Determination of Aqueous Inorganic Carbon and Calculated Carbonate Alkalinity of Fresh/Estuarine/Coastal Waters.

1. SCOPE and APPLICATION

1.1 Aqueous inorganic carbon (TIC) is determined by wet chemical analysis where the sample is injected into a receptacle of phosphoric acid. The carbonates are reduced to CO_2 and are detected using a non-dispersive infrared detector (NDIR) of an organic carbon analyzer. Carbonate alkalinity is calculated using the TIC concentration. The method is used to analyze all ranges of salinity.

1.2 A Method Detection Limit (MDL) of 0.17 mg/L TIC 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 TIC was set at 0.05 mg/L C.

1.4 This procedure should be used by analysts experienced in the theory and application of inorganic carbon analysis. Three months experience with an experienced analyst, trained in the analysis using the organic carbon analyzer, is required.

1.5 This method can be used for all programs that require analysis of aqueous inorganic carbon.

1.6 This procedure follows the procedures set forth within the operating manual of the Shimadzu TOC5000A.

2. SUMMARY

2.1 The Shimadzu TOC5000A is a high temperature combustion instrument used to analyze aqueous samples for TIC, TOC and non-purge-able organic carbon (NPOC). Although the TIC sample is not injected onto the hot catalyst bed, the furnace must be on for the analysis to proceed.

2.2 An aliquot of sample is injected into a receptacle of 25% v/v phosphoric acid (H_3PO_4). The carbonates within the sample are reduced to 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.

2.3 Carbonate alkalinity is then calculated after the concentration of inorganic carbon is determined.

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 250 µl syringe and 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 if 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 (CRM) – 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 (ASTM Type I) 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 (sodium carbonate/sodium bicarbonate (Na_2CO_3/$NaHCO_3$)) 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 filed 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 Shimadzu5000A TOC analyzer. 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 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 Carbon dioxide is readily absorbed from the air into an aqueous sample. Care must be taken to avoid this. Sample collection bottles should be

filled to the brim with no head space. Standards should be prepared in small batches and used within 1-2 days of analysis. Sample vials should be filled full and covered when placed in the auto sampler.

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 CBL Associate Director of Administration of the incident. Contact the CBL Associate Director of Administration 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
Sodium Carbonate, Anhydrous	1	0	1	2	Green
Sodium Bicarbonate	1	1	1	1	Green
Phosphoric 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

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 TOC5000A is used in this laboratory.
6.2 Refrigerator, capable of maintaining $+4 \pm 4°$ 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 and rinsed copiously with DI (ASTM Type I) water.

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 Sodium Hydrogen Carbonate ($NaHCO_3$) and Sodium Carbonate (Na_2CO_3) – primary standard for inorganic carbon.

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
Reagent H_2O	500 ml

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

7.4 Phosphoric Acid (H_3PO_4), 25% v/v –

Phosphoric Acid (H3PO4), concentrated,	25 ml
Reagent water, q.s.	100 ml

In a 100 ml volumetric flask, add 25 ml of concentrated phosphoric acid to ~ 50 ml of reagent water. Dilute to 100 ml with reagent water.

7.5 Blanks – ASTM D1193, Type I water is used for the Laboratory Reagent Blank. The LRB is comprised of the instrument blank. The area of the LRB is subtracted from the area of the standards.

7.6 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 (Na_2CO_3/$NaHCO_3$).

8 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Water collected for TIC is unfiltered whole water and should not be acidified. The sample container may be any container which has been adequately cleaned. Freshwater samples should be frozen in Teflon or plastic to prevent breakage.

8.2 Frozen TIC 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.

8.3 TIC samples stored at 4° C should be analyzed within 28 days.

8.4 Sample containers should be filled to the brim with no head space if refrigerated. If frozen, enough space for expansion should be left at the top of the container to prevent breakage.

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 ± 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, analyze 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:

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

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 ASTM Type I 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 ± 3σ 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 graphed, and the slope, y-intercept, and r squared data are compiled and tracked.

