



**PROCEDURE FOR ORGANIC CARBON AND ELEMENTAL CARBON
(OC/EC) ANALYSIS OF VEHICULAR EXHAUST PARTICULATE
MATTER (PM) ON QUARTZ FILTERS**

**SOP MV-AEROSOL-139 Version 1.2
Effective Date: September 1, 2019**

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SOP MV-AEROSOL-139

PROCEDURE FOR
ORGANIC CARBON AND ELEMENTAL CARBON (OC/EC)
ANALYSIS OF VEHICULAR EXHAUST PARTICULATE MATTER (PM)
ON QUARTZ FILTERS

1 SCOPE

This document is a standard operating procedure (SOP) for the quantification of organic carbon (OC) and elemental carbon (EC) in vehicular exhaust particulate matter (PM) collected on quartz fiber filters, by following the IMPROVE_A Thermal/Optical Carbon Analysis.

2 SUMMARY OF METHOD

The method is based on the preferential evaporation/oxidation of OC and EC at different temperatures and under different oxygen/helium conditions. The analysis follows the IMPROVE_A (Interagency Monitoring of PROtected Visual Environments_A) protocol. The IMPROVE_A protocol bases upon the temperature plateaus for defining each carbon fractions: OC of 140 °C (OC1), 280 °C (OC2), 480 °C (OC3), 580 °C (OC4) and temperature plateaus for EC of 580 °C (EC1), 740 °C (EC2), 840 °C (EC3). However, other protocols such as the IMPROVE or NIOSH (National Institute of Occupational Safety and Health) or STN (Speciation Trends Network) protocol can also be used with the same instrument/analyzer.

- 2.1 A 5/16 inch diameter (0.5 cm² nominal area) sample is taken from a quartz fiber filter deposited with vehicular exhaust PM, placed inside the carbon analyzer on a sample holder and heated to selected temperatures under selected oxygen/helium atmospheres.
- 2.2 At low temperatures (not greater than 580 °C) and in a helium (He) only atmosphere, carbonaceous compounds that can volatilize at each plateaus temperature are defined as OC1, OC2, OC3, and OC4 sbufractions. The volatilized OC is swept by helium over a hot oxidizer (manganese dioxide, MnO₂) and converted to carbon dioxide (CO₂).
- 2.3 After all OC volatilizes, the sample is continuously heated in 2% oxygen (in helium) atmosphere. At the temperature starting from 580 °C, carbonaceous materials that can volatilize at each temperature plateaus are defined as EC1, EC2, and EC3 subfractions. The volatilized EC is swept over a hot oxidizer and converted to CO₂, the same as OC.
- 2.4 Pyrolysis can happen during the OC analysis by charring of OC compounds to EC. To avoid underestimation of OC and overestimation of EC due to pyrolyzed OC (OCPyro), it is necessary to make a correction for the pyrolysis.

The pyrolysis during the sample analysis is determined by sample light reflectance and/or transmittance, which are continuously measured throughout an analysis cycle with seven modulated diode lasers and photo

detectors at wavelengths from 405 to 980 nm. The corrections of OC and EC calculations use the pyrolysis quantified at wavelength 635 nm.

- 2.5 The resulting CO₂ for OC and EC subfractions are quantified by a nondispersive infrared (NDIR) detector. With a calibration factor, the amounts of OC and EC can be calculated from the NDIR peak areas. The quantification can also be achieved with FID, after CO₂ in Section 2.2 and 2.3 being converted to H₂ with a reducing agent [nickel(II) nitrate hexahydrate, Ni(NO₃)₂ · 6H₂O].
- 2.6 Organic carbon (OC) is defined as the carbon volatilized from the sample in a He-only atmosphere at 140 °C, 280 °C, 480 °C, and 580 °C plus pyrolyzed organic carbon. Elemental carbon (EC) is the carbon volatilized from the sample in a 98% He/2% O₂ atmosphere at 580 °C, 740 °C, and 840 °C minus any pyrolyzed OC. Total carbon (TC) is the sum of EC and OC.

3 INTERFERENCES

- 3.1 The presence of carbonate carbon presents significant interference in carbon analysis if it constitutes more than 5% of total measured carbon. Acid pretreatment of the filter samples can reduce the carbonate interference (Section 11, Carbonate Analysis). In routine analysis, carbonate is not removed, as it is expected to be at the trace level in vehicular exhaust particulate matter.
- 3.2 The presence of minerals and colored materials can affect the laser correction for pyrolysis:
 - 3.2.1 Some minerals change color as the sample filter is heated, generally resulting in a darker sample.
 - 3.2.2 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.
 - 3.2.3 Colored organic compounds can affect the laser correction causing increased reflectance as these compounds are removed.
 - 3.2.4 The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr) as part of the deposit material has been shown to catalyze the removal of elemental carbon at lower temperatures.
- 3.3 Moisture in the sample and filter might affect the NDIR baseline and peak area integration. An adequate delay time for the sample filter to dry in the analyzer by passing helium over the filter punch will reduce this interference.
- 3.4 Sample filters can be contaminated by the PM in the environment. Using clean surfaces, storing filters in clean containers, and handling filters carefully in a clean environment will minimize contamination.

