

Determination of Dissolved Organic Carbon (NPOC), and Total Organic Carbon Fresh/Estuarine/Coastal Waters using High Temperature Combustion and Infrared Detection.

1. SCOPE and APPLICATION

- 1.1 High temperature combustion (680°C) is used to determine dissolved organic carbon (DOC), also known as non-purge able organic carbon (NPOC), total organic carbon (TOC), and total carbon (TC), using a non-dispersive infrared detector (NDIR). The method is used to analyze all ranges of salinity.
- 1.2 A Method Detection Limit (MDL) of 0.24 mg/L DOC was determined using the Student's *t* value (3.14) times the standard deviation of 7 replicates. If more than seven replicates are used to determine the MDL, refer to the Student's *t* test table for the appropriate n-1 value.
- 1.3 The quantitation limit for DOC was set at 0.05 mg/L C.
- 1.4 This procedure should be used by analysts experienced in the theory and application of organic carbon analysis. Three months experience with an experienced analyst, certified in the analysis using the organic carbon analyzer, is required.
- 1.5 This method can be used for all programs that require analysis of dissolved and total organic and inorganic carbon.
- 1.6 This procedure conforms to EPA Method 415.1.

2. SUMMARY

- 2.1 The Shimadzu TOC-L uses a high temperature combustion method to analyze aqueous samples for total carbon (TC), total organic carbon (TOC) and dissolved organic carbon (DOC), also known as non-purge-able organic carbon (NPOC). TOC and TC concentrations are derived from whole unfiltered water and water used for NPOC has been filtered through a 0.7 um (nominal pore size) GF/F glass fiber filter, or equivalent.
- 2.2 TOC and NPOC samples are acidified and sparged with ultra pure carrier grade air to drive off inorganic carbon. TC samples are injected directly onto the catalyst bed with no pretreatment and measure inorganic as well as organic carbon. High temperature combustion (680°C) on a catalyst bed of platinum-coated alumina balls breaks down all carbon compounds into carbon dioxide (CO₂). The CO₂ is carried by ultra pure air to a non-dispersive infrared detector (NDIR) where CO₂ is detected.

3. DEFINITIONS

- 3.1 Acceptance Criteria – Specified limits placed on characteristics of an item, process, or service defined in a requirement document. (ASQC)
- 3.2 Accuracy – The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS)
- 3.3 Aliquot – A discrete, measured, representative portion of a sample taken for analysis. (EPA QAD Glossary)
- 3.4 Analytical Range - 100 ppb - 4000 ppm using a 4 - 100 µl injection volume, using regular sensitivity catalyst.
- 3.5 Batch – Environmental samples, which are prepared and /or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates, or concentrates) and/or those samples not requiring preparation, which are analyzed together as a group using the same calibration curve or factor. An analytical batch can include samples originating from various environmental matrices and can exceed 20 samples. (NELAC/EPA)
- 3.6 Blank- A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC)
- 3.7 Calibrate- To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)
- 3.8 Calibration – The set of operations which establish, under specified conditions, the relationship between values indicated by a measuring device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)
- 3.9 Calibration Curve – The graphical relationship between known values, such as concentrations, or a series of calibration standards and their analytical response. (NELAC)
- 3.10 Calibration Method – A defined technical procedure for performing a calibration. (NELAC)
- 3.11 Calibration Standard – A substance or reference material used to calibrate an instrument. (QAMS)
 - 3.11.1 Initial Calibration Standard (STD) – A series of standard solutions used to initially establish instrument calibration responses and develop calibration curves for individual target analytes.
 - 3.11.2 Initial Calibration Verification (ICV) – An individual standard, analyzed initially, prior to any sample analysis, which verifies

acceptability of the calibration curve or previously established calibration curve.

