1.0 TITLE

Determination of Total or Dissolved Organic and Inorganic Carbon in Water by Combustion, Oxidation, and Infrared Detection

2.0 LOCATION

Inorganic Instrument Laboratory.

3.0 SCOPE & APPLICATION

This method is applicable for the determination of Total Organic Carbon (TOC) or Dissolved Organic Carbon (DOC) in aqueous samples including drinking water, surface water, ground water, saline water, domestic and industrial waste waters, and leachates. For ACZ's purposes all references to Total Organic Carbon (TOC) actually signify Non-Purgeable Organic Carbon (NPOC). This SOP will solely mention TOC. TOC is determined by measuring Total Carbon (TC) after all inorganic carbon has been removed by acidification and sparging. TC is measured using a combustion furnace. TIC can be measured using an oxidation reaction.

The organic carbon in aqueous samples is composed of a variety of organic compounds in different oxidation states, some of which can be further oxidized by biological or chemical processes – Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) may be used to characterize these fractions. TOC is independent of the oxidation state of the organic matter and does not measure other organically bound elements and inorganics that can contribute to the oxygen demand measured by BOD and COD. TOC measurement is a direct expression of total organic content, and cannot replace BOD or COD testing.

4.0 SUMMARY

The TOC instrument uses a non-dispersive infrared detector (NDIR) to detect Carbon Dioxide (CO2) in compressed air stream. CO2 is first evolved from the sample using an oxidative catalyst inside a furnace heated to 850-900°C, which converts all forms of carbon (TC) present in the sample to CO2. Inorganic carbon is measured when a sample is acidified by the instrument to convert all inorganic forms of carbon to CO2. The working range for the TOC instrument is 1 – 200 mg/L total carbon. The working range for the DOC low level product (DOC_LL) is 0.5 – 200 mg/L total carbon.

5.0 REFERENCES

5.1 Standard Methods for the Examination of Water and Wastewater, Online Edition, Method 5310B, (2000).

5.2 Standard Methods for the Examination of Water and Wastewater, Online Edition, Method 5310B, (2011).

5.3 FORMACS^{HT} TOC/TN Analyzer User Manual, Skalar, October 2009.

5.4 TOC-LCPH/CPN User's Manual, Shimadzu, 2011-2016

6.0 SAMPLE COLLECTION, HANDLING & PRESERVATION

6.1 Samples for TOC are collected in glass or plastic (polyethylene or fluoropolymer) bottles and are preserved to pH < 2 with Trace metal Grade (TMG) Sulfuric Acid (H_2SO_4). "Yellow-dot" bottles are unfiltered and are used for TOC determination. "Blue-dot" bottles are filtered with a 0.45µm membrane filter and are used for DOC determination. Samples are maintained at 0-6.0 ºC in the South inorganic walk-in cooler. Protect from sunlight and atmospheric oxygen as these sample types are used for other analyses.

6.2 Samples for TIC analysis are unfiltered and unpreserved (Raw). Samples for DIC are filtered and unpreserved (White). Samples are maintained at 0-6.0 ºC in the North inorganic walk-in cooler.

6.3 Samples for TC analysis are unfiltered and unpreserved (RAW). Samples for DC analysis are filtered and unpreserved (WHITE). Samples are maintained at 0-6.0 ºC in the North inorganic walk-in cooler.

6.4 The hold time for TOC is 28 days from collection. Sample prep and analysis must be completed within the hold time.

6.5 The hold time for TIC/TC is not specified. ACZ observes a hold time of 28 days from collection. Sample prep and analysis must be completed within this time.

6.6 There is no specified hold time for soils extracts between time of sampling and time of extraction. Post extraction hold time is 28 days. Extracted samples are stored at 0-6.0 ºC in the Organic Walk-in cooler.

Table 6.1: Hold Times

Parameter Description	Matrix	Hold Time Starts – Ends With
TOC/DOC/DOC_LL/TC/TIC/DIC	Liquid	28 days from collect date to analysis
	Solid with Extraction	28 days from extraction time out to analysis

7.0 APPARATUS & SUPPLIES

7.1 FORMACS^{HT} TOC Analyzer
7.2 LAS-160 Autosampler
7.3 PC interfaced with TOC analyzer, with HT Access operational software
7.4 Four place analytical balance, calibration verified daily or before use (refer to SOPAD013)
7.5 100-1000µl and 2-10ml adjustable pipettes, accurate delivery verified (refer to SOPAD013)
7.6 Class A pipettes and volumetric flasks
7.7 16X100mm Borosilicate tubes
7.8 Compressed Air

7.9 Type 1 water system
7.10 0.45 mm filter verified by lot to be free of contamination from carbon.
7.11 Lot verified centrifuge tubes for spiking/dilutions

8.0 REAGENTS & STANDARDS[1]

NOTE: All glassware is rinsed with copious amounts of DI H_2O before preparing standards or reagents.

8.1 Reagent Water: Type I water with specifications consistent with SOPAD013. Obtain directly from Type I water tap in the Inorganic Inst Lab.

8.2 0.05M HCl (Shimadzu TOC-L): In a 200mL volumetric flask, add 1.2mL of 12N HCl to ~100mL of Type I water. Bring to 200mL volume using Type I water. Store in glass container at 0.0-6.0 ºC in the reagent room cooler for up to 1 year.

8.3 1M HCl (Shimadzu TOC-L): In a 200mL volumetric flask, add 16.7mL of 12N HCl to ~100mL of Type I water. Bring to 200mL volume with Type I water. Store in glass container at 0.0-6.0 ºC in the reagent room cooler for up to 1 year.

8.4 Phosphoric Acid (2% V/V): In a 100mL volumetric flask, add 2.35mL of Reagent Grade H_3PO_4 (85%) to ~ 50mL of Type I water. Bring the volume to 100mL using Type I water. Make fresh daily when TIC samples are to be analyzed.

8.5 Diluent (0.4% H_2SO_4): In a 1L glass bottle, add 4mL concentrated H_2SO_4 to ~ 500mL of Type I water. QS to 1L. Store in glass container at 0-6.0 ºC in the reagent cooler for up to 1 year.

8.6 5000 mg/L TC/TOC/DOC/DOC_LL Calibration Stock Solution: Purchased pre-made from vendor. Manufacturer's expiration date apply. Store at 0-6.0 ºC in the reagent cooler.

8.7 1000 mg/L TIC/DIC Calibration Stock Solution: Purchased pre-made from vendor. Manufacturer's expiration date apply. Store at 0-6.0 ºC in the reagent cooler.

8.8 Working Calibration Standards:

NOTE: All standards are prepared using Class A Glassware and 0.4% H_2SO_4. Store at 0-6.0 ºC in the reagent cooler. Expires after 90 days, or at manufacturer's expiration date, whichever is sooner.

Table 8.1: TC/TOC/DOC Working Calibration Standards (Skalar TOC)

Standard	Amount of 5000mg/L TC Stock (mL)	Amount of H_2SO_4 (mL)	Volumetric Size (mL)	Final Concentration (mg/L)
C1	8	0.8	200	200
C2	4	0.8	200	100
C3/CCV	10	4	1000	50
C4	1	0.8	200	25
C5	0.2	0.8	200	5 ++

Calibration Blank (C6) = 0.4% H_2SO_4

++ There must be a standard in the calibration curve with a concentration = PQL.

[1] ACZ has found inconsistency between different manufacturer's storage recommendations of standards and has decided that storing them at 0-6.0˚C in the reagent cooler is sound practice. Samples that are tested for these parameters are also stored at 0-6.0˚C. (CAR 1211)

Table 8.2: DOC_Low Level Working Calibration Standards (Skalar TOC)

Standard	Amount of 5000mg/L TC Stock (mL)	Amount of H_2SO_4 (mL)	Volumetric Size (mL)	Final Concentration (mg/L)
C1	8	0.8	200	200
C2	4	0.8	200	100
C3/CCV	10	4	1000	50
C4	1	0.8	200	25
C5	0.2	0.8	200	5
C6	0.1	0.8	200	2.5^{++}

Calibration Blank (C7) = 0.4% H_2SO_4

$^{++}$ There must be a standard in the calibration curve with a concentration = PQL.

