





# CALIFORNIA

## AIR RESOURCES BOARD

### Standard Operating Procedure For Organic and Elemental Carbon Analysis of Exposed Quartz Microfiber Filters

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Approval Signatures	Approval Date
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# Standard Operating Procedure for Organic and Elemental Carbon Analysis of Exposed Quartz Microfiber Filters

## 1. SCOPE AND APPLICATION

This document describes the analysis of exposed quartz microfiber filters for organic carbon (OC) and elemental carbon (EC) using a Desert Research Institute (DRI) Thermal/Optical Carbon Analyzer.

## 2. SUMMARY OF METHOD

The analysis method used is **ImproveA**. The method is based on the preferential oxidation of organic carbon and elemental carbon compounds at different temperatures. Organic compounds are volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The carbon compounds are liberated under temperature and oxidation environments from a small sample using a 5/16 inch diameter punch (0.512 cm<sup>2</sup> area) taken from a quartz fiber filter.

These compounds are converted to carbon dioxide (CO<sub>2</sub>) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO<sub>2</sub>). The CO<sub>2</sub> is reduced to methane (CH<sub>4</sub>) by passing the flow through a methanator (hydrogen – enriched nickel catalyst). A flame ionization detector (FID) is used to quantify the methane.

The optical component of the analyzer is used to correct for pyrolysis of the organic compounds to elemental carbon in order to avoid underestimation of OC and overestimation of EC. The sample reflectance and transmission are continuously monitored by a helium-neon laser and a photodetector throughout an analysis cycle. When pyrolysis takes place, there is an increase in light absorption resulting in a decrease in reflectance and transmission. Thus, by monitoring the reflectance/transmission, the portion of the elemental carbon peak corresponding to pyrolyzed organic carbon can be correctly assigned to the organic fraction.

PM<sub>2.5</sub> carbon data, quality control data, and documentation detailing pertinent information, is compiled into a data package. Next, the data package is reviewed by the PM<sub>2.5</sub> carbon analyst, a second level reviewer (peer reviewer), and finally reviewed and approved by NLB management. PM<sub>2.5</sub> carbon data is then submitted to U.S. EPA's Air Quality System (AQS) database.

PM2.5 carbon filters are archived for at least five years, plus the current year, in compliance with U.S. EPA guidelines.

### 3. ACRONYMS AND DEFINITIONS

g	Grams
°C	Degrees Celsius
cm	Centimeter
mg	Milligram
ml	Milliliter
mm Hg	Millimeters mercury
mm	Millimeter
μl	Microliter
μg	Microgram
μg/m <sup>3</sup>	Microgram per cubic meter
ACS	American Chemical Society
AIO	Analog Input/Output
AQS	Air Quality System
DIO	Digital Input/Output
DPM	Digital panel meter
DRI	Desert Research Institute
FID	Flame Ionization Detector
IDOC	Initial Demonstration Of Capability
KHP	Potassium hydrogen phthalate
LIMS	Laboratory Information Management System: Database containing sample metadata, raw and reported concentration results, and quality control samples and results.
MDL	Method Detection Limit
NIST	National Institute of Standards and Technology
NLB	Northern Laboratory Branch
OC/EC	Organic Carbon/Elemental Carbon
PM2.5	Particulate matter with an aerodynamic diameter less than or equal to a nominal 2.5 micrometers
PPM	Parts Per Million
QC	Quality Control
SOP	Standard operating procedure
U.S. EPA	United States Environmental Protection Agency

### 4. INTERFERENCES

- 4.1. The presence of certain minerals can affect the laser correction for pyrolysis. These minerals change color as the sample punch is heated, generally resulting in a sample that is darker. Some minerals may affect

the laser reflectance by temporarily changing color or changing the surface texture of the deposit residue. These changes are reversible and highly temperature dependent. Colored organic compounds can affect the laser correction causing increased reflectance as these compounds are removed. The presence of certain elements (chromium, cobalt, copper, lead, nickel, manganese, potassium, sodium, and vanadium) as part of the deposit material has been shown to catalyze the removal of elemental carbon at lower temperatures.

- 4.2. Water vapor can shift the FID baseline. Allowing adequate time for the sample punch to dry in the analyzer by passing gases over it will eliminate this effect.
- 4.3. All surfaces are cleaned so that no contamination occurs. Filters are carefully handled with tweezers in order not to contaminate them.