- 3.11.3 Continuing Calibration Verification (CCV) – An individual standard which is analyzed after every 10-15 field sample analysis.
- 3.12 Certified Reference Material – A reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (ISO 17025)
- 3.13 Combustion tube – Quartz tube filled with platinum catalyst, heated to 680° C, into which the sample aliquot is injected.
- 3.14 Conditioning Blank – DI water run before the calibration curve to decrease the instrument blank and stabilize the column conditions.
- 3.15 Corrective Action – Action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)
- 3.16 Deficiency – An unauthorized deviation from acceptable procedures or practices. (ASQC)
- 3.17 Demonstration of Capability – A procedure to establish the ability of the analyst to generate acceptable accuracy. (NELAC)
- 3.18 Detection Limit – The lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated degree of confidence.
- 3.19 Duplicate Analysis – The analyses of measurements of the variable of interest performed identically on two sub samples (aliquots) of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory. (EPA-QAD)
- 3.20 External Standard (ES) – A pure analyte (potassium hydrogen phthalate (KHP)) that is measured in an experiment separate from the experiment used to measure the analyte(s) in the sample. The signal observed for a known quantity of the pure external standard is used to calibrate the instrument response for the corresponding analyte(s). The instrument response is used to calculate the concentrations of the analyte(s) in the unknown sample.
- 3.21 Field Duplicates (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 provide a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
- 3.22 Field Reagent Blank (FRB) – A aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all

analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

- 3.23 Furnace – Heats the combustion tube to the operating temperature of 680° C.
- 3.24 Holding time – The maximum time that samples may be held prior to analysis and still be considered valid. (40 CFR Part 136) The time elapsed from the time of sampling to the time of extraction or analysis, as appropriate.
- 3.25 Injection – The sample aliquot that is drawn into the syringe and injected into the combustion tube.
- 3.26 Instrument Detection Limit (IDL) – The minimum quantity of analyte of the concentration equivalent which gives an analyte signal equal to three times the standard deviation of the background signal at the selected wavelength, mass, retention time absorbance line, etc.
- 3.27 Laboratory Duplicates (LD1 and LD2) – Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.28 Laboratory Reagent Blank (LRB) – A matrix blank (i.e., DI water) that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the instrument.
- 3.29 Laboratory Control Sample (LCS) – A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standard or a material containing known and verified amounts of analytes. The LCS is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system. (NELAC)
- 3.30 Limit of Detection (LOD) – The lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. (ACS)
- 3.31 Limit of Quantitation (LOQ) – The minimum levels, concentrations, or quantities of a target variable (target analyte) that can be reported with a specified degree of confidence. The LOQ is set at 3 to 10 times the LOD, depending on the degree of confidence desired.
- 3.32 Linear Dynamic Range (LDR) – The absolute quantity over which the instrument response to an analyte is linear. This specification is also referred to as the Linear Calibration Range (LCR).
- 3.33 Material Safety Data Sheets (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.
- 3.34 May – Denotes permitted action, but not required action. (NELAC)

- 3.35 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.36 Must – Denotes a requirement that must be met. (Random House College Dictionary)
- 3.37 Non-Dispersive Infrared Detector (NDIR) – The detector found in the Shimadzu TOC-L and TOC5000A analyzers. Carbon dioxide is detected.
- 3.38 Precision – The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (NELAC)
- 3.39 Preservation – Refrigeration, freezing, and/or reagents added at the time of sample collection (or later) to maintain the chemical and or biological integrity of the sample.
- 3.40 Quality Control Sample (QCS) – A sample of analytes of known and certified concentrations. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.
- 3.41 Run – One sample analysis from start to finish, including printout.
- 3.42 Run Cycle – Typically a day of operation – the entire analytical sequence of runs from the first run to the last run and including the transfer of run cycle data to the disc.
- 3.43 Sample Volume – Amount of sample injected into the combustion tube.
- 3.44 Sensitivity – The capability of a test method or instrument to discriminate between measurement responses representing different levels (concentrations) of a variable of interest.
- 3.45 Shall – Denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there be no deviation. (ANSI)
- 3.46 Should – Denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (ANSI)
- 3.47 Sparge Time – The time required to aerate an acidified sample with ultra pure air to remove inorganic carbon to determine the concentration of organic carbon.
- 3.48 Standard Reference Material (SRM) – Material which has been certified for specific analytes by a variety of analytical techniques and/or by numerous laboratories using similar analytical techniques. These may consist of pure chemicals, buffers, or compositional standards. The materials are used as an indication of the accuracy of a specific analytical technique.

