USGS Water Science Center Laboratory, Troy, NY

Dissolved Inorganic Carbon

Standard Operating Procedure

1. Scope and Application

1.1 Analytes

Dissolved inorganic carbon (DIC)

1.2 Reporting Limit

41.63 μmol C/L

1.3 Applicable Matrices

This method is used to determine the concentrations of dissolved inorganic carbon in precipitation, dilute surface waters and soil waters.

1.4 Dynamic Range

The analytical range for the determination of DIC is from 8.326 μmoles C/L (0.1 mg C/L) to 832.6 μmoles C/L (10.0 mg C/L). Sample concentrations that exceed this range must be diluted and reanalyzed. Sample concentrations below the reporting limit are flagged "<" in the Laboratory Information Management System (LIMS).

1.5 Interferences

Method interferences (positive bias) may be caused by contaminants in the carrier gas, dilution water, reagents, glassware, or other sample processing hardware (i.e. filtering apparatus).

2. Summary of Procedure

The sample is acidified with phosphoric acid and sparged with ultra-high purity nitrogen. This process converts the inorganic carbon to carbon dioxide which is subsequently measured by an infrared detector.

3. Safety Issues

3.1 Chemical Hazards

A. Handle phosphoric acid (H_3PO_4) with care.
B. All strong acids and bases should be mixed in a fume hood.
C. Gloves, safety glasses, and lab coats should be worn when preparing and performing this analysis.
D. For proper handling techniques for specific chemicals, consult the appropriate Safety Data Sheet (SDS).

4. Sample Preservation, Containers, Processing and Analysis Times

4.1 Sample Preservation

Samples are unfiltered and stored at 4°C.

4.2 Containers

Samples are stored in 40-mL amber glass vials with Teflon septa seals. The vials are new or have been recycled and cleaned using the laboratory dishwasher. The septa seals are replaced after each use.

4.3 Processing and Analysis Times

Sample processing: none
Lab analysis: one week
LIMS entry: one week

5. Reagents and Standards

5.1 General Information

All reagents are commercially purchased, reagent grade or higher quality, and should be stored in the original container. Date the reagent bottles when received and when opened. Note expiration date, if any. No verification of the reagents is necessary.

5.2 Reagents

A. Nitrogen

Use commercially purchased ultra-high purity (UHP) nitrogen.

B. 21% Phosphoric Acid

1. Add 37 mL concentrated phosphoric acid (H_3PO_4) to a 500-mL volumetric flask that contains 188 mL of Milli-Q water.
2. Mix thoroughly.
3. Pour into designated glass reagent bottle.
4. Prepare monthly or as needed.

5.3 Standards

A. Inorganic Carbon Standard Stock Solution, 1000 mg C/L

1. Dry about 5 g anhydrous sodium carbonate (Na_2CO_3) at 105°C for 2 hours and allow to cool in desiccator.
2. Dry about 5 g of anhydrous sodium bicarbonate ($NaHCO_3$) at 105°C for 2 hours and allow to cool in desiccator.
3. Dissolve 1.103 g dried Na_2CO_3 in a 250-mL volumetric flask containing about 100 mL Milli-Q water. Add 0.874 g of $NaHCO_3$ and dissolve.
4. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
5. Store in an amber glass bottle at 4°C; label and date.
6. Prepare every six months.
7. To avoid contamination, aliquots of stock solution must not be withdrawn directly from the bottle.

B. Inorganic Carbon Standard Substock Solution

1. Pipet 1.0 mL of standard stock solution into a 100-mL volumetric flask containing 50 mL of Milli-Q water.

2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
3. Prepare daily.
4. The instrument automatically dilutes the 10 mg C/L substock into the following calibration standards.

Standard	IC Concentration
1	0.0 μmol/L (0.0 mg/L)
2	8.326 μmol/L (0.10 mg/L)
3	20.81 μmol/L (0.25 mg/L)
4	41.63 μmol/L (0.5 mg/L)
5	83.26 μmol/L (1.0 mg/L)
6	208.15 μmol/L (2.5 mg/L)
7	416.3 μmol/L (5.0 mg/L)
8	832.6 μmol/L (10.0 mg/L)

C. Inorganic Carbon Quality Control Stock Solution, 1000 mg C/L
1. The compounds must be from a manufacturer or lot different from those used to prepare the standard stock.
2. Dry about 5 g anhydrous sodium carbonate (Na_2CO_3) at 105°C for 2 hours and allow to cool in desiccator.
3. Dry about 5 g of anhydrous sodium bicarbonate ($NaHCO_3$) at 105°C for 2 hours and allow to cool in desiccator.
4. Dissolve 1.103 g dried Na_2CO_3 in a 250-mL volumetric flask containing about 100 mL Milli-Q water. Add 0.874 g of $NaHCO_3$ and dissolve.
5. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
6. Store in an amber glass bottle at 4°C; label and date.
7. Prepare every six months.
8. To avoid contamination, aliquots of stock solution must not be withdrawn directly from the bottle.

