ANALYSIS OF TOTAL NITROGEN (TN), DISSOLVED NITROGEN (DN), TOTAL ORGANIC CARBON (TOC), AND DISSOLVED ORGANIC CARBON (DOC) USING SHIMADZU TOC INSTRUMENTS EQUIPPED WITH TOTAL NITROGEN MODULES (TNM-L)

TABLE OF CONTENTS:

Page

1. SCOPE AND APPLICATION 2
2. SUMMARY OF THE METHOD 2
3. EQUIPMENT AND SUPPLIES 3
4. CHEMICALS, REAGENTS, AND STANDARDS 5
5. SAMPLE HANDLING AND PRESERVATION 12
6. SAMPLE PREPARATION AND ANALYSIS 12
7. DATA ARCHIVAL/VALIDATION 18
8. MAINTENANCE/TROUBLESHOOTING 18
9. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES 20
10. SAFETY/WASTE MANAGEMENT/POLLUTION PREVENTION 21
11. REFERENCES 22

APPENDIX I: INTRUMENTS SETTINGS-PARAMETERS 23

APPENDIX OF SIGNIFICANT CHANGES 26

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1. SCOPE AND APPLICATION

1.1. This SOP details the analysis of Total Nitrogen (TN), Dissolved Nitrogen (DN), Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) in surface waters, ground waters, salt water, effluents and influents. The tests covered by this SOP are: W-TN, W-DN, W-TOC, and W-DOC.

Key method parameters:

	W-TOC/W-DOC	W-TN/W-DN
Calibration range	0.0 – 100.0 mg C/L	0.0 – 5.0 mg N/L
Minimum Detection Limit (MDL)	0.50 mg C/L	0.10 mg N/L
Practical Quantitation Limit (PQL)	1.0 mg C/L	0.5 mg N/L

1.2. Samples with concentration of TN/DN greater than 5.0 mg N/L are reported after dilution into the range or qualified appropriately. Samples with TN concentrations below the PQL will be re-analyzed following SOP NU-105, or qualified appropriately, if needed. Samples with concentration of TOC/DOC greater than 100.0 mg C/L are reported after dilution into the range or qualified appropriately.

2. SUMMARY OF THE METHOD

2.1. The described procedure is based on ASTM D8083-16 for TN/DN analysis and Standard Methods 5310 B-2014 for DOC/TOC analysis. The method was modified to not implement blank subtraction. A study was performed that demonstrated that there is no significant TOC contribution from the labs DI water used to prepare standards and dilutions. It shows that the method described in this SOP gives compatible or better method performance than the published method. These methods allow for either use of internal or external sparging as described in 2.2.

Note: *Only the **TOC-N-CPH** instrument is equipped with the external sparge kit for mixing. See APPENDIX I for further details.*

2.2. The analyst has the option of analyzing the samples with internal or external sparging. In the external sparging procedure, the acidified samples are purged with ultra-high purity (UHP) air using an external sparge kit for a duration of 360 seconds prior to injection in order to remove the inorganic carbon fraction. In the internal sparging procedure, the acidified samples are purged with ultra-high purity (UHP) air for the duration of 90 seconds in the syringe/plunger prior to injection in order to remove the inorganic carbon fraction. Samples (50 ul) are introduced by the sample injector into a combustion tube.

2.3. The organic carbon and nitrogen components of the sample are combusted at 720ºC in the presence of a platinum catalyst to form carbon dioxide and nitrogen oxide (NO), respectively. Carbon dioxide is detected by infrared analysis. Nitrogen oxide reacts with ozone to form excited state NO_2. As the NO_2 returns to the ground state, the emitted radiation is detected using a chemiluminescence detector.

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2.4. The method measures nonpurgeable organic carbon (NPOC). In many surface and ground waters, the purgeable organic carbon contribution to TOC is negligible. Therefore, in practice, the nonpurgeable organic carbon determination is substituted for TOC. Elemental carbon may not be oxidized at the furnace temperature, but it is not expected to be a constituent of the water samples analyzed. In addition, the method does not measure N_2 as gas.

2.5. The method requires the analysis of at least **4 injections** of **TONCHCK** (Organic Nitrogen Test Solution) (4.3.8.) at the same volume as samples to be analyzed. To satisfy this requirement, **TONCHCK** is put on the run sequence at least twice (for a minimum total injection of 6 and up to 10 injections).

2.6. This procedure is applicable only to nitrogenous and organic matter in the sample that can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. An external sparging procedure may be used as a mixing mechanism to suspend small particles that may otherwise settle over time. The openings of the autosampler needle and injection syringe limit the maximum size of particles included in the analysis.

2.7. Interferences:

2.7.1. Acid preservation of samples minimizes interferences that can cause results to be low. Gases of halide components may interfere with the detection system. They are eliminated by passing the reaction gas through a halogen scrubber. Samples with a high particulate loading may need to be homogenized prior to analysis. Samples containing high total suspended solids (TSS) may cause TN/TOC analysis to be biased low. Dissolved inorganics in the sample that are not volatized may result in devitrification or solidify in the catalyst tube resulting in decreased flow rates. Total organic carbon (TOC) up to 300 mg/L does not interfere with the TN analysis.

2.7.2. Saline samples may impair the effectiveness of the catalyst and reduce its lifespan. Samples with a conductivity of ≥15,000 µmhos/cm and ≤30,000 µmhos/cm and/or a salinity of 9 PPTh or greater are batched as salt samples and are diluted 1:2. Salt samples with a conductivity of >30,000 µmhos/cm are diluted 1:4. HCL and/or H_2SO_4 rinses are added between the samples and at the end of the run in order to minimize residue build up on the catalyst (see 6.12.3).

3. EQUIPMENT AND SUPPLIES

3.1. Instrumentation

Instrumentation	Component	Manufacturer	Model/Product #
W-TOC-N-CPH	Total Organic Carbon Analyzer	Shimadzu	TOC-LCPH
	Autosampler ASI-L for 24 mL, ROHS - compliant	Shimadzu	638-93199-58
	TNM-L Total Nitrogen Module, ROHS	Shimadzu	638-91108-58
	External Sparge Kit for ASI-L	Shimadzu	638-77183-41

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	TOC Control L Software	Shimadzu	Ver. 1.08
W-TOC-O-CSH	Total Organic Carbon Analyzer	Shimadzu	TOC-L-CSH
	Autosampler ASI-L for 24 mL, ROHS - compliant	Shimadzu	638-93199-58
	TNM-L Total Nitrogen Module, ROHS	Shimadzu	638-91151-43
	External Sparge Kit for ASI-L	Shimadzu	638-77183-41
	TOC Control L Software	Shimadzu	Ver. 1.09
W-TOC-P-CSH	Total Organic Carbon Analyzer	Shimadzu	TOC-L-CSH
	Autosampler ASI-L for 24 mL, ROHS - compliant	Shimadzu	638-93199-58
	TNM-L Total Nitrogen Module, ROHS	Shimadzu	638-91151-43
	External Sparge Kit for ASI-L	Shimadzu	638-77183-41
	TOC Control L Software	Shimadzu	Ver. 1.09

3.2. Instrument Accessories

Accessory	Manufacturer/Vendor	Model(s) / Catalog Number
Combustion Tube	Shimadzu	638-41323-00
Platinum Screen 2 Sheets TOC	Shimadzu	630-00105-01
O-Ring, 4D P 10AX5	Shimadzu	03-11209-84
O-Ring, PTFE Maintenance Parts	Shimadzu	638-15025

3.3. Equipment

Equipment	Manufacturer/ Vendor[1]	Model(s)/Catalog Number
Analytical Balance	Mettler Toledo/Fisher	XSR105DU
Adjustable Pipette, 10-100 µL	Eppendorf/Fisher	3123000047/13690029
Adjustable Pipette, 100 -1000 µL	Eppendorf/Fisher	3123000063/13690032
Adjustable Pipette, 1-10 mL	Eppendorf/Fisher	3123000080/13690034
Volumetric Flask, Class- A, Assorted	Pyrex/Fisher (SR)	10-208M, 10-212-5L, 10-240E; 10-212B
Graduated Cylinder, assorted	KIMAX/Fisher (SR)	08-564A
Glass Funnel	Fisher (SR)	10-346-5B
Desiccator	Fisher Scientific	08-645-6
Or Equivalent [1]**Note:** (SR) designates chemical is typically ordered through the in-house stockroom		