## **5. PERSONNEL QUALIFICATIONS AND TRAINING**

Prior to performing this method, new personnel must be trained by experienced staff. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, and LIMS functionality pertaining to the program.

Personnel should provide an initial demonstration of capability (IDOC) prior to performing this method on real-world samples (i.e. data for record).

Training will be documented and maintained by the laboratory supervisor.

## **6. SAFETY REQUIREMENTS**

All personnel must follow the general health and safety requirements found in Northern Laboratory Branch (NLB) Chemical Hygiene Plan. Wear appropriate eye protection at all times while handling chemicals.

- 6.1. Wear suitable protective clothing (lab coat), including gloves if necessary, that are resistant to the chemicals.
- 6.2. Prepare chemical solutions under the fume hood that is suitable for the chemicals used.
- 6.3. Clean-up chemical spills immediately using the appropriate equipment and supplies, such as spill clean-up kits.

- 6.4. Handle gas cylinders properly. Use a suitable hand truck after making sure that the valve cap is securely in place and that the cylinder is properly fastened to the hand truck.

## **7. HANDLING AND DISPOSAL OF CHEMICALS**

All chemicals that are used in this method must be disposed of in proper disposal containers.

- 7.1. The analyst is responsible for ensuring the responsible purchase and subsequent safe storage of all chemicals associated with this method.
- 7.2. Contact the NLB's Health and Safety Coordinator for the proper disposal of the chemicals associated with this method (Refer to the NLB Chemical Hygiene Plan).

## **8. EQUIPMENT, SUPPLIES, AND CHEMICALS**

Equipment, supplies, chemicals necessary to meet requirements for PM2.5 carbon analysis are described below.

- 8.1. Desert Research Institute (DRI) Thermal/Optical Carbon Analyzer Model 2001 or 2001A.
- 8.2. 5/16 inch diameter steel punching tool.
- 8.3. Furnace-4800 Barnstead/Thermolyne Corporation.
- 8.4. Analytical balance equipped with a balance pan in a glass enclosure. Balance must have a minimum resolution of 0.1 mg and minimum precision of 0.5 mg.
- 8.5. Gases:
  - (a) Compressed air for the pneumatic actuation of the sample boat inlet bridge.
  - (b) Ultra zero air for flame ionization detector (FID).
  - (c) Hydrogen using a hydrogen generator.
  - (d) 10% oxygen balance helium gas – NIST certified.
  - (e) Grade 5 helium gas.
  - (f) 5% methane balance helium gas –NIST traceable standard.

(g) 5% carbon dioxide balance helium gas – NIST traceable standard.

8.6. Chemicals:

(a) Potassium hydrogen phthalate (KHP) American Chemical Society (ACS) grade for calibration standards.

(b) Potassium hydrogen phthalate (KHP) ACS grade used as a second source for control standards.

(c) Sucrose ACS grade used for calibration standard.

(d) Manganese dioxide ( $\text{MnO}_2$ ), crystalline, as an oxidizer in the oxygen oven.

(e) Nickelous nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], crystalline, used as a reducer in the methanator.

(f) Chromosorb 60/80 mesh, used as a support for nickel catalyst in methanator. Both nickelous nitrate and this support are for preparing the reduction catalyst in the methanator.

(g) Hydrochloric acid concentrated (36.5 – 38.0%) ACS or better grade.

(h) Nanopure water with resistivity of 16.5 megohm centimeter or better.

8.7. Traps:

(a) Oxygen trap for the helium gas.

(b) Hydrocarbon trap for the helium gas and hydrogen generator.

(c) Moisture trap for helium gas and hydrogen generator.

8.8. Porcelain Coors dishes for firing the quartz filters.

8.9. Tweezers, flat tip, metal.

8.10. Quartz 25 mm PALL filters.

8.11. Glass petri dish.

8.12. Kimwipes.

- 8.13. Lighter to light FID.
- 8.14. Pasteur glass pipet.
- 8.15. Syringes:
  - (a) Gas-tight 1000  $\mu$ l and 2500  $\mu$ l syringes for gas calibration injections.
  - (b) 10  $\mu$ l and 25  $\mu$ l syringes for liquid calibration injections.

