AMQAW DOC SOP DRAFT

Determination of Dissolved Organic Carbon (DOC), Non-Purgeable Organic Carbon (NPOC), and Total Organic Carbon (TOC) in Fresh/Estuarine/Coastal Waters using High Temperature Combustion with 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), and total organic carbon (TOC) using a non-dispersive infrared detector (NDIR). The method is used to analyze all ranges of salinity.

1.2 A Method Detection Limit (MDL) should be determined yearly using the Student's *t* value (99% confidence) times the standard deviation of a minimum of 7 replicates of a low concentration natural sample. Refer to the Student's *t* test table for the appropriate n-1 value.

1.3 This procedure should be used by analysts experienced in the theory and application of organic carbon analysis. Demonstration of capability should be documented after training with an experienced analyst, certified in the analysis using the organic carbon analyzer.

1.4 This method can be used for all programs that require analysis of dissolved and total organic carbon. This procedure is applicable for carbon analysis ranging from 0.5 mg/L and higher.

1.5 The method utilized is based on EPA method 415.1 and SM 5310 B, 20th Edition.

2. SUMMARY

2.1 This method uses high temperature combustion to analyze aqueous samples for Total Carbon (TC) and non-purge-able organic carbon (NPOC).

2.2 NPOC samples are treated with hydrochloric acid 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. High temperature combustion (680EC) on a catalyst bed breaks down all carbon compounds into carbon dioxide (CO_2). The CO_2 is carried by ultra pure air to a non-dispersive infrared detector (NDIR) where CO_2 is detected.

3. INTERFERENCES

3.1 Carbonates and bicarbonates will interfere with the determination of organic carbon by increasing the concentration of CO_2 detected. These are

removed by lowering the pH of the sample to less than 2, then sparging with an ultra high purity carbon dioxide-free gas for a predetermined time.

4. SAFETY

4.1 Safety precautions must be taken when handling reagents, samples and equipment in the laboratory. Protective clothing including lab coats, safety glasses or goggles 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 and call out for assistance. If solutions come in contact with skin, wash thoroughly with soap and water.

4.2 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.

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

4.4 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.

5. EQUIPMENT AND SUPPLIES

5.1 A Total Organic Carbon Analyzer capable of maintaining a combustion temperature of 680° C and analyzing for organic and inorganic carbon.
5.2 An Auto Sampler is recommended.
5.3 Data Station with instrument software.
5.4 Freezer, capable of maintaining -20 ± 5° C.
5.5 Lab ware – All reusable lab ware (glass, Teflon, plastic, etc) should be sufficiently clean for the task objectives. A laboratory's glassware cleaning method will be considered sufficient if all quality control samples are within the expected ranges.

6. REAGENTS AND STANDARDS

6.1 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.
6.2 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.
6.3 Potassium Hydrogen Phthalate (KHP) C_6H_4 (COOK) (COOH) – primary standard for organic carbon.
6.4 Sodium Hydrogen Carbonate ($NaHCO_3$) and Sodium Carbonate (Na_2CO_3) – primary standard for inorganic carbon. This standard is also used to check the sparging efficiency for NPOC samples.

6.5 Hydrochloric Acid, 2 N –
Hydrochloric acid (HCl), concentrated, 166 ml
Deionized water, q.s. 1000 ml

In a 1000 ml volumetric flask, add 166 ml of concentrated hydrochloric acid to ~600 ml of deionized water. Dilute to 1000 ml with deionized water.

6.6 Organic Carbon Stock Standard: Potassium Hydrogen Phthalate (KHP) Standard, 1000 mg/l

Potassium hydrogen phthalate ($HOCOC_6H_4COOK$), Dried at 45 C	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.

6.7 Inorganic Carbon Stock Standard: Sodium Hydrogen Carbonate/ Sodium Carbonate ($NaHCO_3/Na_2CO_3$) Standard, 1000 mg/l

Sodium Hydrogen Carbonate ($NaHCO_3$)	1.75 g
Sodium Carbonate, Anhydrous (Na_2CO_3)	2.205 g
Deionized H_2O	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.

6.8 Blanks – ASTM D1193 Type I water is used for the Laboratory Reagent Blank.

6.9 Quality Control Sample (QCS) or Certified Reference Material (CRM)– For this procedure, the QCS/CRM can be any certified dissolved sample obtained from an external source. If a certified sample is not available, then use an appropriate source of organic carbon.

7 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Water collected for DOC should be filtered through a Whatman GF/F glass fiber filter (nominal pore size 0.7 μm), or equivalent.