3.4. Supplies and Consumables

Equipment	Manufacturer/ Vendor[1]	Model(s)/Catalog Number
Pipette Tips, 200 µL	Eppendorf/Fisher (SR)	05-403-41
Pipette Tips, 1000 µL	Eppendorf/Fisher (SR)	05-403-43
Pipette Tips, 1-10 mL	Eppendorf/Fisher (SR)	05-403-116
Weigh Dish, Hexagonal 1 ½ X 1	Fisher (SR)	02-202-100
Weigh Dish, Hexagonal 4 X 3	Fisher (SR)	02-202-102
Weigh Dish, Aluminum, 60 mm	Fisher (SR)	08-732-101
Transfer Pipet, 5 mL	Fisher (SR)	13-711-5AM
Parafilm	Fisher (SR)	13-374-12

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Vial, Glass Shell	Fisher (SR)	03-339-30H
DWK Kimble Glass Screw-Thread Vials with PTFE/Silicone Septa**	Fisher**	03-340-47D
Sample Beakers, Polystyrene, Assorted	Fisher (SR)	08-732-120, 08-732-122
Kimwipes, SM 4.5” x 8.5”	Fisher (SR)	06-666A
Or Equivalent		
[1]**Note:** (SR) designates chemical is typically ordered through the in-house stockroom		
** A substitute to these vials is available through Shimadzu (Cat. # 220-95316-01) in case of supply disruptions at Fisher.		

4. CHEMICALS, REAGENTS, AND STANDARDS (SEE DEP SOPs NU-041, NU-042, and LB-030)

Purchased chemicals, reagents, and standards are processed according to the provisions in SOPs NU-041, NU-042 and LB-030. Before use they are entered into the laboratories LIMS system and labeled with a unique ID and expiration date. Remember that expiration dates on purchased materials can be found either on the container or the certificate of analysis, if available. If no explicit expiration dates are assigned by the manufacturer follow the protocol outlined in the aforementioned SOP’s.

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

Note: All reagent and standard preparations must be documented in the specific TOC-TN Reagent and Standard Logsheet for W-TN/W-TOC analysis. This excel sheet (NU-RGTSTD-TOCTN) is specific to TOC-TN analysis and located in the following subfolder: \\floridadep\data\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\MetaData\TOC-TN\Forms

It needs to be updated whenever a reagent or standard is newly prepared. For every analysis file print the TOC-TN Reagent and Standard Logsheet and place it into the analysis folder.

Note: Reagent and standard preparations must be documented in the Laboratory Information Management System (LIMS) ‘Standard Preparation Tracker’ module. Unique ID numbers for each standard and reagent are generated in the module and documented in the reagent and standard sheet submitted with each analysis folder. If available, a Certificate of Analysis for each purchased reagent and standard is maintained in the REAGENT_PREP folder on the Nutrients drive located in the subfolder: \\floridadep\data\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\MetaData\TOC-TN\CertificatesofAnalysis. All containers holding standards or reagents must be labeled with their unique ID and expiration date. In-House deionized water, used for reagent and standard preparation, stored in containers is replaced daily.

Note: Prior to using the chemicals in this analysis, please read their MSDS and the safety notes found in Section 11 of this SOP.

4.1. Chemicals

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	Chemical	Alias	Manufacturer[1]	Catalog Number	Purity	Storage
4.1.1.	Deionized (DI) Water	H_2O	In-House	N/A	N/A	N/A
4.1.2.	Air, Compressed	Air Ultra Zero	Airgas	AI UZ300	Ultra Zero Grade	Room Temp
4.1.3.	Sulfuric Acid	H_2SO_4	Fisher (SR)	A300S-212	Certified ACS Plus	Room Temp
4.1.4.	Hydrochloric Acid	HCl	Fisher (SR)	A144S-212	36.5 – 38.0% (w/w), Certified ACS Plus	Room Temp
4.1.5.	Potassium Hydrogen Phthalate	KHP	Fisher (SR)	P243-100	≥98.5%, meets ACS	Room Temp
4.1.6.	Anhydrous Dextrose (Ground)	$C_6H_{12}O_6$	Fisher (SR)	D16-500	Certified ACS	Desiccator
4.1.7.	Potassium Nitrate	KNO_3	Sigma-Aldrich	221295-500G	≥99.0%, Certified ACS	Room Temp
4.1.8.	Ammonium Sulfate	$(NH_4)_2SO_4$	Fisher	A702-500	≥99.0%, Certified ACS	Room Temp
4.1.9.	Glycine	$C_2H_5NO_2$	Sigma-Aldrich	G7126-100G	≥99% (HPLC), ReagentPlus®	Desiccator
4.1.10.	Anhydrous Sodium Carbonate	Na_2CO_3	Fisher (SR)	S263-500	≥99.5% Certified ACS	Desiccator
4.1.11.	Demand certified standard	TOC/DOC ALTQC	ERA	516	N/A	Fridge/ Room Temp ok
4.1.12.	Simple Nutrients Certified Standard	TN/DN ALTQC	ERA	505	N/A	Fridge/ Room Temp ok
4.1.13.	Sodium Hydroxide	NaOH	Fisher (SR)	S318-3	≥97.0 %, Pellets/Certified ACS	Room Temp
4.1.14.	Drierite 10-20 Mesh, White	$CaSO_4$, Desiccant	W.A. Hammond Drierite Co. LTD (SR)	14005/07-577-4B	≥99.5% $CaSO_4$	Room Temp
4.1.15.	Drierite 8 Mesh, Blue	$CaSO_4$ and $CoCl_2$ Desiccant	W.A. Hammond Drierite Co. LTD (SR)	23005/S692-212	≥98% $CaSO_4$,<2% $CoCl_2$	Room Temp
4.1.16.	Platinum Catalyst, 20g	Catalyst	Shimadzu	638-60202-01	Normal Sensitivity	Room Temp
4.1.17.	Halogen Scrubber (Copper)	Halogen Scrubber	Shimadzu	630-00992-00	≥99% Copper	Room Temp
4.1.18.	Synthetic Seawater without Heavy Metal	Synthetic Seawater	RICCA (SR)	8363-5	N/A	Room Temp

4.2. Stock standards, spiking solutions, & reagents

4.2.1. **Stock Standard Solution (TN/DN; 1000 mg N/L)** –

Potassium Nitrate (4.1.7.) 3.609 g

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Ammonium Sulfate (4.1.8.)	2.360 g
Sulfuric Acid (4.1.3.)	2 mL
DI Water (4.1.1.)	to 1000 mL

Dry 8 g of Potassium Nitrate and 5 g of Ammonium Sulfate at 120°C for 2 hours. Cool in a desiccator.

Weigh out 3.609 g of dried KNO_3 into a weighing boat. In a separate weighing boat, weigh out 2.360 g of dried $(NH_4)_2SO_4$.

In a 1 L volumetric flask containing approx. 800 mL of water, add 2 mL of H_2SO_4. Swirl to mix. Next, rinse the contents of the weighing boats into the flask using DI Water. Dilute to the mark and invert several times to mix thoroughly. Label this flask **'TN STOCK 1000 PPM'**.

This solution is used for the preparation of the TN/DN calibration standards. Holding time, 180 days.

Note: This solution is also used for low-level TN analysis. See SOP NU-105.

4.2.2. **KNO_3 Stock (TN/DN; 1000 mg N/L)** –

Potassium Nitrate (4.1.7.)	1.803 g
Sulfuric Acid (4.1.3.)	0.5 mL
DI Water (4.1.1.)	to 250 mL

Dry 4g of Potassium Nitrate at 120 °C for two hours. Cool in a desiccator.

Weigh out 1.803 g of dried KNO_3 in a weighing boat. In a 250 mL flask containing approx. 100 mL of DI water, add 0.5 mL of concentrated H_2SO_4. Swirl to mix. Next, rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and invert several times to mix thoroughly. Label this bottle **'1000 PPM KNO3'**.

This solution is used for the preparation of the Continuing Calibration Verification (CCV) standard for TN/DN analysis. Holding time, 180 days.

4.2.3. **Stock Standard Solution (TOC; 1000 mg C/L)** –

KHP (4.1.5.)	2.1254 g
Sulfuric Acid (4.1.3.)	2 mL
DI Water (4.1.1.)	to 1000 mL

Dry 5 g of primary grade potassium hydrogen phthalate (KHP) at 120 ºC for 12 hrs. Cool in a desiccator.