Table 8.3: TC/TOC/DOC High Level Working Calibration Standards (Shimadzu TOC-L)

Standard	Amount of 5000mg/L TC Stock (mL)	Amount of H_2SO_4 (mL)	Volumetric Size (mL)	Final Concentration (mg/L)
C1	8	0.8	200	200
C2	4	0.8	200	100
C3/CCV	10	4	1000	50
C4	1	0.8	200	25

Table 8.4: TOC-DOC Low Level Working Calibration Standards (Shimadzu TOC-L)

Standard	Amount of 5000mg/L TC Stock (mL)	Amount of H_2SO_4 (mL)	Volumetric Size (mL)	Final Concentration (mg/L)
C4	1	0.8	200	25
C5	0.4	0.8	200	10
C6	0.2	0.8	200	5^{++}
C7	0.1	0.8	200	2.5^{++}

Calibration Blank (C8) = 0.4% H_2SO_4

$^{++}$ There must be a standard in the calibration curve with a concentration = PQL.

8.9 TIC Calibration Standards:

NOTE: Prepare standards using Class A glassware and Type I water**. Do not acidify the TIC standards!** Store at 0-6.0 ºC in the reagent cooler. Expires at 90 days, or at manufacturer's expiration date, whichever is sooner.

Table 8.5: TIC Calibration Standards (Skalar TOC)

Standard	Amount of 1000 mg/L TIC Stock (mL)	Volumetric Size (mL)	Final Concentration(mg/L)
C1	40	200	200
C2	20	200	100
C3/CCV	50	1000	50
C4	5	200	25
C5	1	200	5^{++}

Calibration Blank (C6) = Type I H_2O

++ There must be a standard in the calibration curve with a concentration = PQL.

Table 8.6: TIC High Level Calibration Standards (Shimadzu TOC-L)

Standard	Amount of 1000 mg/L TIC Stock (mL)	Volumetric Size (mL)	Final Concentration(mg/L)
C1	40	200	200
C2	20	200	100
C3/CCV	50	1000	50
C4	5	200	25

Table 8.7: TIC Low Level Calibration Standards (Shimadzu TOC-L)

Standard	Amount of 1000 mg/L TIC Stock (mL)	Volumetric Size (mL)	Final Concentration(mg/L)
C4	5	200	25
C5	2	200	10
C6	1	200	5++
C7	0.5	200	2.5

Calibration Blank (C8) = Type I H_2O

++ There must be a standard in the calibration curve with a concentration = PQL.

8.10 1000 mg/L TC/TOC/DOC/DOC_LL ICV Stock Solution: Purchased pre-made from vendor. This stock must be from a separate source/lot number than the calibration stock. Manufacturer's expiration date applies. Store at 0-6.0 ºC in the reagent cooler.

8.11 TC/TOC/DOC/DOC_LL Working ICV (True Value = 100 mg/L): In a 1000mL volumetric flask, add 100 mL of the 1000mg/L ICV Stock and 4mL H_2SO_4 into ~ 500 mL Type 1 water. QS to 1000 mL. Store in a glass bottle at 0-6.0 ºC in the reagent cooler. Shelf life is 3 months

8.12 TC/TOC/DOC/DOC_LL AS/LFB (True Value = 50 mg/L): Add 0.1mL of the 5000 mg/L TC/TOC/DOC/DOC_LL Calibration Stock Solution into 10mL sample for an AS or into 10 mL 0.4% H_2SO_4 for the LFB.

8.13 Practical Quantitation Verification (PQV) standard (True Value = 5mg/L): In a 1000mL volumetric flask, add 1mL of the 5000 mg/L TC/TOC/DOC Calibration Stock Solution and 4mL H_2SO_4 to ~500mL Type 1 water. QS to 1000mL. Store in a glass bottle at 0-6.0 ºC in the reagent cooler. Shelf life is 3 months. PQV is C5 calibration standard.

8.14 DOC_LL Practical Quantitation Verification (PQV) standard (True Value = 2.5mg/L): In a 200mL volumetric flask, add 0.1mL of the 5000mg/L TC/TOC/DOC/DOC_LL Calibration Stock Solution and 0.8mL H_2SO_4 to ~100mL Type 1 water. QS to 200mL. Store in a glass bottle at 0-6.0 ºC in the reagent cooler. Shelf life is 3 months. PQV is C6 calibration standard.

8.15 1000mg/L TIC/DIC ICV Stock Solution: In a 1L volumetric flask containing ~500mL of Type I H_2O, dissolve 4.4122g anhydrous sodium carbonate and 3.497g anhydrous sodium bicarbonate. QS to 1L mark with Type I H_2O. Store in a glass bottle at 0-6 ºC in the cyanide prep lab cooler. Shelf life is 3 months. Stock may also be purchased pre-made from vendor, but must be from a separate source/lot number that the calibration stock. Manufacturer's expiration date apply. Store at 0-6.0 ºC in the reagent cooler.

8.16 TIC/DIC Working ICV (True Value=100mg/L): In a 1L volumetric flask containing ~500mL of Type I H_2O add 100mL of 1000mg/L TIC ICV solution. QS to 1L. Store in a glass bottle at 0-6.0 ºC in the reagent cooler. Shelf life is 3 months.

8.17 TIC/DIC AS/LFB (50 mg/L): Add 0.5 mL of 1000 mg/L TIC/DIC calibration stock to 10 mL sample for AS or 10 mL Type I H_2O for the LFB.

8.18 TC/DC AS/LFB (50 mg/L): Add 0.1 mL of 5000 mg/L TC/TOC/DOC Calibration Stock Solution into 10mL sample for an AS or into 10 mL Type I H_2O for the LFB.

9.0 SAFETY

9.1 HAZARDS

This procedure does not propose to address all safety issues associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous.

9.2 SAFETY TECHNIQUE

9.2.1 Safety glasses are required and the use of gloves and lab coat is strongly recommended. Shorts and open-toed shoes are not allowed in the lab.

9.2.2 Use care when pouring and pipetting reagents. Always add acid to water. Use the proper method when washing glassware.

9.2.3 Do not eat or use tobacco products in the lab.

9.2.4 Wipe up ALL spills immediately. Implement the Emergency Response Plan if necessary.

9.2.5 Do not wear gloves or lab coat outside of the laboratory. Remove gloves before using a computer, telephone, etc. Computers within lab areas may be designated for use with gloves.

9.2.6 Do not conduct “experiments” unrelated to the analysis.

9.3 PROTECTIVE EQUIPMENT

9.3.1 Use a fume hood when there is a potential for strong fumes.

9.3.2 A fire extinguisher is located in each analytical laboratory.

9.3.3 An emergency shower and eye wash station are located in the metals prep lab.

10.0 INTERFERENCES

10.1 Method Interferences:

Carbon is ubiquitous in nature, so reagents, water and glassware can all contribute contamination. Method interferences may be caused by contaminants in the carrier gas, dilution water, reagents, glassware, or other sample processes. Careful observation of initial and continuing calibration blanks can be used to check for systematic contamination. The use of high purity reagents and

gases help to minimize interference problems.

10.2 Interference by Non- Carbon Dioxide Gases:

The IR detector is sensitized to carbon dioxide and accomplishes virtually complete rejection of responses from other gases, which absorb energy in the IR region. Trapping and desorption of carbon dioxide on the molecular sieve trap isolates this component of interest and allows the complete absence of interference in the system from gases other than carbon dioxide.

10.3 Sampling Interference:

Sampling containers should be free of organic contaminants. Plastic bottles can leach carbon into water samples. Keep sample bottles closed when possible and store at 0-6 ºC in the dark.

10.3.1 Carbonate and bicarbonate forms of carbon represent interference under the terms of this test and are accounted for in the final calculations.

10.3.2 Samples must be homogeneous and free of large particulate matter.

11.0 PROCEDURE (SKALAR TOC)

11.1 Starting the TOC:

11.1.1 Turn on the Compressed Air located near the South inorganic walk-in cooler and set flow to ~30 psi on tank regulator. Check the pressure on the regulator; if < 500 psi then change the tank. Record the change in the logbook.

11.1.2 Turn on the main power switch on the back panel of the instrument and the display screen on top of instrument, watch to see that the screen comes on, and then turn on the power switch on the back of the autosampler. The autosampler will reset itself.

11.1.3 When the autosampler stops moving, open the HT Access software. Press **Esc** to begin and enter user name (wetchem) and password (logbook). Click on **Connect** then **Auto Connect**. The settings screen will automatically open, check to see that settings are appropriate (furnace should be set to 900 ºC, flow should be set to On and sparge should be set to 240 s), click **Send Settings to Analyzer** (green check marks will appear next to parameters), then **OK**. This screen may also be accessed through **Settings** then **Analyzer Settings.** NOTE: The furnace does not need to be turned on if only analyzing TIC or DIC.

