Standard Operating Procedure

Title: Operation and Calibration of Sievers 820 TOC Analyser

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Preparation of Calibration Standards

1. 25 ppm IC as Sodium Carbonate - standard preparation procedure

Materials and Equipment:

Materials:

Sodium Carbonate anhydrous, Na_2CO_3 Analytical Reagent Grade (Mol wt. 105.99 g/mol)

Para film

Equipment:

Milli-Q water

100mL volumetric flask, Class A

50mL volumetric pipette, Class A

1 L volumetric flask, Class A

Procedure:

1.1. Obtain required glassware and thoroughly rinse 5 times with Milli-Q water.
Note: For Calibration solutions dedicated glassware must be used, therefore use only glassware identified for the standard being prepared. Ensure all pipettes are cleaned and thoroughly rinsed with Milli-Q water.

1.2. Obtain an "Inorganic Carbon Standard Worksheet" (Form 615).

1.2.1. Record the current date and name of preparer in line 1.

1.2.2. Record the lot number of the Na_2CO_3 in line 2.

1.3. Dry approximately 1-2 grams Na_2CO_3 in an oven.

1.3.1. Place the Na_2CO_3 into a clean beaker and place in a 110°C oven for not less than 2 hours.

1.3.2. Transfer the Na_2CO_3 into a desiccator and allow the material to cool to room temperature.

1.4. Weigh dried Na_2CO_3 for preparation of standard.

1.4.1. Record the weight of the weigh boat in line 4 of the "Inorganic Carbon Standard Worksheet" **(Form 615).**

1.4.2. Accurately weigh out approximately 0.441 $\pm$ 0.0001g Na_2CO_3 in the weigh boat, and record the value in line 3 of the "Inorganic Carbon Standard Worksheet".

1.4.3. Calculate the difference in line 5 of the "Inorganic Carbon Standard Worksheet".

1.5. Transfer to 100mL volumetric flask.

1.5.1. Dilute solid with Milli-Q water while it is in the weigh boat.

1.5.2. Verify the water used in preparation contains less than 100 ppb TC and IC.

2.3.1. Place the KHP into a clean beaker and place in a 110°C oven for not less than 2 hours.

2.3.2. Transfer the KHP into a desiccator and allow the material to cool to room temperature.

2.4. Weigh dried KHP for preparation of standard.

2.4.1. Record the weight of the weigh boat in line 4 of the "Organic Carbon Standard Worksheet".

2.4.2. Weigh out approximately 0.425 ± 0.0001g KHP in the weigh boat, and record the value in line 3 of the "Organic Carbon Standard Worksheet".

2.4.3. Calculate the difference in line 5 of the "Organic Carbon Standard Worksheet".

2.5. Transfer to 100mL volumetric flask

2.5.1. Dilute solid with Milli-Q water while it is in the weigh boat

2.5.2. Verify the water used in preparation contains less than 100 ppb TC and IC.

2.5.3. Transfer the contents of the weigh boat into the 100mL volumetric flask.

2.5.4. Using Milli-Q water, wash down the weigh boat, flask neck, and ground glass joint and allow the rinse water to flow into the 100mL volumetric flask.

2.5.5. Add Milli-Q water until the 100mL volumetric flask is approximately 50 % full.

2.5.6. Ensure that the KHP is fully dissolved.

2.6. Dilute the solution to 100mL.

2.6.1. Add Milli-Q water to the 100mL volumetric flask to bring the total volume to 100mL

2.6.2. Cover the flask with volumetric lid and than with the clean side of a 4" x 4" square of Para film.

2.6.3. Invert the flask not less than 3 times and mix well.

2.7. Calculate the carbon concentration of the stock solution

$$\text{conc. of stock TC std (ppm)} = \frac{\text{Weight of KHP (g)} \times 8 \text{ mol C/mol KHP} \times 12.01\text{g C/mol} \times 1000}{(0.1\text{L}) \times (204.22 \text{ g/mol KHP})}$$

2.7.1. Record the result in line 6, Table 1 of the "Organic Carbon Standard Worksheet".

2.8. Prepare the dilute TC standard

2.8.1. Rinse a 25mL pipette with approximately 20mL of stock solution and discard.

2.8.2. Pipette 25mL of stock solution into a 2L volumetric flask.

2.8.3. Dilute to 2L with Milli-Q water, washing down the neck and ground glass joint of the 2L volumetric flask.

2.8.4. Cover the flask with volumetric lid and than with a 4" x 4"square of Para film.

2.8.5. Invert the flask not less than three times and mix well.

2.8.6. Calculate the final carbon content of the dilute solution.
Conc. of dilute TC standard (ppm) = Conc. of stock (ppm) x 0.0125

2.8.7. Record the final concentration of the dilute standard in line 7, Table 2 of the "Organic Carbon Standard Worksheet".