Weigh out 2.1254 g of dried KHP into a weighing boat. In a 1 L volumetric flask containing approx. 800 mL of DI water, add 2 mL of H_2SO_4. Swirl to mix. Next, rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and invert several times to mix thoroughly. Pour this solution into a reagent bottle labeled **'TOC STOCK: 1000 PPM'**.

Note: This solution is used for the low spike (V1) for W-TOC salt samples,

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laboratory fortified blank (LFB_V1) on salt batches for W-TOC, and the continuing calibration verification (CCV) standard. Holding time, 180 days.

4.2.4. **Stock Standard Solution (10000 mg C/L)** –

Dextrose (4.1.6.)	2.505 g
Sulfuric Acid (4.1.3.)	0.2 mL
DI Water (4.1.1.)	to 100 mL

Dry 5 g of primary grade dextrose at 120ºC for 12 hrs. Cool in a desiccator.

Weigh out 2.505 g of the dried dextrose into a weighing boat. In a 100 mL volumetric flask containing approx. 20 mL of DI water, add 0.2 mL of H_2SO_4. Swirl to mix. Next, rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and invert several times to mix thoroughly. Pour this solution into a reagent bottle labeled **'STOCK DEX 10000'**.

This solution is used for the calibration standards and the practical quantitation limit (PQCK4). Holding time, 180 days.

4.2.5. **Mixed Spiking Solution (500 mg N/L, 10000 mg C/L)** –

Dextrose (4.1.6.)	2.505 g
Potassium Nitrate (4.1.7.)	0.3609 g
Sulfuric Acid (4.1.3.)	0.2 mL
DI Water (4.1.1.)	to 100 mL

Dry about 6 g of dextrose at 120ºC for 12 hours and 1 g of potassium nitrate at 120ºC for 2 hours. Cool in a desiccator.

Weigh out 2.505 g of dried dextrose into a weighing boat. In a separate weighing boat, weigh out 0.3609 g of dried KNO_3.

In a 100 mL volumetric flask containing approx. 50 mL of DI water, add 0.2 mL of H_2SO_4. Swirl to mix. Next, rinse the contents of both weighing boats into the flask using DI water. Dilute to the mark and invert several times to mix thoroughly. Label this flask **'MIXED SPK'**.

Used for the mixed W-TOC/W-TN spike (M1, and H1) and mixed Laboratory Fortified Blank (LFB_M1 or H1). Holding time, 180 days.

4.2.6. **Inorganic Carbon Removal Check (ICRC, 103 PPM)**

4.2.6.1 **Inorganic Spiking Solution (10000 mg C/L)**

Sodium Carbonate Anhydrous (4.1.10.)	8.8500 g
DI Water (4.1.1.)	to 100 mL

Dry approx. 10 g of Sodium Carbonate Anhydrous (Na_2CO_3) at 120°C for 12 hours. Cool in a desiccator.

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Weigh out 8.8500 g of the dried Na_2CO_3 into a weighing boat. Rinse the contents of the weighing boat into a 100 mL volumetric flask containing approx. 70 mL of DI water. Dilute to the mark and invert several times to mix thoroughly. Label this flask **'IC SPK 10000 PPM'**.

Do not acidify this standard. Holding time, 180 days.

4.2.6.2. **Synthetic Seawater: DI (1:10 solution)**

In a clean graduated cylinder, measure 100 mL of Synthetic Seawater (4.1.18.). Pour the Seawater into a clean 1 L volumetric flask. Add approximately 500 mL of DI water to the flask. Add 2 mL of H2SO4 (4.1.3.) to the solution in the flask to acidify it to 0.2% concentration.

Spike this solution with 10 mL of IC SPK 10000 PPM (4.2.6.1.). Dilute to the mark for the final volume of 1L. Label this solution "**ICRC 103 PPM**". This solution has a holding time of 30 days.

Note: The 1:10 dilution of Synthetic Seawater has approximately 3 PPM inherent inorganic C. The spike adds 100 inorganic C PPM for a total of 103 PPM inorganic carbon.

Note: The ICRC sample is used to assess instrument's capability to remove inorganic carbon (IC Removal Check).

4.2.7. **Glycine ($C_2H_5NO_2$); Purity 99+%, Organic Nitrogen Stock Solution (1000 mg N/L) –**

Glycine (4.1.9.)	1.3392 g
Sulfuric Acid (4.1.3.)	0.50 mL
DI Water (4.1.1.)	to 250 mL

Dry about 3 g of glycine at 120°C for 2 hours. Cool in a desiccator.

Weigh out 1.3392 g of dried glycine into a weighing boat. In a 250 mL volumetric flask containing approx. 150 mL of DI water, add 0.50 mL of H_2SO_4. Swirl to mix. Next, rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and invert several times to mix thoroughly. Label this flask **'ORGANIC NITROGEN STOCK 1000 PPM'**.

This is used for the preparation of the Total Organic Nitrogen Check Solution. Holding time, 180 days.

Note: This solution is also used for low-level TN analysis. See SOP NU-105.

4.2.8. **Acid Rinse (HCL RINSE)** for Catalyst Regeneration –

Hydrochloric Acid (4.1.4.)	164 mL
DI Water (4.1.1.)	to 1000 mL

To a 1 L volumetric flask containing approx. 800 mL of DI water, carefully add 164 mL of concentrated HCL. Dilute to the mark and mix

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thoroughly.

Holding time, 90 days.

4.3. Preparation of QC and Calibration Standards –

4.3.1. **ALTQCs** – Two individual ALTQC standards are prepared to verify the TOC and TN calibrations.

4.3.2. **ALTQC TOC**: This solution serves as an Initial Calibration Verification (**ICV**) and a Calibration Check Sample. The TOC ALTQC is a certified quality control standard purchased from ERA. Prepare the standard to the certified concentration as instructed by the manufacturer. If the certified concentration is 10 PPM-40 PPM, then this standard is the working ALTQC standard and should be labeled **ALTQC##_TOC**. It can be used directly for analysis. In this case the holding time is 30 days. If the certified concentration is > 40 PPM, the prepared solution is an intermediate ALTQC and should be labeled **ALTQC##_TOC Intermediate**. It has a holding time of 30 days as well. Dilute the intermediate appropriately so that the working concentration is within the 10 PPM-40 PPM range.

Holding time of the diluted standard is 30 days. Refer to the manufacturer's certificate of analysis for the expiration date of the purchased stock ampule.

Note: The initial ALTQC solution prepared from the ampule to the "certified concentration" must be acidified with the appropriate volume of H_2SO_4 to the concentration of 0.2% H_2SO_4. Any further dilution of this solution to the appropriate ALTQC working concentration must be done with diluent (4.3.4.).

4.3.3. **ALTQC TN:** This solution is used as an Initial Calibration Verification **(ICV)** and an Independent Reference Material **(IRM)**. The ALTQCTN is prepared by diluting the "NOX ERA STOCK ##" to a working concentration range of 1.0 – 4.0 mg N/L and should be labeled **ALTQCTN##**. NOX ERA STOCK is prepared from an ERA "Simple Nutrients" ampule, where the sum of the certified values for Ammonia and Nitrate/Nitrite is the concentration for TN.

Holding time of the ALTQCTN standard is 30 days.

Note: The ALTQCTN solution must be acidified with the appropriate volume of H_2SO_4 to the concentration of 0.2% H_2SO_4.

4.3.4. **Blank Standard/Diluent (0 mg C/L, 0 mg N/L)** –

Sulfuric Acid (4.1.3.)	4 mL
DI Water (4.1.1.)	to 2000 mL

To a 2 L volumetric flask containing approx. 1.5 L of DI water, carefully add 4.0 mL of concentrated H_2SO_4. Dilute to the mark and invert several times to mix thoroughly.

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Used for the method blank (MBLK) and continuing calibration blank (CCB) and rinses (RINSE). Holding time, 30 days.

Note: This solution is also used for W-TN analysis following SOP NU-105 (low level TN).

4.3.5. **PQCK4 (1.0 mg C/L PQL) –**

10000 mg C/L Stock (4.2.4.)	0.1 mL
Diluent (4.3.4.)	to 1000 mL

To a 1 L volumetric flask containing approx. 900 mL of diluent, add 0.1 mL of the 10000 mg C/L stock standard. Fill up to the mark with diluent and invert several times to mix thoroughly.