4 APPARATUS AND MATERIALS

- 4.1 DRI (Desert Research Institute) Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer, or equivalent.
- 4.2 Quartz fiber filters, 47 mm (Pall Corporation, Tissuquartz filter, Part No. 7202 (pre-heat-treated) or No. 7194 (non-heat-treated), and filter containers (Millipore Petrislide, Cat. No, PD1504700), or equivalents.
- 4.3 Steel punching tool, 5/16 inch diameter, 0.5 cm² nominal area for removing small sample punches from quartz filters. This punching tool must be kept clean and sharp.
- 4.4 Glass petri dish or a glass plate with a flat surface, for cutting 5/16-in sample punch from filter with punching tool.
- 4.5 Tweezers, flat tip.
- 4.6 Thermolyne furnace, Model 30400, or equivalent.
- 4.7 Coors porcelain plates, 230 mm diameter.
- 4.8 Gases:

The following gases should be ultra-high purity (UHP) grade or better:

- (a) Nitrogen gas from liquid nitrogen or compressed air with carbon dioxide scrubber for pneumatic activation, regulated to ~25 psi.
 - (b) 10% oxygen by volume in helium, Airgas USA, LLC, catalog # X02HE90P15A1040, or equivalent, regulated to 15 psi.
 - (c) 5% methane by volume in helium (Cal Gas), Airgas USA, LLC, catalog # X02HE95P15AE260, or equivalent, regulated to 20 psi.
 - (d) 5% carbon dioxide by volume in helium, Airgas USA, LLC, catalog # X02HE95P15A7533, or equivalent, regulated to 15 psi.
 - (e) Helium, Ultrapure, 99.9995%, regulated at 20 psi.
- 4.9 Chemicals:
- (a) Potassium hydrogen phthalate (KHP), ultrapure (Spectrum Chemical, Catalog # P1960, or equivalent), CAS 877-24-7.
 - (b) Sucrose, ultrapure (Spectrum Chemical, catalog # S1697, or equivalent), CAS 57-50-1.
 - (c) Manganese dioxide (MnO₂), reagent, as an oxidizer in the oxygen oven (Spectrum Chemical, catalog # M1107, or equivalent), CAS 1313-13-9.
 - (d) Soda Lime 4-8 mesh for carbon dioxide scrubber for compressed air as the makeup gas (VWR, catalog # JT3447-1, or equivalent).
 - (e) Hydrochloric acid (HCl), 36.5–38% for preparing KHP reagent (VWR, catalog # BDH3026-500MLP, or equivalent), CAS 7647-01-0.
 - (f) Hydrochloric acid (HCl), 0.4 M, for carbonate analysis (Spectrum Chemical, # H-130, or equivalent).
 - (g) Nanopure water (18 megohm purity).

- 4.10 Gas purification traps:
 - (a) Oxygen trap for helium.
 - (b) Hydrocarbon trap for helium.
- 4.11 Syringes:
 - (a) Gas-tight syringes, 500 μ L, 1000 μ L and 2500 μ L (SGE, P/N 007200, 008100, and 008500, respectively, or equivalents).
 - (b) Liquid syringe, 25 μ L (Hamilton, P/N 80400, or equivalent).
- 4.12 Volumetric flasks, 100 mL.

5 PREPARATION OF FILTERS

Quartz fiber filters must be pre-baked to remove any traces of carbon compounds before use.

- 5.1 Visually inspect all quartz filters for damage. Place a batch of inspected filters on Coors porcelain plates using tweezers.
- 5.2 Place the porcelain plates and filters inside the oven of a Thermolyne 30400 Furnace oven.
- 5.3 Set the oven to heat to 900 °C.
- 5.4 When oven temperature has reached 900 °C, bake the quartz filters for four hours at 900 °C.

SAFETY CAUTION: Do not open the hot furnace door as this can cause serious bodily injuries.
- 5.5 Set oven temperature to room temperature and let the oven and filters cool down to room temperature.
- 5.6 Remove porcelain plates with the filters from the oven. Remove filters with tweezers and place each filter into an individually labeled filter container. Be careful to avoid damaging filters.
- 5.7 Place the filters and containers in a desiccator or a refrigerator for storage until use.
- 5.8 After baking treatment, choose random 4% of total baked filters or at least three filters per batch, whichever is larger, and analyze for lab blank OC and EC. The blank filter must have OC < 11 μ g C/filter and EC < 2.0 μ g C/filter. If any lab blank filter has a carbon loading over the above limits, analyze three more filters. If the OC and/or EC are still over these limits, all filters from the same batch are discarded.

6 PREPARATION OF STANDARDS

6.1 The following four standards are used to calibrate the analyzer:

- (1) Cal Gas (5% CH₄ in helium).
- (2) 5% CO₂ in helium.
- (3) Potassium hydrogen phthalate (KHP) solution.
- (4) Sucrose solution.

The gaseous standards are commercially available from Airgas USA, LLC or equivalent. The KHP and sucrose solutions are prepared as follows.

