

SOP 402

Standard Operating Procedure for Thermal/Optical Carbon Analysis of CSN Samples Using a Sunset Thermal/Optical- Reflectance/Transmittance Carbon Analyzer

Quartz Carbon Analysis Laboratory
Air Quality Research Center
CNL-Jungerman Hall, UC Davis, One Shields Ave, Davis, CA 95616

Prepared by: _Xiaolu Zhang_____ Date: _____

Reviewed by: Krystyna Trzepla_____ Date: _____

Approved by: _Nicole Hyslop_____ Date: _____

TABLE OF CONTENTS

	<u>Page</u>
TABLE OF CONTENTS	2
1. PURPOSE AND APPLICABILITY	5
2. SUMMARY OF METHOD.....	5
3. INTERFERENCES.....	6
3.1 Pyrolytically-Produced Elemental Carbon (Pyrol C)	6
3.2 Carbonate Carbon	6
4. SAFETY	6
4.1 Laser safety	6
4.2 Gas cylinders.....	7
5. PERSONNEL QUALIFICATIONS	7
6. APPARATUS	7
6.1 Thermal-Optical Transmittance/Reflectance Carbon Aerosol Analyzer (Sunset Laboratory Inc.)	7
6.2 Precision Punch.....	8
6.3 Automatic Pipettors.....	8
6.4 Forceps	8
6.5 Pre-fired Quartz-Fiber Filters	8
6.6 Volumetric Flasks, Class A.....	8
<u>7. REAGENTS.....</u>	<u>8</u>

8.	STANDARD PREPARATION AND CALIBRATION	9
8.1	Preparation of Standards	9
8.2	Calibration with External Standards	10
8.3	Internal Standard	11
9.	PROCEDURE OF CARBON ANALYSIS ON CSN SAMPLE.....	11
9.1	Work Area Preparation.....	11
9.2	Startup	11
9.3	Running a Sample	12
9.4	Shutdown	13
10.	CALCULATIONS	14
10.1	Blank Correction	14
10.2	Concentrations of Carbon Fractions on the Filter (in $\mu\text{g C}/\text{cm}^2$).....	14
10.3	Masses of Carbon Fractions on the Filter (in $\mu\text{g C}$)	14
10.4	Concentrations of Carbon Fractions in Air.....	14
10.5	Measurement Uncertainty	15
11.	Quality Assurance and Quality Control	16
11.2	Calibrations.....	18
11.3	Duplicates	19
11.3.1	CSN SAMPLE Replication Analysis.....	19
11.4	FID Response to Internal Standard	20
11.5	Start Integration Times for OC Fractions.....	20
11.6	Transit Time	21

11.7 Laser Transmittance 21

12. References 22



1. PURPOSE AND APPLICABILITY

This standard operating procedure is intended to provide a basic understanding of the principles of carbon analysis and to describe the process for the determination of organic carbon (OC), elemental carbon (EC), carbonate carbon (CC), and total carbon (TC) in particulate matter collected on quartz-fiber filters using the Sunset Laboratory Thermal/Optical OC/EC analyzers.

2. SUMMARY OF METHOD

This is a Thermal-Optical method that speciates carbon in particulate matter collected on a quartz-fiber filter into OC, EC, and CC using the IMPROVE_A temperature protocol (Table 1). A standard sized punch (0.581 cm²) is removed from a quartz filter sample and placed in the quartz oven. Once the oven is purged with helium to remove ambient air, a stepped temperature ramp increases the oven temperature to 580°C, thermally desorbing the organic and carbonate carbon. The oven is then partially cooled to 500°C, and the original flow of helium is switched to an oxidizing carrier gas (He with 10% O₂). In the second (or oxidizing) heating stage, the original EC component plus pyrolyzed OC (Pyrol C) formed during the first heating stage are oxidized and desorbed from the filter with another series of controlled temperature ramps. All carbon evolved from the sample is converted to CO₂ gas in a manganese dioxide (MnO₂) oxidizing oven immediately downstream from the desorption oven. The CO₂ then flows with the helium stream and mixed with hydrogen gas before entering a heated methanator oven where it is quantitatively reduced to methane (CH₄). The CH₄ is subsequently measured using a flame ionization detector (FID).

With the IMPROVE_A temperature protocol, the FID response for OC can be divided into five separate measurements. These measurements correspond to the OC evolved during each of the four separate heating ramps in the first (or non-oxidizing) heating stage of the analysis (Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC) and to the OC evolved during the second (or oxidizing) heating stage that is counted as Pyrol C. EC measurements are divided into three fractions (EC1, EC2 and EC3) that correspond to the EC evolved during each of the three heating ramps in the second (or oxidizing) heating stage of the analysis. The separation between OC and EC as well as the correction for the charring (Pyrol C) is performed using both the Thermo-Optical Reflectance (TOR) and Thermo-Optical Transmittance (TOT) methods (detailed in Section 3.1).