9.3.5 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 ($Na_2CO_3/NaHCO_3$), and are to be within TV ± 3σ. 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 0.5 ml of the highest carbonate standard in the curve is added to 5.0 ml of sample for a total volume of 5.5 ml.

9.4.3 0.5 ml standard 0.5/5.5 = 0.09

9.4.4 0.09 X STD conc.

9.4.5 5.0 ml sample 5.0/5.5 = 0.91

9.4.6 (original sample conc. X 0.91) + (0.09 x std conc.) = (expected conc.) mg/L

9.5 Data Assessment and Acceptance Criteria for Quality Control Measures

9.5.1 The Acceptance Criteria for TIC 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. Four point calibration is used with the Shimadzu TOC 5000A.

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

$$mg\ TIC/L = (A_{STD} - A_{H2OBLK})/\ m$$

Where: A_{STD} = Area of the standard

A_{H2OBLK} = Area of water blank
m = slope of the regression line

TIC sample concentration is calculated using the following equation:

$$mg\ TIC/L = A_S / m$$

Where: A_S = area of the sample,
m = slope of the regression line

Carbonate Alkalinity sample concentration is calculated using the following equation:

$mg\ CO_3 = (mg\ TIC/1) * (1\ moles\ C/12\ g\ C) *(48\ g\ CO3/\ 1\ mole)$

example: 17.0 mg TIC/L = (17.0 * 48)/12 = 68.0 mg CO_3/L

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)	± 20%	If QCS value is outside ± 20% of the target value reject the run, correct the problem and rerun samples.	Beginning of run following the ICV.
Initial Calibration Verification (ICV)	± 20%	Recalibrate if outside acceptance limits.	Beginning of run following standard curve.
Continuing Calibration Verification (CCV)	± 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)	≤ 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	Following the ICV, after every 10-12 samples following the CCV and at the end of the run.

		quantitation limit.	
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 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.	1/20
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

11.0 References

Instruction Manual Total Organic Carbon Analyzer Model TOC-5000A. Shimadzu Scientific Corporation. 7102 River wood Drive, Columbia, Maryland 21046-2502. Phone: 410 381-1227.

Appendix I

How to run the Shimadzu 5000A

- Turn on the gas.
- Turn on instrument. The power switch is located on the left side of the instrument.
- Instrument checks when turning on: Check level of liquid in the humidifier, located in the lower right corner inside. The level should be between the two lines. If low—add ASTM Type I water. Unscrew cap on the side and squirt in up to upper line.
- Press F5 to initialize the ASI. Make sure the turntable is in place to avoid error messages.
- Use the F keys to navigate. Go to NEXT (F1) which opens the MAIN MENU. Press 3 and Enter for General Conditions.
- Using arrow keys, scroll down to TOC furnace. Press 1 and Enter to turn on furnace. Return to MAIN MENU (F2). Make sure liquid in the TIC chamber —plastic reservoir inside in upper center— is bubbling. If not, there is a leak.
- Press 8 and Enter to go to the MAINTENANCE SCREEN. Toggle down to Regenerate IC Solution, select and press START. Do this twice before starting each run.
- Press 6 and Enter to get to MONITOR SCREEN. This screen allows you to monitor instrument conditions. It takes 20-30 minutes to come to temperature.
- Loading Samples: Decide on standard curve.
  TIC: The samples are analyzed using a curve of 0-30 ppm Na_2CO_3/$NaHCO_3$ and an injection volume of 20 µl in range 1. If the samples fall within the low end of the curve, the curve range and injection volume are adjusted accordingly. If the samples fall off scale, they are diluted and reanalyzed.
- Use the large sample vials for the curve stds. Examples of sample protocol can be found in the data sheet notebook.
- Always load several reagent water samples (at least 3) as conditioning blanks.
- Fill std vials ~ 1/3 to 1/2 full.
- Fill sample vials to within a millimeter or so of the top and cover with foil. DO NOT acidify TIC samples.
- Data sheets are found in the EXCEL TOC5000 folder.
- When the turntable is loaded, place in the ASI. Align the pin on the carousel with the slot on the ASI. Line up

arrow on cover with arrow on ASI. The cover will fit into a slot. Sample needles will Z if the top is not properly aligned.

