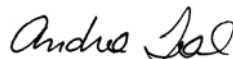



**CARBON CONTENT IN WATER:
Total Carbon (TC), Total Organic Carbon (TOC), and Total Inorganic
Carbon (TIC)**

(Methods: EPA 9060, EPA 9060A, SM5310B, & EPA 415.1)

Approvals (Signature/Date):

 November 12, 2009
Andrea Teal Date
Quality Assurance Manager

 November 12, 2009
Benjamin Gulizia Date
Laboratory Director/Lead Technical Director

 December 3, 2009
Ernest Walton Date
EH&S Coordinator / Technical Manager

 November 25, 2009
Carol Webb Date
Department Manager

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1.0 **Scope and Application**

This SOP gives the procedures for the determination of total carbon (TC), total inorganic carbon (TIC), and total organic carbon (TOC) in water samples by combustion.

Total carbon is comprised of total organic carbon and total inorganic carbon.

- If TOC is requested, the sample is acidified upon collection and analyzed.
- If TC is requested, an unacidified sample is collected and analyzed.
- If TIC is requested, the sample is collected and analyzed twice (once for the acidified portion and once for the unacidified portion) and the TOC result is subtracted from the TC result to obtain TIC.

Note: The determination of TOC involves purging the sample which eliminates any volatile organic compounds (VOCs) from the sample matrix. For this reason, the TOC reported is actually the non-purgeable TOC. The determination of TC or TIC involves analyzing the sample without purging the VOCs from the sample matrix.

This procedure can also be used for the determination of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and dissolved carbon (DC) by performing a filtration on the sample prior to acidification and analysis.

The reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 **Summary of Method**

Total organic carbon (TOC) is measured by purging an acid-preserved sample to eliminate the inorganic carbon present in the sample. The acid converts any carbonates present in the sample to CO₂, which is then purged out of the sample. The sample is then combusted at 680°C. The carbon is converted to carbon dioxide and is measured by an infrared (IR) detector.

Total carbon is performed in the same manner as TOC using unpreserved vials and eliminating the purging step. TIC is determined using a calculation by subtracting the TOC result from the TC result.

Dissolved organic carbon (DOC) is performed by filtering an aliquot of unpreserved sample with a 0.45um filter and preserving the filtrate to a pH of <2 with 50% HCl. The filtered sample is analyzed using the same procedures and equipment as the TOC analysis.

The following equation shows the relationship between the various forms of carbon that can be measured with this procedure:

$$TC = TOC + TIC$$

Where:

TC = total carbon

TOC = total organic carbon

TIC = total inorganic carbon

- 2.3 This SOP is based on the following methods: EPA Method 415.1, Standard Methods 5310B, EPA Method 9060, and EPA Method 9060A.

3.0 **Definitions**

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 **Interferences**

4.1 **Procedural Interferences**

- 4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.
- 4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.
- 4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.
- 4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 **Matrix Interferences**

- 4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences.
- 4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.
- 4.2.3 Sample particulates that are larger than the syringe will not be included in the carbon determination. This condition may cause low results if the particulates contain

measurable levels of carbon. The analyst must be cognizant of samples that may clog the sample syringe, and initiate an NCM, as applicable, to address this situation.

- 4.2.4 Liquid samples containing oil or that are oily in nature will deactivate the catalyst which may require regeneration or replacement prior to running other samples.
- 4.2.5 It is very important that the inorganic carbon be removed from the sample prior to the direct determination of the TOC (non-purgeable TOC). Failure to remove the inorganic component of the sample may result in artificially high TOC results.

5.0 **Safety**

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 **Specific Safety Concerns or Requirements**

- 5.1.1 The furnace on the carbon analyzer must be cooled to room temperature before maintenance is performed. The temperature of the analyzer furnace can reach 680°C. The analyst must be careful to avoid touching these very hot surfaces.
- 5.1.2 Care must be taken when handling hydrochloric acid (HCl) and solutions of hydrochloric acid. The 2N HCl must be handled with caution.

Hydrochloric acid is extremely hazardous as an oxidizer, a corrosive, a poison, and is reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage. The acid should be added slowly to minimize potentially violent reactions that will splatter acid.

