STANDARD OPERATING PROCEDURE

Water TOC Analysis Using the Shimadzu TOC-VCSN and ASI-V Autosampler

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KEY WORDS

TOC-V, total carbon, inorganic carbon, oxygen, NPOC, HCl, calibration curve

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1.0 INTRODUCTION

1.1. Purpose

The Shimadzu Total Organic Carbon (TOC) Analyzer in combination with the ASI-V automated sampler is used to measure TOC in water samples. The amount of TOC in a water sample can be an indicator of the amount of pollution in a sample.

2.0 MATERIALS

2.1 TOC-V CSH/CSN component (herein after referred to as TOC-V)

2.2 ASI-V autosampler

2.3 2M HCl

2.4 DI water

2.5 Low TOC water (certified < 100 ppb TOC)

2.6 40 ml vials

2.7 Parafilm®M (cut into 1 inch squares)

2.8 Calibration standard(s)

2.9 Alconox® or Liquinox®

2.10 Potassium hydrogen phthalate (KHP [$KHC_8H_4O_4$])

3.0 PROCEDURES

3.1 Equipment Checks

3.1.1 Open the front door of the TOC-V to check the DRAIN VESSEL volume (back of machine). If needed, fill with DI water to the level indicated by the drain discharge tube on the side of the container. Use DI wash bottle to fill the container through the slits in the top of the black cap *in situ*. Do not remove the cap or unclip the bottle from its current location.

3.1.2 With the door open, check the HUMIDIFIER water container level in the front of the TOC-V; fill if needed. Add low TOC water using a

wash bottle to fill the container to the 'Hi' level mark. Squirt water through the water supply port opening in the top of the container. Close the door of the TOC-V.

3.1.3 Fill the RINSE BOTTLE with DI water to the 2000 ml mark (outside the ASI-V).

3.1.4 Fill the DILUTION WATER BOTTLE (located between the ASI-V and TOC-V) with low TOC water. Verify that the intake tubing nearly reaches to the bottom.

3.1.5 Check the ACID BOTTLE located between ASI-V and TOC-V. Ensure acid tube is near the bottom of the acid bottle and that the bottle is at least 50% full. If not, fill with 2M HCl. Recap bottle at the end of the day (or seal with Parafilm®M). If making up 2M HCl, always wear gloves and safety glasses with side shields (or goggles) and prepare under the hood. Always add concentrated HCl to the low TOC water (acid to water). If you spill some acid on your skin, IMMEDIATELY wash it off with copious amounts of running cold water and seek medical attention.

3.1.6 Monitor the PRINTER PAPER by removing the cover to the paper roll. Replace the paper roll if necessary (to run a full tray of 68 vials will take approximately 10 feet of printer paper).

Figure 1. TOC-V machine

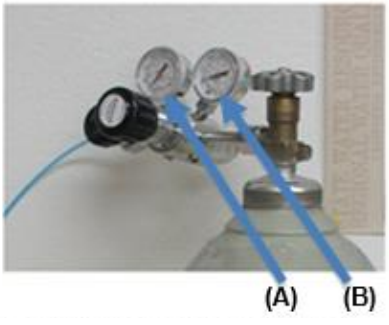

Figure 2. Oxygen tank; gas pressure (A) and tank volume (B)

3.2 Turning on the TOC-V

3.2.1 Press the “Power” button located in the lower right hand corner to power on the TOC-V (Figure 1). It will take 20 to 30 min to reach the operating temperature. The TOC-V is at the correct operating temperature when the green light below the READY signage on the keypad is steady green (not flashing).

3.2.2 Immediately after turning the machine on, supply oxygen by turning the knob on the oxygen tank counter-clockwise. Use the two gauges on the top of the tank to regulate the amount of oxygen available to the TOC-V. The right gauge measures the amount of O_2 gas in the tank whereas the left gauge regulates the pressure of the gas entering the TOC-V (Figure 2). The needle of the left gauge should be between 44-87 psi; 60 psi is the optimum operating pressure. If the needle of the right gauge is below 400 psi, there may not be enough O_2 to properly conduct an analysis and the oxygen tank should be replaced.