PQL Check standard for W-TOC initial QC. Holding time, 30 days.

4.3.6. **Continuing Calibration Verification (CCV).**

Three different checks are prepared because TOC analysis requires a low, mid and high check to be analyzed on a rotating basis. The TN level in each check is not varied.

CCV1 (1 mg C/L, 2 mg N/L) –

1000 mg C/L Stock (4.2.3.)	500 uL
1000 mg N/L KNO3 Stock (4.2.2.)	1 mL
Diluent (4.3.4.)	to 500 mL

To a 500 mL volumetric flask containing approx. 400 mL of diluent, add 500 uL of the 1000 mg C/L stock standard and1 mL of the 1000 mg N/L KNO_3 Stock. Fill up to the mark with diluent and invert several times to mix thoroughly.

CCV20 (20 mg C/L, 2 mg N/L)

1000 mg C/L Stock (4.2.3.)	10 mL
1000 mg N/L KNO3 Stock (4.2.2.)	1 mL
Diluent (4.3.4.)	to 500 mL

To a 500 mL volumetric flask containing approx. 400 mL of diluent (4.3.4.), add 10 mL of the 1000 mg C/L stock standard (4.2.3.), add 1 mL of the 1000 mg N/L KNO_3 Stock (4.2.2.), and fill up to the mark with diluent and mix thoroughly.

CCV80 (80 mg C/L, 2 mg N/L)

1000 mg C/L Stock (4.2.3.)	40 mL
1000 mg N/L KNO3 Stock (4.2.2.)	1 mL
Diluent (4.3.4.)	to 500 mL

To a 500 mL volumetric flask containing approx. 400 mL of diluent (4.3.4.), add 40 mL of the 1000 mg C/L stock standard (4.2.3.), add 1 mL of the 1000 mg N/L KNO_3 Stock (4.2.2.), and fill up to the mark with

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diluent and mix thoroughly.

Holding time, 30 days.

4.3.7. **Mixed TOC TN calibration standards –**

Stock Dex 10000 (4.2.4.)	See Table
TN Stock 1000 PPM (4.2.1.)	See Table
Diluent (4.3.4.)	to 500 mL

In a 500 mL volumetric flask containing approx. 250 mL of diluent, add volumes of the stock solutions as described in the table below. Fill to the mark with diluent and invert several times to mix thoroughly.

Holding time, 30 days.

Standard Name	Vol. of TOC Stock (4.2.4.) [mL]	Vol. of TN Stock (4.2.1.) [mL]	Final Vol. [mL]	TN conc. [mg N/L]	TOC conc. [mg C/L]
MDLSPK	0.04	0.25	500	0.50	0.80
CAL STD 1	0.05	0.40	500	0.80	1.0
CAL STD 5	0.25	0.625	500	1.25	5.0
CAL STD 20	1.0	1.0	500	2.0	20
CAL STD 100	5.0	2.5	500	5.0	100

4.3.8. **Total Organic Nitrogen Check (TONCHCK, 2 mg N/L)-**

1000 mg N/L Glycine Stock (4.2.7.)	0.5 mL
Diluent (4.3.4.)	to 250 mL

To a 250 mL volumetric flask containing approx. 100 mL of diluent, add 0.5 mL of the 1000 mg N/L glycine stock solution. Dilute to mark with diluent and invert several times to mix thoroughly. Label this flask '**TONCHCK 2 PPM N**'.

Holding time, 30 days.

5. SAMPLE HANDLING AND PRESERVATION

5.1. Samples are preserved with sulfuric acid at collection and stored on ice or at ≤ 6 °C (not frozen). Samples submitted to the laboratory for DN/DOC analysis must be filtered in the field prior to acidification. All samples must be analyzed within 28 days of collection date for results to be reported unqualified.

5.2. Samples are stored in the Nutrient refrigerators in the receiving room of the FDEP laboratory. Allow samples to come to room temperature before processing.

6. SAMPLE PREPARATION AND ANALYSIS (SEE DEP SOP NU-033)

6.1. Open program TOC-CONTROL-L.

6.2. Choose Sample Table Editor icon →hit ok.

6.3. To start a new file and run: Click on the *New* button in the top left corner. Select

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the H/W settings on the drop-down menu → **TOC-N-CPH-SPARGE** (External Sparge) or **TOC-N-CPH, TOC-O-CSH, TOC-P-CSH** (Internal Sparge). To save the file, click *Save* and name the file YYMMDDN(/P/O)#_TOC_HTN (where # is a number 1, 2, etc., that indicates the 1st, 2nd, etc., run of the day.). → *Save*.

6.4. In some cases, it may be helpful to perform an optional rinse before the calibration. To add the rinse sequence to the beginning of the run (the rinse blank result will be calculated from a previous calibration), highlight line 1, right click, and select *Insert*→ *Multiple Samples*. This opens the Sample Group Wizard.

6.4.1. Page 1 Sample Source: Select *Method* option and browse button. Then select option a or b depending on the type of run:

a. 'NPOC_TN_EXSPARGE.met' → *Open* → *Next.* (external sparge run)
b. 'NPOC-TN.met' → *Open* → *Next.* (internal sparge run)

6.4.2. Page 2 Sample Parameters. Set options as follows:

Number of Samples = 1
Start Vial = 0
Sample Name = Enter file name (Ex.200101N1)
Sample ID = RINSE→ Finish

6.5. To setup a calibration sequence, highlight line two, right-click, and select *Insert- Calibration Curve* → Select appropriate cal file depending on the type of run:

a. 'NPOC CAL CURVE-EXSPARGE.cal' → *Open* (external sparge run)
b. 'NPOC CALIBRATION.cal'→ *Open* (internal sparge run)

6.6. After inserting the calibration, select the autosampler image in top right corner.

Assign vial numbers as follows:

0 mg C/L standard = 1 (diluent, 4.3.4.)
0.8 mg C/L standard = 2 (MDLSPK, TABLE 4.3.7.)
1.0 mg C/L standard = 3 (CAL STD 1, TABLE 4.3.7.)
5.0 mg C/L standard = 4 (CAL STD 5, TABLE 4.3.7.)
20.0 mg C/L standard = 5 (CAL STD 20, TABLE 4.3.7)
100.0 mg C/L standard = 6 (CAL STD 100, TABLE 4.3.7)

Select *OK* to complete. The vial column numbers should read 1,2,3,4,5,6.

Note: Calibration sequence for both types of run external and internal sparge will be the same.

6.7. To setup the next calibration sequence, highlight the next line (3, if a rinse was run at the beginning), right-click, and select *Insert- Calibration Curve* → Select appropriate cal file depending on the type of run:

a. 'TN CAL CURVE_EXSPARGE.cal' → *Open* (external sparge run)

b. 'HTN CALIBRATION.cal' → *Open* (internal sparge run)

6.8. After inserting the calibration, select the autosampler image in top right corner. Assign vial numbers as follows:

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0 mg C/L standard = 7 (diluent, 4.3.4.)
0.8 mg C/L standard = 8 (MDLSPK, TABLE 4.3.7.)
1.0 mg C/L standard = 9 (CAL STD 1, TABLE 4.3.7.)
5.0 mg C/L standard = 10 (CAL STD 5, TABLE 4.3.7.)
20.0 mg C/L standard = 11 (CAL STD 20, TABLE 4.3.7)
100.0 mg C/L standard = 12 (CAL STD 100, TABLE 4.3.7)

Select *OK* to complete. The vial column numbers should read 7,8,9,10,11,12.

Note: Calibration sequence for both types of run external and internal sparge will be the same.

6.9. To setup a sample sequence, highlight the next line, select *Insert -Multiple Samples*. This will open the Sample Group Wizard.

6.9.1. Page 1 Sample Source; Select Method option and browse button. Then select method depending on sample and run type:

a. For external sparge samples requiring both TN and TOC analysis, select 'NPOC_TN_EXSPARGE.met'→ *Next*
b. For external sparge samples requiring TOC analysis only, select 'NPOC_EXSPARGE.cal'→ *Next*
c. For internal sparge samples requiring both TN and TOC analysis, select 'NPOC-TN.met'→ *Next*
d. 'For internal sparge samples requiring TOC analysis only, select 'NPOC CALIBRATION.cal'→ *Next*
e. 'For internal sparge samples requiring TN analysis only, select 'HTN CALIBRATION.cal'→ *Next*

6.9.2. Page 2 Sample Parameters; Set options as follows:

Number of Samples = number of lines needed to complete the run.
Start Vial = 7 or 13 depending on use of one or two cal curves.
Sample Name = Enter file name. (YYMMDDN(/P/O)#_TOC_HTN)
Sample ID = Leave blank
→ Finish → OK.