## 9. PROCEDURES

- 9.1. The following standards are used to calibrate the carbon analyzer: 5% CH<sub>4</sub> in helium, 5% CO<sub>2</sub> in helium, sucrose, and potassium hydrogen phthalate (KHP).
- 9.2. Preparation of 1800 ppm KHP.
  - 9.2.1. KHP is dried at 110°C for two hours in a beaker before preparation of a solution.
  - 9.2.2. After the KHP has cooled to room temperature weigh out and transfer 0.3826 g of KHP into a clean, dry, glass 100 ml volumetric flask. Store unused portion in a desiccator.
  - 9.2.3. Dissolve the KHP in the flask with about 50 ml of nanopure water.
  - 9.2.4. Add 0.2 ml of concentrated HCl and dilute to volume with nanopure water.
  - 9.2.5. Mix the KHP solution thoroughly to make an 1800 ppm carbon solution of KHP.
  - 9.2.6. Label the flask with chemical name, date of preparation, the initials of the chemist preparing the solution, and the concentration.
  - 9.2.7. Store the KHP solution in a refrigerator until it is needed for calibration. The KHP solution is good for 30 days.
  - 9.2.8. A second solution of KHP, the control, is prepared the same as the calibration solution using a different source of KHP. The solution is stored in the refrigerator and is good for 30 days.



9.3. Preparation of 1800 ppm sucrose.

- 9.3.1. Weigh and transfer 0.428 g of sucrose into a clean, dry 100 ml volumetric flask.
- 9.3.2. Dissolve the sucrose in the flask with nanopure water. This will make 1800 ppm carbon solution in sucrose. Store in refrigerator until ready to use. The sucrose solution is good for 30 days.

9.4. Keithley DriverLINX Software Setup Panel.

- 9.4.1. Click on the software Analog Input/Output panel (AIO) to open the Keithley DriverLINX software. The meter panel is used in setting and checking signal levels, while Digital Input/Output panel (DIO) is used for checking the operation of valves, and sample boat positioning (See Operations Manual for Model 2001 or 2001A OC/EC instrument).
- 9.4.2. Click DIO to open the DIO panel. Then select output of channel 1 in DIO configuration panel. Click on channel 1 from the digital output panel (middle panel). Then boxes (0 – 7) under output bits can be selected to activate the designated functions of the analyzer. Once turned on, the box will light up. Clicking on the same box will turn off that line.
- 9.4.3. The assignment of the output bits:
- 9.4.4.

Carle Valve Load	0
Back Valves	1
Carle Valve Inject	2
Front Valves	3
Sample Oven Fan	4
Sample Load	5
Sample Calibrate	6
Sample Analyze	7

9.5. System Leak Checking.

- 9.5.1. The two toggle shut-off valves in conjunction with the System Oven Pressure digital panel meter (DPM) located on front of

the instrument above the rotameters are used for detecting leaks in the analyzer. The Oven Outlet toggle valve is located on the right side panel. The Oven Inlet toggle is on the front of the instrument.

- 9.5.2. Make sure that toggles He-1, He-2, and the pneumatic air are flowing and that the bridge of the sample boat inlet is closed. If not, manually switch the sample boat to "Calibrate" to ensure the bridge is sealed.
- 9.5.3. Close (flip downward on the handle) the Oven Outlet toggle valve. The Sample Oven Pressure should increase. When the pressure reaches about 5 psig, close the Oven Inlet toggle. The pressure should not decline much over several minutes, if so there may be a leak. Normally, leaks are prone at the Teflon ferrules around the thermocouple push rod and the quartz oven inlet and outlet. Tightening the nut should stop the leak. Also, check the septum ports and the top and bottom seals of the quartz oven cross, or the oven may have a crack. If the leak persists, replace the ferrules, seals, septum, or quartz oven cross as needed, and then repeat leak test.
- 9.5.4. When the system leaks checks are satisfactory, open the toggles to re-establish flow.

## 9.6. Flow Balancing

- 9.6.1. Three needle valves on the analyzer's right side panel provide adjustments needed to balance the flow.
- 9.6.2. Make sure the sample boat inlet bridge is closed, and that the flow rates have been set correctly and all gases (helium, compressed air, 10% oxygen balance helium, and 5% methane balance helium) are flowing. The settings are located on each rotameter.
- 9.6.3. Set the Watlow Controller Settings as follows: Warm up the FID temperature to 125°C (Model 2001) or 150°C (Model 2001A). Heat up the oxidation and methanator ovens stepwise in approximately 150°C increments with approximately 20 minute holding time at each step until the oxidation oven is at 900°C, and the methanator is at 420°C. Temperature can be

set by holding down the set button of the controller and using the up or down arrows to adjust the setting (See the Instruction Manual for the 2001 or 2001A analyzer).