Table 1. IMPROVE_A TOT/TOR Method Parameters

Temperature Ramp (Duration)	Carrier Gas	Carbon Fraction
Heater off (90s)	He Purge	----
140°C (150-580s)	He	OC1
280°C (150-580s)	He	OC2

480°C (150-580s)	He	OC3
580°C (150-580s)	He	OC4
580°C (150-580s)	He/O ₂	EC1
740°C (150-580s)	He/O ₂	EC2
840°C (150-580s)	He/O ₂	EC3
Heater off (200s)	He/O ₂ + CH ₄	

3. INTERFERENCES

3.1 Pyrolytically-Produced Elemental Carbon (Pyrol C)

Laser transmittance and reflectance signals are used to optically correct for pyrolytically-produced elemental carbon (or char or Pyrol C) formed from organic compounds during the initial non-oxidizing stage of the analysis. Formation of Pyrol C decreases the transmittance/reflectance of the laser beam through the system. During the second (oxidizing) stage of the analysis, all EC (including Pyrol C) is oxidized from the filter. The split point between OC and EC is determined during the oxidation of EC when the transmittance or reflectance of the laser beam rises back to its initial value at the beginning of the analysis. Once the point is found, it is assumed that the EC which evolves after this point is quantitatively equal to the original EC of the sample. Pyrol C is defined as carbon evolved between the addition of oxygen and the OC/EC split point. If the OC/EC split occurs before the addition of oxygen, Pyrol C is zero and Pk4 OC ends at the split time.

3.2 Carbonate Carbon

Carbonate carbon (from calcium carbonate) is volatilized near the end of the first (or non-oxidizing) heating stage and is therefore initially included with organic carbon. The FID response for the distinctive carbonate peak can be integrated manually and subtracted from the total area assigned to organic carbon, which allows calculation of separate values for organic and carbonate carbon. Alternatively, a separate filter punch can be exposed to hydrogen chloride (HCl) vapors (which react with carbonate to form gaseous CO₂ and removes carbonate carbon from the filter) and organic and elemental carbon can be quantified (in the absence of carbonate carbon) in a second analysis. The first method is usually adequate for PM_{2.5} samples and can be accomplished with a single analysis.

NOTE: Carbonate carbon is not generally present in PM_{2.5} at quantities above the absolute uncertainty of the method.

2. SAFETY

2.1 Laser safety

The Sunset Laboratory OCEC Carbon Aerosol Analyzers uses a 658 nm laser diode for the optical light source during the sample analysis. While the analyzer itself is classified as a Class 1 Laser Product, meaning that there is no harmful laser radiation exposure to the operator during normal operation and maintenance, the internal source laser diode is rated as a Class 3b product and emits sufficient optical power to constitute a possible hazard to the human eye if directly exposed to the laser beam. Therefore, all repair and service must be performed by a trained technician.

2.2 Gas cylinders

Use caution when handling all support gas cylinders and regulators, always have cylinders properly chained to a safety rack.

NOTE: Hydrogen is a flammable gas and extra precautions should be used with the hydrogen gas lines from the supply cylinder to ensure all fitting are connected and must be leak tested each time a new cylinder is installed. The pressure of the hydrogen gas line should be kept under 15psi at all times.

3. PERSONNEL QUALIFICATIONS

Before performing carbon analysis, all operators in the laboratory, including student assistants and laboratory technicians, should read and understand the Standard Operating Procedure (SOP) and the companion Technical Instructions (that are stored under U:\IMPROVE_Lab\Carbon Analysis Lab\Daily Operation files\Instructions, including routine system calibration, sample analysis, gas cylinder replacement and trouble-shooting.

The responsibilities of the Quartz Carbon Laboratory Supervisor are: to ensure that the carbon analyses procedures are properly followed; to train new operators on handling the quartz filters and operating the analyzers; to review and examine all thermograms and data for blanks, standards and samples; to designate samples for reanalysis; to arrange for maintenance and repair of instruments; to verify an adequate quantity of supplies and gases are in stock to ensure uninterrupted analysis; and to deliver the sample analysis results in database format to the Laboratory Manager, within the specified time period. In addition, the Quartz Carbon Laboratory Supervisor is responsible for preparing monthly QC reports, including presentation of findings and evaluation of data with recommendations.

4. APPARATUS

4.1 Thermal-Optical Transmittance/Reflectance Carbon Aerosol Analyzer (Sunset Laboratory Inc.)

6.1.1 Computer system that meets Sunset Laboratory's specifications for running the analyzer, storing the analysis data, and performing calculations

6.1.2 Sunset Laboratory instrument operation software version 1109 (OCECInst1109.exe) or higher

6.1.3 Sunset Laboratory calculation software version 414(Calc414UCD.exe) or higher

4.2 Precision Punch

For removal of filter sample portion, nominal punch size of 0.581 cm²; punch areas are calculated using inside diameter measurements, made with a micrometer caliper, of the circular punch)

NOTE: Each punch is inspected regularly for any unevenness around the sharp edges, and punches with one or more significant notches in the sharp edges are replaced.

NOTE: The punch is cleaned between samples by rubbing the cutting edges with a piece of clean quartz filter.

4.3 Automatic Pipettors

Calibrated; capable of accurately pipetting standard solutions

4.4 Forceps

Silicone-coated and uncoated wide tip forceps for manipulation of the quartz boat during sample loading/unloading; uncoated metal forceps with narrow tips for manipulation of quartz filter samples and punches.

NOTE: The metal forceps are cleaned between samples by rubbing the gripping edges with a piece of clean quartz filter.

4.5 Pre-fired Quartz-Fiber Filters

Quartz fiber filters (PALL Corporation, 25 mm) are pre-fired by placing a batch (typically 100) of the filters (covered in aluminum foil) in a muffle furnace (Lindberg/Blue M No. BF51732PBC Box Furnace, or equivalent), heating the filters at 850°C for at least 3 hours under a low flow of air and allowing the filters to cool down to room temperature for at least 2 hours in the furnace.