6.2 KHP standard solution

6.2.1 Dry KHP at 110 °C for two hours before preparation of a solution.

6.2.2 After the KHP has cooled to room temperature, weigh and transfer 0.3826 g of KHP into a clean, dry 100 mL volumetric flask.

6.2.3 Dissolve the KHP in the flask with about 50 mL nanopure water.

6.2.4 Add 0.2 mL of concentrated HCl and dilute to volume with nanopure water.

6.2.5 Mix the KHP solution thoroughly. This will make an 1800 ppm carbon (1.80 µg C/µL) solution of KHP.

6.2.6 Label the flask and store the KHP solution in a refrigerator until needed. Do not freeze solution. This solution is good for 40 days.

6.2.7 The actual concentration of the KHP solution is calculated by:

$$\begin{aligned} \text{Actual } \mu\text{gC}/\mu\text{L} &= \left(\frac{\text{wt of KHP}}{\text{vol of solution}} \right) \left(\frac{\text{no of carbon in KHP} \times 12}{\text{mol wt of KHP}} \right) \\ &= \left(\frac{\text{wt of KHP in g}}{100 \text{ mL}} \right) \left(\frac{8 \times 12}{204.23} \right) \left(\frac{10^{-3} \text{ ml}}{\mu\text{L}} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right) \end{aligned}$$

6.3 Sucrose standard solution

6.3.1 Weigh and transfer 0.4280 g of sucrose into a clean, dry 100 mL volumetric flask.

6.3.2 Dissolve sucrose in nanopure water and dilute to volume. Mix thoroughly. This will make an 1800 ppm carbon (or 1.80 µg C/µL) solution of sucrose.

6.3.3 Label the flask and store the sucrose solution in a refrigerator until needed. Do not freeze solution. This solution is good for 40 days.

6.3.4 The actual concentration of the sucrose solution is calculated by:

$$\begin{aligned} \text{Actual } \mu\text{gC}/\mu\text{L} &= \left(\frac{\text{wt of sucrose}}{\text{vol of solution}} \right) \left(\frac{\text{no of carbon in sucrose} \times 12}{\text{mol wt of sucrose}} \right) \\ &= \left(\frac{\text{wt of sucrose in g}}{100 \text{ mL}} \right) \left(\frac{12 \times 12}{342.31} \right) \left(\frac{10^{-3} \text{ mL}}{\mu\text{L}} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right) \end{aligned}$$

6.4 Blank solution

Prepare a blank solution using the same procedure as in Sections 6.2 or 6.3 without KHP or sucrose.

7 ANALYZER START-UP

7.1 Set temperatures

If the Analyzer is turned on for the first time, or after an extended period of non-operation, it will take a period of conditioning to reach a stable system background. At the start, allow all gases to purge through the system for about 15 minutes before heating methane heater and the oxidation oven (Oxygenator), containing MnO₂. The set points and heating steps for both heating zone are as follows:

Oxygenator: 912 °C

Heat the MnO₂ to 110 °C for approximately 30 minutes, heat up stepwise in ~100 °C increments with at least ~30 minutes holding time at each temperature until the final temperature of 912 °C is reached.

Methane Heater: 50 °C

7.2 Set gas flows

7.2.1 Check all gas cylinder pressures. Cylinders with gas pressures less than 500 psi should be replaced before beginning the day's analysis.

7.2.2 Start the Carbon2015 program, select Calibration Controls, and select the Flow Calibration tab. The cylinder pressures and the gas flow rates are set as below. The gas flow rates are factory calibrated. (Reference 15.1 pp. 4-8)

Cylinder regulator pressures (psi):

Cal Gas	20
He/O ₂ , CO ₂ /He	15
He	20
Pneumatic gas	25

Gas flow rates (mL/min):

He-1	40
He-2	10
He-O ₂	10
Makeup	140
Total Flow	200

7.3 System leak check

Perform system gas leak checks daily to detect leakage in the sample oven. The leak check valves are operated by the Carbon2015 software.

- 7.3.1 From the Software Selection window, click the “Calibration Controls” button.
- 7.3.2 Set the He/O₂ flow to Zero, turn off the on/off toggle valve on that line connected to the side arm of the quartz cross.
- 7.3.3 In the Calibration Controls window, toggle the back valve to direct flow to the leak check valve (from green to red color).
- 7.3.4 In the Calibration Controls window, toggle the leak check valve switch on. This seals the analysis region between the two leak check valves off from other components and the gas inlet.
- 7.3.5 Observe the pressure reading. It will initially drop quickly and then stabilize. If it drops more than 0.1 psi per second after that, and does not stabilize, there is a leak in the system. Find and fix the leak.

Note: Normally, the most likely leaks are the Teflon ferrules around the thermocouple push rod and the quartz oven inlet and outlet. A slight turn on the nut should seal the leak. Also, check the septum port. The two remaining areas are the top and bottom seals of the quartz oven cross. If the leak persists, the oven may have a crack. Over tightening the nuts and ferrules may crack the quartz components.

- 7.3.6 When the system leak checks are satisfactory, toggle the leak check valves off in the Carbon2015 software.