- 9.6.4. Turn on the Front valves (I/O line 3) at the Keithley DIO panel and note the absence of ball movement at the He-2 rotameter. If the ball jumps up, turn the front (He/O<sub>2</sub>/HE adjust) needle valve clockwise slightly. If the ball drops, turn the needle valve counter clockwise slightly. Turn off the Front valves and let the flow stabilize for a couple of minutes. Repeat this step until no ball movement is observed (See Instruction Manual for the 2001 or 2001A analyzer).
- 9.6.5. Turn on the Back valves (I/O line 1) at the Keithley DIO panel. Adjust the middle (oven flow adjust) needle valve until the sample oven pressure increases by ~0.2 psi. The stability of the oven pressure is important so the baseline does not fluctuate.
- 9.6.6. Turn off the Back valves and observe the system oven pressure. The oven pressure should be stable with little or no change.

## 9.7. Calibration

- 9.7.1. The instrument is calibrated every six months or when the gas standard is changed, whichever comes first. The following are used to calibrate the instrument: 5% CO<sub>2</sub> in helium, 5% CH<sub>4</sub> in helium, KHP, and sucrose. The 5% CH<sub>4</sub> in helium is also used as the end-of-run calibration, automatically injected by the instrument. In addition, the manual calibration injections of 5% CO<sub>2</sub> in helium and 5% CH<sub>4</sub> in helium are performed at the beginning and end of each analysis day to verify proper analyzer performance.
- 9.7.2. A 5% CO<sub>2</sub> in helium gas is injected in the following volumes for calibration: 20 µl, 40 µl, 100 µl, 200 µl, 500 µl, 1000 µl, and 1500 µl, respectively.
- 9.7.3. A 5% CH<sub>4</sub> in helium gas is injected in the following volumes for calibration: 20 µl, 40 µl, 100 µl, 200 µl, 500 µl, 1000 µl, and 1500 µl, respectively.

- 9.7.4. Then an 1800 ppm carbon KHP standard is injected in the following volumes: 5  $\mu\text{l}$ , 10  $\mu\text{l}$ , 15  $\mu\text{l}$ , and 20  $\mu\text{l}$ , respectively. This gives a concentration of carbon as 9  $\mu\text{g}$ , 18  $\mu\text{g}$ , 27 $\mu\text{g}$ , and 36  $\mu\text{g}$ , respectively.
  - 9.7.5. Next, an 1800 ppm sucrose standard is injected in the following volumes: 5  $\mu\text{l}$ , 10  $\mu\text{l}$ , 15  $\mu\text{l}$ , and 20  $\mu\text{l}$ , respectively. This gives a concentration of carbon as 9  $\mu\text{g}$ , 18  $\mu\text{g}$ , 27 $\mu\text{g}$ , and 36  $\mu\text{g}$ , respectively.
  - 9.7.6. The gas standard concentrations are corrected for temperature and pressure at the laboratory conditions using the Ideal Gas Law (See Section 12.1).
  - 9.7.7. The slope is determined by plotting calculated carbon in  $\mu\text{g}$  vs. peak area/calibration peak area. The line is forced through zero.
  - 9.7.8. The slope value determined from the four calibration standards is entered into the "carbon.par" table (ASCII file) (See Section 12.2 and Table 1 for criteria).
- 9.8. System Blanks
- 9.8.1. A system blank is analyzed once a day at the beginning of the run before samples are analyzed to check to see if the system is clean.
  - 9.8.2. A clean blank filter punch is placed in the boat. After baking the system at least three times, the analysis is started. The system blank should be < 0.2  $\mu\text{g}$  total carbon before analyzing any samples.
- 9.9. Routine OC/EC Analysis
- 9.9.1. Check the regulators on all gas cylinders to make sure there is enough gas for the day. Turn on the gases and adjust the regulators on the gas tanks. Also, check the water level on the hydrogen generator and add nanopure water if needed.
  - 9.9.2. Light the FID with a lighter. Check that the FID is lit by holding the bottom of a small beaker or a pair of tweezers over the FID exhaust stack and watching for condensation. After the FID is

lit, adjust the rotameter to the operating setting (See the Instruction Manual for 2001 or 2001A analyzer for specific instructions).