11.1.4 Monitor the flow of air in the system by watching the info screen on the upper left corner of the computer monitor, or by watching the display screen on top of the instrument. Flow should be ~200 units, but will fluctuate until the furnace has reached temperature. The gas flow can be adjusted using the flow adjuster knob, situated against the back panel in the front compartment. If there is not proper flow, turn off the furnace and allow it to cool down then perform a leak/blockage check. See Trouble shooting section in User Manual for instruction.

11.1.5 Fill rinse container with Type I H_2O. Check Waste is automatically pulled from instrument to plumbing, but check waste line connections for sign of wear or damage.

11.1.6 Empty and fill IC reactor with fresh 2% H_3PO_4 if TIC samples are to be analyzed. To fill the IC reactor:

1) Release the two bolts on the IC reactor holder and pull the holder down. Then carefully pull the IC reactor down. Glass reactor is fragile.

2) Remove old acid from reactor and refill with new acid up to the overflow tube using a transfer pipette.

3) Carefully replace the reactor and reactor holder and tighten the bolts.

11.1.7 Once furnace has reached temperature, ~ 900 ºC, monitor the base line by clicking on **View, Live Monitor.** The base line should be at 20000, if not, click on **Auto Zero** and wait for it to stabilize. Make sure flow is ~200 units and adjust if necessary.

11.2 Calibrating the TOC Analyzer: A TC/ TIC calibration must be performed when two consecutive analyses of the ICV or CCV fail, or when a significant hardware change or maintenance event has taken place. Recalibrating in the event of two consecutive failures of either an ICV or CCV can be avoided as long as two consecutive passing ICV's or CCV's is observed prior to generating client data. This is possible when the QC failures can be attributed to operator error or a technical malfunction rather than a drift in detection from the original calibration.

11.2.1 Creating a TC Calibration Sequence:

NOTE: §11.2.1.1-11.2.1.3 have been performed and saved as "CALtemplate" in the HTAccess software. The calibration template does not need to be re-created for each calibration, but can be edited to fit desired run needs. To use this prior created calibration template, click on **Template**, **Edit**, and select "CALtemplate". The following directions are to create a new cal template.

11.2.1.1 Click on **Template**, **New**, file name "CALtemplate", click on **Add Pos,** label as **Tracer 100mg/L,** under TYPE, select **Unknown,** under INJECTION, select **TC** and **sparge.** This standard is used to stabilize the system**.**

11.2.1.2 Next, click on **Standards** and a list of the available TC standards appears. Click on TC 0, select **Add to Template**, then follow with TC 5, TC 25, TC 50, TC 100, TC 200. Standards will appear in template in order clicked and parameters for testing will be TC and sparge. To add or change available TC Standards this must be done from the main menu home screen under **View, Standards.**

11.2.1.3 For TC ICV/ICB, select **Add Pos**, label standard, under TYPE, select **Quality Sample 2,** under Injection, select **TC.**
NOTE: ALL TC injection volumes should be set to 100µL for TC/TOC/DOC calibrations and workgroups.

11.2.2 Creating a DOC_LL Calibration Sequence:

NOTE: §11.2.2.1-11.2.2.3 have been performed and saved as "CAL_LL Template" in the HTAccess software. The calibration template does not need to be re-created for each calibration, but can be edited to fit desired run needs. To use this prior created calibration template, click on **Template**, **Edit**, and select "CAL_LL Template". The following

directions are to create a new cal template.

11.2.2.1 Click on **Template**, **New**, file name "CAL_LL Template", click on **Add Pos,** label as **Tracer 100mg/L,** under TYPE, select **Unknown,** under INJECTION, select **TC** and **sparge.** This standard is used to stabilize the system**.**

11.2.2.2 Next, click on **Standards** and a list of the available TC standards appears. Click on TC 0, select **Add to Template**, then follow with TC2.5, TC 5, TC 25, TC 50, TC 100, TC 200. Standards will appear in template in order clicked and parameters for testing will be TC and sparge. To add or change available TC Standards this must be done from the main menu home screen under **View, Standards.**

11.2.2.3 For TC ICV/ICB, select **Add Pos**, label standard, under TYPE, select **Quality Sample 2,** under Injection, select **TC.**
NOTE: ALL TC injection volumes should be set to 200µL for DOC_LL calibrations and workgroups.

11.2.3 Creating a TIC Calibration Sequence:

NOTE: §11.2.3.1-11.2.3.3 have been performed and saved as TICCALtemplate in the HTAccess software. The calibration template does not need to be re-created for each calibration, but can be edited to fit desired run needs.

11.2.3.1 Click on **Template**, **New**, file name "TICCALtemplate", click on **Add Pos,** label as **Tracer 100mg/L,** under TYPE, select **Unknown,** under INJECTION, select **TIC.** This standard is used to stabilize the system.

11.2.3.2 Next, select IC in the upper left corner and a list of the IC standards appears. Click on IC 0, select **Add to Template**, follow with IC 5, IC 25, IC 50, IC 100, IC 200. Standards will appear in template in order clicked and parameters for testing will be IC. To add or change available IC Standards this must be done from the main menu home screen under **View, Standards.**

11.2.3.3 For IC ICV/ICB, select **Add Pos**, label standard, under TYPE, select **Quality Sample 2**, under Injection, select **IC**.
NOTE: ALL IC injection volumes should be set to 100µL for IC calibrations and workgroups.

11.2.4 At the bottom of each template there are different options to choose. For all templates the options should be:
Element: Carbon
Integration Time: 60s
Sample (TC/IC): 2
Extra Sample (TC/IC):2
Max CV: 5%
Sample Time: 300s

11.2.5 To edit the calibration template click on desired **Template**, **Edit**, file name "CAL Template", "TICCAL Template", or "CAL_LL Template" A calibration can be run alone or with a Workgroup. Save the template by going to **File, Save As** and save as WorkgroupnumberCAL.

11.2.5.1 If running just a calibration then the template is ready.

11.2.5.2 If adding a Workgroup to the calibration template go to §11.3 before running the calibration.

11.2.5.3 Once template has been edited to reflect desired run, view the template by selecting **Print** and review to be sure all parameters are correct and the positions are in the correct order. To print, select **Print.** Exit out of print screen and select OK.

11.2.6 Running a Calibration

11.2.6.1 Go to **Analysis, New** and name the run as the WorkgroupCAL then hit **Save.** Software will prompt you to select a template. Select the template you created in §11.2.1, §11.2.2, or §11.2.3 and **Open.**

11.2.6.2 Label glass culture tubes according to run sequence and pour off standards (and samples if running Workgroup. See §11.3 and §11.4) Load carousel according to template starting with position 1. Samples should never be placed in position 0.

11.2.6.3 Monitor baseline by selecting **Graph Peaks**. If baseline is not ~ 20000 adjust by selecting **Auto Zero.**

11.2.6.4 On Analysis screen make sure correct analysis name and template are entered and select "Switch on flexible sample time" and "Allow direct calculations." If instrument will run overnight also select "Go to Stand-by after analysis"

11.2.6.5 If running a new calibration, prior curves still left in default settings should be deselected. This can be done by selecting **Results**, **Calibration Curves**, and unchecking the unwanted curve(s). This can also be done following the completion of a run and then clicking **Calculate Results** in the results screen. The final new calibration should only be selected to reference curve titled "This Analysis".

11.2.6.6 Once all of the correct selections are made and the baseline has stabilized, select **Start Analysis.** Once the carousel resets, if all parameters are correct select **Continue.**

11.2.6.7 Follow the progress of the calibration by selecting **Graph Peaks**, which display the peaks as they appear, or select **Results**, and view the Raw values.

11.2.6.8 When all samples are analyzed a message is displayed that the analysis is ready. Click **OK** to close message.

11.2.6.9 To view Calibration results go to **Results, Calibration Curves.** Select TC or IC "This Analysis" and **Show Graph.** Verify that the calibration correlation coefficient (r^2) is >0.995. if generating a new curve, print a copy of the calibration graph and include with the workgroup.

11.2.6.10 Return to the Analysis screen and **Print Results.** Verify ICV/ICB passing.

11.2.6.11 If everything is passing, select the calibration as the calibration to be used for analyses. From the main screen, select **Settings, Default Calibration Curves.** Click on **TC** and **Add Curve**. Select desired curve and do the same for **IC**. Delete unwanted curves by highlighting curve and then click **Remove Curve.** Adding and removing curves can also be done in the Results screen.