4. INTERFERENCES

4.1 Carbonates and bicarbonates may interfere with the determination of organic carbon by increasing the concentration of CO₂ detected. These are removed by adding enough acid to the sample to bring the pH to 2 or below, then sparging with ultra-pure air for a predetermined time.

5. SAFETY

5.1 Safety precautions must be taken when handling reagents, samples and equipment in the laboratory. Protective clothing including lab coats, safety glasses and enclosed shoes should be worn. In certain situations, it will be necessary to also use gloves and/or a face shield. If solutions come in contact with eyes, flush with water continuously for 15 minutes. If solutions come in contact with skin, wash thoroughly with soap and water. Contact Solomons Rescue Squad (911) if emergency treatment is needed and also inform the Chesapeake Biological Laboratory (CBL) Business Manager of the incident. Contact the CBL Business Manager if additional treatment is required.

5.2 The toxicity or carcinogenicity of each reagent used in this procedure may not have been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known hazardous materials and procedures.

5.3 Do not wear jewelry when troubleshooting electrical components. Even low voltage points are dangerous and can injure if allowed to short circuit.

5.4 The following hazard classifications are listed for the chemicals used in this procedure. Detailed information is provided on Material Safety Data Sheets (MSDS).

| Chemical | Health | Flammability | Reactivity | Contact | Storage |
|------------------------------------|--------|--------------|------------|---------|--------------|
| Potassium Hydrogen Phthalate | 0 | 1 | 0 | 1 | Green |
| Sodium Carbonate, Anhydrous | 1 | 0 | 1 | 2 | Green |
| Sodium Bicarbonate | 1 | 1 | 1 | 1 | Green |
| Phosphoric Acid | 3 | 0 | 2 | 4 | White |
| Hydrochloric Acid | 3 | 0 | 2 | 4 | White |
| Sodium Hydroxide | 3 | 0 | 2 | 4 | White Stripe |
| Platinum Catalyst on Alumina Beads | 1 | 0 | 1 | 1 | Green |
| Soda Lime | 1 | 0 | 1 | 3 | White |
| Sulfuric Acid | 4 | 0 | 2 | 4 | White |

On a scale of 0 to 4 the substance is rated on four hazard categories: health, flammability, reactivity, and contact. (0 is non-hazardous and 4 is extremely hazardous)

STORAGE

Red – Flammability Hazard: Store in a flammable liquid storage area.

Blue – Health Hazard: Store in a secure poison area.

Yellow – Reactivity Hazard: Keep separate from flammable and combustible materials.

White – Contact Hazard: Store in a corrosion-proof area.

Green – Use general chemical storage (On older labels, this category was orange).

Striped – Incompatible materials of the same color class have striped labels. These products should not be stored adjacent to substances with the same color label. Proper storage must be individually determined.

6. EQUIPMENT AND SUPPLIES

6.1 A Total Organic Carbon Analyzer capable of maintaining a combustion temperature of 680° C and analyzing for organic and inorganic carbon. The Shimadzu TOC-L is used in this laboratory.

6.2 Freezer, capable of maintaining $-20 \pm 5^{\circ}$ C.

6.3 Lab ware – All reusable lab ware (glass, Teflon, plastic, etc) should be sufficiently clean for the task objectives. This laboratory soaks all lab ware related to this method in a 10% HCl (v/v) acid bath overnight.

7. REAGENTS AND STANDARDS

7.1 Purity of Water – Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specification D 1193, Type I. Freshly prepared water should be used for making the standards intended for calibration. The detection limits of this method will be limited by the purity of the water and reagents used to make the standards.

7.2 Purity of Reagents – Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without compromising the accuracy of the determination.