D. Inorganic Carbon QC Samples
1. Pipet desired amount of QC stock into a 250-mL volumetric flask containing about 100 mL Milli-Q water.
2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
3. Prepare daily.

QC Sample	DIC Concentration	QC Stock Added (mL)
QC-low	41.63 μmol/L (0.50 mg/L)	0.125
QC-high	249.78 μmol/L (3.0 mg/L)	0.750

6. Laboratory Performance

A. A Method Blank (MB) comprised of Milli-Q water is analyzed immediately after the first set of QCs. The result should be less than the instrument reporting limit.

B. Laboratory duplicates are analyzed once per run. Laboratory duplicates should be no more than 10 percent different between the samples. Only the first Sample value of the duplicate is entered into the database.

7. QC Procedure

A. The standard curve is a linear plot of standard concentration vs. the peak area. An eight standard linear regression is used for calibration. A new calibration is performed each day the instrument is run. The curve is accepted if the correlation coefficient is 0.99875 or greater.

B. Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run.

C. A quality control sample is acceptable if the analyzed value is within 10 percent of the QC-high known value and 25 percent of the QC-low known value.

D. If one of the QC samples fails the acceptance criteria, the run is stopped and the QC sample is re-run. If the QC sample fails again the run is stopped, the QC sample is remade, and/or the instrument is re-calibrated. Samples associated with the failed QC sample are re-analyzed.

8. Chemical Analysis Procedure

8.1 Instrumentation

Tekmar-Dohrmann Fusion TOC Analyzer
Teklink software v 1.1.5.2

8.2 Start-up

A. Remove standards and QC stock solutions from the refrigerator and allow to warm to room temperature before use.

B. Check the waste container daily. If nearing capacity, empty the waste down the hood drain and flush the drain with water.

C. Open the UHP nitrogen tank valve. The tank pressure of the gas supply should be above 200 psi. If the reading is 200 psi or lower, change the tank. The delivery pressure should be 80 psi for the proper functioning of the instrument.

D. Double click on the **Fusion** icon.

E. Login using username: hhollist and password: fusion2017. Click **OK**.

F. **Connect** to the Fusion using RS232COM1 connection.

G. Click the **Ready** tab.

H. Check supply of phosphoric acid and fill if necessary.

I. If the acid has been replaced, under dropdown **Tools**, click **Maintenance Tasks**, then **Prime the Acid**.
J. Change supply of Milli-Q water in 2-L bottle daily. After replenishment, under dropdown **Tools**, click **Maintenance Tasks**, **Prime the Water**.
K. Allow the instrument to warm up, the UV lamp to fully illuminate, and the baseline stabilize, approximately 5 minutes.

8.3 Blank and Calibration

A. Under **File**, **OPEN**, **Schedule** choose the previous DIC run, click **OK**. Click **Use** for the Clean, Reagent/Acid Blank, and Calibration Standards. Under **File**, **Save run as** a new run with mmddyyyyDIC format.
B. If the **Clean** procedure was run at the end of the previous day's run, the clean procedure doesn't not need to be run at the start of a new run.
C. Fill the designated 125-mL amber glass bottle with the 10 mg/L (832.6 µmol/L) standard substock solution and place in Position A on the autosampler tray.
D. Click on **Start**.
E. The instrument will clean, perform daily blanks on reagents, and perform the calibration.
F. Once the calibration has finished, under **File**, open **Calibration**. Open the new calibration. The software ensures the calibration has met criteria before it proceeds, if not recalibrate. If the calibration is acceptable, print the calibration and proceed with samples.
G. Close calibration window.