3.2.3 Open the front door of the machine and adjust the two carrier gas regulators (Figure 3). The round CARRIER GAS PRESSURE REGULATOR is the located on the left hand side of the TOC-V. Use the knob below the gauge to adjust the carrier gas pressure to 200 KPa. The long rectangular CARRIER GAS FLOW METER is located on the right hand side. Adjust the carrier flow using the carrier gas knob to the left of the gauge. The bottom of the ball should be level to the 150 mL/min increment in the scale. Close door.

3.3 Preparing Samples for Analysis

3.3.1 As the TOC-V comes up to operating temperature, prepare the water samples. Using a Sharpie®, label the vials according to your protocol. Fill the glass vials with approximately 35 mL of water with the meniscus just below the shoulders of the vial and cap or cover with a 1-inch square of parafilm®M. Do not let the parafilm®M hang below the threads on the vial.

Figure 3. Setting the carrier gas pressure and flow.

3.3.2 Set vials into the sampling rack. To ensure the correct QA/QC for the analysis it is recommended that for every 20 vials analyzed, include one sample of each: 1) low TOC water; 2) lab duplicate; and 3) concentration standard. Repeat this pattern for every 20 samples. Check with project lead to confirm. Set rack into the ASI-V Autosampler.

3.3.3 No visible sediment or organic matter should be included in the water samples as this could clog the uptake needle.

3.4 Programming Conditions

3.4.1 In the INITIAL DISPLAY screen, press the F4 key on the keypad to access the CONDITIONS screen. Set the parameters for conducting a water TOC analysis (Figure 4). To change any of the parameters use the arrow keys to scroll down and highlight the selected measurement. Press the SELECT key and scroll through the options until the desired setting is highlighted. Press the ENTER key to change the parameter.

3.4.2 Next, press the F4 key again to access the MEASUREMENT CONDITIONS screen. Ensure that the parameters are set correctly (Figure 5). Use the arrow keys to change any parameters in the same manner used in 3.4.1.

3.4.3 Press the F1 (RETURN) key to return to the Initial Display screen.

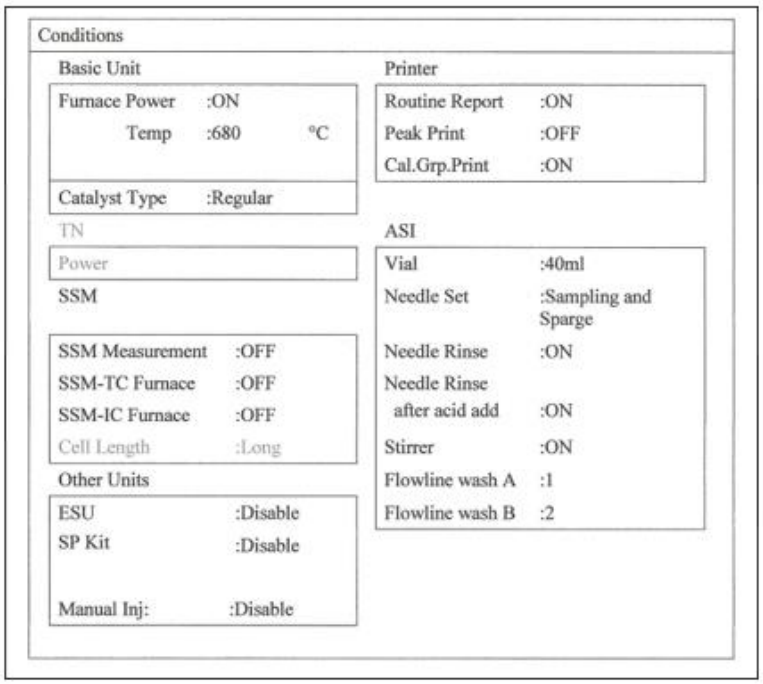

Figure 4. Parameters on the Conditions screen (F4) for conducting a TOC water analysis.