- 5.1.3 The carrier gas MUST remain on while the instrument is in operation. The analyst must ensure that there is sufficient carrier gas available in the tank to complete the run. Failure to have carrier gas running through the instrument while the combustion furnace is at the operating temperature may result in melting of the combustion tubes.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the “MSDS Online” button on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit ¹	Signs and Symptoms of Exposure
Hydrochloric Acid	Corrosive Poison	5ppm - Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
¹ Exposure limit refers to the OSHA regulatory exposure limit.			
Note – Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Shimadzu TOC-VCPN Carbon Analyzer

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

Disposable Transfer Pipettes – various sizes

Filters – 0.45um, disposable

Syringes – 10mL, disposable

Autosampler vials – 25mL

pH paper – provides a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step. pH paper should be checked upon receipt, as follows, to make sure that it is functioning properly.

- Examine the pH paper. If the paper is discolored or looks worn, it may be defective.
- Place a piece of pH paper on a watch glass or other suitable surface and add a few drops of a certified buffer solution onto the paper.
- Compare the color of the pH paper to the reference colors. If the colors match, the paper can be used. If not, acquire new paper.

Detergent – Liquinox, used for washing non-disposable labware.

Ultra pure compressed air, regulator, and appropriate fittings – The compressed air must contain less than 1ppm of carbon dioxide. This gas is used as the carrier and sparge gas for the analysis of aqueous samples.

Stir plate

Stir bars – Teflon

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The sample collection containers supplied by the laboratory are purchased with Certificate of Analysis attesting to purity. The routine bottle kits supplied are as follows:

Analyte	Bottle Type	Preservative	Other Equipment
TOC	125mL amber glass	2mL 50% HCl	None
TC	40mL VOA	None	None
TIC	125mL amber glass	2mL 50% HCl	None
	40mL VOA	None	None
DOC	125mL amber glass	2mL 50% HCl	10mL syringe 0.45um filter
DC	40mL VOA	None	10mL syringe 0.45um filter
DIC	125mL amber glass	2mL 50% HCl	10mL syringe 0.45um filter
	40mL VOA	None	10mL syringe 0.45um filter

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard must not exceed the expiration date of the standard that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Traceability*.

Hydrochloric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Laboratory Reagent Water – ASTM Type II.

7.2.2 Hydrochloric acid (HCl) – concentrated, reagent grade or better. Store in original container at room temperature.

Storage: reagent cabinet

Expiration: manufacturer's expiration date or 2 years from the date opened, whichever is sooner

7.2.3 Hydrochloric acid solution (50% HCl) – Add approximately 400mL of laboratory reagent water to a 2-L beaker. Place the beaker on a magnetic stir plate located under a hood. Add a Teflon stir bar to the laboratory reagent water and turn the stir plate on. Slowly add 500mL of concentrated HCl to the beaker in small aliquots. After the entire 500mL of HCl has been added, continue mixing and allow the solution to cool. After the solution has cooled, transfer to a 1-L volumetric flask and dilute to volume with laboratory reagent water. This solution must be stored in a glass container at room temperature. **Caution: Hydrochloric acid is extremely toxic, has a suffocating odor, and can cause severe chemical burns.**

Storage: Acid storage cabinet, away from incompatibles

Expiration: 2 years from the date prepared or the expiration date of the parent reagent, whichever is sooner

7.2.4 2N HCl Solution – Slowly add 42mL of concentrated HCl to approximately 150mL of laboratory reagent water contained in a 250-mL volumetric flask. Dilute to volume with laboratory reagent water. Transfer the reagent to a glass container. This reagent must be prepared under a hood. This solution must be stored in a glass container at room temperature. **Caution: Hydrochloric acid is extremely toxic, has a suffocating odor, and can cause severe chemical burns.**

Storage: reagent cabinet

Expiration: 2 years from the date prepared or the expiration date of the parent reagent, whichever is sooner

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Traceability*. Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

- 7.3.1 Potassium hydrogen phthalate (KHP) solution – 5,000mg/L, purchased from Aqua Solutions. Store in the original container.
Storage: Refrigerated at 4°C
Expiration: manufacturer's expiration date or 2 years from the date opened, whichever is sooner

7.3.2 Calibration Standards

Prepare the calibration standards according to the recipe in the following table. Smaller volumes and different concentrations may be prepared if approved by the department manager.