8.4 Analysis

A. Take samples out of the refrigerator and equilibrate to room temperature.
B. If the SSNs haven't already been added in the schedule, edit the SSN's and set the status of the samples, QCs, and to **Use**. Analyze one sample in duplicate once during each run. Save the changes.
C. At the end of the schedule, include a **Clean** procedure as the Sample Type. If timing does not allow for the **Clean** procedure to be run at the end of the day, it can be run before the next day's run, see 8.3.
D. Print out the schedule which serves as the bench sheet.
E. Load the samples and blank in the sample tray on the autosampler in the order corresponding to the bench sheet.
F. Pour the QC samples into the designated 40-mL vials and load QC-high in position 29 and QC-low in position 30.
G. Click on **Start**.
H. The QC samples will be evaluated automatically before running samples, during the run after every 10 samples, and at the end of the run. If all QC samples pass, the run will proceed until the tray is finished.

I. If the QC samples fail verification at any time during the run, a message will pop up and analysis will cease. Re-pour the QC samples and reset the status of the QC samples to **Use** in the **Report** window.
J. Click on **Start** to re-run QCs.
K. If QC samples fail again, remake the QC samples from the stock and/or recalibrate and re-run the last 10 samples.
L. Review the sample peaks and analysis data as the run progresses.
M. Note any bad peaks, samples of questionable results, or dilutions needed.

8.5 Shutdown

A. Under **File**, **OPEN**, **Schedule** choose **CLEAN**, click **OK**. Click **Start.**
B. When the clean run has completed, log out of Teklink software if desired.
C. Turn off the UHP nitrogen gas.
D. Rinse amber bottles with DI water and soak filled with DI water overnight. Rinse again and air or oven dry.

8.6 Maintenance

A. Check to ensure that the gas/liquid separator water level is filled to the waste outlet.
B. The tin and copper in the scrubber should be replaced every 6 months or when the copper becomes discolored, whichever occurs first.

8.7 Data Processing and LIMS Entry

A. Under **File, Open Report**, open the appropriate files for the run date. The files are in a date time format: mmddyyyytttt. There may be multiple files for each day.
B. Export the report(s) as a .csv and save to \LAB_DATA\DOC\DOC-20XX-data\CSV.
C. Export the report(s) as a .html and save to \LAB_DATA\DOC\DOC-20XX-data\HTML.
D. Open the report file(s) in Excel and edit as needed. Compile into a single Excel file with the data in chronological order. Do not include any data from the priming, cleaning, or calibration files.
E. Save as an .xls in \LAB_DATA\DOC\DOC-20XX-data\EXCEL\mmddyyyyDIC format.
F. Print the file.
G. Double click on the **Watershed LIMS** icon.
H. Click **Import Data**.
I. Under the **Import** drop down, choose **Water Carbon**.
J. Choose and open the desired file.
K. Choose **Client**, **Analysis**, **Units**, type in the **Test Date**, and choose **Analyst**.
L. Exclude and/or edit any data necessary.
M. Click **Client ID** to **Sample No**.
N. Click **Check RL Flag**.

O. Click **Set Data**.
P. Investigate problems for data that did not transfer or are duplicated.

9. Calculations and Data Reporting

A. Data are output from the instrument in units of milligrams per liter. During the import to the LIMS, the results are automatically converted to micromoles per liter by multiplying the results from the instrument by the IC conversion factor of 83.26.
B. This method has been assigned USGS National Water Information System (NWIS) method code IR005.
C. Data that are uploaded to NWIS must be converted to mass units (mg/L). Multiply data by the conversion factor of 0.012011 and store under the parameter code 00685.

10. Archiving

A. Data files are backed up daily by an automated back-up program. Hard copies of the runs are filed and retained indefinitely. The laboratory LIMS system is backed up daily by an automated back-up program.
B. Samples are stored at room temperature until the data can be verified.

11. References

Fusion User Manual; Tekmar Company.

Rice, E.W., Baird, R.B, Eaton, A.D., Clesceri, L.S. eds., 2012, Standard Methods For the Examination of Water and Wastewater, 22nd Edition: American Public Health Association, p. 5-25-5-27.

12. Key Words

Carbon, dissolved inorganic carbon, water samples, chemical analysis, water analysis.

13. Revision Record

The SOP will be revised and approved as changes are required. A review will be performed no later than every two years from the last approval date and the SOP revised if necessary.

Revision	Date	Responsible Person	Description of Change
1.1	Pre 01/14/2020	Hannah Ingleston	All released prior to the addition of the revision record table.
1.2	01/14/2020	Hannah Ingleston	Updated to reflect housekeeping and incidental edits.
1.3	01/20/2022	Hannah Ingleston	Updated to reflect addition of MB, new QA officer, and incidental edits.