8 CALIBRATION

There are three types of calibration: an annual calibration to verify the calibration factor, a routine daily calibration to verify performance of the analyzer, and an end-of-run calibration for NDIR peak area quantitation.

8.1 Annual calibration

The instrument is calibrated every year, when the gas standard is changed, or when the instrument has a major service. The following four standards are used to calibrate the instrument: 5% CH₄ in helium (Cal Gas), 5% CO₂ in helium, KHP solution and a sucrose solution. At the end of each analysis a 1-mL sample of the Cal Gas is also automatically injected by a Carle valve (in a constant temperature compartment). When the Cal Gas is used as the calibration standard it is used for dual purposes: as the internal standard and as the analyte manually injected in different quantities.

8.1.1 Calibration with gaseous standards (CH₄ and CO₂)

The calibration is done by injection of a known volume of the standard CH₄ or CO₂ to yield a calibration curve of peak area ratio of injected carbon to Cal Gas (internal standard) versus µg C injected.

- 8.1.1.1 Select "Analyze Samples" from the Software Selection Screen of the Carbon2015 program.
- 8.1.1.2 Select "Setup Analysis".
- 8.1.1.3 Under "Protocol" drop down menu, select "He_Only". The project name should be "CALIB", Batch # should be "CARBON", Sub-batch # should be "YYYYmmdd" for the year, month, and day. Fill out the Sample ID, Run #, and Tech Initials fields.
- 8.1.1.4 Set the "Drying Time" to 0.
- 8.1.1.5 Under "Load Sample Boat?" drop down menu, select "Unload".
- 8.1.1.6 Click "Press to Continue" to start.
- 8.1.1.7 Load syringe with CH₄ or CO₂ in the following volumes (µL):

<u>Volume</u>	<u>Total Carbon</u>
100 µL (using a 500 µL syringe)	2.68 µg C
250 µL (using a 500 µL syringe)	6.70 µg C
500 µL (using a 1000 µL syringe)	13.4 µg C
1000 µL (using a 1000 µL syringe)	26.8 µg C
1500 µL (using a 2500 µL syringe)	40.2 µg C

- 8.1.1.8 Inject the sample through the injection port between 0-50 seconds after the analysis starts.
- 8.1.1.9 Obtain the integrated peak counts and CH₄ internal calibration peak counts, and calculate the calibration slope.

At STP, for the 5% CH₄ Cal Gas or the CO₂ gas, the carbon concentration is 0.0268 µg C/µL. This gives a series of carbon concentrations as shown above. Depending on the CH₄ or CO₂ certified concentrations provided by the standards manufacturer, the actual carbon concentrations can be calculated. These carbon concentrations are then corrected for the temperature and pressure at the laboratory using the following formula derived from the Ideal Gas Law:

$$\text{Actual } \mu\text{g C}/\mu\text{L} = \left(\frac{\text{Pa}}{760}\right) \left(\frac{1}{(T + 273.15)}\right) \left(\frac{1}{0.08206}\right) \left(\frac{\% \text{ conc of gas}}{100}\right) \times 12$$

where Pa is the atmospheric pressure in mm Hg and T is the room temperature in °C. Divide the CH₄ or CO₂ peak area by the internal standard peak area to obtain the peak area ratio for the corresponding total carbon (μg C).

8.1.2 Calibration with KHP and sucrose standard solutions

- 8.1.2.1 Perform a system blank before running KHP or sucrose.
- 8.1.2.2 A clean blank quartz punch is baked in the analyzer oven at 900 °C for 10 minutes using the “Bake” protocol.
- 8.1.2.3 Follow the same steps 1 – 4 of Section 8.1.1. Under “Protocol” drop down menu, select “IMPROVE_A”. The Punch area and Deposit area should be “1” for the filter being analyzed
- 8.1.2.4 The filter must be dried before analysis starts. Enter the length of time in seconds you wish to delay the beginning of the analysis. Set “Drying Time” to allow at least ~1.5 - 2 minutes of purge time for every μL of solution deposited (i.e., 5 μL= 600s, 10 μL= 900s, 15 μL= 1200s, and 20 μL = 1500s).
- 8.1.2.5 After the sample oven has cooled to below 50°C, the KHP or sucrose solution is injected onto the punch using a 25 μL syringe. The following volumes are used:
 - 5 μL KHP or sucrose solution
 - 10 μL KHP or sucrose solution
 - 15 μL KHP or sucrose solution
 - 20 μL KHP or sucrose solution

Calculate the carbon concentrations of KHP (Section 6.2) and sucrose (Section 6.3) in each analysis. After each analysis, add peak areas of all subfractions of total carbon (TC, TC=OC1+OC2+OC3+OC4+EC1+EC2+C3) and divide by the CH₄ internal standard peak area to obtain the area ratio for the corresponding total carbon (μg C).

- 8.1.3 Repeat the above injection procedure (Section 8.1.2) using the blank solution (Section 6.4) with the same injection volumes. Add peak areas of all subfractions (OC1 through EC3). If the peak areas from the blank solutions (normally around system blank level) are significant when compared to those of the corresponding volumes of the standard solutions, subtract the blank areas from the areas of the standard peaks before calculating the peak area ratios.
- 8.1.4 Slowly spike the solution in the center of a quartz fiber filter punch.