7.3 Potassium Hydrogen Phthalate (KHP) $C_6H_4(COOK)(COOH)$ – primary standard for organic carbon.

7.4 Sodium Hydrogen Carbonate ($NaHCO_3$) and Sodium Carbonate (Na_2CO_3) – primary standard for inorganic carbon and also determining sparging efficiency.

- 7.5 Sulfuric Acid, 9 N –
- | | |
|--|---------|
| Sulfuric acid (H ₂ SO ₄), concentrated, | 250 ml |
| Deionized water, q.s. | 1000 ml |

In a 1000 ml volumetric flask, add 250 ml of concentrated sulfuric acid to ~600 ml of deionized water. Dilute to 1000 ml with deionized water. Allow solution to cool to near room temperature before filling completely to the graduated mark on the flask

- 7.6 Organic Carbon Stock Standard: Potassium Hydrogen Phthalate (KHP) Standard, 1000 mg/l
- | | |
|--|---------|
| Potassium hydrogen phthalate (HOCOC ₆ H ₄ COOK), | |
| Dried at 45° C, min. 1 hour | 2.125 g |
| Deionized water | 1000 ml |

In a 1000 ml volumetric flask, dissolve 2.125 g of potassium hydrogen phthalate in ~800 ml of deionized water. Dilute to 1000 ml with deionized water. Make fresh every 4 - 6 months. Store at 4° C.

- 7.7 Inorganic Carbon Stock Standard: Sodium Hydrogen Carbonate/ Sodium Carbonate (NaHCO₃/Na₂CO₃) Standard, 1000 mg/l
- | | |
|--|---------|
| Sodium Hydrogen Carbonate (NaHCO ₃) | 1.75 g |
| Sodium Carbonate, Anhydrous (Na ₂ CO ₃) | 2.205 g |
| Deionized H ₂ O | 500 ml |

In a 500 ml volumetric flask, dissolve 1.75 g NaHCO₃ and 2.205 g Na₂CO₃ in ~300 ml deionized H₂O. Dilute to 500 ml with deionized H₂O. Make fresh every 4 months. Store at 4° C.

- 7.8 Blanks – ASTM D1193, Type I water is used for the Laboratory Reagent Blank.
- 7.9 Quality Control Sample (QCS) – For this procedure, the QCS can be any certified dissolved sample which is obtained from an external source. If a certified sample is not available, then use the standard material (KHP).

8 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1 Water collected for DOC should be filtered through a Whatman GF/F glass fiber filter (nominal pore size 0.7 µm), or equivalent.
- 8.2 Water collected for DOC should be frozen at -20° C, or acidified with 9N H₂SO₄ to a pH of ≤2. The sample container should be either borosilicate glass or Teflon. Plastic containers may be used if well cleaned and aged. Freshwater samples should be frozen in Teflon or plastic to prevent breakage.

- 8.3 Frozen DOC samples may be stored longer than 28 days. It has been shown that frozen QCS samples up to a year old still fall well within the control limits.
- 8.4 Acidified DOC samples should be frozen, as above, or refrigerated at 4° C for no longer than 28 days.

9 QUALITY CONTROL

9.1 The laboratory is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the continued analysis of laboratory instrument blanks and calibration standard material, analyzed as samples, as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data generated.

9.2 Initial Demonstration of Capability

9.2.1 The initial demonstration of capability (DOC) – is used to characterize instrument performance (MDLs) and laboratory performance (analysis of QC samples) prior to the analyses conducted by this procedure.

9.2.2 Quality Control Sample (QCS/SRM) – When using this procedure, a quality control sample is required to be analyzed at the beginning and end of the run, to verify data quality and acceptable instrument performance. If the determined concentrations are not within $\pm 10\%$ of the certified values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with analyses.

9.2.3 Method Detection Limits (MDLs) – MDLs should be established for DOC and DIC using a low level ambient water sample. To determine the MDL values, analyzed seven replicate aliquots of water. Perform all calculations defined in the procedure (Section 10) and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$\text{MDL} = S t_{(n-1, 1-\alpha=0.99)}$$

Where, $t_{(n-1, 1-\alpha=0.99)}$ = Student's *t* value for the 99% confidence level with n-1 degrees of freedom ($t = 3.14$ for 7 replicates)

n = number of replicates

S = Standard Deviation of the replicate analyses.