- 9.9.3. Check all gas flows at the analyzer. The correct settings are located on each rotameter. Adjust through the center of the ball. Allow the instrument to stabilize for about 30 minutes.
- 9.9.4. On the computer, click the **DRICarb** shortcut icon to start the carbon program.
- 9.9.5. Leak test the system (See Section 9.5). Make sure the sample boat position is in the calibration position so that the bridge is closed before performing test. Once the leak test is satisfactory, open the toggles to re-establish flow.
- 9.9.6. Balance the flow by adjusting the sample oven pressure (See Section 9.6).
- 9.9.7. Once the flow has been balanced, a clean blank filter punch is loaded onto the boat, and the oven is baked at least three times. This is done by clicking on the analysis button on the computer screen, selecting sample, the **cmdBakeOven or cmdBakeOvenImproveA**. Click OK, and then run. Repeat the bake oven procedure three times in order to clean the oven.
- 9.9.8. Make sure that the printer has enough paper, the printer cartridge is okay, and the printer is on.
- 9.9.9. A system blank is analyzed after the oven has been baked by selecting the **cmdImproveA** protocol from the command table.
- 9.9.10. If the system blank is  $<0.2 \mu\text{g}$  total carbon, a 5%  $\text{CO}_2$  in helium or 5%  $\text{CH}_4$  in helium gas standard can be analyzed. Instead of selecting sample, calibrate is selected in the analysis program and **cmdCalib-HeO2** from the command table. The syringe is conditioned by analyst three times before loading. Once the software indicates to do so, load a 1000  $\mu\text{l}$  syringe with 5%  $\text{CO}_2$  in helium or 5%  $\text{CH}_4$  in helium, and then inject into the septum port of the analyzer.

- 9.9.11. After the gas standard has been analyzed, 10  $\mu\text{l}$  of an 1800 ppm carbon KHP control standard is analyzed. Sample is selected on the analysis program and **cmdImproveA** from the command. The analysis page containing the fields, sample ID, punch area (1.0  $\text{cm}^2$ ), deposit area (1.0  $\text{cm}^2$ ), and Tech initials are filled in. Click OK and then run. The syringe is conditioned by analyst three times before loading. When the software has prompted to do so, load the 10  $\mu\text{l}$  of KHP slowly on to the filter punch. Click OK and then enter the delay time required to dry the liquid standard on the filter punch. For each  $\mu\text{l}$  of liquid on the filter punch, 60 seconds of drying time (delay time) is required before the analysis will proceed. In this case, enter 600 seconds and click OK.
- 9.9.12. Once the KHP standard has been analyzed and is within  $\pm 10\%$  of the expected value, the samples can be analyzed. The KHP control standard is also analyzed after every ten samples and at the end of the day's sample run before analyzing the gas check standard.
- 9.9.13. Make sure that the tweezers, punch tool, and surface area used to punch on are thoroughly wiped clean with a dry kimwipe.
- 9.9.14. Remove the sample petri dish from the refrigerator. On the computer screen, after sample and **cmdImproveA** are selected, record the site name, sample ID (barcode), punch area, filter exposure area, and chemist's initials. Remove the filter from the sample petri dish with tweezers onto the glass petri dish. A sample punch is removed by gently pushing down on the punching tool. Place the punching tool on a clean kimwipe surface and return the filter to the petri dish. Remove the sample punch from the punching tool by grasping the bottom edge with the tweezers. Place one sample filter in the sample boat, and gently push the sample punch using the large end of a Pasteur (glass) pipet to make sure that the sample punch is seated in the well of the boat.
- 9.9.15. Click OK after loading sample punch. Then OK when the software prompts for delay time. The default value is 60 seconds. The sample will go through the sample analysis.