4.6 Volumetric Flasks, 100 ml, Class A

4.7 Analytical Balance, capable of weighing to 0.0001g.

5. REAGENTS

7.1 Helium, ultra-high purity (UHP)

7.2 Hydrogen, ultra-high purity (UHP)

7.3 Oxygen (10%) in helium, premixed, purified

7.4 Methane (5%) in helium, premixed, certified

7.5 Air, Ultra Zero

7.6 Sucrose, 99.5% reagent grade

7.7 Organic-Free Water, generated in-house with a de-ionized water unit (MilliQ Academic)

6. STANDARD PREPARATION AND CALIBRATION

A set of external liquid calibration standards containing sucrose in organic-free water is used to establish the linearity of the FID response and to calibrate the gaseous internal standard (5% methane in helium) that is injected at the end of each analysis.

8.1 Preparation of Standards

8.1.1 Sucrose Stock Solution--Prepare a sucrose stock solution by weighing 1.000±0.010 g sucrose (verify balance accuracy using NIST-traceable Class 1 10-g check weight before weighing out sucrose) into a 100 mL volumetric flask and diluting to the mark with organic-free water.

NOTE: 1.000 g of sucrose (C₁₂H₂₂O₁₁, MW 342.31) in 100.00 mL of solution has a carbon (C, AW 12.01) concentration of 4.210 µgC/µL.

$$\left(\frac{1.000g \text{ sucrose}}{100 \text{ mL soln}}\right) \left(\frac{(12)(12.01gC)}{342.31g \text{ sucrose}}\right) \left(\frac{1mL}{10^3\mu L}\right) \left(\frac{10^6\mu g}{1g}\right) = 4.210 \frac{\mu gC}{\mu L \text{ soln}}$$

8.1.2 Calibration Standards--Prepare at least three calibration standards that span the measurement range of the CSN samples. Calibration standards are prepared either (1) by weighing appropriate masses of sucrose into a 100 ml volumetric flask and diluting to the mark with organic-free water, or (2) by diluting aliquots of the sucrose stock solution (Section 8.1.1) with organic-free water in a 10 ml glass vial (Table 2). Calculation template can be found in: U:/IMPROVE_Lab/Carbon Analysis Lab/Template_sucrose.xlsx.

Table 2. Sucrose standard concentrations

	Sucrose Stock (µgC/10µL)	Volume of Stock (ml)	Volume Final (ml)	Final Concentration (µgC/10µL)
Standard 1	42.10	----	100 ml	42.10
Standard 2	42.10	5 ml	10 ml	21.05
Standard 3	42.10	2.5 ml	10 ml	10.53
Standard 4	42.10	1 ml	10 ml	4.21
Standard 5	42.10	0.5 ml	10 ml	2.105

8.1.3 Store sucrose stock solution and sucrose calibration standards in a refrigerator at ≤4°C.

8.1.4 Prepare new stock solution and calibration standards at least every 6 months.

8.2 Calibration with External Standards

External standards are used to establish linearity of FID response and to calibrate the 5% methane in helium internal standard loop. Prepare and spike filter punches with external standards for calibration and analyze them according to the following instructions:

8.2.1 Punch out a new, clean section of a quartz filter and place the section on the quartz filter boat in the analysis oven.

NOTE: The filter punch section remaining in the oven from the last analysis can be used instead of a new punch of filter.

8.2.2 Run a “Clean Oven” cycle to completely clean the filter section; then run an “Instrument Blank”

8.2.3 Open the quartz door to the oven and pull out the quartz filter boat containing the cleaned filter punch.

8.2.4 Use a calibrated Eppendorf pipettor (or equivalent) to dispense 10.0 μL of a standard sucrose solution (Section 6.1.2) to the clean filter punch without removing the punch from the filter boat.

NOTE: Deposit the standard on the center of the punch that will be directly in the path of the laser during analysis.

8.2.5 Push the filter boat into the oven, close the quartz door of the oven, run a “dry wet filter” cycle.

8.2.6 Choose “Sucrose” as the punch area and click the “Start Analysis” button.

8.2.7 Repeat Sections 8.2.3 through 8.2.6 until **all three standards have been analyzed and all of the following criteria have been met:**

- The 3-point calibration has an $R^2 \geq 0.998$ (linear least-squares fit forced through the origin of a plot of total FID area counts vs. mass of carbon spiked);
- Each of the three analyses shows a percent recovery of 95% to 105% of theoretical (μgC measured/ μgC spiked);
- Each of the three analyses gives an FID response to the internal standard within 90% to 110% of the average FID response to the internal standard for the three calibration analyses; and

8.2.8 If the criteria are not met, investigate and if valid reason, change the calibration constant to a value that gives an average percent recovery of 99.95% to 100.05% when the new calibration constant is used to recalculate results from the 3-point calibration analyses. A new constant is calculated by dividing the current constant by the slope (percent recovery) determined in 8.2.7.

8.2.9. The new constant must be saved in: “C:\OCEC1109\OCECPAR\InstrumentParameter.txt” for each instrument. Values in the “InstrumentParameter.txt” file are default parameters used by

the instrument and will be embedded into every raw data text file associated with each analysis. By default, the calculation software uses the information imbedded in the raw data to compute carbon concentrations.