Caution: If the solution is spiked too quickly, it will bead up and run off

the punch.

- 8.1.5 For each of the four calibrations, plot calculated carbon concentrations in $\mu\text{g C}$ (y-axis) versus area ratios or corrected area ratios (x-axis). Force the curves through the origin and calculate the four slopes. Calculate the average value of the four slopes. These four slopes must be within $\pm 20\%$ from the average slope.
- 8.1.6 Open the Carbon2015 program, select Calibration Controls, and select the Calibration Analysis Parameters tab, check the Alter Calibration Values box, enter the average slope into the Carbon Calibration Slope field and the new date into the Parameter Version field, uncheck the Alter Calibration Values box.

The new response factor is normally within $\pm 20\%$ of the previous value unless major Analyzer changes have been made.

8.2 Routine daily calibrations

Routine daily calibrations are to be performed at the beginning and at the end of each analysis day using Cal Gas standard and the automatic routine calibration "AutoCalib" protocol. The automated calibration uses the Carle valve to inject the Cal Gas standard three times: first in a He-only atmosphere (peak 1), then in a He/O₂ atmosphere (peak 2), and finally, the normal calibration peak at the end of analysis (peak 3). These three peaks should have similar peak areas if the catalyst MnO₂ is in good condition and the calibration factor holds. Use the following steps to perform this automated calibration.

- 8.2.1 From the Carbon2015 Software Selection screen, click the "Analyze Sample" button.
- 8.2.2 Select the "AutoCalib" protocol from the drop-down menu.
- 8.2.3 Enter "Calib" for project name, "YYYYMM" for the Batch #, "YYYYMMDD" for the Subbatch #, and "Autocal YYMMDD" for sample ID, where YYMMDD is the year, month and date for the day of analysis.
- 8.2.4 Enter the Punch Number # "1" for first calibration of the day and "2" for second calibration of the day, etc. Enter "1" in the Punch area and Deposit area fields, and enter "0" in the Drying Time field. Select "Unload" in the Load Sample Boat? Field. Click the "Press to Continue" button to start the analysis.
- 8.2.5 After the run, review the thermogram and record the three peak area counts in the logbook and in the control charts (Section 13-3). The three calibration peak integrated counts (OC3, EC1, and CAL) should be 15,000 – 25,000 and must be within $\pm 20\%$ of other runs.

8.2.6 Whenever the MnO₂ catalyst is replaced, an automated routine calibration should be run to confirm that the previous calibration curve holds.

8.3 End-of-run calibration

The carbon analysis program uses the internal standard calibration method to quantify all NDIR peaks. At the end of each analysis, the Carbon Analysis program automatically injects a set quantity of Cal Gas (the internal standard). All NDIR peak areas are normalized to the Cal Gas peak area to minimize the effects of NDIR performance and electronic drift over time. The end-of-run calibration occurs automatically at the end of each analysis and requires no operator's intervention. After each run, the Cal Gas peak area count should be checked and compared to the Cal Gas peak area counts from previous runs. If the area count is within $\pm 20\%$ from previous counts, the Analyzer is considered operating properly.

8.4 Currently there is no NIST-traceable primary standard available for carbon analysis. The current calibration procedure is for the total carbon, and there is no existing routine procedure to check the accuracy of the OC/EC split.

9 MINIMUM DETECTION LIMIT

The minimum detection limit (MDL) is calculated from the sum of mean (total OC and EC) and three times the standard deviations obtained from the analysis of at least 7 pre-fired blank filters. Total OC and EC are calculated based on the sample collection area (11.34 cm²) and the punch area (0.537 cm²). When calculating the MDL for different size sampling media, the actual sample collection area needs to be taken into consideration.

MDLs for EC and OC are determined independently due to the heightened interest in a black carbon emission standard whereby the EC may play a surrogate role.

- 9.1 Total OC is the sum of OC subfractions with a charring correction due to pyrolysis (OC1+OC2+OC3+OC4+OCPyro). The total EC is the sum of EC fractions after correction OC charring (EC1+EC2+EC3-OCPyro).
- 9.2 The previous version of SOP specified the MDLs was effective since September 2011. These MDLs were determined for the EC and OC based on results collected from 200 quartz fiber filter blanks on DRI Model 2001 OC/EC Carbon Analyzer. These filters were baked and analyzed during the period of April 29, 2008 through July 14, 2011. The average level for the EC was 0.34 ± 0.55 $\mu\text{g C/filter}$, the average level for the OC was 4.08 ± 2.04 $\mu\text{g C/filter}$. The MDLs were determined to be 2.00 $\mu\text{g C/filter}$ for the EC and 11.00 $\mu\text{g C/filter}$ for the OC.
- 9.3 These MDL values were further verified by analyzing thirty-eight quartz filter blanks on DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer. The filter blanks were collected between September 22, 2017 and June 27, 2018. The average level for the EC was 0.12 ± 0.28 $\mu\text{g C/filter}$ and the average level for the OC was 5.06 ± 1.68 $\mu\text{g C/filter}$; the corresponding EC MDL was 1.00 $\mu\text{g C/filter}$, OC MDL was 11.00 $\mu\text{g C/filter}$.