Calibration Standard Level	5,000mg C/L Stock Standard Volume (mL)	Final Volume (mL)	Calibration Standard Concentration (mg/L)
1	100	1000	500
2	40	1000	200
3	20	1000	100
4	10	1000	50
5	2.0	1000	10
6	1.0	1000	5.0
7	0.20	1000	1.0
8	0.0	1000	0.0

Adjust the pH of each standard to less than 2 with 50% HCl. Transfer the calibration standards to amber storage bottles.

Storage: Refrigerated at 4°C

Expiration: 3 months from the date prepared or the expiration date of the parent reagent, whichever is sooner

7.3.3 Initial Calibration Verification (ICV)

Potassium hydrogen phthalate (KHP) – reagent grade, purchased from Fisher Scientific. Note: The ICV standard must be purchased from a source independent of that used to prepare the calibration standards. Store in original container at room temperature.

Storage: Desiccator

Expiration: manufacturer's expiration date or 5 years from the date opened, whichever is sooner

This material must be lightly crushed, to break up lumps, and dried at 120°C prior to preparation of the stock standard.

Potassium acid phthalate (KHP) ICV Stock Standard – Transfer 0.85g of the second source KHP to a 1-L volumetric and dissolve in a small amount of laboratory reagent water. Dilute to volume with laboratory reagent water. The stock standard has a concentration of 400mg C/L. Transfer the stock standard to an amber storage bottle.
Storage: Refrigerated at 4°C

Expiration: 3 months from the date prepared or the expiration date of the parent reagent, whichever is sooner

- 7.3.4 Laboratory Control Sample (LCS) Solution (20mg/L) – Place approximately 400mL of laboratory reagent water in a 500-mL volumetric flask. Add 2.0mL of the 5,000mg/L Potassium hydrogen phthalate (KHP) solution. Dilute to 500mL with laboratory reagent water. Adjust the pH to less than 2 with 50% HCl. Transfer the stock standard to an amber storage bottle.

Storage: Refrigerated at 4°C

Expiration: 3 months from the date prepared or the expiration date of the parent reagent, whichever is sooner

- 7.3.5 Matrix Spike (MS) Spiking Solution (1000mg/L) – Place approximately 50mL of laboratory reagent water in a 100-mL volumetric flask. Add 20mL of the 5,000mg/L Potassium hydrogen phthalate (KHP) solution. Dilute to 100mL with laboratory reagent water. Adjust the pH to less than 2 with 50% HCl. Transfer the stock standard to an amber storage bottle.

Storage: Refrigerated at 4°C

Expiration: 3 months from the date prepared or the expiration date of the parent reagent, whichever is sooner

- 7.3.6 Sodium Carbonate (NaCO_3) – reagent grade. Store in original container at room temperature.

Storage: reagent cabinet

Expiration: manufacturer's expiration date or 5 years from the date opened, whichever is sooner

- 7.3.7 Sodium Bicarbonate (NaHCO_3) – reagent grade. Store in original container at room temperature.

Storage: reagent cabinet

Expiration: manufacturer's expiration date or 5 years from the date opened, whichever is sooner

- 7.3.8 Carbonate/Bicarbonate TIC Check Solution – Place approximately 800mL of laboratory reagent water in a 1-L volumetric flask. Add 1.38g NaHCO_3 and 1.77g NaCO_3 and mix until all solid is dissolved into solution. Dilute to 1L with laboratory reagent water and adjust the pH to <2 with 50% HCl. Transfer to an amber glass container and store at room temperature.

Storage: reagent cabinet

Expiration: 2 years from the date prepared or the expiration date of the parent reagent, whichever is sooner

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

All aqueous samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of analysis. Samples must be analyzed within 28 days of collection.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives. NCMs must be initiated for samples for TC and/or TIC analysis that are received containing headspace.

8.1.1 TOC

Aqueous samples for TOC are routinely collected in 125mL amber glass containers containing 2.0mL of 50% hydrochloric acid preservative is added to the container. This preservative should be sufficient to achieve a sample pH of <2.

8.1.2 TC

Aqueous samples for TC are routinely collected in 40mL VOA vials with no preservative. The 40mL VOA must be filled with no headspace to minimize the loss of the volatile organic components.