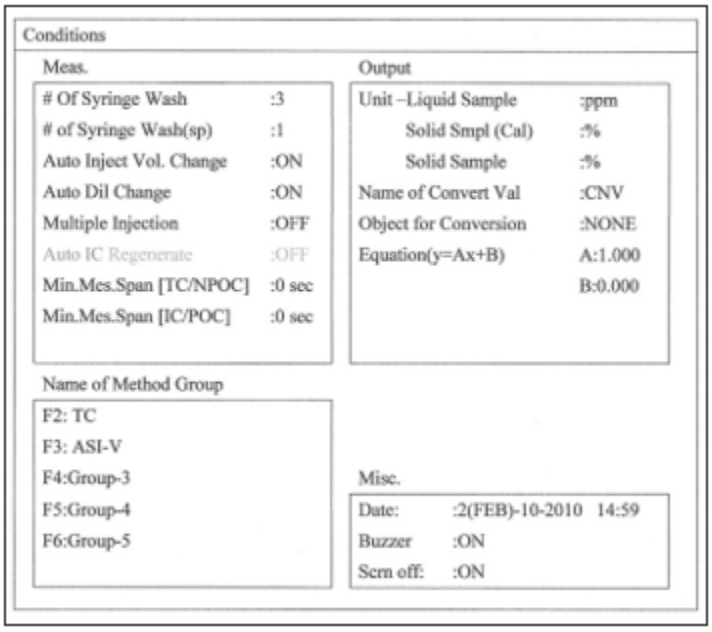

Figure 5. Default parameters on the Measurement Conditions screen (F4, then F4 again) for conducting a TOC water analysis.

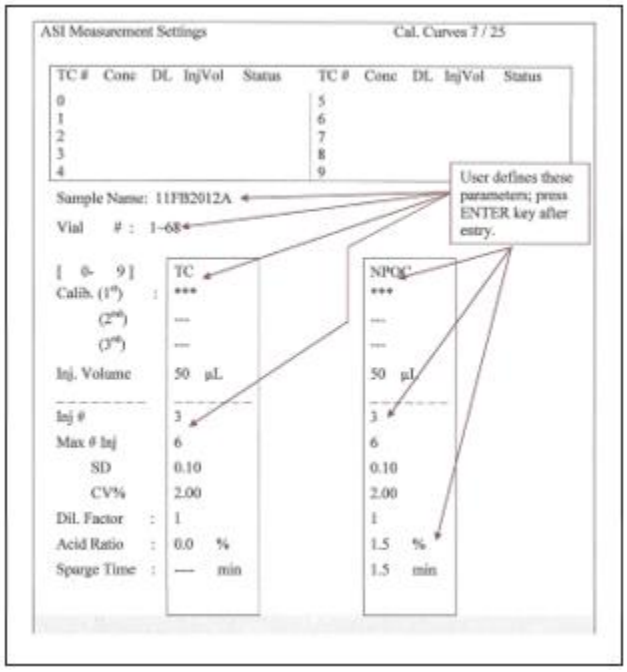

Figure 6. Recommended settings on the ASI Measuring Setting screen. Most of the parameters are user defined.

3.5 Conducting a TOC water analysis using the ASI-V autosampler

3.5.1 In the Initial Display screen, press the ASI key to select the ASI SETTING screen.

3.5.2 Move the cursor to an empty row in the ASI Schedule Setting screen. Press the MEASURE SAMPLE key and the ASI Measurement Setting screen will appear.

3.5.3 In the ASI Measurement Setting screen, enter a unique sample name and the total number vials that will be processed (1 ~ n; n = total number of vials). Select the SHIFT key to toggle between numbers/alphabet (Figure 6).

3.5.4 Press the F5 key to select NPOC. Most analyses will be acidified with 2M HCl to convert inorganic carbon into CO_2, then purged with oxygen to remove the CO_2. Hence most analyses will be processed using Non Purgeable Organic Carbon (NPOC) method. Using the Total Carbon (TC) method instead of the NPOC method will analyze CO_2 as part of the TC.

3.5.5 Set other parameters in ASI Measurement Setting screen, including calibration curve and number of injections (Figure 6). More than one calibration curve may be selected. Only select acid ratio and sparge time if samples have not already been acidified with HCl.

3.5.6 Press the NEXT key to complete the setup. The schedule has been stored and the display will return to the ASI Schedule Settings screen. The sample name and analysis mode of the schedule will be displayed with the message “Not Measured”.

3.5.7 Using arrow keys highlight the desired row for analysis.

3.5.8 Press the NEXT key

3.5.9 Select which option is to be performed when analysis is completed:

1) POWER OFF [F3], powers off 30 minutes after completion and carrier gas flow (oxygen) is halted; 2) SLEEP [F4], temporarily stopped, and will start again at a specified time and date; or 3) WAITING [F5], will remain on, ready to run another analysis. For

most analyses, including ones to be conducted over night, select POWER OFF [F3].