8.3 Internal Standard

The internal standard is 5% methane in helium, an aliquot of which is injected through a fixed-volume loop near the end of the analysis. The mass of carbon in an aliquot injected from the loop must be determined using the external standards described above. The response factor from the 3-point calibration is used to determine the mass of carbon in the internal standard loop.

7. PROCEDURE OF CARBON ANALYSIS ON CSN SAMPLE

9.1 Work Area Preparation

9.1.1 In a designated area near the OC/EC instrument, clear an area that can be maintained free of clutter, dust and chemicals. Cover the plastic dish with a layer of clean aluminum foil. Press down the edges so that the foil is secured.

9.1.2 At the beginning of each analytical session, get a new, clean section of quartz filter and roll it around the forceps. Use this to scrub an area about 2 inches in diameter on the aluminum foil to be used for cutting filter punches.

9.2 Startup

9.2.1 Ensure that the gas cylinders have at least 200-300 psi. If any of the gas cylinders need replacement, pause the analysis and notify the lab manager.

9.2.2 From standby click on “Out-of-Standby” button (if program has been exited double clicking on the “OCECINST” icon will start the analyzer).

9.2.3 Wait 10-15 seconds for the gas flows to stabilize. The actual gas flows should be close to their pre-set values shown below:

	Idle	Purge Offline	Purge Online	Analysis Helium	Analyzing Oxygen	Standby
Air (cc/min)	280	280	280	280	280	0
H ₂ (cc/min)	55	55	55	55	55	0
He1 (cc/min)	25	90	57	57	49	3
He3 (cc/min)	68	68	3	3	11	5
He/Ox (cc/min)	2	8	8	8	8	5

Cal (cc/min)	0	10	10	10	10	0
-----------------	---	----	----	----	----	---

NOTE: Use the recommended gas flow ranges displayed by the vendor-supplied software unless specifically directed by the vendor's technical support staff to use a different range.

NOTE: Check the oven pressure (PSIG). In the off-line mode it should be in the range of 0.05-0.15 psi. While analyzing on-line it should increase to about 0.6-0.7 psi. This oven pressure will change, depending upon flow rates and resistance of the MnO₂ oxidizer bed and methanator oven.

9.2.4 Ignite the FID flame by pushing the red button on the FID box and run a “Clean Oven” cycle (detailed in “TI Daily operation”)

9.2.5 Select the “Improve a.par” Parameter file and enter the name of the output file into the Raw Data file text box in the following format:
MMDDYYYY_INTRUMENT NAME.txt. Raw output files are saved under: U:\CSN\Carbon analyzers\Data\.

9.3 Running a Sample

Quartz filters are stored in a freezer at -15°C or below. An individual batch containing up to 50 filters may be kept in a refrigerator at 4°C during analysis of that batch.

Allow each petri slide holder containing a quartz filter sample to warm to room temperature just before opening it to take a punch from the filter for analysis. Return the quartz filter to the petri slide holder immediately after starting the analysis.

Punches from filter samples should only be placed in the oven while the computer is in the “Safe to put in a new sample” mode.

9.3.1 Use the precision punch to remove a section from the quartz fiber filter sample for analysis.

9.3.2 Open the quartz door to the oven.

9.3.3 Partially remove the quartz filter boat from the oven with silicone-coated forceps, and place the sample filter punch centrally into the boat's designated area with uncoated forceps. Make sure the deposited side of the sample is facing up.

9.3.4 Use the silicone-coated forceps to gently slide the boat into the oven until it is stopped by the tip of the oven thermocouple.

9.3.5 Close the quartz oven door making sure that the o-ring seals tightly in the oven ball joint and place a clamp on the ball joint.

9.3.6 Check the pressure reading on the monitor screen to make sure no warning flag appears (which would indicate a leak).

- 9.3.7 Check the Laser Transmittance signal to make sure the filter punch is in the laser pathway (Laser Transmittance signal should be less than 20000). If not, open the oven door and re-adjust the position of the boat.
- 9.3.8 At the computer, type in (or scan the bar code of) a sample identification name or number in the SAMPLE ID # field. Enter the operator's initial. Check the Parameter file and Output Raw Data file name to make sure they are correct.
- 9.3.9 Enter the sample ID and operator's name in the lab notebook and the electronic logbook, along with any notes about the appearance of the filter.
- 9.3.10 Press the "Start Analysis" button.

9.4 Shutdown

- 9.4.1 If intending to return to the analyzer later in the day or at some time over the next couple days, click on the STANDBY box. In STANDBY the back oven and methanator oven will be maintained at a lower than normal operating temperature to increase heating coil life. Also the laser will be off and the pressure will be near zero, since there is very little flow.
- 9.4.2 If not intending to use the instrument for several days, turn off the power to the FID detector and main oven and wait for the methanator oven to cool below 100°C. Shut off the gas flows and choose EXIT from the file menu (for details follow TI instructions (Startup_Shutdown.docx" for full shutdown).
-

8. CALCULATIONS

10.1 Blank Correction

In accordance with current EPA guidance, speciated carbon measurements will not be blank-corrected by laboratory personnel.

10.2 Concentrations of Carbon Fractions on the Filter (in $\mu\text{g C}/\text{cm}^2$)

10.2.1 The software application used to run the analyzer (OCECInst1109.exe) automatically stores data acquired during an analysis in comma-delimited ASCII text format for later computation, display, and printing.