3. Calibration Procedure

Materials and Equipment:

25 ppm Inorganic Carbon standard (Sodium Carbonate Anhydrous)

25 ppm Total Carbon standard (Potassium Acid Phthalate)

"Calibration Worksheet for Autosampler Calibration" **(**Form 615**).**

Powder-free gloves

4. Performing Calibration - Prepare the following Calibration Protocol file using the Sievers program

The sampling schedule is as follows:

Sample	Sample No.	Acid Flow° Rate No.	Oxidiser Flow° Rate (µL/min)	No. of Replicates/ Sample (µL/min)
DI blank	1,2,3	0.75	0.00	4
25 ppm TC (KHP)	4,5,6	0.75	2.50	4
25 ppm IC (Na_2CO_3)	7,8,9	0.75	0.00	4
Cleanup (DI)	10	--.---	--.---	--

Select Create New Protocol from the Files menu.

Enter the protocol file name without an extension at the prompt.

An empty protocol file will be displayed for editing.

Highlight the protocol file window then use the ▲ button to zoom the window to full screen.

Edit the protocol by typing in the following:

No.	Group Name	Samp./group	Rep./Sample	Acid Rate	Oxid. Rate
1	DI water blank	1	4	0.75	0.00
2	25 ppm TC (KHP)	1	4	0.75	2.50
3	25 ppm IC (Na_2CO_3)	1	4	0.75	0.00

The software will automatically add the cleanup vial to the Table when you save the protocol.

Type over any defaults in the columns for each group.

Check the table in the protocol program to ensure it is correct.

Select Save Displayed Protocol from the Files menu.

Use Save and return to menu to save the protocol.

Use Save As ____ and return to menu to select a new name or path.'

Use the ▲▼ button to zoom the windows to normal size.

4.1. Prepare a water blank flask

Fill 3 x 40mL vials with the same water used to prepare the 25 ppm standards. Label as "DI Blank".

4.2. Fill the sample vials and load in Autosampler

4.2.1. Always use clean sample vials, caps, and septa and rinse the solution to be analysed 3 times into the vial.

4.2.2. Label each vial with the standard name, including the blanks and the cleanup vial.

4.2.3. Obtain a standard or blank to be measured in the protocol.

4.2.4. Fill three vials directly from the standard flask.

4.2.5. Re-seal the standard flask.

4.2.6. Repeat for each remaining standard.

4.2.7. Fill one cleanup vial with Milli-Q water.

4.2.8. Load the vials sequentially into the Autosampler according to the sampling schedule.

4.2.9. Ensure that the cleanup vial is the last vial in the sequence.

4.2.10. Using the index button on the left rear of the Autosampler, index the vials until the first blank vial is directly under the sampling needle.

4.3. Run the protocol file from the Autosampler software

4.3.1. Select the Run Current Protocol from the Start menu.

Para film

Milli-Q water

1L volumetric flask, Class A

500mL volumetric flask, Class A

10.0mL volumetric pipette, Class A

Procedure:

5.1.1. Obtain required glassware and ensure it has been cleaned in the Laboratory dishwasher and thoroughly rinsed 5 times with Milli-Q Water.
Note: For Calibration solutions dedicated glassware must be used, therefore use only glassware identified for the standard being prepared. Ensure all pipettes are cleaned and thoroughly rinsed with Milli-Q water.

5.1.2. Record relevant Sucrose information in the "500 ppb Sucrose Standard Worksheet" **(Form 615)** for Sucrose preparation.

5.1.3. Prepare nominal 25,000 ppb stock standard solution.

1. Dry the sucrose at 105°C for 4 hours. Let it cool in a desiccator.
2. Accurately weigh approximately 0.059 ± 0.0001g sucrose for preparation of stock standard solution and record in "500 ppb Sucrose Standard Worksheet".
3. Transfer to 1L volumetric flask and make up to volume using Milli-Q water washing down weigh boat and flask to ensure 100% transfer. Verify that water used is low TOC i.e. less than 100ppb and prepare a blank sample of this water.

5.1.4. Calculate the concentration of the stock as follows:
conc. of stock (ppb C) = weight of sucrose (g) x carbon content x 10^6

5.1.5. Prepare the dilute standard.

1. Use standards as soon after preparation as possible.
2. Using a 500mL volumetric flask, partially fill it with Milli-Q water.
3. Using a 10mL volumetric pipette, pipette the stock solution into the partially filled 500mL volumetric flask, mix and make up to 500mL.

5.1.6. Calculate the dilute standard concentration:

$$\text{conc. of dilute standard (ppb C)} = \frac{\text{conc. of stock (ppb C)}}{50}$$

5.1.7. Record the calculated concentration on line 8 of the "500 ppb Sucrose Standard Worksheet".

6. Preparation of 500 ppb Benzoquinone standard

Materials and Equipment

1,4-Benzoquinone (Mol wt. 108.10g/mol)

Para film

Milli-Q water

Two x 1L volumetric flasks, Class A

10.0mL volumetric pipette, Class A

Procedure

6.1. Obtain required glassware and ensure it has been cleaned in the Laboratory dishwasher and thoroughly rinsed 5 times with Milli-Q Water.
Note: For Calibration solutions dedicated glassware must be used therefore use only glassware identified for the standard being prepared. Ensure all pipettes are cleaned and thoroughly rinsed with Milli-Q Water.