6.10. For sample and QC that only need to be analyzed for W-TN or W-TOC, highlight the row where you want to insert the sample, select *Insert-Calibration Curve* and select the corresponding file (6.5. or 6.7.) and add a single sample as before.

6.11. Template for both internal and external sparge runs have been created so that a new run sequence does not need to be performed for every analysis. Click *open* in the top left of the software. Select the appropriate template for High Level run. Insert the sample IDs and save the file name. Then go to File→*print*. This will be the bench sheet.

6.12. Use appropriate vials for analysis based on the type of run:

External sparge runs: DWK Kimble Glass Screw-Thread Vials with PTFE/Silicone Septa 24 mL (Table 3.4.)

Internal sparge runs: Glass Shell Vials (Table 3.4.)

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For internal sparge runs, samples, QC standards, and calibration standards can be poured directly into Glass Shell Vials (Table 3.4.). For external sparge runs, all samples and standards must be pipetted into labeled 24 mL Glass Screw-Thread Vials (Table 3.4.) according to the run sequence. Place them in the autosampler rack and return rack to turntable for realignment. Make sure that all vials are correctly seated.

6.13. **Batch Preparation and Run Sequence:**

6.13.1. Batch Quality Control (Spiking): For each batch (10 samples or less): Select a quality control sample prepared in duplicate to assess precision for W-TOC and W-TOC/TN.

The sequence for Fresh, and Effluent samples:

- Sample
- Sample_M1(for TOC/TN) or Sample_H1(for TOC only)
- Sample_M1 (for TOC/TN) or Sample_H1(for TOC only)

The sequence for Salt samples:

- Sample
- Sample_V1
- Sample_V1

Prepare a 2 mg N/L and 40 mg C/L matrix spike (spike code M1 or H1) by adding 80 µL of the MIXED SPK (4.2.5.) to one 20 mL portion of the selected sample. For salt samples matrix spike preparation (spike code V1), add 400 uL of **'TOC STOCK: 1000 ppm' (4.2.3.)** to one 20 mL portion of the selected sample.

Prepare a laboratory fortified blank (LFB). The LFB spike must match the spiking code (M1, H1 or V1) with respect to the quality control sample, following the same procedure as for the matrix spikes by substituting blank standard (4.3.4.) for the sample. Effluent samples are batched separately.

6.13.2. Inorganic Carbon Solution (ICRC 103 PPM): For each analytical run including TOC analysis, prepare one inorganic carbon solution by pouring approximately 20 mL of ICRC 103 PPM (4.2.6.2.) directly into a glass vial. The vial can be analyzed similar to any other standards or samples as part of the run sequence.

6.13.3. Samples with a conductivity of ≥15,000 µmhos/cm and ≤30,000 µmhos/cm and/or a salinity of 9 PPTh or greater are batched as salt samples and are diluted 1:2. Salt samples with conductivity of >30,000 µmhos/cm are diluted 1:4. A 2N hydrochloric (HCl) acid rinse (4.2.8.) is run every 5 cups in order to minimize residue build up on the catalyst. An

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additional diluent rinse (RINSE, 4.3.4.) may be added after every salt sample to further clean the catalyst. Salt batch is placed at the end of a run and no more than fifteen salt samples should be analyzed per run. The run should end with at least 1 HCL rinse and 4 diluent rinses to further minimize residue build up on the catalyst.

6.13.4. Each run begins with the following sequence:

Rinse (6.4.) (optional)
Calibration/s (6.6., 6.8.)
CCB (Run CCB immediately after the highest TOC calibration standard of 100 PPM as a carryover check)
MDLSPK (PQL-level for TN, Table 4.3.7.)
ICRC (4.2.6.)
TONCHCK (4.3.8.)
TONCHCK (4.3.8.)
TONCHCK must be run twice.
PQCK4 (PQL TOC only, 4.3.5.)
ALTQC##_TOC (4.3.2.)
ALTQCTN## (4.3.3.)
CCV1 (Mixed Check for TOC & TN, 4.3.7.)
Batched samples including **MBLKs** (4.3.4.), **LFBs** (6.12.1.), duplicate samples and spiked samples (6.12.1.)
CCV20, CCV80, CCV1 on rotating basis (CCV 4.3.7.)
CCB (Blank Standard 4.3.4.)

Note: CCV and CCB checks are scheduled to bracket every 10th sample on the run. The first CCV is the CCV1 (1 PPM C, 2 PPM N). Following the first CCV, checks will alternate in the following pattern: CCV20 → CCV80 → CCV1→ CCV20 → CCV80…

6.13.5. It is recommended to end each run with 8 rinses (RINSE 4.3.4., 6.4.) to clean the catalyst.

6.14. Connect Instrument: Click *Connect.* Wait for connection and ready indicator (highlighted green when ready), then press *Start*→ Check Shut down instrument box → press Run to start the run.

Note: Print the run file that was just created by going to *file* → *print*→ *sample table*.

6.15. Post-run Procedure: Results are exported as an ASCII file and converted into a raw file in the QC manager for performing calculations and uploading to LIMS.

6.15.1.*File* → *ASCII Export Setting* → *Detail* → *Data.* Check the following export options; Sample ID, Dilution, Date/Time, Mean Conc., Result, and Vial. Also make sure the export data box is checked. Under the "Misc" tab that asks for the separator settings, choose "tabulator," and check the box for "Export strings in quotation marks…".

6.15.2.To export file: *File* → *ASCII Export* → *Detail* (Include Injection Data) →

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Filename → *Save.*

6.15.3. There are 3 TOC-L model instruments used for W-TOC or W-TOC/W-TN analysis as part of this SOP. Be cautious to save data in the correct instrument's respective folders and subfolders.Export to the appropriate instrument data subfolder C:\TOC-'X'_TN\Data for TOC-L'X' (where X represents instruments N, O, or P) in the current years' subfolder. This is the local drive for the instrument workstation.

6.15.4. Open C:\TOC-L'X' (X is N, or O or P) in Windows Explorer. Locate the text file you just created, as well as the peak (*.pkt), calibration (*.cal) and sample table (*.t32 or *.tlx) files associated with the analysis and copy all four files from the local drive to the appropriate instrument folder (TOC-N or O or P) in the current year's subfolder located at:

\\floridadep\data\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\TotalOrganicCarbonAnalyzers\

Note: The exact location of the data files within instrument folder structure is determined by the software settings (Tools > Organize Files; please see User manuals for details).

6.15.5. Print a copy of the final report and data table containing injection peaks by selecting: *File* → *Print* → *Sample Report –All*, then *File* → *Print* → *Sample Table.*

6.16. Quantitation/Calculations:

6.16.1. To upload the file, log into LIMS, select QC Manager (QCM), and select the appropriate instrument. Click the 'Convert File" button, and the selection the appropriate folder (current year). The Text File that was exported (6.14.3.) should be available for conversion. Select the appropriate file and follow the QC Manager's (QCM) instructions.

6.16.2. The instrument will give the values for NPOC in mg C/L and Total Nitrogen in mg N/L. The results for TN and NPOC calculated by the instrument is the average of three out of five injections for a given sample with a Max CV of 5 %. The calibration consists of five standards plus a blank. The regression model applied is linear.

6.16.3. The QC Manager will calculate spike and standard recoveries and RPDs. For general calculations including RPDs and spike recoveries, see the FDEP Quality Manual Section 5.9.

6.16.4. The calibrants are all prepared manually (Section 4.3.4. and 4.3.7.). The correlation coefficient for the calibration is calculated by the instrument software. Use the current NU-TOC_TN form located at: \\floridadep\data\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\MetaData\TOC-TN\Forms to calculate the recoveries of the calibrants. Open the form, enter the header information and the slope, intercept, and mean area results to calculate the recovery of calibrants. Acceptance limits for the recoveries of the calibration standards above the PQL are 90 – 110%

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and 70 – 130% for the PQL-level standard. For TOC, the 0.8 mg C/L standard (MDLSPK) acceptance limits are 62.5 – 150%. The acceptance limits for the blank calibration point results are below the MDL and above the negative value of the MDL (-MDL < blank < MDL)

7. DATA ARCHIVAL/VALIDATION

7.1. The raw data is archived in paper format. A report folder is created for each analytical run. Occasionally more than one run may be in one folder. The folder is labeled with the test (W-TOC/W-TN), filename/s(Ex:YYMMDDN(/P/O)#_TOC_HTN) and initials of the analyst.