Note: a 125mL amber glass container may also be used, provided the sample is collected with no headspace.

8.1.3 TIC

Aqueous samples for TIC require 2 sets of bottles to be supplied:

- 1 set as outlined above for TOC
- 1 set as outlined above for TC

8.1.4 DOC

Aqueous samples for DOC should be filtered in the field, within 2 hours of collection, using a 0.45um filter. The filtrate should be collected in a 125mL container containing hydrochloric acid preservative sufficient to achieve a sample pH of <2.

Note: Samples for DOC may be collected in unpreserved containers, filtered in the lab upon receipt, and then preserved with HCl; however, this is not recommended as the 2-hour holding time will not be met. An NCM must be initiated for samples collected and preserved in this manner.

8.1.5 DC

Aqueous samples for DC should be filtered in the field, within 2 hours of collection, using a 0.45um filter. The filtrate should be collected in a 40mL VOA vial with no preservative. The 40mL VOA must be filled with no headspace to minimize the loss of the volatile organic components.

Note: a 125mL amber glass container may also be used, provided the sample is collected

with no headspace.

8.1.6 DIC

Aqueous samples for DIC require 2 sets of bottles to be supplied:

- 1 set as outlined above for DOC
- 1 set as outlined above for DC

8.1.7 Preservation Checks

8.1.7.1 pH Verification

For each preserved sample,

- Place a piece of pH paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the pH paper.
- If the pH is greater than 2, initiate a Nonconformance Memo. Adjust the sample pH to <2 using 50% HCl.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the pH paper into the sample container. The pH paper dye may bleed into the sample and affect sample results.

9.0 **Quality Control**

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 4 provide requirements for evaluating QC data.

9.1 **Batch QC**

An analytical batch consists of up to 20 environment samples and the associated quality control items. The minimum QC items required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD) or sample duplicate (SD).

If there is insufficient sample to perform the MS or sample duplicate, an NCM must be initiated and the LCS must be prepared in duplicate (i.e., LCSD must be performed).

Batch QC must meet the criteria given in Attachment 4 of this SOP.

9.2 **Instrument QC**

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve contains 3 ranges. Each range consists of a minimum of 4 standards.

The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

The initial calibration standard concentrations currently in use in the laboratory are as follows:

Range	Calibration Level	Calibration Standard Level	Concentration (mg/L)
1	1	8	0
1	2	7	1.0
1	3	6	5.0
1	4	5	10
2	5	7	1.0
2	6	5	10
2	7	4	50
2	8	3	100
3	9	7	1.0
3	10	3	100
3	11	2	200
3	12	1	500

Refer to Section 7.3.2 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-041.

The purge is turned off to analyze the initial calibration. Each initial calibration standard is analyzed by the instrument up to 5 times. The instrument chooses the best 3 of the 5 analyses and averages this result to determine the response for the associated concentration.

9.2.1.1 ICAL Criteria

The correlation coefficient (r) of the regression curve must be greater than 0.995 for the initial calibration curve to be acceptable.

Note: The calibration must be performed quarterly (i.e., once every 3 months) at a minimum.

9.2.2 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified after the initial calibration is established, prior to any sample analyses, in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The initial calibration verification standard concentration currently in use in the laboratory is 400mg/L. Refer to Section 7.3.3 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

The ICV must be within +/-10% of the true value to be acceptable.

9.2.3 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed immediately following the initial calibration. Continuing calibration blanks are analyzed at the beginning and end of each batch.

Initial and continuing calibration blanks must be $<1/2RL$ to be acceptable.

9.2.4 Continuing Calibration Verification

The initial calibration curve must be verified every 10 analyses with a mid-level standard.

The CCV must be within +/-10% of the true value to be acceptable.

The continuing calibration verification standard concentrations currently in use in the laboratory are equivalent to the 5.0, 50, and 200mg/L levels of the ICAL. Refer to Section 7.3.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

9.2.5 Carbonate/Bicarbonate TIC Check Solution

This solution is analyzed once daily as a check of the efficiency of the acidification and sparging to remove inorganic carbon from samples being analyzed for TOC.

Transfer an aliquot of the Carbonate/Bicarbonate TIC Solution to a labeled autosampler vial.

Adjust the pH of the solution to <2 with 50% HCl and analyze.