3.5.10 Ensure that the vials are in the sample rack in the correct order.

3.5.11 Press the flashing START key to begin the analysis.

3.5.12 If POWER OFF is not selected, return to ASI Settings Screen. Highlight your analysis (message should display “Measure End”) and select Delete (F4), Edit (F5), or Reset Schedule (F6). Press F6 (Yes) to complete.

3.5.13 Deselect the ASI key to return to the Initial Display screen.

3.6 Creating a Calibration Curve using the ASI-V

3.6.1 While in the Initial Display screen press the ASI key.

3.6.2 Move the cursor to an empty row in the ASI Schedule Setting screen.

3.6.3 Press the CAL key; this will display the ASI Calibration Settings screen (Figure 7). A list of previously generated calibration curves will appear at the top of the screen.

3.6.4 Press the F2 (TC) key to create a new calibration curve.

3.6.5 Enter the user defined parameters (press ENTER after each entry):

3.6.5.1 calibration curve number not previously used

3.6.5.2 vial number

3.6.5.3 calibration standard concentration(s)

3.6.5.4 number of injections

3.6.5.5 maximum number of injections

3.6.5.6 injection volume.

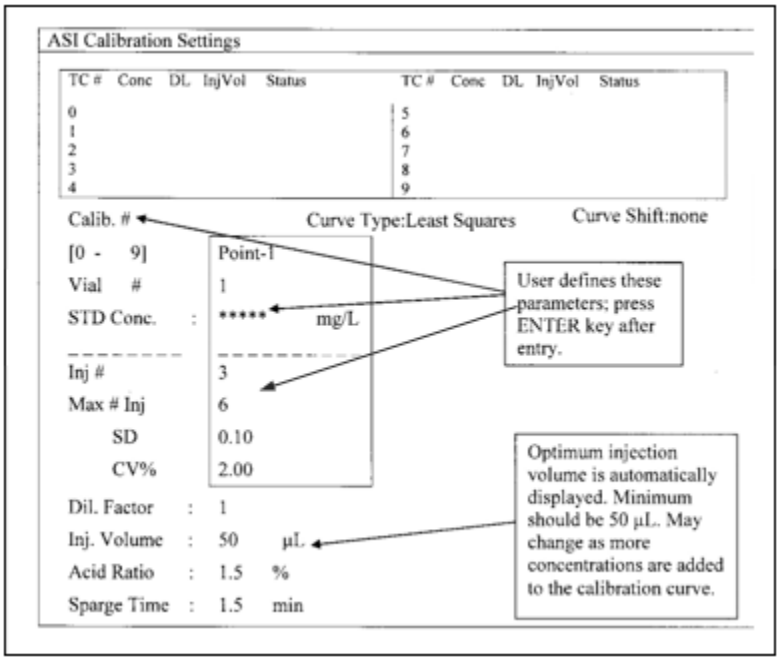

Figure 7. ASI Calibration Setting screen.

3.6.6 Additional concentration points may be added in the same manner once the parameters box for the first calibration point has been completed. With “Point-1” highlighted, press the right facing arrow key to display the parameters box for the second concentration point.

3.6.7 If more than five concentration points are required use the arrow keys to toggle between parameter boxes. To delete a point, highlight the parameters box for that point and press the F6 [DELETE] key.

3.6.8 When all desired points are added to the curve, press the NEXT key. This returns the user to the ASI Schedule Setting.

3.6.9 Check that all of the vials are in their correct position in the sample rack. Highlight the row for analysis. Once verified, press the NEXT key to run the analysis.

3.6.10 When instructed, press the flashing START key. A calibration curve will be generated at the completion of the analysis. The curve will be stored and may be used in future TOC sample analyses.

3.6.11 When the calibration curve is completed, return to the ASI Schedule Settings Screen. Highlight your analysis (message should display “Measure End”). Select Delete (F4), Edit (F5), or Reset Schedule (F6).

3.6.12 Press F6 (Yes) to complete selection.

3.6.13 Deselect the ASI key to return to the Initial Display screen.

3.7 Housekeeping

3.7.1 Cleanup: remove all vials from sample rack, erase labeling, and wash vials with Alconox® or Liquinox® and triple rinse with DI water.

3.7.2 Deleting data. Data is stored internally in the TOC machine. Delete your data after confirming the printout of the data is complete.