11.3 Creating a Sequence

11.3.1 Create a workgroup in SAGE.

11.3.2 Print a copy of the current standards and reagents form to attach to the workgroup.

11.3.3 From the main screen, click on **Template**, **Edit.** Determine if a calibration will be run with the Workgroup. If so select file name "CALtemplate", "CAL_LL Template", or"TICCAL Template" which will include a TC or TIC calibration prior to samples. If a calibration is not necessary, depending on analysis being run, select file name "Tracer Template", "LLTracer Template", or "TICTracer Template" which will begin with just a Tracer sample (100 mg/L TC or TIC standard depending on the analysis to be run) and end with several rinses (rinses are not required, but have been found to help keep the TC chamber clean.). Before making any changes to the selected template go to **File, Save As** and enter the Workgroup number as the file name. If running multiple groups as one template, use the numbering pattern WGXXXXXX-XXX (for example, WG418429 and WG418430 run under one template would be saved as WG418429-430). Highlight the sample in the template that will precede the workgroup (generally the tracer or a rinse following the tracer) and select **Import.** Select Workgroup number to be imported as well as the number of positions needed. Workgroups can also be made manually in the **Template** screen.

NOTE: The software will import the workgroup samples the exact same way that the highlighted sample is set up. If the analysis is for TOC, **TC** and **sparge** should be selected for the injection type and "unknown" as the sample type. If the analysis is for TIC the highlighted sample should have IC for the injection type.

11.3.4 **TOC/DOC Analysis:** For **Type**, select **Quality 2** for all QC samples (ICV, ICB, CCV, and CCB) and **TC** and **sparge** for injections. For client samples, analytical spikes, LFB, PQV and duplicates, select **Unknown** for **Type** and TC and **sparge** for **injections**. Enter correct dilution factors. Injection volume will be 100 µl for all samples. If samples contain sediment, select **Stirrer** so samples will be stirred before analysis.

11.3.5 **TIC/DIC Analysis:** For **Type**, select **Quality 2** for all QC samples (ICV, ICB, CCV, and CCB) and **TIC** for injections. For client samples, analytical spikes, LFB, PQV and duplicates, select **Unknown** for **Type** and **TIC** for **injections**. Enter correct dilution factors. Injection volume will be 100 µl for all samples. If samples contain sediment, select **Stirrer** so samples will be stirred before analysis. .

11.3.6 **TC/DC Analysis:** For **Type**, select **Quality 2** for all QC samples (ICV, ICB, CCV, and CCB) and **TC** for injections. For client samples, analytical spikes, LFB, PQV and duplicates, select **Unknown** for **Type** and **TC** for **injections**. Enter correct dilution factors. Injection volume will be 100 ul for all samples. If samples contain sediment, select **Stirrer** so samples will be stirred before analysis. Make sure that sparge is NOT selected for TC analysis.

11.3.7 **DOC_LL Analysis:** For **Type**, select **Quality 2** for all QC samples (ICV, ICB, CCV, and CCB) and **TC** and **sparge** for injections. For client samples, analytical spikes, LFB, PQV and duplicates, select **Unknown** for **Type** and TC and **sparge** for **injections**. Enter correct dilution factors. Injection volume will be 200 µl for all samples. If samples contain sediment, select **Stirrer** so samples will be stirred before analysis.

11.3.8 Once template has been edited to reflect desired run, print template by selecting **Print** and review to be sure all parameters are correct, any dilution factors are correct, and the positions are in the correct order(if not in order, select **Renumber,** and software will automatically update positions, starting with 1). To print select **Print.** Exit out of print screen and select OK.

11.4 Running a Sequence

NOTE: Prepare all TOC/DOC/DOC_LL dilutions using 0.4% H_2SO_4 and all TIC/DIC and TC/DC dilutions using Type I H_2O. Dilutions are to be performed with a calibrated mechanical pipette and lot verified centrifuge tubes.

11.4.1 Setting up Carousel Tray

11.4.1.1 Collect the **yellow-dot** bottles for TOC or **blue-dot** bottles for DOC and DOC_LL.

NOTE: Verify blue-dot samples have been filtered. If necessary, create a FILT-AC-B workgroup in SAGE and filter samples using a 0.45 µm membrane filter and acidify with Trace Metal Grade Sulfuric Acid **before** analysis. Refer to SOPWC050.

11.4.1.2 Collect RAW bottles for TIC or TC analysis or WHITE bottles for DIC or DC analysis.

11.4.1.3 Label glass culture tubes according to run sequence using either Eltron printer labels or a sharpie pen.

11.4.1.4 Fill each tube with corresponding sample or QC standard.

NOTE: For each client sample, verify that the sample Log-in number on the workgroup matches the sample number on the bottle. This ensures that samples are not inadvertently switched when they are poured off.

11.4.1.5 If any dilutions are necessary, use calibrated pipettes to add the appropriate amounts of sample and 0.4% H_2SO_4 diluent or Type I H_2O, depending on the analysis, to the lot verified centrifuge tube. Cover with parafilm and mix well, then pour diluted sample into glass tube. Common reasons for dilutions are high pH (> pH 6), odor, reactivity with acid, oily matrix, high

TDS, or high amounts of sediment.

11.4.1.6 Place each vial in the correct location on the carousel according to the template sequence. Place the carousel into TOC autosampler by lining up the arrow with the wash station at the back of the autosampler.

11.4.2 Starting a Sequence

11.4.2.1 Go to **Analysis, New** and name run the same as the earlier created template, then hit **Save.** Software will prompt you to select a template. Select the template you created in §11.3 and **Open.**

11.4.2.2 Monitor baseline by selecting **Graph Peaks.** If baseline is not ~ 20000, adjust by selecting **Auto Zero.**

11.4.2.3 On Analysis screen make sure correct analysis name and template are entered and select "Switch on flexible sample time" and "Allow direct calculations." If instrument will run overnight select "Go to Stand-by after analysis."

11.4.2.4 If running a TC/TOC/DOC workgroup, the higher injection volume DOC_LL calibration curve should be deselected. If running a DOC_LL workgroup, the lower injection volume TC/TOC/DOC calibration curve should be deselected. This can be done by selecting **Results**, **Calibration Curves**, and unchecking the unwanted TC curve. This can also be done following the completion of a run and then clicking **Calculate Results** in the results screen.

11.4.2.5 Once all of the correct selections are made and the baseline has stabilized, select **Start Analysis**. Once the carousel resets, if all parameters are correct select **Continue.**

11.4.2.6 Follow the progress of the analysis by selecting **Graph Peaks,** which displays the peaks as they appear, or select **Results** and view the Raw values.

11.4.2.7 When all samples are analyzed a message is displayed that the analysis is ready. Click **OK** to close message.

11.4.2.8 Results can be viewed in the **Results** screen or **Graph peaks** screen.

11.4.2.9 Return to the analysis page to **Print Results**. On the analysis data printout, make sure the correct curve is being referenced under the "SEL" header. Any curve that is selected will say "YES", while any deselected curve will have a dash mark "-". If selected curve needs to be changed, see §11.4.2.4.

11.4.3 Upload Data to SAGE

11.4.3.1 On the analysis page select **Export Results**. Save as the WG#.csv

11.4.3.2 After exporting data from HT Access it will be in the U:\WaitLoad\toc2 folder.

11.4.3.3 Send the file to U:\AutoLoad\toc2. If workgroup needs editing, make necessary changes in WaitLoad, before sending to AutoLoad. Any editing of file data should be done in Notepad if possible. Opening and closing the files in Excel can sometimes cause upload problems.

NOTE: Any changes made to upload files must be documented with the workgroup.

11.4.4 Review the workgroup in the SAGE AREV screen, completing a data review checklist. Attach all raw data and supporting documentation and submit the data package to the department supervisor for SREV.

11.5 Shutting down the TOC instrument

11.5.1 Close the HT Access software program; turn off the sampler and Formacs HT by keeping the On/Off button pressed until a beep is heard. A message is displayed on the screen that the analyzer is shutting down, but that this procedure can be stopped within 8 seconds by shortly pressing the button and the analyzer will stay on.