7.2. Each report folder should contain the following items - run report including raw data and calibration curve, calibration standard recovery sheet, results report, bench sheet, Reagent and Standard Logsheet (ensure TOC-TN specific Reagent and Standard Logsheet NU-RGTSTD-TOCTN is used), and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

7.3. The report folders are on file with the nutrients supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

7.4. Instrument raw data files, including peak (*.pkt), calibration (*.cal) and sample table (*.t32 or *.tlx) files, are backed up from instrument PCs and stored on the Nutrients drive in the appropriate instrument folder (TOC-N) in the current year's subfolder located at:

\\floridadep\data\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\TotalOrganicCarbonAnalyzers\

7.5. TOC/TN instrument data text transfer files for upload to QC manager are stored in electronic format in the appropriate instrument folder (TOC-N or O or P) in the current year's subfolder located at

\\floridadep\data\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\TotalOrganicCarbonAnalyzers\

7.6 Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in

\\floridadep\data\DEAR\Labs\Lab5\Chemistry\Inorganic\Nutrient\Validations

8. MAINTENANCE/TROUBLESHOOTING

Note: Make sure all maintenance performed is documented in the instrument's maintenance log.

8.1. Maintenance:

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8.1.1. Before beginning sample analysis, conduct a general inspection of the instrument to ensure that everything is in order, and that there is enough UHP Air to complete the run.

8.1.2. The Humidifier and Dehumidifier vessels should be filled with DI water to the fill line on the vessel. Once a month, the humidifier vessel should be drained and refilled with fresh DI water. This prevents contamination.

8.1.3. Inspect the Drain Port (on the side of the instrument) weekly. Drain Port should be drained and refilled with fresh DI water once a month (Refer to user's manual for instructions and details).

8.1.4. Keep the rinse water bottle filled with DI water. If running samples overnight, fill the bottle with DI water before starting the run.

8.1.5. The diluent bottle should be changed with fresh Blank Standard/Diluent (4.3.4.) at least once per month.

8.1.6. Make sure the HCL Intake is changed with fresh 2N HCL (4.2.8.) at least once every three months.

8.1.7. Inspect the slider and O-rings before analysis and clean with DI water if needed.

8.1.8. Check the waste line daily to ensure proper flow. Waste backup will damage the autosampler. Dump waste down the drain as needed.

8.1.9. Regeneration of TC catalyst should be performed on a case by case basis TC catalyst regeneration has little effect on TN analysis. See instrument manual for regeneration procedure. Regeneration should be followed with a run of at least 20 CCBs and a few CCVs.

8.1.10. Other maintenance may be required periodically, such as replacing catalyst, replacing halogen-scrubber, maintaining syringe and 8-port valve. Refer to user's manuals for instructions and details.

8.2. Troubleshooting Notes:

8.2.1. To stop the run at any point and delete the calibration:

Click *Stop* button → *Stop* (stop all processes immediately).

8.2.2. To interrupt the run at any point and save the calibration:

Click *Stop* button → *Stop* (after current sample is completed).

8.2.3. In order to restart a run in progress (for example, if there is a QC failure at the beginning of a run) and keep the sample table set up for a new run, previous data gathered or attempted must be deleted prior to restart. Highlight the lines to delete, go to *Edit* → *Clear Measured Data* → *Highlighted* → *Yes*, then click *View Vial Settings* → Assign the vial numbers for rerun samples.

8.2.4. Treat samples suspected to contain humic acids as follows:

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a. Split a well-mixed sample into two portions.
b. Keep one portion at pH ≤ 2 and adjust the other to pH 5-7 with 10 N Sodium Hydroxide to increase the solubility of humic acid.
c. Cap and allow both portions to sit at room temperature for ½ hour.
d. Analyze both splits and report the highest result.

9. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE NU-038 AND NU-043)

9.1. A new calibration must be performed at the beginning of the analysis and the linear calibration range (LCR) must be verified (see 9.2.). Consecutive runs on one day may use the same calibration. The linear calibration consists of five standards (CAL STD 100, CAL STD 20, CAL STD 5, CAL STD 1, MDLSPK) and a blank. A CCB (blank check) must be analyzed immediately after the highest calibration standard of 100 PPM. The CCB must be below the MDL of 0.5 mg C/L and 0.10 mg N/L. It is followed by a sequence listed in 6.12.4.

9.2. LCR: See the FDEP Quality Manual Appendix B, Section 7.0, 'Protocol for Determining the Test Method Range of Applicability'. The correlation coefficient of the linear regression (r^2) must be equal to or larger than 0.995. Acceptance limits for the recoveries of the calibration standards above the PQL are 90 – 110% and 70 – 130% for the PQL-level standard. The acceptance limit for the **TOC** MDLSPK standard (below the PQL) is 62.5 – 150% recovery. The acceptance limits for the blank calibration point results are below the MDL and above the negative value of the MDL (-MDL < blank < MDL).

9.3. Each analytical run may contain a number of sample batches, with no more than 10 samples per batch. Each batch is required to have an MBLK, an LFB, a matrix spike, and a duplicate sample and/or duplicate matrix spike. The spikes are prepared according to section 6.13.1. Acceptance limits for the LFB and spike recoveries are 85-115%. The RPD acceptance criterium for TOC is <15% and for TN is <20 % for results above the PQL.

9.4. TN: On every analytical run the organic nitrogen check (TONCHCK) is run at least twice at the beginning of the run (6.13.14.). The result must be between 85-115% recovery. If the recovery is outside the control limit the samples must be reanalyzed or reported qualified. The instrument should be checked to ensure that it is operating correctly.

Note: The method requires the analysis of at least **4 portions** of **TONCHCK** (Organic Nitrogen Test Solution) (4.3.8.) at the same volume as samples to be analyzed. To satisfy this requirement, **TONCHCK** is put on the run sequence at least twice (for a minimum total injection of 6 and up to 10 injections).

9.5. One AltQC standard for TN and one AltQC for TOC are analyzed with every analytical run. Acceptable limits for the recovery of the ALTQC are 90 – 110% unless the manufacturer's certified limits are more stringent, in which case, the manufacturer's limits apply. (Refer to 4.3.2., 4.3.3.)

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9.6. One MDLSPK (MDLSPK, TABLE 4.3.7.) is analyzed for every analytical run. MBLK and MDLSPK results are used for ongoing MDL and PQL verification. The acceptance limit for the MDLSPK standard for TOC (below the PQL) is 62.5 – 150% recovery, for TN 70 – 130% recovery. The MDLSPK serves as the PQL-level standard for TN.

9.7. One PQL (PQCK 4.3.6., MDLSPK, Table 4.3.7) level standard for TOC and TN is analyzed for every analytical run. For analytical runs that are longer than 24 hours, at least one PQL standard is analyzed every 24 hrs. Acceptance limits for the PQCK recovery are 70-130%.

9.8. A CCV (CCV 4.3.7., 6.13.4.) and a blank (CCB 4.3.4.) standard are run at the beginning of every run, after every 10^{th} sample, and at the end of the run. CCV1, CCV20, and CCV 80 are analyzed in a rotating pattern throughout the run. The first CCV is the CCV1 (1 PPM C, 2 PPM N). Following the first CCV, all checks will alternate in the following pattern after every 10^{th} sample – the rotation will be repeated until the run is complete.

The acceptance limit for the recovery of the CCV for TN is 85 – 115% in each level. The acceptance limit for the recovery of TOC in CCV1 is 70 – 130 % (PQL level) and is 85 – 115% in CCV20 and CCV80.

CCV1 (1 C mg/L, 2 N mg/L)
CCV20 (20 C mg/L, 2 N mg/L)
CCV80 (80 C mg/L, 2 N mg/L)

9.9. Acceptance limits for the blanks (MBLKs and CCBs) are < 0.10 and > -0.10 mg N/L for TN and < 0.50 and > -0.50 mg C/L for TOC.