Evaluate the result. If the TIC Check standard is less than the RL, continue with the sequence. If not, check the pH of the standard to make sure that it is less than 2.0, remake the standard, and reanalyze the standard. If the result is still greater than 2.0, contact the supervisor immediately. The instrument may need to be serviced.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 4. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Remove the samples from the refrigerator and allow them to come to room temperature.

10.2 QC Sample Preparation

Prepare the method blank by adding 25mL of laboratory reagent water that has been adjusted to a pH of <2 with 50% HCl to an autosampler vial.

Prepare the LCS by adding 25mL of LCS solution to an autosampler vial.

Prepare the MS by adding 0.50mL of the 1000mg/L Matrix Spike Spiking Solution to 25mL of sample.

Prepare a sample duplicate.

10.3 Analysis

10.3.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 2 of this SOP.

Turn the Shimadzu TOC-VCPN on and set the following parameters:

Analyzer Furnace: 680°C

Carrier Gas: 150mL/min (ultrapure compressed air)

Purge Gas: 50mL/min (ultrapure compressed air)

Minimum Number of Replicates: 3

Maximum Number of Replicates: 5

Allow the instrument to equilibrate and the furnace to reach the set point before processing samples.

10.3.2 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.1. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.2, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.4.

10.3.3 Sample Analysis

The sample must be analyzed using the same volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be

analyzed after suspected high concentration samples to allow the detector response to stabilize.

Each sample must be analyzed in quadruplicate for EPA 9060 and EPA 9060A, and in triplicate for SM5310B and EPA 415.1. If a sample contains a concentration of TOC greater than the linear range of the calibration curve on range 3, the sample must be diluted and re-analyzed. The average of the quadruplicate analyses results is reported as the final result in LIMS.

Note: The laboratory purges the acidified sample during analysis to remove the inorganic and purgeable organic carbon from the sample matrix; therefore, the non-purgeable TOC (nTOC) or non-purgeable DOC (nDOC) concentration is determined.

In order to determine the total carbon (TC) or dissolved carbon (DC) concentration an aliquot of the un-preserved sample is analyzed without purging the inorganic and purgeable organic carbon from the sample.

10.3.4 Example Analytical Sequence

An example analytical sequence is listed below.

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source: 400mg/L
ICB	Used as method blank
Bicarbonate/Carbonate TIC Check Standard	
LCS	
Samples	Up to 10 sample analyses, including MS/MSD
CCV	5mg/L
CCB	
Samples & Batch QC Items	Up to 10 analyses, including MS/MSD
CCV	50mg/L
CCB	
Samples & Batch QC Items	Up to 10 sample analyses, including MS/MSD
CCV	200mg/L
CCB	

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and*

Review.

11.1.1 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.2 Chemical Relationships

When available, the following chemical relationships must be evaluated for each sample. If these relationships are not met the Department Manager must be contacted immediately.

- Total Results \geq Dissolved results
- COD \geq TOC
- TC \geq TOC + TIC

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The following equations show the relationship between the various forms of carbon that can be measured with this procedure:

$$TC = TOC + TIC$$

Where:

TC = total carbon

TOC = total organic carbon

TIC = total inorganic carbon

$$DC = DOC + DIC$$

Where:

DC = dissolved carbon

DOC = dissolved organic carbon

DIC = dissolved inorganic carbon

11.2.3 The calculation to determine final concentration is given as follows:

$$C(\text{mg} / \text{L}) = C_{\text{curve}} \otimes DF$$

Where:

C_{curve} = concentration of TOC from curve

DF = dilution factor

12.0 **Method Performance**

12.1 **Method Detection Limit Study (MDL)**

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and annually thereafter, and verified annually in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

Note: MDLs are determined for TOC and TC, only. These TOC and TC MDLs are used to satisfy the DOC and DC MDLs, respectively. TIC and DIC are obtained using a calculation; therefore, these MDL values are defined as the higher of the values between TOC and TC (or DOC and DC).

12.2 **Demonstrations of Capability**

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures*.

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), or via acceptable results on a PT study. The CDOC must be documented and routed to the QA Department for filing.

