USGS District Laboratory, Troy, NY

Organic Carbon Analysis

Standard Operating Procedure

1. Scope and Application

1.1 Analytes

Dissolved organic carbon (DOC)

1.2 Reporting Limit

41.0 μmol/L

1.3 Applicable Matrices

This method is used to determine the DOC concentrations in precipitation, dilute surface waters and soil waters.

1.4 Dynamic Range

The analytical range for the determination of dissolved organic carbon is from 20.0 μmol C/L to 1665.2 μmol C/L. Sample concentrations that exceed this range must be diluted and reanalyzed.

2. Summary of Procedure

The sample is acidified with phosphoric acid and sparged with ultra-high purity nitrogen. This removes inorganic carbon from the sample. Dissolved organic carbon is then converted to carbon dioxide by ultraviolet radiation and persulfate oxidation. The carbon dioxide produced is measured by an infrared detector.

3. Safety Issues

3.1 Chemical Hazards

A. Handle phosphoric acid (H_3PO_4) and sodium persulfate ($Na_2S_2O_8$) 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 Material Safety Data Sheets (MSDS).

4. Sample Preservation, Containers, Processing and Analysis Times

4.1 Sample Preservation

Samples are filtered through a 47 mm glass-fiber filter (GF/F with a particle retention size of 0.7 µm and greater) and stored at 4°C.

4.2 Containers

Samples are stored in 40-mL amber acid-washed glass vials with Teflon seals.

4.3 Processing and Analysis Times

Sample processing: one week

Lab analysis: two weeks
LIMS entry: one week

5. Reagents and Standards

5.1 General Information

All reagents are commercially purchased 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 flask that contains 188 mL of Milli-Q water.
2. Mix thoroughly.
3. Store in a polyethylene bottle; label and date.
4. Prepare monthly.

C. Sodium Persulfate

1. Use 98+% purity sodium persulfate ($Na_2S_2O_8$).
2. Add 25.0 g sodium persulfate to a flask that contains 213 mL Milli-Q water.
3. Add 9 mL of concentrated H_3PO_4.
4. Mix thoroughly.
5. Store in a polyethylene bottle; label and date.
6. Prepare weekly.

5.3 Standards

A. DOC Standard Stock Solution, 1000 mg C/L

1. Dry about 10 g potassium biphthalate (KHP) at 105°C for 2 hours and allow to cool in dessicator.
2. Dissolve 2.1254 g dried KHP in a 1,000-mL volumetric flask containing about 800 mL Milli-Q water.
3. Add 2 mL concentrated H_3PO_4.
4. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
5. Store in a 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. DOC Working Standards

1. Pipet desired amount of standard stock into a 100-mL volumetric flask.
2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
3. Store in a brown glass bottle at 4°C; label and date.

4. Prepare every other day or as needed.

Working Standard	DOC Concentration	Standard Stock Added (mL)	Final Volume (mL)
1	0.0 μmol/L (0.0 mg/L)	0.0	100
2	83 μmol/L (1.0 mg/L)	0.1	100
3	167 μmol/L (2.0 mg/L)	0.2	100
4	416 μmol/L (5.0 mg/L)	0.5	100
5	833 μmol/L (10.0 mg/L)	1.0	100
6	1666 μmol/L (20.0 mg/L)	2.0	100

C. DOC Quality Control (QC) Stock Solution, 1000 mg C/L
   1. Use KHP from a manufacturer or lot different from that of the KHP used for the standard stock solution.
   2. Dry about 10 g potassium biphthalate (KHP) at 105°C for 2 hours and allow to cool in a dessicator.
   3. Dissolve 2.1254 g dried KHP in a 1,000-mL volumetric flask containing about 800 mL Milli-Q water.
   4. Add 2 mL concentrated H_3PO_4.
   5. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
   6. Store in a 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. DOC QC Samples:
   1. Pipet desired amount of QC stock into a 500-mL volumetric flask.
   2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
   3. Store in a glass bottle at 4°C; label and date.
   4. Prepare daily or as needed.

QC Sample	DOC Concentration	QC Stock Added (mL)	Final Volume (mL)
Low	83 μmol/L (1.0 mg/L)	0.5	500
High	416 μmol/L (5.0 mg/L)	2.5	500

6. QC Procedure

A. The standard curve is a linear plot of standard concentration vs. the peak area obtained from the working standards. The best-fit line is drawn, and 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 range known value and 15 percent of the QC-low range 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 from the substock, and/or the instrument is re-calibrated. Samples associated with the failed QC sample are re-analyzed.