6.2. Record the relevant Benzoquinone information in the "500 ppb Benzoquinone Standard Worksheet" (Form 615) for 500 ppb Benzoquinone preparation.

6.3. Prepare nominal 50,000 ppb stock standard solution.

9. Routine Maintenance

Item	Part No.	Replacement Schedule	Notes
60 µm filter element	**MRF 94401**	Every 3 months or as required	In-line filter applies only to on-line measurement. The filter element replacement schedule depends on the level of particulates in the water being sampled. A clogged filter may be detected by decreasing pressure on the sample inlet pressure gauge, or by a decrease in flow from the sample bypass waste line. At a minimum, the filter status should be checked every 3 months on the same schedule as replacement of the oxidiser reagent reservoir.

Continued

15% Ammonium Persulfate Reagent reservoir	**APF 80020**	Every 3 months	Because of loss of activity of the oxidiser over time, the 3-month replacement schedule is independent of whether the instrument is used for measurements, or is idle. The lifetime of the oxidiser reagent is tracked by the instrument with date/time information in non-volatile RAM, and Error 14 is reported when the lifetime has been exceeded. Error 13 is reported when the amount of oxidiser available is less than 10 percent of the full reservoir value.
6M Phosphoric Acid Reagent reservoir	**APF 80010**	as required	Replacement schedule of the acid reservoir, sample pump tubing, and ultraviolet lamp depends on the total time the instrument is on and/or making measurements. Lifetime of these items is tracked by the instrument with date/time information in non-volatile RAM, and specific errors are reported when the lifetime has been exceeded for any item. **Error 12** is reported when the amount of acid available is less than 10 percent of the full reservoir value.
Sample Pump Tubing assembly	**ATU 00644**	Every 12 months	**Error 16** is reported when the age of the sample pump tubing has exceeded the planned life expectancy.
Ultraviolet Lamp assembly	**EMI 00800**	Every 6 months	**Error 15** is reported when the age of the UV lamp has exceeded the planned life expectancy.
Refill DI Water reservoir	n/a	Every 2-12 weeks as required	Small amounts of DI water can be lost from the DI reservoir over time. The level of water in the DI reservoir should be periodically checked and the reservoir refilled if necessary. The procedure for checking and filling the reservoir is detailed in the Operation and Service Manual. The required inspection schedule depends on the mode of measurement. For on-line use, check the reservoir every 3 months, on the same schedule as replacement of the oxidiser reagent reservoir. For container sampling or Autosampler use, check the reservoir every 2 weeks.

Detailed procedures to replace all maintenance items and perform other maintenance procedures are given in Chapter 11 of the Operation and Service Manual.

10. Summary of Changes

Version #	Revision History
MICLAB 115	New

End of Procedure

Toc Analyser Calibration Worksheets

(Ref. MICLAB 115)

Calculation of Calibration Constants

Current TC calibration constant		$=TC_{cal,old}$

New TC calibration constant	$= TC_{cal,old} \bullet \frac{TC_{adj,TC}}{TC_{ave,TC}}$	$=TC_{cal,new}$

Current IC calibration constant		$=IC_{cal,old}$

New IC calibration constant = $IC_{cal,old}$	$\bullet \frac{TC_{adj,TC}}{TC_{ave,TC}} \bullet \frac{TC_{ave,IC}}{IC_{ave,IC}}$	$=IC_{cal,new}$

Verification of Calibration

Average TC of 3rd TC (KHP) standard		$=TC_{ave,chk,TC}$
Average TC of 3rd IC(Na_2CO_3) standard		$=TC_{ave,chk,IC}$
Average IC of 3rd IC (Na_2CO_3) standard		$=IC_{ave,chk,IC}$
New TC $_{adj,TC}$ = $TC(KHP)_{std}$ + average TC 3rd DI Blank =		
TC Std % difference = $\frac{(\text{New TC}_{adj,TC} - TC_{ave,chk,TC}) \times 100}{\text{New TC}_{adj,TC}}$ =		(NMT 3%)
IC Std % difference = $\frac{(TC_{ave,chk,IC} - IC_{ave,chk,IC}) \times 100}{TC_{ave,chk,IC}}$ =		(NMT 3%)

500 ppb Sucrose Standard Worksheet

Date, Name of Preparer	line 1

Lot No. of Sucrose used	line 2

Carbon Assay (% value / 100) nominal 0.421	line 3

Gross Weight (Sucrose + Boat)	line 4

Tare Weight of Weigh Boat	line 5