- Go to the MAIN MENU — Press 9 and Enter for the AUTOSAMPLER.
- Determine analysis type: Press 2 for IC, one line per curve. The instrument can store up to 18 curves.
- Create 2 std curves for TIC. Using the number keys, toggle the sample type to TIC. Enter sample positions under IS and FS, and curve # under C1. Curve #1 is used as the conditioning curve with at least 3 vials of reagent water and the std reagent in position (S1). (5 max 6 injections, 100 µl, range = 1, and curve not through zero.) Curves 2-18 are used as sample curves.
- Enter curve # under C1 and ENTER. This opens the screen to input curve data. Use arrow keys to navigate. Enter std conc. & position (S1, S2, etc.).

  TIC: Range = 1, inj. vol 20 µl for 0-30 ppm curve. 3 max 5 injections, 200 SD, 2.0% CV.
- Return to SAMPLE CONDITIONS. Make sure sample conditions match curve conditions. Ex: # of inj, sparge time, etc.
- When all is set, press F1 (NEXT)
- Decide whether to leave instrument in 1 (Finish), 2 (Running), or 3 (No Change)
- Press F1 (NEXT)
- Press Start
- Check paper supply
- Make sure the Rinse Reservoir is full.
- Make sure the waste bottle has room.

Shutdown procedure for the TOC5000A.

- Make sure the Autosampler needles are in the home position.
- Open MAIN MENU (F2).
- Enter 7 for STANBY OPTIONS
- Press STANBY (F1) to shutdown. This turns the furnace off and closes the main pressure valve.
- Wait 30 minutes before turning off power.

Maintenance Schedule for the TOC5000A

Daily:

- Check liquid level in humidifier. Add ASTM Type I water to top line if level is too low. Keep level between top and bottom scored lines on vessel.
- Check paper supply if using in Stand Alone Mode.
- Make sure that the liquid in the IC pot is bubbling once the furnace is on. Lack of bubbling means a leak is present.
- Main instrument gas pressure setting @ 4.5 kg/cm^2.
- Carrier gas setting @ 150 cc.
- Sparge gas setting @ ~30-60 cc when in use.
- Check the level of the rinse container.
- Carrier gas pressure. Set the 2^{nd} stage of the regulator to 90-95 psi. Use Ultra Zero grade Air from Airgas or comparable grade. UZ Air is a synthetic blend containing 20-22% oxygen, < 1 ppm CO + CO_2 combined, < 2% H_2O, < 0.1% THC.

Monthly, approximately or after 15-18 analytical batches:

- Consumables parts list:
  PN 017-42801-01 TC catalyst, regular sensitivity
  PN 036-11209-84 Black o-rings, injection port; 5/pk
  PN 036-11408-84 Teflon o-rings (white), 5/pk
  PN 630-01565-00 injection port needle
  PN 638-41323-00 TC combustion tube
  PN 220-91101-00 syringe plunger w/tip
  PN 630-00105-01 platinum screens, 2/pk
  PN 630-02674-01 mist trap filter ball
  PN 036-11219-84 large black o-ring for IC reaction vessel.
  PN 200-91532-02 printer paper
  PN 638-41314-00 cooling coil, changed yearly or as needed.
  PN 638-41284-00 ASI sampling needles, changed yearly or as needed.
  PN 630-01566-00 Teflon coated o-ring, changed every 6 months.
  PN 630-00962-01 Na_2CO_3, primary std
  PN 630-00963-01 NaHCO3, primary std

- Make sure oven is off and cooled to room temperature.
- Remove the old column by unscrewing the two side screws on the mounting plate.
- Remove the injection port slide, and the injection block.
- Release the TC gas line from the side of the block.
- Remove the syringe from under the 4 port valve.
- Rinse the syringe and replace the old plunger and tip with a new plunger and tip.