- 9.4 The MDLs for the consistent reporting value will remain at the same levels as those of specified in the previous version of the SOP. More quartz filter blanks data are acquired to evaluate the EC MDL and OC MDL of DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer for future update.

10 ROUTINE OC/EC ANALYSIS

- 10.1 Open the Carbon2015 software. When all components are “green” on the Query Status screen click “Continue” and the Software Selection Screen will appear.
- 10.2 Check that the temperature of the Oxygenator and Methane Heater are in the correct setting. From the Software Selection window, click the “Calibration Controls” button, and select the Oven Calibration tab (Section 7.1).
- 10.3 Check that all mass flow meters are outputting the correct flows. From the “Calibration Controls” window, select the Flow Calibration tab (Section 7.2.2).
- 10.4 Perform the system leak check (Section 7.3).
- 10.5 Exit the “Calibration Controls” window.
- 10.6 From the Software Selection window, click the “Analyze Sample” button to bring up the analysis window.
- 10.7 Click “Setup Analysis” button in the analysis window to bring up the analysis details and protocol selection window.
- 10.8 Before analyzing samples, run the bake oven, system blank, and routine daily calibration first.
- 10.9 Click on the folder icon in the upper right corner to select the analysis protocol. To clean the oven, select “Bake”; for system blank analyses, select “IMPROVE_A”; and to run an auto calibration, select “AutoCalib” (Section 8.2).
- 10.10 Fill out the information about each analysis, including: Project Name, Batch #, Sub-batch #, Sample ID, Run Number, Punch, and Deposit area of the filter. Enter analyst’s initials in the “Tech initials” field.
- 10.11 Under “Load Sample Boat”, the default is on in order to have it automatically load once “Press to Continue” is clicked. Toggle this off if needed.
- 10.12 For a “Bake”, system blank run, and “AutoCalib” run, set the “Drying Time” to 0, the “Punch Area” and “Filter Deposit” to 1, toggle the “Load Sample Boat” off, and click “Press to Continue”.
- 10.12.1 Repeat the oven bake procedure if necessary.
- 10.12.2 The system blank should have total carbon concentration < 3 µg C/filter before analyzing any samples. If not, repeat oven bake until

system blank total carbon concentration is $< 3 \mu\text{g C/filter}$.

Monitor the reflectance (LR) and transmittance (LT) of 635 nm laser. A difference $>5\%$ between initial and final indicates significant laser drift.

- 10.12.3 Routine daily calibration is for verifying the Analyzer's performance (Section 8.2). The three calibration peak integrated counts (OC3, EC1, and CAL) should also be within $\pm 20\%$ of the areas of other runs. If not, repeat the daily calibration.
- 10.12.4 Record the information and data in a logbook.
- 10.13 For a sample filter or a blank filter analysis, set the drying time to 90 seconds, the "Punch Area" around 0.5 cm^2 (Section 4.3), and the "Filter Deposit" around 12 cm^2 for a 47 mm quartz filter.
- 10.13.1 It should be noted that the reported Total OC, Total EC, and Total Carbon concentrations per filter are calculated based on the values entered in the "Punch Area" and "Filter Deposit". The circular boundary of the deposit area is not a clear-cut boundary, and so the accuracy of the reported values of carbon amount per filter/sample is highly dependent on the accuracy of the deposit area determination. For consistency purposes, measure the inside diameters of the punching tool and the filter holder and use these values to calculate the punch area and deposit area.
- 10.13.2 Verification of the punch area is performed by removing 10 punches from a 47 mm quartz-fiber filter (17.35 cm^2), then calculating the punch area: $\text{Punch Area} = [17.35 \text{ cm}^2 \times (\text{the initial filter weight} - \text{the final weight after punches have been removed}) / 10 \times \text{the initial filter weight}]$.
- 10.13.3 Further verification can be done by taking a precise measurement of the punching tool.
- 10.13.4 If the punching tool is resharpened, the punch area must be re-verified.
- 10.13.5 The "Filter Deposit" area is determined by the inside diameter of the sampling media pack used to hold the quartz filter in the sample collection process.
- 10.13.6 Before analyzing a sample filter or a blank filter, make sure the tweezers, the punching tool, and the glass surface area used to punch on are cleaned with a dry kimwipe.

Note: the blank filter analysis is optional and useful in trouble shooting. The blank filter should have organic carbon/filter $\leq 11 \mu\text{g C/filter}$, elemental carbon concentration/filter $\leq 2 \mu\text{g C/filter}$, total carbon concentration/filter $\leq 13 \mu\text{g C/filter}$ (Section 9.2). If not, repeat the filter blank analysis.

