Arikaree Environmental Laboratory
Revision 1
Date: April 30, 2020

Total Organic Carbon/Dissolved Organic Carbon

Total Nitrogen/Total Dissolved Nitrogen

TITLE: EPA 9060A & 415.1

ANALYTES: TOC/DOC/TN/TDN

1) Applicable Matrices

a) This method is applicable to ground, surface, and waste waters**.**

b) The method is applicable in the range from 0 to 50.0 mg/L for TOC/DOC and 0 to 5.0 mg/L for TN/TDN

2) Scope and Application

a) Samples are combusted using a Shimadzu TOC-L/TNM-L analyzer.

3) Interferences

a) Any sample with residual inorganic carbon will interfere with TOC accuracy. Acidification and purging samples with high purity air eliminates this interference.

4) Equipment and Supplies

a) Analytical balance capable with 0.0001g sensitivity.

b) Top loading balance with 0.01g sensitivity.

c) Adjustable Pipets capable of precisely dispensing1.0-10.0mL and 0.1-1.0mL

d) Pipet tips appropriate for each pipet.

e) 100mL graduated cylinder

f) Class A volumetric flasks and pipets for reagent and standard preparation.

g) Shimadzu TOC-L/TNM-L Instrument

h) Water purifier for preparation of ASTM Type I water (Ultrapure).

i) Glass vials to hold sample in autosampler

j) Ultra-high purity compressed air

5) Reagents and Standards

1,000ppm TOC Stock Standard

1) Dry 2.5g of Potassium Hydrogen Pthalate (KHP) at 110°C for 2 hours. Cover and allow to cool in a desiccator.

2) Once the KHP has been cooled to room temperature, in a 1,000mL Class A volumetric flask, dissolve 2.1254g of KHP in about 500mL of ultrapure water. Do not use a magnetic stir bar. Instead, dissolve the KHP by swirling the flask contents by hand until completely dissolved.

3) Dilute to the 1,000mL mark on the flask with ultrapure water. Replace the stopper and invert to mix. Store stock standard in a clean, burned 1L brown glass bottle. Stable for 6 mos. when refrigerated.

1,000ppm TN Stock Standard

1) Dry Potassium Nitrate (KNO_3) primary standard at 110°C for 2 hours. Cover and allow to cool in a desiccator.

2) Once the KNO_3 has been cooled to room temperature, in a 1,000mL class A volumetric flask, dissolve 3.6091g KNO_3 in about 500mL of ultrapure water. Do not use a magnetic stir bar. Instead, dissolve the KHP by swirling the flask contents by hand until completely dissolved.

3) Dilute to the 1,000mL mark on the flask with ultrapure water. Replace stopper and invert to mix. Store stock standard in a clean, burned 1L brown glass bottle. Stable for 1 year when refrigerated.

TOC/TN Matrix Spike Solution

1) In a class A 100mL flask, dilute 25.0mL of 1,000ppm TOC stock standard and 2.5mL of TN stock standard. Dilute to 100mL mark and invert to mix. Store in a clean, burned 125mL brown glass bottle and refrigerate.

Sodium Bicarbonate Inorganic Carbon Check Standard

1) Use the 163.9μEq/L Sodium Carbonate standard for ANC as the carbonate check.

1:1 Hydrochloric Acid

1) In a 500mL clean, burned brown glass bottle, add 200mL of ultrapure water using a graduated cylinder to measure. In a fume hood, while wearing a lab coat, safety glasses and gloves, dilute 200mL of concentrated Hydrochloric Acid in the 200mL of ultrapure water using a graduated cylinder to measure. Cap bottle and invert. Store in acid cabinet beneath fume hood.

6) Sample Collection, Preservation, Shipment, and Storage

a) Collect and filter samples in acid washed, combusted bottles (sample bottles shall be combusted at 450°C for at least 4 hours). Samples for DOC/TDN shall be filtered through a Whatmann GF/F glass fiber filter. Keep samples refrigerated between 0-4°C.

7) Quality Control

a) Calibrate the Shimadzu once a month or after maintenance or column change. Analyze Instrument Performance Check (IPC)/ from a second source standard every analytical run. Calibration r-value is required to be > 0.995, if not re-calibrate.

b) Run an initial calibration verification blank (ICVB) at the beginning of each run and then once every 10 samples. ICVB must be <LOD. If not, re-analyze, if still out of control qualify data. Subsequent blanks (CCVB) must be <LOD, or less than 10% of the measured concentration in the samples from the adjacent set.

c) Analyze an Initial Calibration Verification Standard (ICVS) at the beginning of each run and Continuing Calibration Verification Standard (CCVS) with every 10 samples. Standard must be within 10% of known value. If not, reanalyze. If still out of control, recalibrate.

d) A duplicate and matrix spike must be analyzed every 10 samples (10%). Prepare a spiked sample by pipetting 0.2mL of Matrix Spike Solution (see matrix spike solution in section 5) into empty TOC 0sample tube. Pipet 9.8mL of sample into the same tube. Swirl tube carefully to mix. Place in correct location in autosampler rack.

8) Calibration

a) Prepare calibration standards as listed below. Use only clean class A volumetric pipets and flasks. Dilute using ultrapure water. Store in clean, burned, brown glass bottles.