10.2.2 Results from the raw datafiles are calculated using a second software application.. The data for each sample can be printed in graphic form (referred to as a thermogram) with temperature, laser transmittance/reflectance and absorbance, and FID profiles. Text output on the thermogram includes calculated loadings of OC (transmittance and/or reflectance), EC (transmittance and/or reflectance), and TC, as well as Pk1 OC, Pk2 OC, Pk3 OC, Pk4 OC, and Pyrol C on the filter (each in $\mu\text{g C}/\text{cm}^2$). The uncertainty associated with the OC, EC, and TC measurements are also given on the thermogram. Uncertainty is not estimated by the software for CC, Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC because the limits of integration for these are manually set by the analyst. Uncertainty is also not included with the Pyrol C measurement, which has integration boundaries set by the software (time of addition of oxygen to the calculated OC-EC split time). Other text outputs include EC/TC ratio, date, time, calibration constant, punch area, FID1 and FID2 status, calibration area, split time, manual split time, initial absorbance, absorption coefficient of original elemental carbon, instrument name, analyst, laser correction factor, and transit time.

10.3 Masses of Carbon Fractions on the Filter (in $\mu\text{g C}$)

The mass (in μgC) of OC, EC, TC, CC, Pk1 OC, Pk2 OC, Pk3 OC, Pk4 OC, and Pyrol C on the filter are calculated by multiplying the concentration (c) of each type of carbon ($\mu\text{g C}/\text{cm}^2$) by the deposit area (A) of the filter in cm^2 .

$$m = cA$$

NOTE: The filter deposit area is 3.53 cm^2 for a 25-mm quartz fiber filter used for sampling in a filter cassette with a 21.2-mm inside diameter, which defines the deposit area.

$$A = \pi r^2 = (3.14159) \left(\frac{21.2 \text{ mm} \left(\frac{1 \text{ cm}}{10 \text{ mm}} \right)}{2} \right)^2 = 3.53 \text{ cm}^2$$

10.4 Concentrations of Carbon Fractions in Air

Mass (m , in $\mu\text{g C}$) of each type of carbon on a filter can be divided by the volume (V_{air}) of air sampled (in m^3) to calculate concentrations (c_{air}) of each type of carbon in the air sampled.

$$C_{\text{air}} = \frac{m}{V_{\text{air}}}$$

10.5 Measurement Uncertainty

Uncertainties of measurements for OC, EC, and TC are calculated by the data analysis software according to the following equations, each of which contains both an absolute uncertainty and a relative uncertainty.

$$\begin{aligned} OC_{\text{unc}} &= \pm \left[0.20 \frac{\mu\text{gC}}{\text{cm}^2} + 0.05 \times \left(\text{meas conc of OC in } \frac{\mu\text{gC}}{\text{cm}^2} \right) \right] \\ EC_{\text{unc}} &= \pm \left[0.20 \frac{\mu\text{gC}}{\text{cm}^2} + 0.05 \times \left(\text{meas conc of EC in } \frac{\mu\text{gC}}{\text{cm}^2} \right) \right] \\ TC_{\text{unc}} &= \pm \left[0.20 \frac{\mu\text{gC}}{\text{cm}^2} + 0.05 \times \left(\text{meas conc of TC in } \frac{\mu\text{gC}}{\text{cm}^2} \right) \right] \end{aligned}$$

DRAFT

9. Quality Assurance and Quality Control

Figure 1 illustrates the general flow of the Quartz Carbon laboratory for CSN network sample receiving and analysis. A series of quality assurance and quality control (QA/QC) measures are taken on a regular basis to ensure the data quality of the OC/EC analysis. Table 3 summarizes the various QC checks performed. Detailed descriptions are provided in the following sub-sections.