11.5.2 Turn off compressed air (instrument will stop air flow, but turning off air at the tank will prevent leaks).

11.5.3 Empty sample tubes.

11.5.4 If the instrument will not be used for a few days, release the tubing from the pumps.

11.6 **TROUBLESHOOTING/MAINTENANCE**

Preventative maintenance and troubleshooting are necessary to ensure the instrument will run smoothly and efficiently. If any difficulties arise (failing QC, inconsistent flow rate, abnormal peak shape, etc.) verify the following and/or consult the Operator's Manual. **Document all maintenance, troubleshooting, repairs and support calls in the instrument logbook.**

- Is the compressed air turned on? Is the gas tank pressure greater than 500psi?
- Is the flow rate ~190-210 mL/min?
- Are there any gas leaks?
- Make sure TC/IC heads are tightened to correct tightness with torque wrench.
- Check o-rings in TC/IC head for damage. Replace if necessary
- If there is no instrument response when starting a run, check that the autosampler is sampling properly.
- Is the Halide scrubber discolored? Cracked? If so, replace.
- Does the catalyst in the combustion tube need replacing? If so, consult the User Manual for instructions.
- Is the combustion tube cracked? If so, replace.
- If blanks are failing check that the rinse receptacle is full.
- Verify that there is enough Phosphoric Acid reagent in the Acid receptacle.
- Check for any clogs in the tubing.
- Replace tubing if flat/dirty
- If QC continues to fail after verifying the above, try recalibrating the instrument.
- Consult the User Manual for scheduled and unscheduled preventative maintenance.
- Contact technical support at Skalar if problems persist (800-782-4994).

12 PROCEDURES (SHIMADZU TOC-L)

12.1 Starting the TOC:

12.1.1 Turn on the Compressed Air located near behind the Shimadzu TOC-L bench and set to ~30 psi on tank regulator. Check the pressure on the regulator; if < 500 psi then change the tank. Record the change in the logbook.

12.1.2 Press the button on the front of the instrument to turn it on (Do NOT flip the switch located on the right side of the instrument! If turned off while combustion tube is hot, the teflon valve on top will melt leading to an expensive repair). The indicator light on the front of the instrument will change color depending on the state of the instrument (see **Table 12.1** below for relationship between indicator light and the status of the instrument).

Table 12.1: Relationship Between Indicator Light and Instrument Status

Power Switch	Indicator Light	Instrument State
Lit Green	Lit Orange	Ready condition not established
Lit Green	Lit Green	Ready condition established
Lit Green	Lit Blue	Measurement in progress
Lit Green	Flashing Orange	In editing mode
Lit Green	Flashing Blue	Sleep state
Lit Green	Flashing Green	Firmware update in progress
Lit Green	Flashing Red	Error occurred
Lit Green	Lit Red	Warning occurred
Flashing Orange	Off	Shutting down
Lit Orange	Off	Shut down
Off	Off	Main power switch off

12.1.3 Open the TOC-Control L software and click on “Sample Table Editor.” A dialog box saying “Please enter the user name” will appear. Leave blank and click “Ok” to open the sample table editor.

12.1.4 Once you sample table is created (see section §12.3 below for details on how to create a sample table), click the “Connect” button in the top right corner. This will connect the instrument to the created sample table. Once connected, click the “Monitor” button to see the instrument status. Make sure all instrument parameters are at the levels listed below. Once the system is stabilized, you will see green checkmarks next to each parameter in the Background Monitor and the status, in the upper right corner of the Sample Table Editor, will change from “Not Ready” to “Ready.”

Supply Gas Pressure = 200 ± 10 kPa
Carrier Gas Flow = 150.0 mL/min
Furnace = 680 ºC (it takes ~30min to reach temperature at startup)

12.1.5 Make sure all containers are filled with their respective solutions.
12.1.5.1 Fill the acid container, located on the left side of the instrument, with 1M HCl.
12.1.5.2 Fill the B-Type Halogen Scrubber, located on the front of the instrument, to the bottom of the writing with 0.05M HCl.

12.1.5.3 Fill the humidifier, located on the right side of the front panel, to the MAX Fill line with Type I water.

12.1.5.4 Rinse out and fill the dilution water bottle, located on the left side of the instrument, with Type I water.

12.1.5.5 Fill the cooler drain vessel with Type I water by removing the rubber cap on top and pouring water in using a Type I wash bottle. This vessel is located towards the back of the containers on the left side of the instrument.

12.1.5.6 Rinse and fill the autosampler rinse bottle, located behind the autosampler, with Type I water.

12.1.6 Check the waste lines running from the autosampler and instrument for green algal growth and clean out if necessary. These lines lead to a waste container located on the floor behind the instrument. If full, discard waste down the sink drain and place tubes back into the container.

12.1.7 Once everything is setup and ready, click the Start button at the top of the screen. A dialog box will appear asking what the instrument should do at the completion of the analysis. Select the "Shut down instrument" option and click Start.

NOTE: If you are planning to analyze samples the following morning, you can select the "Sleep" option and set the time and date for when you would like the instrument to start up again. This is useful as it will allow the instrument to heat up and stabilize prior to your arrival the next morning without the instrument running all night.

12.2 Calibrating the TOC Analyzer: A TOC/DOC/TC/TIC/DIC calibration must be performed when two consecutive analyses of the ICV or CCV fail, or when a significant hardware change or maintenance event has taken place. Recalibrating in the event of two consecutive failures of either an ICV or CCV can be avoided as long as two consecutive passing ICV's or CCV's is observed prior to generating client data. This is possible when the QC failures can be attributed to operator error or a technical malfunction rather than a drift in detection from the original calibration.

12.2.1 Creating a TC Calibration Sequence and Sample Table:

12.2.1.1 Click on the "Calibration Curve" tab located at the bottom of the left file viewer window. Click the "New" button at the top and a stepwise wizard dialog box will appear.

12.2.1.1.1 **Page 1:** System = TOC-L CPN, User = blank, Comment: blank

12.2.1.1.2 **Page 2:** Select "Normal"

12.2.1.1.3 **Page 3:** Analysis = TC, Default Sample Name and Default Sample ID = TC Cal (Date), Calibration Method = Linear Regression, unselect "Zero Shift", select "Multiple Injections", File Name = TC Cal (Date) saved in 'C:\TOC-L\CalCurves.'

12.2.1.1.4 **Page 4:** Leaving everything else the same, change the CV Max: to 5.00.

12.2.1.1.5 **Page 5:** This is where you will add your calibration standards. Click the "Add" button and add standards in increasing order from 0.0 mg/L to 200.0 mg/L.

12.2.1.1.6 **Page 6:** Make sure the "Use default settings" option is checked and select the "Correlation Coeff. Check" option. For "Failure Action (1st time)" select "Repeat" and for the "Failure Action (2nd

time)" select "Stop." Make sure the "Lower Limit" is set to 0.995 and click "Finish."

NOTE: For reference, a printed copy of the above steps can be found in the Shimadzu binder located near the instrument.

12.2.1.2 Once created, click and drag the calibration from the Calibration Curves file viewer window into the blank sample table.

NOTE: The entire calibration will appear on one line of the sample table. If the analysis is paused or cancelled midway through the calibration, the entire calibration will have to be re-analyzed.

12.2.1.3 Assign the calibration to the method before importing samples by selecting the "Method" tab, right clicking and opening associated method, selecting "NPOC" tab and selecting the new calibration. Click "OK" once new calibration is selected.

12.2.1.4 Make sure the calibration is followed by an ICV/ICB and the entire analysis is bracketed by blank rinses.

12.2.1.4.1 The referenced calibration for all QC samples will have to be changed to the current calibration. Double click on each QC sample individually and in the "TC" tab click the button with three dots to the right of the "Calibration Curve 1" space. Select the current calibration and click "Ok."

NOTE: For analyses requiring two calibrations, the referenced calibrations for each QC sample will have to be changed to the current calibrations being performed.

12.2.1.5 Assign each sample a vial number by clicking the  button in the upper right-hand corner. This will bring up the Vial Setting menu. Assign each blank rinse vial "0" and double click the vial position in the sample rack picture to assign each sample to its respective spot on the sample rack. Once finished click "Ok."

12.2.1.6 With the sample table still open, click the "Save" button in the top left corner and save in 'C:\TOC-L\Data' as the initial calibration workgroup number (ie. WG######).

12.2.2 Creating a TOC/DOC/DOC_LL Calibration Sequence and Sample Table:

12.2.2.1 Click on the "Calibration Curve" tab located at the bottom of the left file viewer window. Click the "New" button at the top and a stepwise wizard dialog box will appear.

12.2.2.1.1 **Page 1:** System = TOC-L CPN, User = blank, Comment: blank
12.2.2.1.2 **Page 2:** Select "Normal"
12.2.2.1.3 **Page 3:** Analysis = NPOC, Default Sample Name and Default Sample ID = TOC-DOC (LL/HL) Cal (Date), Calibration Method = Linear Regression, unselect "Zero Shift", select "Multiple Injections",

File Name = TOC-DOC (LL/HL) Cal (Date) saved in 'C:\TOC-L\CalCurves.'

12.2.2.1.4 **Page 4:** Leaving everything else the same, change the CV Max: to 5.00.