3.7.2.1 In the Initial Display, press the F6 [Data Report] key.

3.7.2.2 The Data Report – Measurement Log screen is displayed.

3.7.2.3 Press the F4 [Clear All] key.

3.7.2.4 Press the F6 [Yes] key to delete data.

3.7.2.5 Press F1 key to return to the Initial Display.

3.7.3 Manual shutdown. Prior to turning off the TOC-V manually, follow the sequence below to ensure the furnace cools without damage.

3.7.3.1 Press the Press F1 [STANDBY OPTION] key in the Initial Display screen.

3.7.3.2 Press F5 [POWER OFF], then F6 [Execute]. After the message “Do you want to stop this process?” press the F6 [YES] key to shut down the machine. You will get the message “It is a termination”.

3.7.3.3 It will take the TOC-V about 30–40 minutes to cool. DO NOT turn off the oxygen until the TOC-V has completely

cooled and the furnace has shut down (the green light on the Power Button is off).

3.7.4 Calibration standards and stock solutions. Standard solutions can be purchased or prepared from potassium hydrogen phthalate (KHP [$KHC_8H_4O_4$]). Directions to make a 1000 mg carbon/L (1000 ppm carbon) stock solution:

3.7.4.1 Dry KHP at 105-120°C for 1 hr, then cool to room temperature in a desiccator.

3.7.4.2 Weigh out 1.0625 g KHP and add to a 500 ml volumetric flask.

3.7.4.3 Bring volumetric flask up to volume with low TOC water; ensure that the KHP is completely dissolved.

3.7.4.4 To make up 100 mL of a 10 ppm standard, add 1 ml of the 1000 ppm stock solution to a 100 mL volumetric flask. Add 99 ml of low TOC water to bring up to volume.

3.7.4.5 Confirm concentration with known standard.

3.7.4.6 Store solution in refrigerator; discard after 2-3 weeks.

4.0 CALCULATIONS

4.1 TOC units can be expressed in %, mg/L, µ/L, and ppm. For TOC water, ppm units are recommended. The TOC machine will print out the result of TC or NPOC, the mean (MN), the standard deviation (SD) and the coefficient of variation (CV). No calculations are necessary by the user.

4.2 Accuracy and precision calculations. Accuracy can be measured against the results of a known TOC standard included in the analysis. Precision can be measured by comparing the results of a lab duplicate to the original sample. Both accuracy and precision can be quantified by calculating the relative percent differences (RPD):

$$RPD = \frac{|C_1 - C_2| \times 100\%}{(C_1 + C_2)/2}$$

For Accuracy calculations: C_1 = the results of the known standard, and C_2 = the know value of the standard.

For Precision calculations: C_1 = the result of the original sample; C_2 = the result of the lab duplicate.

TOC readings should be +/- 10% of a known standard and lab duplicate. For example, a 10 ppm known standard should have a reading between 9.4 - 11.06%. If outside of this 10% range, create a new calibration curve and re-analyze the samples.

5.0 REMEDIAL ACTION IN CASE OF FAILURE AND USER HELP

5.1 See DPR video presentations of this SOP: http://www.youtube.com/watch?v=bx7eky_bABc&feature=related (Part I), http://www.youtube.com/watch?v=o9Ln8nCCNfY&feature=related (Part II), and http://www.youtube.com/watch?v=AGW3kTqrDKU&list=UUqC2ZGkVe7XKFBRrKL_3J7g&index=22&feature=plcp (Part III).

5.2 For minor problems, visit Shimadzu's TOC Advisor at https://tocvva.ssi.shimadzu.com/.

5.3 For additional help contact a Shimadzu sales rep at https://www.ssi.shimadzu.com/about/sales-rep-locator.html.

5.4 For supplies, contact Shimadzu store at https://store.shimadzu.com/default.aspx.

6.0 SAFETY

6.1 Wear gloves for personal protection and to prevent sample contamination.

6.2 Wear closed toe shoes when conducting TOC analysis.

6.3 Wear safety glasses with side shields or goggles for eye protection, especially when using HCl.

6.4 Ensure the oxygen tanks are secured to the wall.

6.5 Do not touch hot components or open housing when unit is in use.

6.6 Keep hands away from moving components (i.e., syringe injector). Never remove the sample cover to the automated sampler (ASI-V) when an analysis is in process.

6.7 Ensure that the external drain tubing does not touch the surface of the liquid in the waste container.