7. Chemical Analysis Procedure

7.1 Instrumentation

Tekmar-Dohrmann Phoenix 8000 TOC Analyzer
TOC Talk software v 3.2.105

7.2 Start-up

A. Remove standards and QC samples from the refrigerator and allow to warm to room temperature before analysis.
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 30 psi for the proper functioning of the instrument.
D. Double click on the **Phoenix** icon.
E. Choose **Setup** from the main screen.
F. From the **Setup** window choose **Instrument**.
G. Select the **System**—**Ready** mode.
H. The recommended flow rate for the Phoenix 8000 is 200 cc/min ($^{+}/_{-}$ 10%). If necessary, adjust the pressure from the nitrogen tank regulator until the From Detector reading reaches 200 cc/min.
I. Check supply of reagents and fill if necessary.
J. Change supply of Milli-Q water in 2 L bottle.
K. Allow the instrument to warm up until the UV lamp is at highest brilliance and the baseline has stabilized, approximately 15 minutes.
L. Click on **Run**.
M. Click **Sample Set Up**.
N. Choose **File** from the main screen.
O. Choose **Open**—**Prime**.

P. Reset the status of the three prime cleaning procedures to **Ready**.
Q. Click on **Save/Use**.
R. Click on **Start**.
S. Allow the Phoenix to run through the cleaning procedure, approximately 15 minutes.

7.3 Calibration

A. Under **Sample Set Up**, open the **Calibration** file and reset the status for the calibration standards to **Ready**.
B. Click on **Save/Use**.
C. Pour standards into glass vials and place in the appropriate positions in the sample tray on the autosampler.
D. Click on **Start**.
E. Allow the Phoenix to run through the calibration procedure, approximately 45 minutes.
F. Once the calibration has finished, select the daily calibration results to check the correlation coefficient. If the calibration is acceptable, proceed with samples.

7.4 Analysis

A. Under **Sample Set Up**, open the **Daily** file. Change the SSN's and reset the status of the samples to **Ready**.
B. Click on **Save/Use**.
C. Go back to the **Daily** file under **Sample Setup** and print out the file which serves as the bench sheet.
D. Click on **Save/Use**.
E. Place the samples in the sample tray on the autosampler in the order corresponding to that on the bench sheet.
F. Pour the QC samples into the appropriate vials (QC-high in position 69 and QC-low in position 70).
G. Click on **Start**.
H. The QC samples will be analyzed automatically during the run after every 10 samples. If all QC samples pass, the run will proceed until the tray is finished.
I. If the QC samples fail at any time during the run, a message will pop up and analysis will cease. Re-pour the QC sample and reset the status to **Ready** in the **Sample Setup** window.
J. Click on **Start**.
K. If QC samples fail again, remake the QC samples from the substock and/or recalibrate.
L. Note any bad peaks, and/or samples requiring dilutions or re-runs.

7.5 Shutdown

A. Click on **Exit**.
B. Choose **Setup** on the main screen.

C. From the **Setup** window choose **Instrument**.
D. Select the **System—Standby** mode.
E. Turn off the UHP nitrogen gas.

7.6 Maintenance

A. Check to ensure that the gas/liquid separator water level is filled to the waste outlet.
B. Make sure that the carrier gas flow rate is 200 cc/min $^{+}/_{-}$ 10%.
C. The tin and copper should be replaced in the scrubber every 6 months or when the copper becomes discolored, whichever occurs first.

7.7 Data Processing and LIMS Entry

A. Under **Results--Multiple Analysis**, open the appropriate files for the run date. The files are in a date time format: MMDDTTTT. There are multiple files for each day depending upon how many times the START button was clicked.
B. Once the results are pulled into one data set, under **File** choose **View in Excel**.
C. A series of files will open in Excel with the results. Edit the files as needed and compile into a single Excel file with the data in chronological order. Do not include any data from the priming and calibration files.
D. Save as an Excel worksheet (.xls file extension) in C:\NY_backup\DOC-200* using the format: MMDDYYYY.
E. Print the file.
F. Double click on the **Watershed LIMS** icon.
G. Click **Custom**, then **Import Data**.
H. Under the **Import** drop down, choose **Carbon**.
I. Choose and open the desired file.
J. Choose **Client**, **Units**, type in the **Test Date**, and choose **Analyst**.
K. Exclude and/or edit any data necessary.
L. Click **Client ID** to **Sample No**.
M. Click **Set Data**.
N. Investigate problems for data that did not transfer or are duplicated.

8. Archiving

8.1 Data

Data files are backed up daily by an automatic backup program. Hard copies of the runs are filed and kept indefinitely. The laboratory LIMS system is backed up daily by an automatic backup program.

8.2 Samples

Samples are stored at room temperature until the data can be verified. Sample bottles are cleaned and reused for new samples.

9. References

Phoenix 8000 User Manual; Tekmar Company, 1997-1998.

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies – laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency EPA 600/4-87/026 (variously paged).

10. Keywords

Carbon, dissolved organic carbon, total organic carbon, water, soil water, persulfate oxidation, UV radiation.