- Remove the old mist trap filter ball and replace with a new filter, taking care not to touch with bare fingers.
- Remove the ultra pure water trap, rinse well, and return. There is no need to fill with water.
- Place 2 platinum screens in the bottom of the column. Cover with a very thin layer of quartz wool. Note: pressure problems may arise if the quartz wool is too thick.
- Pour 120 mm of catalyst into the tube. If analyzing for TIC only, it is possible to reuse the catalyst and combustion tube.
- Smear a thin layer of high vacuum silicone grease 1-2 mm below the top of the column. Set aside.
- Remove the old orings from the top of the TC injection block. Rinse the block. Put a thin layer of silicone grease on the new black oring and put into place. Lay a new (white) Teflon oring on top. Do not grease. Note: the Teflon coated oring on the underside of the injection block should be replaced twice yearly.
- Remove the injection needle from the injection slide. Rinse the slide, Replace with a new needle (remove the wire from inside the new needle). Adjust the needle so that only a millimeter or so is showing through the slide, and then tighten the knurled nut. The tip of the needle should not be visible when holding the slide on a horizontal plane. It will score the Teflon oring if it is out too far. Slide the air tubing back onto the needle.
- Insert the column into the bottom of the injection block. Place into the furnace opening, making sure that the drain tube is properly aligned. Insert into the cooling coil and hand tighten.
- Adjust the column height with mounting plate screw.
- Return the TC gas line to its proper position.
- Secure the injection port slide.
- Return the syringe to its proper position.
- Remove the IC reaction chamber and injection block. Replace all o-rings including the large black o-ring under the injection block following the same procedure used for the TC injection block.
- Replace the IC injection port needle using the same procedure for the TC injection needle.
- Turn gas and instrument on. Liquid in the IC block should bubble. If not, check and tighten everything that was loosened.
- Turn the furnace on.
- Fill auto-sampler tubes 1-78 with ASTM Type I water, and acidify with 100 µl 2N HCl. Acidify the water in position S1 standard cup with 300 µl 2N HCl. Set up Curve #1 as NPOC to condition the column, 9 max 10 injections, 1 minute sparge.
- Pull up the maintenance screen and do a Zero Point Detection.
- While in the maintenance screen, Regenerate the IC catalyst.

Semi-annual maintenance:

- Replace the Teflon coated oring.
- Replace the NaOH solution in the humidifier with a 0.3N NaOH solution: 1.2 g NaOH/100 ml H_2O.

Annual maintenance:

- Replace the halogen scrubber and acrodisc filter.
- Replace the soda lime scrubber.
- Replace the 4 port valve.
- If not used frequently, replace the IC port orings and needle. If used regularly, follow the monthly schedule.
- Replace the cooling coil.
- Replace the ASI needles.

Pollution Prevention and Waste Management:

- Liquids generated by this method are safe to put down the sink.
- Spent catalyst may be disposed of in the trash.
- Spent CO_2 absorber (Soda Lime) must be disposed in a proper manner. It should be taken to the Storage Facility on campus to be dealt with as hazardous waste.

SHIMADZU DATA SHEET TIC curve			CRUISE :					
TODAY'S DATE:								
INSTRUMENT USED:								
MANUAL/PC CONTROL			ANALYST: NLK OTHER:					
SPIKE CONC.:			INJECTION VOLUME:			FILE NAME:		
VIAL/STD	AREA		VIAL/ST	AREA			VIAL/STD	AREA
	S1 DHOH		S4	CO3			S7	
	S2 CO3		S5				S8	
	S3 CO3		S6			WORKING STDS MADE:		
VIAL/ID	AREA	VIAL	ID	AREA		VIAL	ID	AREA
1		27				53		
2		28				54		
3		29				55		
4		30				56		
5		31				57		
6		32				58		
7		33				59		
8		34				60		
9		35				61		
10		36				62		
11		37				63		
12		38				64		
13		39				65		
14		40				66		
15		41				67		
16		42				68		
17		43				69		
18		44				70		
19		45				71		
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25		51				77		
26		52				78		