9.2.4 MDLs should be determined yearly.

9.3 Assessing Laboratory Performance

9.3.1 Laboratory Reagent Blank (LRB) – The laboratory must analyze at least one LRB with each batch of samples. The LRB consists of Nanopure water treated the same as the samples. LRB data are used to assess contamination from the laboratory environment.

9.3.2 Quality Control Sample (QCS)/ Standard Reference Material (SRM) – when using this procedure, a quality control sample is required to be analyzed at the beginning of the run and end of the run, to verify data quality and acceptable instrument performance. If the determined concentrations are not within $\pm 3\sigma$ of the certified values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with the analyses. The results of these samples shall be used to determine batch acceptance.

9.3.3 The QCS will be obtained from a source external to the laboratory and different from the source of calibration standards.

9.3.4 Control Charts – The SRM data is tracked.

9.3.5 Continuing Calibration Verification (CCV) – Following every 12-15 samples, one or two CCVs are analyzed to assess instrument performance. The CCVs are made from the same material as calibration standards (KHP), and are to be within $TV \pm 3\sigma$. Failure to meet the criteria constitutes correcting the problem and reanalyzing the samples. If not enough sample exists, the data must be qualified if reported.

9.4 Assessing Analyte Recovery

9.4.1 Matrix spikes are performed on a 20% QA/QC basis.

9.4.2 1.0 ml of the highest KHP standard in the curve is added to 10.0 ml of sample for a total volume of 11.0 ml.

9.4.3 1.0 ml standard $1.0/11.0 = 0.09$

9.4.4 $0.09 \times \text{STD conc.}$

9.4.5 10.0 ml sample $10.0/11.0 = 0.91$

9.4.6 $(\text{original sample conc.} \times 0.91) + (0.09 \times \text{std conc.}) =$
 $(\text{expected conc.}) \text{ mg/L}$

9.4.7 Percent Recovery for each spiked sample should fall within 80-120%. Where:

$$\%SR = \frac{\text{Spiked sample conc.} - \text{actual sample conc.}}{\text{Conc. of spike added}} \times 100$$

9.4.8 Relative Percent Difference (RPD) of duplicated samples should be less than 20%. Where:

$$RPD = \frac{\text{difference of duplicates}}{\text{Average of duplicates}} \times 100$$

Assess whether the analytical result for the CRM/QCS sample confirms the calibration when calculated as follows

$$\% \text{ Recovery} = \text{AMC/CRM} \times 100$$

Where:

AMC = Average measured concentration of the CRM sample

CRM = Certified value of the CRM

The analytical result must fall with the range of 80-120%

9.5 Data Assessment and Acceptance Criteria for Quality Control Measures

9.5.1 The Acceptance Criteria for DOC is 0.9990. If the r^2 is less than acceptable, all blanks and standards analyzed during the run may be averaged into the curve.

9.6 Corrective Actions for Out of Control Data

9.6.1 If the acceptance criteria are still not met, the samples are to be rerun.

10 CALIBRATION AND STANDARDIZATION

10.1 Calibration – Daily calibration must be performed before sample analysis may begin.

10.1.1 Type I water is used as the “zero point” in the calibration. The standards are calculated by the following equation:

$$\text{mg DOC/L} = (A_{\text{STD}}) / m$$

Where: A_{STD} = Area of the standard

m = slope of the regression line

10.1.2 DOC sample concentration is calculated using the following equation:

$$\text{mg DOC/L} = (A_s) / m$$

Where: A_s = area of the sample
 m = slope of the regression line

| QC Indicator | Acceptance/ Action Limits | Action | Frequency (Batch) |
|--|----------------------------------|--|---|
| Correlation Coefficient | ≥ 0.9990 | If < 0.9990 , evaluate data points of the calibration curve. If any data point is outside established limits, reject as outlier. | 1 per batch if acceptable. |
| Quality Control Sample (QCS)/ Certified Reference Material (CRM) | $\pm 20\%$ | If QCS value is outside $\pm 20\%$ of the target value reject the run, correct the problem and rerun samples. | Beginning of run following the ICV. |
| Initial Calibration Verification (ICV) | $\pm 20\%$ | Recalibrate if outside acceptance limits. | Beginning of run following standard curve. |
| Continuing Calibration Verification (CCV) | $\pm 20\%$ | If outside 20%, correct the problem. Rerun all samples following the last in-control CCV. | After every 10-12 samples and at end of batch. |
| Method Blank/Laboratory Reagent Blank (LRB) | \leq Method Quantitation Limit | If the LRB exceeds the quantitation limit, results are suspect. Rerun the LRB. If the concentration still exceeds the quantitation limit, reject or qualify the data, or raise the quantitation limit. | Following the ICV, after every 10-12 samples following the CCV and at the end of the run. |
| Method Quantitation Limit (MQL): The concentration of the lowest standard. | | When the value is outside the predetermined limit and the ICV is acceptable, reanalyze the sample. If the reanalysis is unacceptable, increase the concentration and reanalyze. If this higher concentration meets the acceptance criteria, raise the reporting limit for the batch. | Beginning of run following the LRB. |
| Laboratory Fortified Sample | $\pm 20\%$ | If the recovery of any analyte falls outside the designated | 1/20 |

| | | | |
|----------------------|-------|--|-----------------------------------|
| Matrix Spike | | acceptance limits and the QCS is in control, the recovery problem is judged matrix induced. Repeat the LFM and if the sample results are again outside the acceptable recovery range, the sample should be reported with a “matrix induced bias” qualifier. | |
| Laboratory Duplicate | ± 20% | If the RPD fails to meet the acceptance limits, the samples should be reanalyzed. If the RPD again fails to meet the acceptance limits, the sample must be reported with a qualifier identifying the sample analysis result as not having acceptable RPD for duplicate analysis. | 1/10 recommended 1/20 accepted |

11. References:

- 11.1 EPA Method 415.1. Determination of Total Organic Carbon in Water using Combustion or Oxidation.
- 11.2 Standard Methods for the Examination of Water and Wastewater. Approval date 2000. Method 5310B: High Temperature Combustion Method.
- 11.3 Sugimura, Y. and Y. Suzuki. 1988. A high temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample. Mar. Chem. 24:105-131.

Appendix I

PROCEDURE

Running the TOC-L

Make sure the 2nd stage of the regulator on the air tank (Air Gas Ultra Zero Grade Air, size A) is set at no higher than 30 psi. Replace the tank when the tank pressure falls below 500 psi.

To turn on instrument, push the on/off switch on right side of instrument to on, and then push button located on front of instrument. The front indicator light will turn to orange. The indicator light turns green when the instrument is up to temperature and all parameters are OK. The light will be blue while the instrument is running samples. If the indicator light is red, refer to the software and the manual to determine the problem. If necessary, call Shimadzu (1-800-477-1227) for tech support.

Open software by clicking on the TOC-L sample table icon. There is no password. Just hit enter when password screen appears.

Open a new sample table. Then hit CONNECT located in the tool bar. A sample table must be open to connect the instrument. The furnace automatically turns on.

At this time, refill the dilution, reagent blank, and rinse water bottles. The reagent blank water is in the 500 ml Teflon bottle beside the instrument. The rinse water bottle is located behind the autosampler. The dilution bottle is located on the left side of the instrument along with the 9 N H₂SO₄ bottle and the drain bottle. Check the volume of the 9 N H₂SO₄ bottle and the drain bottle. The liquid level of the drain bottle should be just below the arm. 250 mls of 9 N H₂SO₄ is plenty for several weeks of analysis.

Open the front door of the instrument and check the liquid level of the humidifier located on the right hand side. The level should be between the high and low marks. Add Type A water as needed by removing cap at top.