12.2.2.1.5 **Page 5:** This is where you will add your calibration standards. Click the "Add" button and add standards in increasing order from 0.0 mg/L to 25.0 mg/L (for TOC-DOC LL) and from 25.0 mg/L to 200mg/L (for TOC-DOC HL).

12.2.2.1.6 **Page 6:** Make sure the "Use default settings" option is checked and select the "Correlation Coeff. Check" option. For "Failure Action (1st time)" select "Repeat" and for the "Failure Action (2nd time)" select "Continue." Make sure the "Lower Limit" is set to 0.995 and click "Finish."

NOTE: For reference, a printed copy of the above steps can be found in the Shimadzu binder located near the instrument.

12.2.2.2 Once created, click and drag the calibration from the Calibration Curves file viewer window into the blank sample table.

NOTE: The entire calibration will appear on one line of the sample table. If the analysis is paused or cancelled midway through the calibration, the entire calibration will have to be re-analyzed.

12.2.2.3 Assign the calibration to the method before importing samples by selecting the "Method" tab, right clicking and opening associated method, selecting "NPOC" tab and selecting the new calibration. Click "OK" once new calibration is selected.

12.2.2.4 Make sure the calibration is followed by an ICV/ICB and the entire analysis is bracketed by blank rinses.

12.2.2.4.1 The referenced calibration for all QC samples will have to be changed to the current calibration. Double click on each QC sample individually and in the "NPOC" tab click the button with three dots to the right of the "Calibration Curve 1" space. Select the current calibration and click "Ok."

NOTE: For analyses requiring two calibrations, the referenced calibrations for each QC sample will have to be changed to the current calibrations being performed.

12.2.2.5 Assign each sample a vial number by clicking the  button in the upper right-hand corner. This will bring up the Vial Setting menu. Assign each blank rinse vial "0." Double click the first vial position and enter 1. Click and drag the bottom right of the box to assign positions to the rest of the sample table. Once finished, click "Ok."

12.2.2.6 With the sample table still open, click the "Save" button in the top left corner and save in 'C:\TOC-L\Data' as the initial calibration workgroup number (ie. WG######).

12.2.3 Creating a TIC/DIC Calibration Sequence and Sample Table:

12.2.3.1 Click on the "Calibration Curve" tab located at the bottom of the left file viewer window. Click the "New" button at the top and a stepwise wizard dialog box will appear.

12.2.3.1.1 **Page 1:** System = TOC-L CPN, User = blank, Comment: blank

12.2.3.1.2 **Page 2:** Select "Normal"

12.2.3.1.3 **Page 3:** Analysis = IC, Default Sample Name and Default Sample ID = TIC-DIC Cal (Date), Calibration Method = Linear Regression, unselect "Zero Shift", unselect "Multiple Injections", File Name = TIC-DIC Cal (Date) saved in 'C:\TOC-L\CalCurves.'

12.2.3.1.4 **Page 4:** Leaving everything else the same, change the CV Max: to 5.00.

12.2.3.1.5 **Page 5:** This is where you will add your calibration standards. Click the "Add" button and add standards in increasing order from 0.0 mg/L to 25.0 mg/L (for TIC-DIC LL) and from 25.0 mg/L to 200mg/L (for TIC-DIC HL).

12.2.3.1.6 **Page 6:** Make sure the "Use default settings" option is checked and select the "Correlation Coeff. Check" option. For "Failure Action (1st time)" select "Repeat" and for the "Failure Action (2nd time)" select "Continue." Make sure the "Lower Limit" is set to 0.995 and click "Finish."

NOTE: For reference, a printed copy of the above steps can be found in the Shimadzu binder located near the instrument.

12.2.3.2 Once created, click and drag the calibration from the Calibration Curves file viewer window into the blank sample table.

NOTE: The entire calibration will appear on one line of the sample table. If the analysis is paused or cancelled midway through the calibration, the entire calibration will have to be re-analyzed.

12.2.3.3 Make sure the calibration is followed by an ICV/ICB and the entire analysis is bracketed by blank rinses.

12.2.3.3.1 The referenced calibration for all QC samples will have to be changed to the current calibration. Double click on each QC sample individually and in the "IC" tab click the button with three dots to the right of the "Calibration Curve 1" space. Select the current calibration and click "Ok."

NOTE: For analyses requiring two calibrations, the referenced calibrations for each QC sample will have to be changed to the current calibrations being performed.

12.2.3.4 Assign each sample a vial number by clicking the  button in the upper right-hand corner. This will bring up the Vial Setting menu. Assign each blank rinse vial "0." Double click the first vial position and enter 1. Click and drag the bottom right of the box to assign positions to the rest of the sample table. Once finished, click "Ok."

12.2.3.5 With the sample table still open, click the "Save" button in the top left corner and save in 'C:\TOC-L\Data' as the initial calibration workgroup number (ie. WG######).

12.3 Creating a Sample Table

12.3.1 Create a workgroup in SAGE.

12.3.2 Print a copy of the current standards and reagents form to attach to the workgroup.

12.3.3 Open up the TOC-L Sample Table Editor by double clicking on the desktop icon. Click on the "Schedule" tab located at the bottom of the left file viewer window. Click "New," make sure System = TOC-L CPN and Table Type = Normal, and click "Ok."

12.3.4 Go to "File" and click on "Import Schedule File." This will bring up the a Open file viewer window. The created workgroup can be found in U:\input\toc3. Double click on the workgroup and verify everything has uploaded into the schedule file correctly.

12.3.5 Click on the "Sample Table" tab located at the bottom of the left file viewer window. Click "New," make make sure System = TOC-L CPN and Table Type = Normal, and click "Ok."

12.3.6 Copy the samples from the schedule file into the sample table by completely selecting every row, right clicking in the highlighted area and selecting "Copy." Go to the newly created sample table, select the first row by clicking on the far left "1," right click in the highlighted row and select "Paste." Ensure all QC samples are in the correct places and that the entire workgroup is bracketed by the appropriate blank rinse samples.

12.3.7 Assign each sample a vial number by clicking the  button in the upper right-hand corner. This will bring up the Vial Setting menu. Assign each blank rinse vial "0" and double click the vial position in the sample rack picture to assign each sample to its respective spot on the sample rack. Once finished click "Ok."

12.3.8 With the sample table still open, click the "Save" button in the top left corner and save in 'C:\TOC-L\Data' as the workgroup number (ie. WG######). You can now close the schedule file. When prompted to save changes to the schedule file click "No."

12.3.9 Follow section §12.1.4 to §12.1.7 to start analysis.

12.4 Exporting and Uploading Data to SAGE

12.4.1 Once analysis is complete, check QC to ensure everything is coming out within the specified ranges.

12.4.2 Go to "File," "Ascii Export" and select "Detail(Include injection data)." In the Save as window, save the file as the workgroup number in the TOC3 folder of Waitloads (U:\Waitloads\TOC3). Any modifications can be done while the file is at waitload. Once completed, click and drag the workgroup file from the TOC3 folder in Waitloads to the TOC3 folder in Autoload (U:\Autoload\TOC3).

NOTE: The parameters for a detailed Ascii export should already be specified (refer to the instrument binder located near the instrument for settings of the detailed export).

NOTE: Any changes made to upload files must be documented with the workgroup.

12.4.3 Review the workgroup in the SAGE AREV screen, completing a data review checklist. Attach all raw data and supporting documentation and submit the data package to the department supervisor for SREV.

12.5 Procedure for Generating Paperless Documents

12.5.1 The raw data generated from the Shimadzu TOC-L is not printed, like many other methods, but is instead generated as a PDF file that is later linked the to workgroup in SAGE at review.

12.5.2 Switch the default printer on the TOC3 computer to PDFillPDF & Image Writer. Now anytime a page is printed the printer will create a PDF instead of a printed page. The computer hooked up to the TOC3 instrument should have the PDFillPDF & Image Writer as the default printer. Change this in printer settings if it is not the case. In the "PDF Files" folder on the desktop, create a folder with the workgroup numer as the name. All associated PDF files for the workgroup being worked on will be saved in this folder.

12.5.3 Once the workgroup has completed its run, click the big "Print" icon located at the top. Select "Sample Table". When the Print dialog box pops up make sure PDFillPDF & Image Writer is selected and click "OK". Save as "Sequence.PDF" in the workgroup folder found in "PDF Files" on the desktop. For R-groups, save the sample table file as "SequenceR.PDF".