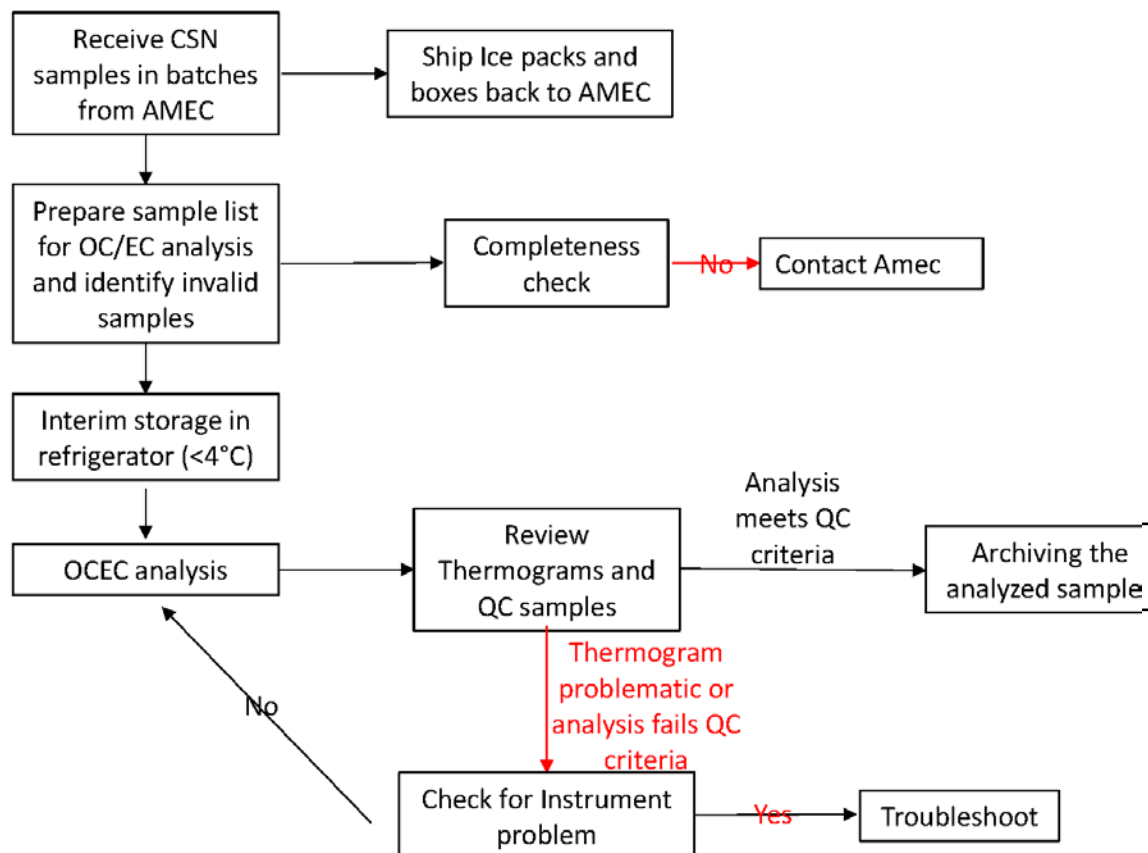


Figure 1. General flow of the Quartz Carbon laboratory for CSN network sample receiving and analysis.

Table 3: QC criteria for OC/EC analysis using the IMPROVE_A TOR/TOT carbon analysis

method

	Frequency	Acceptance Criteria	Corrective Action
Laboratory Blank Check	Beginning of analysis day	$<1.0 \mu\text{g C/cm}^2$	Check filter lots and repeat pre-firing
Instrument Blank Check	Beginning of analysis day	$<0.3 \mu\text{g C/cm}^2$	Check instrument
Single-point Sucrose Standard Check	Beginning of analysis day	Within $\pm 7\%$ of the calculated value	Troubleshoot and correct system before analyzing samples
Calibration Peak Area Check	Every analysis	Within $\pm 5\%$ of the average value for a specific instrument	Void analysis result; Repeat analysis with second filter punch
System Leak Check	Every analysis	Meet criterion set for each instrument	Re-adjust the oven seal before analyzing samples
Laser Performance Check	Beginning of analysis day	Laser Transmittance signal for Instrument blank >5000	Adjust laser position and examine oven for frosting
Network Sample Replicates	Every 20 analyses	See Table 4	Investigate instrument and sample anomalies and rerun replicate when criterion is not met
Inter-instrument Comparison Check	Once per week	$\pm 10\%$ RPD for OC and TC; $\pm 30\%$ RPD for EC	Investigate instrument and sample anomalies and rerun replicate when criterion is not met
Multi-point Sucrose Standard Check	Every six months or after major instrument repair or change of calibration gas cylinder	NA	Calculate new Calibration Constant based on calibration slope and update in the parameter file
Temperature Calibrations	Every six months or after major instrument repair	NA	Change the temperature offset values in IMPROVE_A.par files accordingly
Carrier Gas Cylinder Leak Check	Every time when a gas cylinder is replaced	Regulator pressure reading	Correct for the leak in the gas line

		should not decrease overnight with tank valve closed	
--	--	--	--

11.1 Instrument Blanks

Run an instrument blank, using a punch from a pre-fired 25 mm quartz fiber filter, at the beginning of each day. An instrument blank must meet both of the following criteria:

- TC for the instrument blank must be $\leq 0.3 \mu\text{gC}/\text{cm}^2$.
- The FID response to the internal standard injected at the end of the instrument blank analysis is within 90% to 110% of the average FID response to the internal standard for the last (or current) 3-point calibration.

If the instrument blank fails to meet any one of the criteria above, determine if the problem is with the filter or with the instrument, and, if necessary, initiate corrective action to identify and solve any instrument problem before repeating the instrument blank analysis, which must be acceptable before continuing with analysis of other samples.

11.2 Calibrations

11.2.1 Run a complete set of calibration standards (i.e., three different mass loadings) at least once every six months, or when the calibration gas cylinder is replaced, or a consistent one-sided bias is observed with the daily single-point standard check, whichever comes first. If the least-squares correlation coefficient (r^2) of area counts vs. total mass of carbon, force-fit through the origin (0,0), is not ≥ 0.998 , determine the cause of the non-linearity, and initiate actions that will identify and solve any problem that may have arisen. Then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed. In addition, analysis of each of the three standards must meet both of the following criteria:

- The measured mass of total carbon for the calibration standard is within 93% to 107% of the true value.
- The FID response to the internal standard injected at the end of the calibration standard analysis is within 90% to 110% of the average FID response to the internal standard for all three calibration standards analyses.

If any one of the sucrose standards analyses fails to meet any of the above criteria, repeat the analysis of that standard or initiate corrective action, if necessary, to solve the problem before analyzing samples.

NOTE: The calibration constant (mass of carbon in the fixed-volume internal standard gas loop) will be updated (1) when the calibration gas standard

cylinder is replaced, (2) when measured mass of total carbon for standards differs from the true value by more than 7% on repeat analysis of standards, (3) when the day-to-day measured mass of sucrose standards is consistently higher or consistently lower than the true value by more than 7%, (4) or more frequently at the discretion of the laboratory manager.