- 9.9.16. Wipe the tweezers, petri dish, and punching tool with a clean kimwipe, and then return the sample petri dish to the refrigerator.
  - 9.9.17. Log in the sample ID, date sampled, site name, date analyzed, and chemist initials into the lab notebook.
  - 9.9.18. At the end of the run, a three page report will print out which includes the peak areas, final results, and the thermogram.
  - 9.9.19. A duplicate sample is analyzed for every run and for every ten samples thereafter. A second filter punch is taken from the filter and analyzed.
  - 9.9.20. Once the samples are analyzed for the day, a 1000  $\mu\text{l}$  of 5%  $\text{CO}_2$  in helium or 5%  $\text{CH}_4$  in helium is analyzed for the end of day check by selecting **cmdCalib-HeOnly**. Use the alternate gas standard from the one used in the morning (See Section 9.7.9).
  - 9.9.21. Once the end of the day calibration run has printed, exit the carbon program. Shut off the toggle valves on the instrument for Cal Gas (methane) and He/O<sub>2</sub>. Then close the gas supply valves for the respective gases.
  - 9.9.22. After the results are reviewed, they are entered into the Laboratory Information Management System (LIMS).
- 9.10. Program Software
- 9.10.1. The OC/EC analysis program reads command sequences from and writes data to an Access database file. This file is **C:\Carbon\Access\carbon.mdb**. Clicking on the **DriCarb** shortcut icon will open this file to start the analysis.
  - 9.10.2. The parameter file, **carbon.par**, is an ASCII file which contains analyzer specific information. This is where the calibration slope can be entered (see Section 12.2). The user can only read this file by using the Note Pad word processor.
  - 9.10.3. The command tables are in Microsoft Access. Each command table has all the steps for the analysis program. They contain all of the information for opening and closing the Carle valve,

back valve, front valve, sample oven fan setting, and sample position setting (See the Instruction Manual for the 2001 or 2001A analyzer).

#### 9.11. Preparation of Filters

Filters are pre-fired for the OC/EC analysis before they are placed into the filter holders and shipped out to the field.

- 9.11.1. A Thermolyne 4800 Furnace is set to a temperature of 900°C.
- 9.11.2. Following the annual schedule, the specified number of quartz 25 mm filters are visually checked for damage or holes. All inspected filters are placed into a porcelain dish using tweezers.
- 9.11.3. The porcelain dish with the quartz filters is placed into the furnace oven.
- 9.11.4. After the oven reaches a temperature of 900°C, the porcelain dish with the quartz filter is baked for four hours.
- 9.11.5. Once the filters have baked for four hours at 900°C, the furnace oven is turned off.
- 9.11.6. The next morning, after the oven has cooled, remove the porcelain dish with filters.
- 9.11.7. The filters are removed from the porcelain dish with tweezers, being careful not to damage any of the fragile filters, and placed into a 50 mm covered petri dish (approximately 10 to 12 filters).
- 9.11.8. Before the pre-fired quartz filters go to sample handling, a punch from a pre-fired filter batch is analyzed to make sure no more than 1.0  $\mu\text{g}/\text{cm}^2$  of either organic or elemental carbon exist.
- 9.11.9. The petri dish containing the filters is placed into a desiccator for storage in the sample handling area until use.



## 10. QUALITY CONTROL

- 10.1. The Method Detection Limit (MDL) for the method is determined initially during method development. The MDL is verified annually, or when there is a modification to the instrument that will affect its performance. The MDL is determined by analyzing seven replicates of a KHP standard (1  $\mu$ l of 450 ppm) solution injected onto a filter punch in the boat. This is repeated until seven replicates are analyzed.
  - 10.1.1. A clean filter punch is baked at least three times by the **cmdBakeOven** or **cmdBakeOvenImproveA** protocol from the command table.
  - 10.1.2. Then a system blank is analyzed by the **cmdImproveA** protocol to make sure it is less than 0.2  $\mu$ g total carbon.
  - 10.1.3. After the system blank has been analyzed, a 1  $\mu$ l of the KHP 450 ppm standard is injected onto the filter punch in the boat and analyzed by selecting the cmdImproveA protocol.
  - 10.1.4. Once the analysis is complete, another 1  $\mu$ l of the KHP standard is injected onto the same filter punch in the boat and analyze again.
  - 10.1.5. Repeat until seven replicates have been analyzed.
  - 10.1.6. The standard deviation is determined for the seven replicates.
  - 10.1.7. The standard deviation times the Student's T value (3.143 for seven replicates) equals the MDL (Refer to NLB QC Manual).
- 10.2. The calibration correlation coefficient must be  $\geq 0.980$ .
- 10.3. A system blank is analyzed once daily before any samples are analyzed. The total carbon concentration should be  $< 0.2 \mu$ g before continuing. Blank unexposed filters are not analyzed for this method.
- 10.4. A gas check standard to check the system is analyzed after the system blank and at the end of the run and must be  $\pm 10 \%$  of the expected value.