9.10. For every analytical TOC run, one Inorganic Sample (103 PPM IC) must be analyzed as an inorganic carbon removal check (ICRC) (4.2.6., 6.13.2.). The purpose is to assess instruments efficiency in removing inorganic carbon. The result of the analysis must be below MDL (0.5 PPM C). If the result is not less than MDL, only sample results greater than 10 times the ICRC may be reported without qualification.

9.11. For general method performance and acceptance criteria for QC measures and corrective action for out-of-control data and contingencies for handling out-of-control or unacceptable data, refer to DEP SOPs NU-038 and SOP NU-043. If there are any anomalous results (e.g., differing results for multiple analyses of same sample) or any unusual events (spilled sample, cannot locate sample, etc.), see supervisor for further instruction.

10. SAFETY/WASTE MANAGEMENT/POLLUTION PREVENTION

10.1. Refer to the MSDS notebook for information on safe handling of samples and reagents used with instrument.

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10.2. Flush sample waste (as long as no other known hazards are present) down the sink with plenty of water.

10.3. Review the laboratory Health and Safety Plan (accessible on the intranet at https://www.fldepnet.org/content/dear/bureau-laboratories-safety-documents).

10.4. Safety glasses, gloves and lab coats should be worn at all times while handling samples and reagents.

11. REFERENCES

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use.

11.1. ASTM D8083-16 and Standard Methods Online, 5310 B-2014.

11.2. Shimadzu TOC-L-CPH and TOC-L-CSH user manual

11.3. Quality Manual, Bureau of Laboratories, FDEP.

11.4. DEP SOP NU-062, Determination of Total Organic Carbon (TOC) and dissolved Organic Carbon (DOC) Using the Shimadzu TOC Analyzer

11.5. DEP SOP NU-033, Summary of Analysis Procedures for the General Chemistry and Nutrients Workgroups.

11.6. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

11.7. DEP SOP NU-041, Reagent Preparation Procedure.

11.8. DEP SOP NU-042, Standard Preparation Procedure.

11.9. DEP SOP NU-043, General Chemistry Quality Assurance and Data Authorization Guidelines.

11.10. Laboratory Health and Safety Plan.

11.11. DEP SOP LB-006, Standard operating procedure for records maintenance and storage.

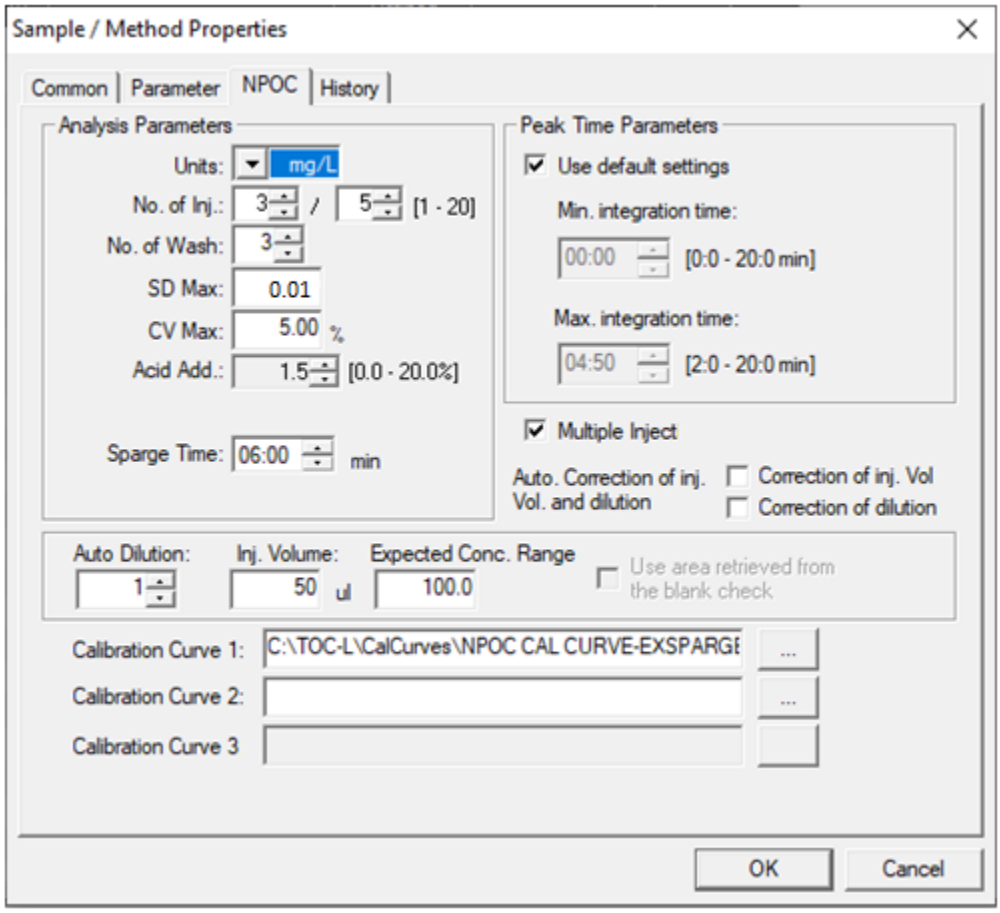
11.12 DEP SOP LB-030, Purchasing and Receiving Laboratory Chemicals and Supplies.

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APPENDIX I: INSTRUMENT SETTINGS- Parameters

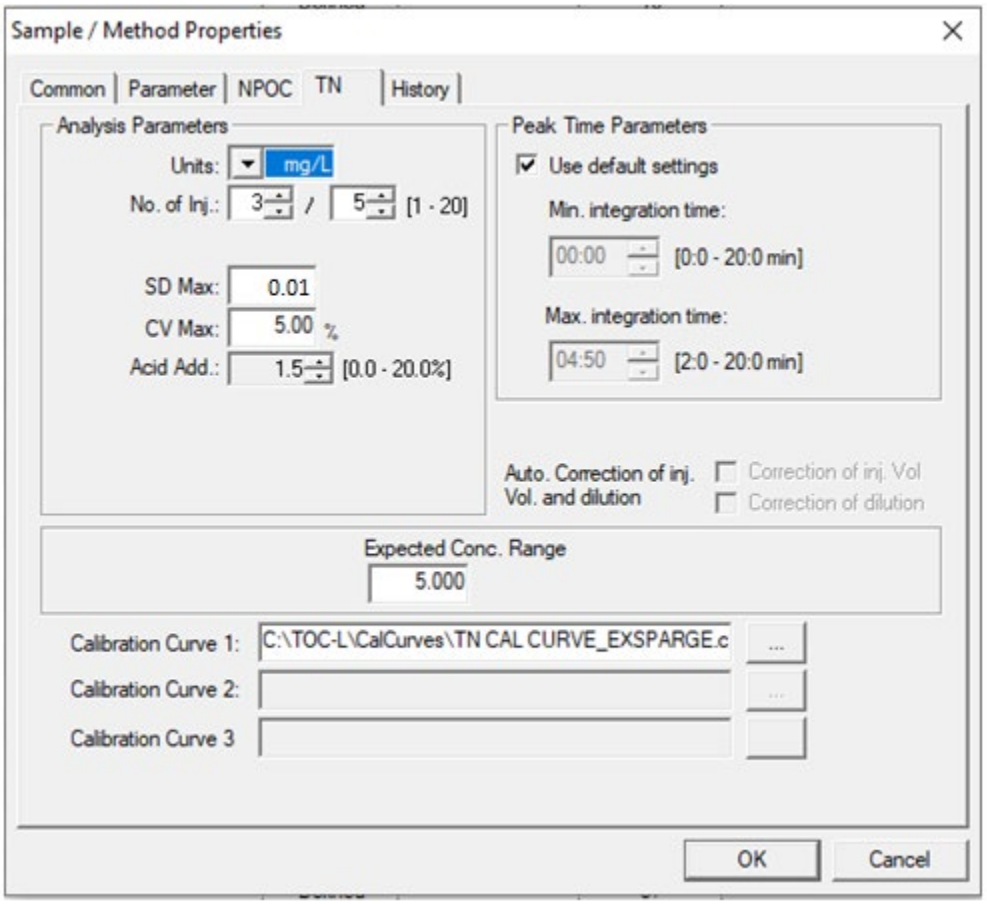
Note: Refer to Shimadzu Software User's Manual for details.