11.2.2 Run a sucrose standard calibration check sample after the initial instrument blank each day. The calibration check sample analysis results are valid if both of the following criteria are met:

- The measured mass of total carbon for the calibration check sample within 93% to 107% of the true value.
- The FID response to the internal standard injected at the end of the calibration standard analysis is within 90% to 110% of the average FID response to the internal standard for all three calibration standards analyses.

If the sucrose standard calibration check sample analysis fails to meet the any of the above criteria, repeat the analysis of the standard or initiate corrective action, if necessary, to solve the problem before analyzing samples.

11.2.3 Run at least seven replicates of a low-level standard to determine the MDL for total carbon. The spike-volume of the low-level standard should be 10-20 μL , and the concentration should be such that about 1.5 μg of carbon is delivered to the clean filter punch.

The MDL is calculated as three times the standard deviation of at least seven replicate measurements of a quantity of carbon no more than two times the estimated practical quantitation limit (PQL). (The PQL is calculated as ten times the standard deviation of the replicate measurements.) If the MDL is $\geq 0.5 \mu\text{g C}/\text{cm}^2$, investigate the source of the problem and initiate corrective action, if necessary, to correct the problem, then repeat the MDL. An acceptable MDL must be obtained before samples can be analyzed.

11.3 Duplicates

11.3.1 CSN Network Sample Replication Analysis

Run a replicate punch every twentieth CSN filter sample. Agreement between replicate total carbon measurements depends upon filter loading and the uniformity of the deposit. Acceptance criterion for replicate measurements at higher filter loadings ($\geq 5 \mu\text{g}/\text{cm}^2$) are based on the relative percent difference (RPD) of the replicate measurements; and the acceptance criterion for replicate measurements at low filter loadings ($< 5 \mu\text{g}/\text{cm}^2$) is based on absolute error ($\pm 0.75 \mu\text{g}/\text{cm}^2$), which dominates the uncertainty of the total carbon measurement at low filter loadings. Acceptance criterion for the various concentration ranges for same-analyzer replication analysis are given in the following table (Acceptance criterion for inter-analyzer replication analysis is given in Section 11.3.2).

Table 4. Acceptance criterion for same-analyzer replication analysis.

Total Carbon Concentration Range	Acceptance Criterion
Values greater than 10 $\mu\text{g}/\text{cm}^2$	Less than 10% RPD
5 - 10 $\mu\text{g}/\text{cm}^2$	Less than 15% RPD
Values less than 5 $\mu\text{g}/\text{cm}^2$	Within 0.75 $\mu\text{g}/\text{cm}^2$

NOTE: Non-uniform filter deposit can cause a difference between duplicate measurements. If the deposit on a filter appears visually to be non-uniform or if a duplicate analysis is run and the duplicate measurements fail the appropriate acceptance criterion in the table above, flag the analysis data for that filter as “Nonuniform Deposit.”

11.3.2 Inter-Instrument Comparison Evaluation

To evaluate instrument performance in terms of instrument inter-comparison, two performance check (PC) samples with enough deposit area for five 0.581 cm^2 punches should be analyzed at least once a week. Ideally the total carbon (TC) mass loading of the PC samples should cover the typical TC range of CSN samples. The measurement bias (%) of each analyzer is calculated by comparing its measurement with the average value obtained from the other four analyzers on the same PC sample. The average measurement bias for a given analyzer should be $\leq 10\%$ for TC and $\leq 30\%$ for EC.

11.4 FID Response to Internal Standard

If the FID response to the internal standard for any sample analysis run on a given day on a given analyzer is outside the range of 95-105% of the average response for all samples run that day on that analyzer, discard the results of that analysis and, if necessary, repeat the analysis with a second punch, if available, from the same filter.

NOTE: An FID response significantly lower than the average occurs when the ball joint at the front of the instrument leaks during the run.

NOTE: See Sections 11.1 and 11.2 for acceptance criteria regarding FID response to the internal standard for instrument blanks and calibration check samples, both of which are run at the beginning of each day.

11.5 Start Integration Times for OC Fractions

Start integration times for Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC are determined from the FID signal in raw data files from analysis of sucrose standard solutions. Start integration times represent the times at which the FID response reaches a minimum or an inflection point between temperature ramps in the non-oxidizing part of the analysis. The start integration times are checked (1) after repair or replacement of the oven or heating coils in an analyzer or (2) after six months from the previous

check or change, whichever comes first.

NOTE: Times at which FID minima occur during analysis of particulate samples can vary between samples by a few seconds because of differences in filter loading and in the composition of material on the filter.

11.6 Transit Time

During TOT analysis, the laser signal monitors the transmittance of the filter in real time while FID response to carbon evolved from the filter lags behind because of the time required for gaseous carbon species to travel from the filter to the FID. This lag time is called the transit time. The transit time for each instrument is used by the calculation software to align FID response properly with laser transmittance for calculation of OC and EC fractions (by integration of FID response) based on the OC/EC split time.

The transit time can be determined by analyzing a $40 \mu\text{g}/\text{cm}^2$ sucrose standard using the "transit.par" parameter file. This parameter file omits the cooling step between the non-oxidizing to oxidizing mode of the heating profile. This permits very rapid oxidation of the char which in turn causes a rapid response of the laser signal. Open the raw data file in a spreadsheet in order to easily examine the FID and laser readings. Examine the data near the beginning of the oxygen mode. Note the row numbers at which the laser readings and the FID readings begin to increase. The difference in row numbers is the transit time in seconds. The transit time can also be determined by plotting the laser signal and FID signal.