Check the level of liquid in the Type B Halogen Scrubber (the long tube next to the syringe which contains the rolled stainless mesh). Add 0.05 M HCl (40 ml dhoh + 1 ml 1N HCl) so that the level is an inch or so above the level of the mesh screen. There is a small drain line attached to the 8-port valve at port 6 which is frequently pulled out of the drain when removing the cap of the Type B Halogen Scrubber. When recapping the scrubber, ALWAYS check that the small tubing from port 6 on the 8 port valve is in the black capped drain port behind the scrubber.

These next three steps should be performed if the instrument has been sitting unused, or if several runs of high salt samples have been analyzed. An explanation of the Maintenance Menus can be found in the User's Manual, Chapter 7.6 p.302-308.

Before running blanks or beginning a sample run, from the program, select Instrument and Maintenance. Click on Residue Removal, then click start. Close when finished.

Next, under Instrument Maintenance, select Replace Flowline Content, and then click start. Close when finished.

Again, under Instrument Maintenance select Regeneration of TC Catalyst, and then click start. This takes several minutes. Close when finished.

Loading samples: Read Section in Full before proceeding.

The volume of the sample vial is 24 mls. The volume of the Teflon bottles is 30 mls, which means, in most cases, the analysis is volume limited. Fill the sample vial between half and $\frac{3}{4}$ full. The absolute minimum volume to use in the sample vial is 10 mls. Choose a sample with maximum volume in the Teflon bottle ahead of time to be the QA sample for duplicates or to make a spike. Cover each sample vial with a foil square and secure the foil with an open septum cap.

Standard Curve:

The reagent blank water is in the 500 ml Teflon bottle beside the instrument. This bottle is considered Position 0 on the sample wheel.

Load the other standards in the curve in the first several slots of the wheel.

QA/QC

Analyze a certified reference control sample (CRM) at least 3-4 times during the run. With each batch of control samples, a method is created in the control sample folder. To insert a control sample, highlight the line in the sample table. Click on INSERT on the tool bar, and then click on Control Sample. Once the folder is open, click on the appropriate file. The control CRM will be inserted in the highlighted line.

Analyze a blank, the lowest standard, and a CRM (or a mid-range standard) every 10-12 samples. The CRM's are frozen in 30-ml bottles. Use 2 bottles if analyzing more than 20 samples. Fill a 24 ml sample vial to the shoulder with CRM, cover with foil and cap. There is enough volume to sample the vial twice. When inserting the control sample in the sample table, assign the same vial position for each time. The autosampler is capable of returning to a particular vial site.

For the sample chosen to duplicate, fill the vial to the shoulder and cover. Indicate on the bench sheet at the appropriate location that the duplicate is to be inserted at that spot. If sample volume is not an issue, two sample vials can be used instead.

For the sample chosen to be spiked, withdraw 10.0 mls of sample using a volumetric pipet and add it to a sample vial. Then add 1.0 ml of the highest standard of the standard curve to the vial. Cover and cap, then gently shake to mix. Put the spiked sample in the proper location in the

sample wheel. With the leftover sample, pour into another sample vial as the original sample. There is usually not enough volume to sample rinse the vial used for the spike or original sample.

Alternate duplicates and spikes every 10-12 samples.

End the run with blanks and standards, with the last control sample inserted between the bracketing standards.

Sample Table:

To create a new calibration file, refer to the User's Manual, Chapter 4.1 pp. 89-93, and follow the Calibration Curve Wizard Setup. Several curve templates are set up and are overwritten with new curve data each time they are used.

Create a method by clicking on File/Open/Method and follow the Method Wizard Setup. Refer to the User's Manual Chapter 4.1 pp.94-96. A new method is created with each run.

Use drop down box to select type of analysis (i.e.: NPOC). Leave default Sample Name and Default Sample ID empty.

Enter desired Calculation Method (i.e.: linear regression). Do not check Zero Shift.

Check Multiple Injections. (This tells the instrument to pull enough sample volume to do several injections while sparging only once.)