12.5.4 Highlight all samples that are associated with the workgroup, including all QC samples and excluding samples that are part of separate workgroups. Click the big "Print" icon and select "Sample Report – Highlighted". When the print dialog box pops up make sure PDFillPDF & Image Writer is selected and click "OK". Save as "Data.PDF" in the workgroup folder found in "PDF Files" on the desktop. For R-groups, save the data file as "DataR.PDF".

12.5.5 Merge all of the above PDF files by using the PDFillPDFTools icon located on the computer's desktop. Double click the icon, select "Merge", "Add PDF File" then move to the appropriate WGnumber directory and select all PDF files for merging, then click "Open". The display will list all PDF files to merge. The files can now be arranged by clicking on the file and using the "Move Up", "Move Down", "Remove File" tabs in the software. The final file order should be Sequence.PDF, Data.PDF, SequenceR.PDF, DataR.PDF and so on. Then click "Save As", move to the appropriate WGnumber directory and save the merged file as WGnumber.PDF. A pdf file will automatically be generated and displayed. Click on the "X" to close the pdf file.

12.5.6 Double click on the PDFill PDF Editor icon on the computer's desktop. Select "File" and then select "Open Project to resume editing". Move to the appropriate directory, select "All Files" in the Files of type" dropdown menu, and select the appropriate WGnumber.PDF file to open.

12.5.6.1 To insert a page, first navigate to the original unmodified sample page, then select "Document", "Insert Pages", select the modified sample PDF page to be inserted, and under "Position in Current Document" select "Page X". This will insert the new page after the current page.

12.5.6.2 To add comments and initials, select “Insert”, “Multiple Line Text”, and then move curor to outline area for new text and type comments along with analyst’s initials and date.

12.5.6.3 Extra or unwanted pages can be deleted by navigating to the unwanted page(s) and selecting “Document”, and “Delete Current Page”.

12.5.7 To save the file as a PDF, sleect the blue “PDF” button, “Save PDF As”, WGnumber.PDF. The original PDF file can now be overwritten. To close out of the editor, click on the “X”. The .pfl file does not need to be saved.

12.5.8 Copy the WGnumber.PDF file to the P:\PDFMerge\TOC3 directory for SREV approval.

12.6 Shutting down the TOC instrument

NOTE: NEVER flip the switch, located on the right side of the instrument, off while the instrument is running as it will turn off the fan that keeps the valve compartment from getting too hot and subsequently melting the valve head (very expensive to replace!).

12.6.1 Once analysis is complete, the instrument should automatically shut down if both the “Shut down instrument” or “Sleep” options had been selected at the start of the analysis.

12.6.2 If the instrument needs to be manually shut down, click the “Shutdown” button in the upper right-hand corner next to the “Monitor” button.

12.6.3 Select the “Shut down instrument” option and click Ok.

12.6.4 Turn off the dry air cylinder located behind the instrument and empty sample the sample rack.

12.7 **TROUBLESHOOTING/MAINTENANCE**

Preventative maintenance and troubleshooting are necessary to ensure the instrument will run smoothly and efficiently. For information on daily and periodic maintenance, consult chapter 7 of the User’s Manual starting on page 271. If any difficulties arise (failing QC, inconsistent flow rate, abnormal peak shape, etc.) verify the following and/or consult the Operator’s Manual. **Document all maintenance, troubleshooting, repairs and support calls in the instrument logbook.**

- Is the compressed air turned on? Is the gas tank pressure greater than 500psi?
- Are there any gas leaks?
- If there is no instrument response when starting a run, check that the autosampler is sampling properly.
- Is the Halide scrubber discolored? Cracked? If so, replace.
- Does the catalyst in the combustion tube need replacing? If so, consult the User Manual for instructions.
- Is the combustion tube cracked? If so, replace.
- If blanks are failing check that the rinse receptacle is full.
- Check for any clogs in the tubing.
- Replace tubing if flat/dirty
- If QC continues to fail after verifying the above, try recalibrating the instrument.
- Consult the User Manual for scheduled and unscheduled preventative maintenance.

12.7.1 Log on to Shimadzu TOC-L Virtual Advisor with any questions. The Virtual Advisor can look at generated data in order to help solve any issues you may be having with the system.

Username: ACZ Labs
Password: Downhill

12.7.2 Contact technical support at Shimadzu if problems persist (877-698-7923).

13 QUALITY CONTROL

12.1 Analyze one ICV and ICB sample immediately after any calibration.
12.2 Analyze a Reagent Water Blank (Type 1 water) prior to the calibration.
12.3 Analyze one CCV and CCB every 10 samples and at the end of each workgroup.
12.4 Analyze one duplicate (DUP) and one analytical spike (AS) for every 10 or less client samples.
12.5 Analyze one LFB for every 20 or less client samples.
12.6 Analyze one PQV immediately after initial ICB/ CCB in all continuing calibration analyses.

Table 12.1 Required QC, Acceptance Limits, and Corrective Actions

Standard	Frequency	Limits	Corrective Action
Calibration	As needed	$r^2 > 0.995$	Recalibrate. Remake standards if necessary.
ICV	Immediately after calibration	90-110%	1 retest OK then recalibrate. Redo samples associated with failed ICV.
ICB	Immediately after ICV	± 3[MDL]	1 retest OK then recalibrate. Redo samples associated with a failed ICB. Some samples may be qualified if large concentration – see B flags in extended qualifier report
CCV	Every 10 samples and at the end of each run. Beginning of runs using prior calibration.	90-110%	Recalibrate if necessary. Rerun/Redo associated samples. Client samples <MDL can be accepted and qualified if CCV fails high.
CCB	Following each CCV	± 3[MDL]	REDO associated samples. Client samples <MDL can be accepted and qualified if CCB fails high.
PQV	Immediately after initial ICB or CCB	70-130%	1 re-test OK, then reanalyze samples. Recalibrate if necessary.
LFB	1 every 20 or less client samples	90-110%	1 re-test OK, then REDO all associated samples. May need to recalibrate. Client samples <MDL can be accepted and qualified if LFB fails high.
AS	1 every 10 or less client samples	90-110%	If instrument QC and LFB passes, qualify associated samples.
DUP	1 every 10 or less client samples	RPD ≤ 20%	1 retest OK, then REDO associated samples if [sx] ≥ 10X MDL. Qualify samples < 10X MDL.

13.0 DATA CALCULATIONS, DATA REPORTING & ARCHIVING

13.1 Calibration standards are analyzed from lowest concentration to highest concentration. The Skalar Formacs TOC Analyzer uses a second order non-linear calibration function with equal weighting.

Note: Blank subtraction as prescribed by SM5310B, §5 is accomplished by including a zero point calibration standard consisting of a reagent water blank. The resulting intercept influences calculated sample results identically to subtracting the reagent water blank from standards & samples. There is no procedural blank as samples do not undergo any pre-treatment or preparation.

13.1.1 Quadratic Calibration Regression Equation

$y=ax^2+bx+c$

where: y=instrument response (A_x)
x= concentration (C_x)
c=intercept

$$x^2 \text{ Coefficient (a)} = \frac{(Sx^2y * Sxx) - (Sxy * Sxx^2)}{(Sxx * Sx^2x^2) - (Sxx^2)^2}$$

$$x \text{ Coefficient (b)} = \frac{(Sxy * Sx^2x^2) - (Sx^2y * Sxx^2)}{(Sxx * Sx^2x^2) - (Sxx^2)^2}$$

$$Sxy = \left(\sum_i^n w_i x_i y_i\right) - \frac{\left(\sum_i^n w_i x_i \times \sum_i^n w_i y_i\right)}{n}$$

$$Sx^2y = \left(\sum_i^n w_i x_i^2 y_i\right) - \frac{\left(\sum_i^n w_i x_i^2 \times \sum_i^n w_i y_i\right)}{n}$$

$$Sxx = \left(\sum_i^n w_i x_i^2\right) - \frac{\left(\sum_i^n w_i x_i^2\right)^2}{n}$$

$$Sx^2x^2 = \left(\sum_i^n w_i x_i^4\right) - \frac{\left(\sum_i^n w_i x_i^2\right)^2}{n}$$

$$Sxx^2 = \left(\sum_i^n w_i x_i^3\right) - \frac{\left(\sum_i^n w_i x_i \times \sum_i^n w_i x_i^2\right)}{n}$$

where: w_i = weighting factor for the i^{th} calibration standard (=1 for all standards)
x_i=expected concentration for the i^{th} calibration standard
y_i=instrument response for the i^{th} calibration standard
n= response factor count
i→n = calibration points in order of increasing concentration

$$\text{Intercept (c)} = \frac{\sum_i^n y_i}{n} - b\left(\frac{\sum_i^n x_i}{n}\right) - a\left(\frac{\sum_i^n x_i^2}{n}\right)$$

$$\text{Concentration (x)} = \frac{\sqrt{(b^2 - 4a(c - y_i))} - b}{2a}$$

Coefficient of Determination (R^2) = $$\frac{\sum_i^n (y_i - \bar{y})^2 - \sum_i^n (y_i - Y_i)^2}{\sum_i^n (y_i - \bar{y})^2}$$

where: y_i= observed instrument response for the i^{th} calibration standard (A_x)
$\bar{y}$= mean observed instrument response from initial calibration
Y_i= Calculated (predicted) instrument response for the i^{th} calibration standard, calculated from $Y_i=ax^2+bx+c$
n= response factor counts
i→n = calibration points in order of increasing concentration

NOTE: FRMQA049 may be used to calculate slope, intercept, calibration coefficient and concentrations. Use the worksheet titled "ESTD EW." See Appendix B for example.