A new transit time must be determined whenever the effective volume of the analysis system between the oven and the FID changes. Such changes include replacement of the oven, replacement of the methanator tube, replacement of the FID, and replacement or modification of any transfer line between the oven and the FID.

11.7 Laser Transmittance

Laser reading (displayed in raw data files under the heading "laser") is an important indicator not only of EC loading on the filter punch but also of the condition of the quartz optical flats used for the boat and for the upper and lower windows of the quartz oven.

11.7.1 A laser reading $<1,000$ for a sample filter punch at the beginning of an analysis indicates a fairly heavy loading of EC in the sample and provides a warning that the OC/EC split point set by the software could be inaccurate because the laser response may "bottom out" during the char-forming, non-oxidizing heating ramp. The absorbance plot on the bottom of the printed thermogram can be used to check the split point.

11.7.2 An initial laser reading $\geq 5,000$ for a clean filter punch and a series of final laser readings that drift slightly upward during the last seconds of an analysis (as the oven cools) generally indicate that the quartz optical flats (boat and oven windows) are adequately free of frosting for an accurate assignment of the OC/EC split. **If the initial laser reading is $<5,000$ or if the laser reading**

drifts slightly downward during the last seconds of an analysis (as the oven cools), the quartz optical flats (boat and oven windows) should be inspected for frosting and the boat or oven or both replaced, if necessary.

NOTE: Sunset Lab's calculation software provides for automatic correction for drifting of the laser during heating and cooling cycles.

11.8 Control Charts

Control charts are used to show instrument performance over time and to compare performance among the five analyzers.

- 11.8.1 Plot measured TC for all laboratory blanks and instrument blanks on all analyzers by date. Show 0.3 $\mu\text{gC}/\text{cm}^2$ bar on the chart.
- 11.8.2 Plot linearity (R^2) of 3-point calibrations on all analyzers by date.
- 11.8.3 Plot FID response to internal calibration standard (Calibration peak area) for all samples (including blanks, sucrose checks and filter samples). Show $\pm 5\%$ bars for average calibration peak area. Note this number is analyzer-specific. Prepare separate plots for each analyzer.
- 11.8.4 Plot percent recovery for all daily calibration checks on all analyzers by date. Show $\pm 7\%$ bars for average percent recovery.
- 11.8.5 Plot relative percent difference of replicate measurements versus average measured TC for all replicate analysis. Prepare separate plots for each analyzer.
- 11.8.6 Plot percentage measurement bias of CSN replication samples and performance check samples versus average measured concentration. Prepare separate plots for OC (both TOT and TOR), EC (both TOT and TOR) and TC for each analyzer.

12. References

NIOSH Method 5040, "Elemental Carbon (Diesel Particulate)," *NIOSH Manual of Analytical Methods*, 4th ed., Cincinnati, Ohio, January 15, 1997.

Peterson, M.R., M.H. Richards, and R.K.M. Jayanty. Thermal-Optical Analysis for Organic, Elemental, Carbonate, and Total Carbon in $\text{PM}_{2.5}$. *EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, Research Triangle Park, NC, September 2000, Session 1, 1st paper.

Peterson, M.R., and M.H. Richards. Thermal-Optical-Transmittance Analysis for Organic, Elemental, Carbonate, Total Carbon, and OCX2 in $\text{PM}_{2.5}$ by the EPA/NIOSH Method. *A&WMA Symposium on Air Quality Measurement Methods and Technology*, San Francisco, CA, November 2002, Session 5, Paper #83.

Peterson, M.R., W.F. Gutknecht, R.L. Perkins, R.K.M. Jayanty, and E.D. Hardison. Laboratory Support for Chemical Speciation of $\text{PM}_{2.5}$. *EM*, August 2000, pp. 17-22.

Peterson, M.R., M.H. Richards, and J.B. Flanagan. Estimation of Uncertainties for Organic Carbon Peaks Data in Thermal-Optical-Transmittance Analysis of PM_{2.5} by the Speciation Trends Network Method. *A&WMA Symposium on Air Quality Measurement Methods and Technology*, Research Triangle Park, NC, May 2006, Extended Abstract #48.

Peterson, M.R., J.B. Flanagan, and M.H. Richards. 2008. *Estimating Uncertainties for Non-Independent Analytes--Thermal-Optical Analysis of Carbon in PM_{2.5}*. Presented at Air & Waste Management Association (A&WMA) 101st Annual Conference & Exhibition, Portland, OR, June 23-27.

Peterson, M.R., and M.H. Richards. 2008. *Evaluating Nonuniformity of Carbon Fractions in PM_{2.5} Collected on Quartz Fiber Filters*. Presented at Air & Waste Management Association (A&WMA) Symposium on Air Quality Measurement Methods and Technology, Chapel Hill, NC, November 3-6.

Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal Optical-Transmittance Carbon Analyzer, Environmental & Industrial Chemistry Department Center for Environmental Measurements and Quality Assurance, Research Triangle Institute, Research Triangle Park, NC, February 16, 2009.

Standard Operating Procedures for DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A. DRI SOP #2-216r2, Desert Research Institute, Reno, NV, July, 2008.

DRAFT