External NPOC Settings:



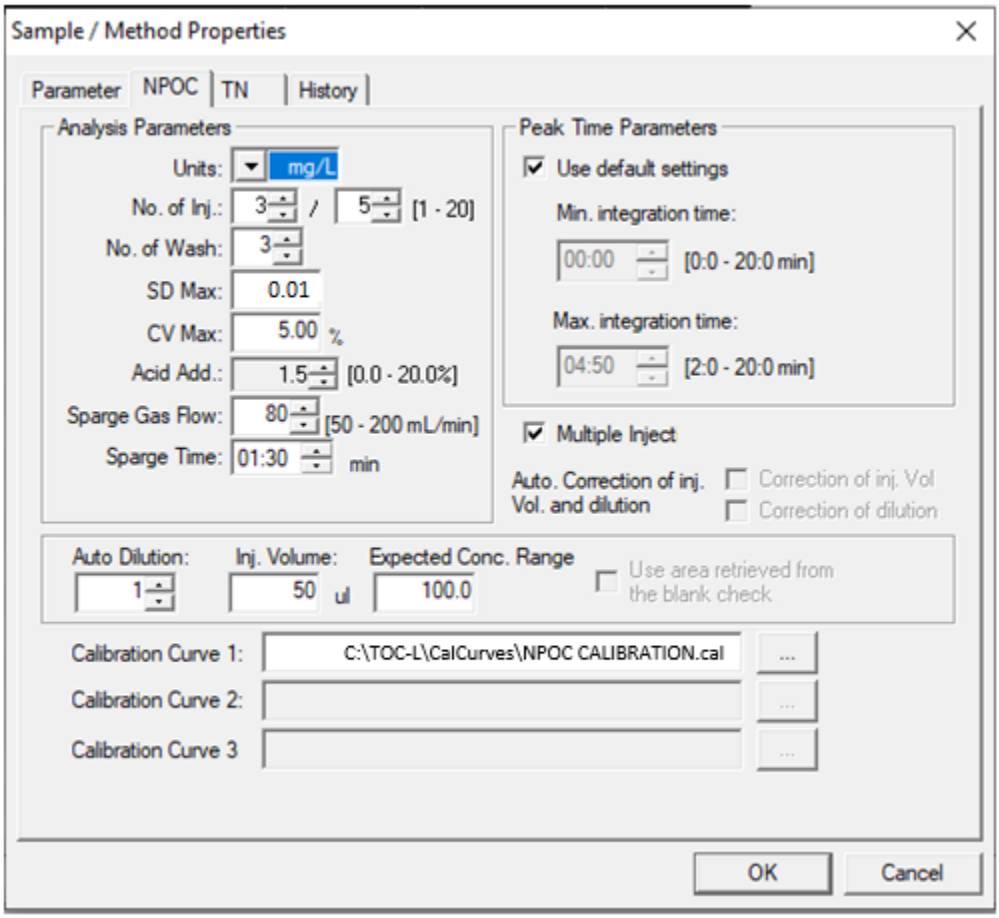
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External TN Settings:



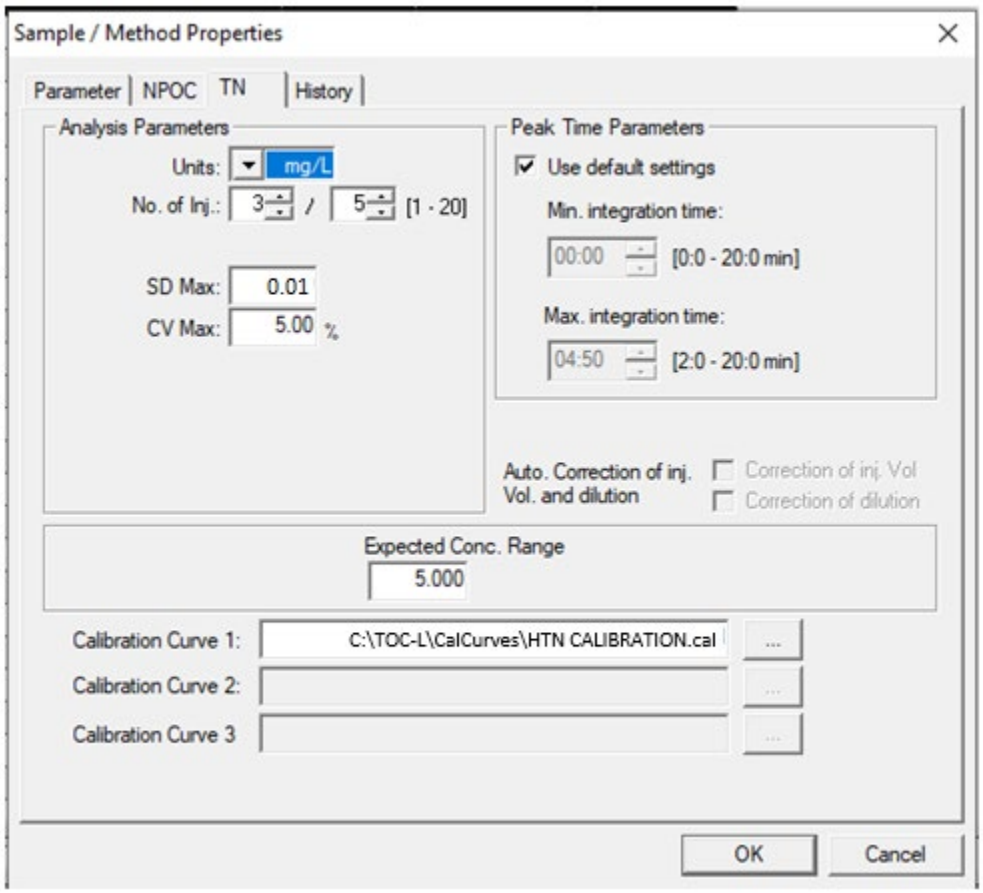
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Internal NPOC Settings:



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Internal TN Settings:



APPENDIX OF SIGNIFICANT CHANGES

01/29/2020 SECTION 4: Added clarification that the ICV/CCV stock solution is prepared from a different source or lot of KNO_3 as used for the calibration standards.

02/14/2020 SECTION 6 AND SECTION 9: Clarified the acceptance limits for the blank calibration point in the calibration curve.

03/17/2021 Added instructions for analyzing high salinity samples.

01/25/2022 Following revisions were made to the SOP:

- Updated Table of Contents
- Added an option to run TOC/TN Analysis on Internal Sparge setting.
- Added tables to include instrumentation information, supplies & consumables, chemicals, and standards.
- Added instructions to run TONCHCK twice to fulfill method requirement.

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- Rearranged the preparation of the stock standards, standards, calibration, and reagents sections to improve SOP flow.
- Updated the run/template set up sections to integrate the Internal Sparge setting and option.
- Added brief instructions on uploading file to QCM.
- Updated the nomenclature of the methods and calibration files for run/template set up sections.
- Updated the maintenance section to include inspection and replacement of DI water of the Drain Port.
- Added the APPENDIX I section to include scanned tables (source of tables is the instrument software) that display the TOC/TN parameters for both internal and external sparge.

03/11/2022 Modified instructions for sample salt samples to allow for 1:4 dilutions of high conductivity samples >30,000 uhm/cm. Added and provided instructions on the use of the Reagent and Standard LogSheet (NU-RGTSTD-TOCTN) specific to TOC/TN analysis.

08/26/2023 Revised SOP to comply with the method 5310 B-2014 update and implementation. The following revisions were made to the SOP:

- New spiking scheme to ensure a duplicate is analyzed every 10 samples.
- For TOC: Immediate analysis of CCB after the highest calibration standard of 100 PPM to check for carryover.
- For TOC: Rotating CCVs. Different CCV concentrations are alternated throughout the analytical run (CCV 1 PPM, CCV 20 PPM, and CCV 80 PPM). CCV acceptance limits updated.
- For TOC: Inorganic spike was replaced with Inorganic Carbon Removal Check 103 PPM, made from Synthetic Seawater.
- Incorporated renaming of instrument TOC-L2 to instrument TOC-N. Added new instruments TOC-O and TOC-P.
- For TOC: Changed RPD acceptance limit to <15 %.
- Clarified acceptance limit for ALTQC’s.

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