- 10.14 When the sample oven temperature is <50 °C (as indicated in the status window) the push rod will retract the boat to the load/unload position and a prompt will appear stating, Press "OK to open Sample Chamber".
- 10.15 Remove the filter from its container with tweezers to a clean glass petri dish or a flat glass surface. Visually inspect the filter. Record any physical damage, non-uniformity or if any unusual deposit is found on the filter. Gently push down a 5/16 inch punching tool on the filter to cut a disc. Remove the cut filter punch with tweezers and place it on the sample boat with the deposit-side facing up. Return the filter to the container for storage or additional analysis. After loading the filter punch, click "OK".
- 10.16 Wipe the tweezers, the glass surface and punching tool with a clean kimwipe, and return the filter with the container to the refrigerator.
- 10.17 When the analysis is complete click "Continue". Record the information and data in a logbook.
- 10.18 At the end of the analysis, data is saved to the database, split times are calculated, carbon peaks are integrated, and tabular and graphical printouts are produced. Examine the thermogram for proper NDIR and laser response, sample oven temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis.
 - 10.18.1 To correctly report the OC and EC concentrations, sample light reflectance and transmittance are continuously monitored by seven modulated diode lasers at wavelengths from 405 to 980 nm and photo detectors throughout an analysis cycle.
 - 10.18.2 As pyrolysis takes place, there is an increase in light absorption resulting in a decrease in reflectance and transmission. By monitoring the reflectance/transmittance, a pyrolytic correction with a portion of the EC peak that corresponds to the pyrolyzed OC, can be accurately assigned to the OC fraction.
 - 10.18.3 The 635 nm laser maintains the constancy with the DRI Model 2001, which uses a He-neon 632.8 nm wavelength laser to correct for pyrolysis charring of OC compounds into EC. The corrected calculation of the OC and EC concentrations is based on the results of the sample light reflectance and transmittance at 635 nm.
- 10.19 Run a replicate analysis for every ten samples or less. Take a second filter punch from one filter and analyze it in the same way (Section 10.13 – 10.18).
- 10.20 Once all samples are analyzed for the day, perform end of the day calibration using "AutoCalib" protocol and record the three peak area counts in the log book. Any values outside the expected ranges should be investigated (Section 8.2). Re-analyze samples with questionable results if necessary.
- 10.21 At the end of the day, leave the Carbon2015 software open. Close the Cal Gas gas supply valve.

11 CARBONATE ANALYSIS

Upon request for carbonate analysis (which is usually not present in vehicular exhaust) the following procedure may be followed.

The analysis is identical to the routine procedure for OC/EC analysis without carbonate removal except that the sample punch will be acidified with 20 μL of 0.4M HCl injected through the septum port when the boat is in the calibrate position. Execute a purge for approximately 20 minutes (1 minute for every μL of liquid) to allow the sample to dry before the run starts.

- 11.1 In the Enter Sample Details screen, enter the Sample ID, Run #, Punch area, Deposit area, and other information. Select "IMPROVEA_Carbonate" analysis protocol.
- 11.2 Follow the steps under Section 10 until the sample punch is loaded into the boat. Load sample and click "OK". When asked if you want to delay or continue analysis, click "OK". After 90 seconds, the punch automatically centers under the acid injection port. The computer will prompt you to inject the hydrochloric acid (HCl), and then will state "Load syringe" and "XX seconds to acid injection".
- 11.3 Flush a 25- μL syringe with 0.4 M hydrochloric acid (HCl) into a waste beaker. When prompted to inject HCl, through the injection port, deposit 20 μL 0.4 M HCl onto the filter punch, ensuring that the needle bevel is turned toward the punch and that the needle tip is touching the top of the punch.
- 11.4 When the analysis is underway, flush the syringe with nanopure water to prevent corrosion of the syringe plunger.
- 11.5 After starting analysis, the program will delay any further analysis for 1200 seconds (~1 to 1.5 minutes for every μL of liquid) to allow the punch to dry.
- 11.6 After the analysis is completed, data is saved to the database and tabular and graphical printouts are produced. Select "cmdImprove_A" from the "Command table" drop-down field and click "OK". Click "Run" on the analysis Setup screen. The program will automatically cycle into the normal OC/EC analysis, using the same Sample ID. Heat from the oxidation oven will dry the sample in this position (for approximately 15 minutes) without prematurely baking carbon from the sample; the sample temperature should not exceed 42 °C. When the punch is dry proceed with normal OC/EC analysis.

12 PROGRAM SOFTWARE

The DRI Model 2015 Carbon Analyzer is a multicomponent instrument controlled using a modular LabVIEW software package Carbon2015. Each software module handles the data processing and controls for its specific hardware component.

- 12.1 The OC/EC analysis program reads command sequences from an exe file located in C:\Program files (x86)\Model 2015 Carbon Analyzer (Carbon2015), writes data to an Access database file located in C:\Multiwavelength Carbon Analyzer\Database [Database(Access 2013)_Trusted Connection] and produces a doc report located in C:\Multiwavelength Carbon Analyzer\Thermograms simultaneously. Double clicking on the "Carbon2015" shortcut icon will open this file to start the carbon analysis program.
- 12.2 The parameter file, Config, is an initialization file which contains specific analyzer information and is located in C:\Multiwavelength Carbon Analyzer. This is where the integration threshold can be entered. Double clicking the "Config" will open this file. Be careful about changing any parameters in this file because any change in this file will affect performance of the Analyzer.
- 12.3 The protocols of carbon analyses are in C:\Multiwavelength Carbon Analyzer\Protocol. Each file has all the steps for the analysis protocol. They contain all the information for operating the analyzer during analysis.
- 12.4 While inside the Carbon Analysis program, closing any window will NOT terminate the analysis program and the ongoing analysis. Use "Exit" to return to the previous window. Only when it is needed, click "Exit" to exit the Carbon2015 program.

