampler
6.1.2 Instrument Controller
6.1.3 Data Collection Software
6.1.4 CO_2 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 60 mL Leur Lock Syringes

6.11 Syringe Filters (0.45 um pore size, nylon filter, 25 mm)

7.0 Reagents and Standards

7.1 Preparation of Reagents

7.1.1 *25% Phosphoric Acid (weight %)*
Dilute 50 mL of concentrated phosphoric acid (85 %) to a final volume of 250 mL with DI water. A final concentration accuracy of ± 2% is acceptable.

7.1.2 *pH 2 Hydrochloric Acid (system rinse)*
Dilute 5 mL of 2N HCl to 1 L with DI water.

7.1.3 *2N Hydrochloric Acid*
Add 25 mL of concentrated HCl to 125 mL of 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
6	7.50
7	10.00
8	15.00
9	20.00

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 for high and low ranges; currently 1.00 and 10.00 mg C/L.

8.0 Sample Handling and Storage

8.1 Unfiltered samples are delivered to the lab in sealed syringes and held refrigerated until time of analysis. Samples are analyzed within 48 hours of delivery to the lab. Immediately prior to analysis, samples are filtered through syringe filters directly into clean analysis vials, minimizing contact with the atmosphere and mixing of air into the sample. Samples are filled to the brim with reverse meniscus and capped immediately with septum caps.

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 the CCAL Laboratory.

9.2 Blank: DI water run before and after the calibration, and after every check standard to monitor drift and carry-over.

9.3 Second Source Check Standard: Run every ten samples to monitor drift and analysis efficiency.

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 if additional syringe is provided.

9.6 Standard recoveries are tracked over time to monitor overall performance.

9.7 When sample volume allows, samples with concentration greater than the highest calibration standard are diluted and reanalyzed.

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	25 % by wt H_3PO_4
Analysis	IC
Calibration Method	Linear Regression
Catalyst	NA
Sparge Time	4 minutes
Washes	2
Combustion Temperature	NA

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. The vials and septum caps are stored in sealed containers 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 Periodic regeneration of the IC solution with phosphoric acid. Regeneration is performed prior to each analysis set if the instrument has not been turned off.

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. Carbon in DI water that is used to prepare calibration standards must be corrected for in determination of sample concentration. The calibration curve is shifted to pass through zero and the sample concentration is determined from this corrected curve.

12.2 When sample volume allows, 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 USEPA. 2004. National Wadeable Streams Assessment: Water Chemistry Laboratory Manual. EPA841-B-04-008. U.S. Environmental Protection Agency, Office of Water and Office of Research and Development, Washington DC.

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.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 NA

18.0 Document Revision History

Original Document: February 2010
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Edit Date: March 2015
New Version: 20A.3
Section 6.2: add Ultra Zero Air requirement
Section 7.2.1: add additional high concentration calibration standards
Section 7.2.2: change to use of prepared standards and add high check standard
Section 13: add NWRI participation
General editing