Standard	mg/L TOC/TN	mL 1,000ppm TOC/TN Standard	Total volume
1	0.2/0.02	25.0 of Cal Std 3	250mL
2	1.0/0.1	25.0 of Cal Std 5	250mL
3	2.0/0.2	25.0 of Cal Std 6	250mL
4	5.0/0.5	50.0 of Cal Std 1	500mL
5	10.0/1.0	10.0/1.0	1,000mL
6	20.0/2.0	20.0/2.0	1,000mL
7	50.0/5.0	50.0/5.0	1,000mL

9) Procedure for Shimadzu TOC-L/TNM-L Set-up and Operation

1) Open the valve on the ultra-high purity air tank all the way. Check the pressure level of the tank.

2) Turn on the Shimadzu by pressing the power button on the front of the instrument. Allow instrument to warm up until the light on the front turns blue.

3) While the instrument is warming up, set up the samples to by analyzed. Start by going through the master data sheets in the office. Record each sample needing TOC/DOC/TN/TDN on a piece of scrap paper.

4) Take the list of samples and a container into the cold room and pull the samples needing analysis. Use only unfiltered, unpreserved samples stored in the burned, brown glass bottles for TOC/TN. For DOC/TDN use filtered, unpreserved samples.

5) Organize samples on a bench in ascending order based on Lab ID#.

6) Print a DOC/TN benchsheet from the Arikaree share folder on the office computer.

7) Record sample numbers on the benchsheet starting in the blank spots. Record the samples in ascending order by Lab ID# (just as the samples should be organized on the bench). Do not forget to include a duplicate and matrix spike every 10 samples.

8) Calibrate adjustable pipets for diluting matrix spikes (0.2mL of matrix spike and 9.8mL of sample) by weighing the RO water dispensed by pipet on an analytical balance. Weights of dispensed water shall be $\pm$0.5% of known weight of water at 20^{o}C. Must have 3 consecutive draws within the limit.

9) Remove auto sampler covers and rack. Move rack to where the samples are organized. Begin pouring standards and check standards into vials. Pour and place standard into proper well in autosampler rack. After standards and check standards are poured and placed, begin pouring samples.

10) After all the samples and standards are poured and placed, pipet 100μL of 1:1 HCl into each sample. Be sure not to dispense HCl into a sample twice or miss a sample.

11) Carry autosampler rack to autosampler. Place rack into auto sampler. Make sure the rack is seated correctly (should not be able to turn rack by hand). Replace covers on autosampler. Autosampler will turn rack.

12) Remove cap and tube from wash bottle behind autosampler. Dump water in the sink. Fill with ultrapure water and replace tube and cap into bottle.

13) Open the front door of the instrument. Check the water level in the reservoir for the humidifier. Dump and fill if low. Close the door.

14) On the computer for the instrument, open the instrument software. Open the most recent run. Click the “File” menu in the top left of the screen. Choose “Save As.” It should automatically name the new file as today’s date. Click save.

15) Go to “Edit.” Choose “Clear All Results in Sample Table.” It will ask you if you’re sure. Ask yourself if you’re sure. Is anyone really sure? Just click yes, as long as you saved the old run.

16) Begin entering the samples from the benchsheet. If you need more spaces for samples, copy rows for samples and paste them at the end until you have enough.

17) If you need to recalibrate, calibrations will have to be inserted. This can be done by right-clicking where you want the calibration, and selecting “Insert Calibration” and choose the calibration folder you need. A separate calibration will be needed for TOC and TN.

18) After standards and samples have been entered, click the icon that looks like a birthday cake in the upper right corner of the sample table. Enter the cup numbers for each sample. This can be done by using the spreadsheet fill function (like Excel). Click “OK.”

19) If the status indicator above the sample table says ready, click “Start.”

20) Check the status of the run periodically. If the autosampler rack is full, the run will take 2 days to complete.

21) After the run is completed, go to “File”=> “Print Sample Table.” Save as a “One Note” document onto a thumb drive. Take thumb drive to the office and print the sample table. These are the results. Staple benchsheet on top of the results.

22) Record and calculate QC data in the DOC/TN QC data file on the Arikaree Share folder.

23) Record results on the master data sheets being mindful of detection limits and significant figures.

24) Three hole punch benchsheet and results and place in DOC binder on top of the other runs.

25) Erase X’s from board in the lab.

26) Remove autosampler tray and dump samples from the vials. Replace rack in autosampler.

27) Clean vials by soaking in 10% HCl over night at least. Remove vials from acid and triple rinse with RO water, then single rinse with ultrapure water. Invert in a wire rack and allow to dry.

10) Corrective Action for Out-of-Control Data

a) Any CCV blank that exceeds the LOD, the analyst must inspect the concentration of the previous sample. If the blank is greater than 10% of the previous sample, reanalyze the blank immediately following the CCVS. No samples can be run until the blank meets requirements.

b) CCV and LCS standards must fall within 10% of true value (90%-110% Recovery). If not re-mix and re-analyze, if still out of range re-calibrate.

11) Contingencies for Handling Out-of-Control Data

a) Samples that fail the CCVB or ICVS will have to be reanalyzed or qualified back to the last sample that the quality control met the above conditions.

12) Waste Management

a) All waste must be collected and disposed of according to CU EHS policies.

13) References

a) U.S. EPA. 2004. “Method 9060A: Total Organic Carbon.” Revision 1.0.

b) U.S. EPA. 1999. “Method 415.1: Total Organic Carbon in Water (Combustion or Oxidation).” Revision 11/16/1999.