7.2 Water collected for DOC may be frozen at -20° C, or acidified 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.

7.3 Frozen DOC samples should be analyzed within 28 days, though it has been shown that frozen QCS samples up to a year old still fall well within the control limits.

7.4 Acidified DOC samples may be frozen, as above, or refrigerated at 4° C for no longer than 28 days.

7.5 DOC samples which have not been acidified and are stored at 4° C should be analyzed within 48 hours.

8 QUALITY CONTROL

8.1 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.

8.2 Initial Demonstration of Capability

8.2.1 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.

8.2.2 Quality Control Sample (QCS/CRM) – 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 established acceptance criteria, the results are unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with analyses.

8.2.3 Method Detection Limits (MDLs) – MDLs should be established for DOC using a low level ambient water sample. To determine the MDL values, a minimum of seven replicate aliquots of water are to be analyzed. Perform all calculations defined in the procedure and report the concentration values in the appropriate units.

8.2.4 Calculate the MDL as follows:

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

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.

8.2.5 MDLs should be determined yearly.

8.3 Assessing Laboratory Performance

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

8.3.2 Quality Control Sample (QCS)/ Certified Reference Material (CRM) – see section 8.2.2.

8.3.3 For this procedure, the QCS/CRM can be any certified dissolved sample obtained from an external source. If a certified sample is not available, then use an appropriate source of organic carbon

8.3.4 Control Charts – The QCS data is tracked via control charts to determine evolving trends.

8.3.5 Continuing Calibration Verification (CCV) – Following every 10-12 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 established acceptance criteria. 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.

8.4 Assessing Analyte Recovery

8.4.1 Matrix spikes and Laboratory duplicates should performed on a minimum 20% QA/QC basis.

8.4.2 Percent recovery for each spiked sample should fall within 80-120%. Where:

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

8.4.3 Percent relative difference (RPD) of duplicated samples should be <20%. Where:

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

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

% Recovery = AMC/CRM x 100%

Where,

AMC = Average measured concentration of the CRM sample

CRM = Certified value of the CRM sample

The analytical result must fall within the range of 90-110%.

8.5 Data Assessment and Acceptance Criteria for Quality Control Measures

8.5.1 The Acceptance Criteria for DOC is 0.9990.

8.5.2 If the r^2 is between 0.9980 – 0.9989, troubleshooting is required before accepting the run.

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

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)	**± 10%**	**If QCS value is outside ± 10% of the target value reject the run, correct the problem and rerun samples.**	**Beginning of run following the ICV.**
Initial Calibration Verification (ICV)	**± 10%**	**Recalibrate if outside acceptance limits.**	**Beginning of run following standard curve.**
Continuing Calibration Verification (CCV)	**± 10%**	**If outside 10%, 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)	**≤ 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		**When the value is outside the predetermined limit and the ICV is acceptable, reanalyze the sample. If the reanalysis is unacceptable, increase the**	**Beginning of run following the LRB.**

concentration of the lowest standard.		**concentration and reanalyze. If this higher concentration meets the acceptance criteria, raise the reporting limit for the batch.**	
Laboratory Fortified Sample Matrix Spike	**± 20%**	**If the recovery of any analyte falls outside the designated 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.**	**At a minimum, alternate every 10-12 samples with Laboratory Duplicates**
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.**	**At a minimum, alternate every 10-12 samples with Laboratory Duplicates.**

9.0 References:

9.1 EPA Method 415.1. Determination of Total Organic Carbon in Water using Combustion or Oxidation.

9.2 Standard Methods for the Examination of Water and Wastewater. 20th Ed. 1998. Method 5310B: High Temperature Combustion Method.

9.3 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.

9.4 Virginia DCLS SOP Technical Procedure 2532, Organic Carbon, Total, and Dissolved, Nonpurgeable, in Drinking, Ground, Surface, and Saline Waters, Domestic and Industrial Wastes by High Temperature Oxidation and NDIR Detection. Revision #6, 10/12/11.

9.5 Old Dominion University, Water Quality Laboratory SOP for Dissolved Organic Carbon in Water and Seawater Using Combustive-Non Dispersive Gas Analysis. Revision #3, 8/31/2009.

9.6 Maryland DHMH Division of Environmental Chemistry SOP for the Determination of Total Organic Carbon (Standard Method 5310B),SOP#IAL-SOP-SM 5310B/R1.0-11, 8/18/11.

9.7 UMCES Chesapeake Biological Laboratory, Nutrient Analytical Services SOP Determination of Dissolved Organic Carbon (NPOC), Total Organic Carbon, and Dissolved Inorganic Carbon in waters of Fresh/Estuarine/Coastal Waters using High Temperature Combustion and Infrared Detection. Revision #2, 5/18/11.

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