12.3 **Training Requirements**

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the TestAmerica Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess samples, reagents, and standards must be disposed in accordance with the TestAmerica Savannah addendum to the Environmental Health and Safety Manual.
- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

15.0 References / Cross-References

- SOP SA-AN-041: *Reagent and Standard Materials Traceability*
- SOP SA-AN-100: *Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Method for Chemical Analysis of Water and Wastes*; U.S. EPA Office of Research and Development: Cincinnati, Ohio, March, 1983

- *Test Methods for the Evaluating Solids Wastes, Third Edition, SW-846*; US EPA Office of Solid Waste and Emergency Response: Washington, DC. (including Updates III and IV)
- *Standard Methods for the Examination of Water and Wastewater*, Online Edition; 2000. APHA, AWWA, WEF.

16.0 Method Modifications and/or Clarifications

- 16.1 Standard Methods 5310B recommends using phosphoric acid to preserve samples and standards. The preservation technique performed by the laboratory has been adopted from EPA Methods 415.1, 9060, and 9060A. These methods use hydrochloric acid to preserve the samples.
- 16.2 The reference methods do not specify a holding time to be used for TC and TIC. The laboratory defaults to 28 days for these analytes (and DC and DIC).
- 16.3 The laboratory allows for lab filtration of DOC samples; however, an NCM must be utilized to indicate the 2-hour holding time was not met.
- 16.4 MDLs are determined for TOC and TC, only. These TOC and TC MDLs are used to satisfy the DOC and DC MDLs, respectively. TIC and DIC are obtained using a calculation; therefore, these MDL values are defined as the higher of the values between TOC and TC (or DOC and DC).
- 16.5 Standard method 5310B specifies that a blank, and an LCS or MS must be performed per 10 analyses with a 2nd source standard. The laboratory uses a same source standard for the LCS and MS; however, a second source ICV is analyzed after each ICAL as a check on the primary source.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

- Attachment 1: Sample Collection, Preservation, and Holding Time Table
Attachment 2: Preventative Maintenance and Troubleshooting
Attachment 3: SOP Summary
Attachment 4: QC Summary

Attachment 1: SOP Summary

Sample Preparation and Analysis Summary

Total organic carbon (TOC) is measured by purging the acid-preserved sample to eliminate the inorganic carbon present in the sample. The acid converts any carbonates present in the sample to CO₂, which is then purged out of the sample. Purging the sample also eliminates any volatile organic compounds (VOC) from the sample matrix; therefore, any direct measurement of TOC is actually non-purgeable TOC. The sample is then combusted at 680°C. The carbon is converted to carbon dioxide and is measured by an infrared (IR) detector. Standards are analyzed under the same instrument conditions as the samples.

Total carbon and total inorganic carbon are performed in the same manner as TOC using unpreserved vials and eliminating the purging step.

Dissolved organic carbon (DOC) is prepared either in the field or immediately upon receipt in the laboratory by filtering an aliquot of unpreserved sample with a 0.45um filter and preserving the filtrate to a pH of <2 with 50% HCl. The dissolved organic carbon is analyzed using the same procedures and equipment as the TOC analysis. The QC samples required for DOC are a filtered method blank and matrix spikes on a filtered sample.

Analytical Sequence

An example analytical sequence is listed below.

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source: 400mg/L
ICB	Used as method blank
Bicarbonate/Carbonate TIC Check Standard	
LCS	
Samples	Up to 10 sample analyses, including MS/MSD
CCV	5mg/L
CCB	
Samples & Batch QC Items	Up to 10 analyses, including MS/MSD
CCV	50mg/L
CCB	
Samples & Batch QC Items	Up to 10 sample analyses, including MS/MSD
CCV	200mg/L
CCB	

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Listed below are the holding times and preservation requirements:

Analyte	Bottle Type	Preservative	Other Equipment	Holding Time
TOC	125mL amber glass	2mL 50% HCl	None	28 Days from Collection
TC	40mL VOA	None	None	28 Days from Collection
TIC	125mL amber glass	2mL 50% HCl	None	28 Days from Collection
	40mL VOA	None	None	28 Days from Collection
DOC	125mL amber glass	2mL 50% HCl	10mL syringe 0.45um filter	Filter: 2 Hours from Collection Analysis: 28 Days from Collection
DC	40mL VOA	None	10mL syringe 0.45um filter	Filter: 2 Hours from Collection Analysis: 28 Days from Collection
DIC	125mL amber glass	2mL 50% HCl	10mL syringe 0.45um filter	Filter: 2 Hours from Collection Analysis: 28 Days from Collection
	40mL VOA	None	10mL syringe 0.45um filter	Filter: 2 Hours from Collection Analysis: 28 Days from Collection