13.2 The method detection limit (MDL) is 1.0 mg/L and the practical quantitation limit (PQL) is 5.0 mg/L. For DOC_LL product, the MDL is 0.5 mg/L and the PQL is 2.5 mg/L.

13.3 All sample results are reported in mg/L.

13.4 Relative Percent Difference (RPD) is determined using the following equation:

RPD = {(S – D) / [(S + D) / 2] } x 100

Where:
S = Sample Value
D = Duplicate Value

13.5 Percent Recovery (%R) is determined using the following equation:

% R = [(measured value) / (true value)] * 100

13.6 Refer to SOPAD044 for details of instrument data backup and archiving.

13.7 Retrieval of Archived Data Files

13.7.1 Go to \\saloon\instrument\TOC2\Program Files\HTAccess\Operators\Wetchem\Analysis.

13.7.2 Save the desired archived folder to the Instrument PC in C:\Program Files\HT Access\Operators\Wetchem\Analysis.

13.7.3 In HT Access go to **Analysis, Edit** and select the desired analysis from C:\Program Files\HT Access\Operators\Wetchem\Analysis.

14.0 METHOD PERFORMANCE/DETECTION LIMITS

14.1 **Method Detection Limit:** An MDL study must be performed during initial method development and whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate the MDL be re-determined.

14.1.1 Spike and analyze at least eight (8) aliquots of reagent blank at 1-5x MDL (at the PQL is recommended) over the course of three separate days. Additionally, analyze eight (8) aliquots of reagent blank (with no analyte spike added) according to the method over the

course of three separate days.The analysis must include at least a passing calibration and ICV/ICB. Enter the data into form FRMAD031. Print the form, sign it and attach all raw data and supporting documentation. Submit the package to the department supervisor for review. Refer to SOPAD001 for additional information.

14.2 An MDL verification is required as part of method development and instrument qualification and on an annual basis thereafter. Prepare a solution fortified with TOC at 2-3X [MDL] and process as a routine sample. Enter the data into form FRMAD031. Print the form, sign it and attach all raw data and supporting documentation. Submit the package to the department supervisor for review. Refer to SOPAD001 for additional information.

14.3 **Quarterly QA MDL Samples:** Each quarter, two QA samples will be logged in for each analysis performed by each instrument. Prepare each sample by spiking reagent blank at the PQL and analyzing according to the method. These samples must be analyzed in separate batches however, they can be pulled into workgroups containing other client samples and passed through SAGE as a normal workgroup. Refer to SOPAD001 for additional information.

14.4 **Demonstration of Capability (DOC):** A successful Initial DOC must be completed and approved by the QA/QC department for each analyst prior to independent generation of client data. A Continuing DOC is required annually for each analyst who routinely performs the method. Refer to §13.6 of SOPAD001 for more information on CDOC qualifications.

14.4.2 Create a workgroup in SAGE and prepare and analyze four individual aliquots of the ICV. Include a passing calibration, ICV/ICB, CCV/CCB. Enter all data in form FRMAD023. Print the completed form, sign it and attach all raw data and supporting documentation. Submit the data package to the department supervisor for review. Refer to SOPAD001 for additional information.

15.0 DOCUMENTATION

15.1 Record the pertinent information for all prepared standards and reagents in SAGE. Include analyst's initials, prep date, expiration date, and the PCN or SCN of any stock standard or reagent used.

15.2 Record the appropriate information in the TOC logbook, noting any maintenance or repairs performed or any problems encountered.

15.3 Label each standard or reagent prepared in §8.0 with the following information:

- standard name
- SCN (or other unique ID)
- preparer's initials
- expiration date
- prep date

15.4 Make sure the following information is included on the Workgroup:

- Printouts of raw data
- Dilution factors
- Analyst's initials
- Any remarks about analysis or samples
- Completed data review checklist form
- Current standard/reagent form

- ICAL WG#
- *ANY OTHER PERTINENT INFORMATION*

15.5 The SOP Revision Form (FRMQA030) must be filled out and approved by QA/QC before changes are made to this procedure.

15.6 Correct all errors according to ACZ protocol (single line cross-out, initialed & dated).

16.0 WASTE MANAGEMENT/POLLUTION PREVENTION

16.1 Waste can be disposed of down the drain with running water.

16.2 Refer to ACZ's Waste Management Plan for appropriate disposal details for this method.

17.0 DEFINITIONS

17.1 LFB- Laboratory Fortified Blank—An aliquot of reagent water to which a known quantity of the method analytes are added. The LFB is analyzed exactly like a sample, and determines whether the methodology is in control, and whether the laboratory is capable of making accurate measurements.

17.2 ICV- Initial Calibration Verification—A solution of method analytes of known concentrations and obtained from a source external to the laboratory and different from the source used to prepare the calibration standards. It is used to determine the validity of the instrument calibration.

17.3 CCV- Continued Calibration Verification—A solution of method analytes of known concentrations. It is analyzed at regular intervals throughout an analysis and confirms that the instrument calibration is still valid.

17.4 ICB- Initial Calibration Blank—An aliquot of reagent water analyzed following initial calibration of the instrument to confirm no background contamination is present in the calibration blank.

17.5 CCB- Continued Calibration Blank—An aliquot of reagent water analyzed at regular intervals throughout an analysis to detect baseline drift in the calibration of the instrument.

17.6 Reagent Water Blank— An aliquot of reagent water analyzed immediately prior to the calibration to confirm that background levels of TC and TIC in the reagent water are negligible in relation to the detection limits of the instrument.

17.7 AS- Analytical Spike—An aliquot of an environmental sample to which a known quantity of method analyte(s) are added. The AS is analyzed exactly like a sample, and determines whether the sample matrix contributes bias to the analytical results.

17.8 DUP- Sample Duplicate—Two aliquots of a sample are analyzed in the same workgroup, under identical circumstances. Analysis of a duplicate sample indicates the precision associated with the laboratory procedure.

17.9 RPD- Relative Percent Difference--The difference between two replicates divided by the average of the two replicates and then multiplied by 100.

17.10 MDL- Method Detection Limit—The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

17.11 PQL-Practical Quantitation Limit— The lowest level that can be reliably achieved within method specified limits during routine operations.

17.12 PQV-Practical Quantitation Verification— An aliquot of reagent water in to which the method analytes are added at the quantitation level. The PQV is analyzed exactly like a sample, and determines whether the methodology is in control, and whether the laboratory is capable of making accurate measurements at the quantitation level.

18.0 TABLES & DIAGRAMS

Table 6.1: Hold Times
Table 8.1: TC Working Calibration Standards
Table 8.2: DOC Low Level Working Calibration Standards
Table 8.3: TIC Calibration Standards
Table 12.1: Required QC, Frequency, Acceptance Limits, Corrective Action

19.0 CORRECTIVE ACTION

19.1 For QC samples that do not meet the method acceptance criteria, refer to Table §12.1. For retests that will occur past the method hold time, check first with the department supervisor to determine if the reanalysis should be conducted.

19.2 For any SOP/method deviation fill out section 1 of a corrective action report (FRMQA001). If necessary, the department supervisor and/or project manager may provide additional information in the appropriate sections; however, QA/QC does not need to close a minor corrective action. Attach a copy of the minor corrective action report to all workgroups affected. A minor corrective action is for documentation purposes – any SOP or method deviation may be noted on the data review checklist or on the workgroup bench sheet in lieu of using FRMQA001.

19.3 For any system failure a major corrective must be opened and the problem investigated. Consult the QA department to open a major corrective action. The corrective action will be assigned a unique tracking number by the QA/QC Officer (or designee) and will be closed by the QA/QC Officer (or designee) once the failure has been resolved. Use FRMQA001.