13 QUALITY CONTROL

13.1 Analyzer performance

13.1.1 System leak check (Sections 7.3, 10.4) and system blanks (Section 10.12.2) are performed at the beginning of each analysis day to confirm the system is clean.

13.1.2 Perform Cal Gas analyses at the beginning and the end of the day to verify the condition of the analyzer including the catalyst MnO₂. (Sections 8.2, 10.6 - 10.11)

13.2 Repeatability

Run a replicate analysis for every ten samples. A second filter punch is taken from the same filter and analyzed (Section 10.19). The total carbon concentrations from the two runs are compared. The values should meet the following criteria:

<u>TC concentration</u>	<u>Criteria</u>
< 10 µg C/cm ²	< ±2.0 µg C/cm ²
≥ 10 µg C/cm ²	≤ ±20 % of average of replicates

Replicates which do not meet these criteria must be investigated for any analyzer or sample anomalies. Analyzer anomalies include poor instrument response (as reflected in the calibration peak areas) or poor laser signals

(affecting the split between OC and EC). Typical sample anomalies are inhomogeneous deposits on the filter and filter contamination from sampling or during analysis. Reanalyze replicates if a reason cannot be found.

13.3 Laser Performance

The reflectance (LR) and transmittance (LT) of system blanks at 635 nm are recorded on the control chart for the initial and final readings. A difference >5% between initial and final indicates significant laser drift. (Section 10.12.2)

13.4 Control Chart

The control chart for the methane standard is updated each analysis day. The data for the methane standard are recorded on the control chart for the three peak areas (Sections 8.2 and 10.6 -10.11): methane calibration peak, peak 1, and peak 2. The control chart contains the peak area and percent deviation of this peak area from a historical mean of the same peak.

13.4.1 The methane calibration peak monitors the overall condition of the analyzer including the NDIR and the condition of the catalyst MnO₂. Instances where any of these peak areas deviate by more than $\pm 20\%$ from their historical means must be investigated and the cause must be corrected.

13.4.2 The historical mean includes the previous three months' data and is updated monthly, or when the methane calibration gas is changed, or when the catalysts are replaced, or when extensive repairs are performed. Normally the analyzer's catalytic efficiencies and NDIR response will decrease with time and the peak areas will also decrease. The control chart monitors these changes.

14 REPORTING DATA

The reporting limits for the total OC and EC are 11.00 and 2.00 $\mu\text{g C}/\text{filter}$, respectively. If the total OC is less than its reporting limit, all the OC subfractions and the total OC are reported as <RL. If the total EC is less than its reporting limit, all the EC subfractions and the total EC are reported as <RL.

15 REFERENCES

- 15.1 DRI Model 2015 OC/EC Carbon Analyzer Installation and Operation Manual, Desert Research Institute, March 5, 2015.
- 15.2 Standard Operating Procedure for Organic and Elemental Carbon Analysis of Exposed Quartz Microfiber Filters, SOP MV-AEROSOL-139 Version 1.1, California Environmental Protection Agency, Air Resources Board, September 2011.
- 15.3 DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A, DRI SOP #2-

226r1, January 25, 2016.

- 15.4 The IMPROVE_A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database. *J Air Waste Manag Assoc.* September 2007; 57(9):1014-23.

16 REVISION HISTORY

- 16.1 First Approval of SOP: May 2006
- 16.2 Revision 1.1: September 2011
- 16.2.1 Revised requirement for calibration when the catalysts are replaced. Section 9.
- 16.2.2 Revised procedure for the MDL determination. New procedure for MDL is based on values collected from 200 blank filters. Previous MDL procedure involved analysis of a dilution of KHP standard. Section 9.1 and 9.2 were incorporated to delineate the new MDL procedure. September 2011.
- 16.2.3 Incorporated section detailing the criteria for reporting the data separately for OC and EC. Section 14.
- 16.3 Revision 2.0: February 2019
- 16.3.1 The purpose of this revision is to reflect the changes of DRI Model 2015 Multiwavelength Thermal/Optical OC/EC Carbon Analyzer from DRI Thermal Optical Carbon Analyzer Model 2001. New DRI Model 2015 uses a nondispersive infrared (NDIR) CO₂ detector instead of a flame ionization detector (FID).
- 16.3.2 Revised SOP name from old convention, SOP MV-AEROSOL-139_Version 1.1, September 2011, to new convention, SOP MV-AEROSOL-139 Version 2.0, February 2019.
- 16.4 Revision 2.1: September 2019
- 16.4.1 Updated Division name due to reorganization.