- 10.5. A control standard of KHP is analyzed just before any samples are analyzed and every ten samples thereafter and after the last sample analyzed. The result should be  $\pm 10\%$  of the expected value.
- 10.6. Duplicate analyses are performed one per run and one for every ten ambient samples analyzed thereafter.
- 10.7. No spike samples are analyzed for this method. The instrument design and operation is incompatible with the preparation and analysis of spike samples.
- 10.8. Table I. Quality Control (QC) Criteria

QC	Acceptance Criteria	Failed Criteria Corrective Action
Calibration	Calibration correlation $\geq 0.980$	Check system. Re-prepare standards and recalibrate
Control KHP	$\pm 10\%$ of the expected value	Check system. Recheck, recalibrate if still out.
Duplicate	Percent difference $< 30\%$ , Not applicable if result and/or duplicate is less than 5 times reporting limit. Analyze one per run and one per every ten samples analyzed.	Recheck if sample available. Otherwise document in data report if criteria not met to notify lab supervisor.
System blank	$< 0.2 \mu\text{g}$ total carbon	Check system. Rerun until $< 0.2 \mu\text{g}$ total carbon before analyzing samples.
System gas check	$\pm 10\%$ of the expected value	Check system. Recheck, recalibrate if still out.

## 11. SAMPLE AND DATA MANAGEMENT

Data management consists of samples logged into the Laboratory Information Management System (LIMS), documentation of unusual occurrences and resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and

maintenance notebooks and/or logbooks are to be kept with instrumentation at all times (Refer to NLB QC Manual).

## 12. CALCULATIONS

12.1. Ideal Gas Law:

$$n = \frac{PV}{RT} = \frac{\left(\frac{P_a}{760}\right) (10^{-6})}{0.08206 (T_a + 273.15)}$$

where,

n = moles/volume of gas

P<sub>a</sub> = ambient pressure in mm Hg

T<sub>a</sub> = ambient temperature in °C

V = volume of gas

R = gas constant

12.2. To determine the calibration slope, the graph of μg of C (carbon) vs. injection peak area /calibration peak area is plotted (See Table I).

12.3. Carbon values per punch are converted to μg C/cm<sup>2</sup> by:

$$\frac{\mu\text{g C}}{\text{cm}^2} = \frac{\frac{\mu\text{g C}}{\text{punch}}}{\text{punch area in cm}^2}$$

12.4. Carbon values are converted to μg C/filter by:

$$\frac{\mu\text{g C}}{\text{filter}} = \left( \frac{\mu\text{g C}}{\text{cm}^2} \right) (\text{filter exposure area in cm}^2)$$

12.5. To determine the micrograms of carbon per cubic meter ( $\mu\text{g}/\text{m}^3$ ):

$$\frac{\mu\text{g}}{\text{m}^3} = \frac{\frac{\mu\text{g C}}{\text{filter}}}{\text{flow rate in m}^3}$$

Or

$$\frac{\mu\text{g}}{\text{m}^3} = \frac{\mu\text{g C}}{(\text{punch area in cm}^2)} \times \frac{(\text{filter exposure area in cm}^2)}{(\text{flow rate in m}^3)}$$

12.6. Method Detection Limit (MDL)=(standard deviation) x (3.143) ,when n = 7

### 13. REVISION HISTORY

METHOD	EFFECTIVE DATE	PRIMARY CHANGE(S) FROM PREVIOUS REVISION
MLD 065 Revision 1.0	June 15, 2007	Changed to ImproveA method, added Tables I-III for Watlow controller settings, and added change from 47 mm to 25 mm quartz filters.
MLD 065 Revision 2.0	July 20, 2018	Reviewed and revised SOP to follow current procedures Removed Tables I –III for Watlow controller settings. Included Model 2001A instrument.

## 14. REFERENCES

- 14.1. Atmoslytic Inc, DRI Model 2001 OC/EC Carbon Analyzer Instruction Manual, October 2001.
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- 14.3. Birck, M.E. and R.A. Cary, "Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust", October 3, 1996, Aerosol Science and Technology.
- 14.4. "Elemental Carbon (Diesel Particulate) 5040", NIOSH Manual of Analytical Methods (NMAM), Fourth Edition.
- 14.5. U.S. Environmental Protection Agency, "PM2.5 Speciation Trends Network Special Study", April 4, 2001.
- 14.6. U.S. Environmental Protection Agency, "Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11", Pt. 136, Appendix B.
- 14.7. Northern Laboratory Branch (NLB) Chemical Hygiene Plan, 2018.
- 14.8. Quality Control Manual of the Monitoring and Laboratory Division, Northern Laboratory Branch, September 2018.