**Attachment 4:
QC Summary**

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration (ICAL) - Minimum of 4 points (with 3 curves)	Upon instrument set-up, and after unsuccessful CCV - Quarterly, at a minimum	$r^2 > 0.995$	Re-calibrate
Second Source Initial Calibration Verification (ICV)	After each ICAL	Within $\pm 10\%$ of the true value	Re-calibrate
Continuing Calibration Verification (CCV)	At the beginning and end of the analysis, and every 10 samples	Within $\pm 10\%$ of the true value	Refer to SOP SA-QA-16
Initial and Continuing Calibration Blank (ICB & CCB)	After ICV and every CCV	$< 1/2RL$	Terminate the analysis; correct the problem; and reanalyze the previous 10 samples
Batch Definition	Analyzed together w/in 24-hr timeframe; not to exceed 10 field samples	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	$< 1/2RL$	Refer to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	Within MLG Limits	Refer to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per extraction batch, when insufficient sample is provided for MS/MSD/SD	Within MLG Limits	Refer to SOP SA-QA-17
Matrix Spike (MS)	One per extraction batch	Within MLG Limits	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per extraction batch	Within MLG Limits	Refer to SOP SA-QA-17

QC Item	Frequency	Criteria	Corrective Action
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Method Detection Limit Study (MDL)	Upon method/instrument set-up, per analyte/method/matrix combination, and then annually thereafter (Includes MDLV)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4: Preventative Maintenance and Troubleshooting

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning.

An extensive spare parts inventory is maintained for routine repairs, consisting of combustion tubes, halogen scrubber, sample needles, o-rings, and platinum catalyst., and other common instrumentation components. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

Preventive Maintenance

Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
Equipment / Item	Service Interval							Service
	D	W	M	Q	SA	A	AN	
Combustion tube							X	Replace as needed
Carrier gas pressure gauge	X							Check daily and replace gas as necessary
Humidifier water level	X							Check daily and refill as necessary

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually;
AN = as needed

Desiccator Maintenance

Upright Desiccators with Doors

The following checks must be performed daily:

- Desiccant is active
- Hygrometer is in the low humidity zone
- Door is making an air tight seal

The desiccator door must remain closed and seated whenever possible.

When the desiccant turns from blue to light purple, discard desiccant, in accordance with the TestAmerica Savannah Addendum to the EHSM, and refill pan with fresh desiccant.

Contingency Plan

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Maintenance Log

A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Instrument Labeling

Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

18.0 **Revision History**

Summary of Changes from Previous Revision:

- Updated to new TestAmerica SOP template. Significant formatting and content changes made. Minor editorial and/or grammatical changes made. Performed review of SOP versus method versus actual laboratory procedure and made changes and/or incorporated Method Modifications and Clarifications, as applicable.
- Changed SOP document control number. This SOP was BA09: *Total Organic Carbon in Water*. SOP BA09 is now obsolete.
- Revised SOP Title.
- Included reference to EPA 9060A.
- Included information for the analysis and/or calculation of Total Carbon (TC) and Total Inorganic Carbon (TIC).
- Included information for the preparation of Dissolved Organic Carbon, Dissolved Carbon, and Dissolved Inorganic Carbon.
- Updated Instrument Parameters to reflect current practice.
- Updated standard and reagent information to reflect current practice.
- Removed TOC Preservation Check Log. This form is obsolete, and this information is now captured in LIMS.
- Added requirement to perform samples for EPA 9060 and EPA 9060A in quadruplicate and samples for EPA 415.1 and SM5310B in triplicate.
- Updated bottle kits to reflect method requirements. Added 2-hour holding time for filtration for determination of dissolved species. Added requirement to collect samples for TC without headspace.
- Added requirement to perform LCS/LCSD if insufficient volume was provided for MS/MSD.
- Added clarification regarding MDLs for dissolved species and calculations.
- Revised method blank criteria from <RL to <1/2RL.