Enter the file name, and then click Next. (Example: dnr st martins041213)

The calibration curve is chosen on the next screen. Click Next again. Confirm the injection parameters to match the calibration curve. Click Next again.

Use default settings on the next page, and None for Pharmaceutical water testing on the last page.

Click Finish. The method is complete.

Editing the Sample Table:

Highlight the first line of the sample table to insert information. From the toolbar at the top, click on Insert.

Insert 3-4 conditioning blanks by clicking on Multiple Samples. Follow the wizard prompts. The water for conditioning blanks is the same as the reagent water in position 0.

Highlight the next available line to insert the calibration curve. Click on Insert/calibration curve. Choose the proper calibration file.

Highlight the next available line to insert multiple samples. Follow the wizard prompts. Leave the Sample Name and Sample ID blank.

Once the sample table has been set up, enter the sample names and IDs.

It is easiest to insert Control samples after the sample names and IDs are in place. Highlight the line below where the control sample is to be inserted. Click on Insert and select Control Sample. Choose the proper file.

When all sample and control information is entered into the table, enter the vial position numbers. Click on the carousel icon (looks like a birthday cake) in the sample table toolbar. The vial positions correspond to the numbered positions on the bench sheet. Be sure replicate samples are numbered to match the original if sampling from the same vial. Click OK when finished.

Proof all entries and save the sample table. Click File/Save As to name the file.

Example: 2013_05_09_dnr st martins 042213

Highlight the first line of the sample table.

Click START. The Measurement Start Window is displayed. Click on the procedure to be performed when the analysis is complete. The instrument is kept running except over weekends. If no samples are to be run the next day, select Keep Running in case samples go off scale and need to be rerun. They can be inserted at the end of the sample table and run.

To open the Sample Window, click on the graph icon on the sample table to view peak information.

Accessing the data:

When the run has finished, click Save on the toolbar.

To save the file to another source (i.e. the P drive or separate flash drive), click File/Save As.

To export data, click File/Ascii Export. Save the file in each form, Normal and Detailed. The Normal file contains only concentration information. The Detailed file includes all injection data. The Ascii files can now be opened in Excel.

To print the calibration curve information, highlight the calibration curve line in the sample table. Select Print on the toolbar, and Highlighted.

SHIMADZU TOC-L DATA SHEET

CRUISE :

TODAY'S DATE:

ANALYST: NLK OTHER:

FILE NAME:

SPIKE CONC.: 10 mg/L...20 mg/L

INJECTION VOLUME: 50 uL

WORKING STDS MADE:

| VIAL# | SAMPLE ID | VIAL# | SAMPLE ID | VIAL# | SAMPLE ID |
|-------|-----------|-------|-----------|-------|-----------|
| 0 | DHOH | 31 | | 62 | |
| 1 | | 32 | | 63 | |
| 2 | | 33 | | 64 | |
| 3 | | 34 | | 65 | |
| 4 | | 35 | | 66 | |
| 5 | | 36 | | 67 | |
| 6 | | 37 | | 68 | |
| 7 | | 38 | | 69 | |
| 8 | | 39 | | 70 | |
| 9 | | 40 | | 71 | |
| 10 | | 41 | | 72 | |
| 11 | | 42 | | 73 | |
| 12 | | 43 | | 74 | |
| 13 | | 44 | | 75 | |
| 14 | | 45 | | 76 | |
| 15 | | 46 | | 77 | |
| 16 | | 47 | | 78 | |
| 17 | | 48 | | 79 | |
| 18 | | 49 | | 80 | |
| 19 | | 50 | | 81 | |
| 20 | | 51 | | 82 | |
| 21 | | 52 | | 83 | |
| 22 | | 53 | | 84 | |
| 23 | | 54 | | 85 | |
| 24 | | 55 | | 86 | |
| 25 | | 56 | | 87 | |
| 26 | | 57 | | 88 | |
| 27 | | 58 | | 89 | |
| 28 | | 59 | | 90 | |
| 29 | | 60 | | 91 | |
| 30 | | 61 | | 92 | |

