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UCD CSN Standard Operating Procedure #402

Thermal/Optical Reflectance (TOR) Carbon Analysis Using a Sunset Carbon Analyzer

Chemical Speciation Network
Air Quality Research Center
University of California, Davis

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DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications
4/2/2020	XZ	3, 8.1, 10.2, 10.3, 10.4	Expanded definition list in Sect. 3. Modified procedures for making sucrose standards in Sect. 8.1. Added Sect. 8.1.1.1 and 8.1.4. Update Sect 10.2 to include new analysis flag and application procedures. Updated Sect. 10.3.7 to reflect the change in the QC tools. Added Sect. 10.3.8. Updated MDL calculations in Sect.10.4. Updated terminologies for consistency throughout the document.

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1. PURPOSE AND APPLICABILITY

This standard operating procedure describes the principles of thermal-optical carbon analysis in addition to the process for routine determination of organic carbon (OC), elemental carbon (EC), and total carbon (TC) in particulate matter collected on quartz-fiber filters using the Sunset Laboratory Thermal-Optical OC/EC analyzers.

2. SUMMARY OF THE METHOD

The Thermal-Optical carbon analysis speciates the carbon in particulate matter, which has been collected on a quartz-fiber filter into OC and EC using the IMPROVE_A temperature protocol (Table 1). A standard sized punch (approximately 0.6 cm^2) is removed from a quartz filter sample and placed in the quartz oven. The oven is prepared through a helium purge to remove ambient air, then a stepped temperature ramp increases the oven temperature to 580 °C, thermally desorbing the organic carbon of the placed sample. The initial flow of helium is then switched to an oxidizing carrier gas (He with 10 % O_2). In the second (or oxidizing) heating stage, the original EC component plus the pyrolyzed OC (OP) 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 CO_2 gas in a manganese dioxide (MnO_2) oxidizing oven immediately downstream from the desorption oven. The CO_2 then flows with the helium stream and is mixed with hydrogen gas before entering a heated methanator oven, where it is reduced to methane (CH_4). The CH_4 is subsequently quantified 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 (OC1, OC2, OC3, and OC4) and to the OC evolved during the second (or oxidizing) heating stage that is counted as OP. 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 (OP) is performed using both the Thermo-Optical Reflectance (TOR) and Thermo-Optical Transmittance (TOT) methods (detailed in Section 6.1).

Table 1. IMPROVE_A TOT/TOR Method Parameters.

Temperature Ramp (Duration)	Carrier Gas	Carbon Fraction
Heater off (90 s)	He Purge	----
140 °C (150-580 s)	He	OC1
280 °C (150-580 s)	He	OC2
480 °C (150-580 s)	He	OC3
580 °C (150-580 s)	He	OC4
580 °C (150-580 s)	He/O_2	EC1
740 °C (150-580 s)	He/O_2	EC2
840 °C (150-580 s)	He/O_2	EC3
Heater off (200s)	He/O_2 + CH_4	

3. DEFINITIONS

- **AQS:** EPA's Air Quality System database.
- **Chemical Speciation Network (CSN):** EPA's $PM_{2.5}$ sampling network, with sites located principally in urban areas.
- **Database:** A normalized, relational data system designed to store unique information about each data point.
- **Ion Chromatography (IC):** An analytical technique used to determine the concentration of ions.
- **Interagency Monitoring of Protected Visual Environments (IMPROVE):** Federal $PM_{2.5}$ and PM_{10} sampling network directed by the National Park Service, with sites located principally in remote rural areas.
- **STI:** Sonoma Tech, Inc. Contractor developing and operating the DART interface.
- **Thermal Optical Analysis (TOA):** An analytical technique used to determine the concentration of carbon.
- **X-Ray Fluorescence (XRF):** An analytical technique used to determine the concentration of elements.
- **Laboratory blank:** Quartz filter pre-fired at 850 °C.
- **Instrumental blank**: Second analysis of the laboratory blank.
- **Laser:** Sunset OCEC analyzer is equipped with a laser diode at 658 nm.
- **Transmittance:** Laser beam transmitted through the filter media.
- **Reflectance:** Laser beam reflected by filter media and oven window.
- **Calibration peak:** CH_4 peak area at the end of the analysis program used for internal calibration.

- **Precision punch:** A custom-made tool used to remove a section of quartz sample for analysis.

4. HEALTH AND SAFETY WARNINGS

4.1 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.

4.2 Gas cylinders

It is recommended that the lab technicians use caution when handling all support gas cylinders and regulators, and 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 fittings 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 15 psi at all times.

5. CAUTIONS

Not applicable.

6. INTERFERENCES

6.1 Pyrolytically-Produced Elemental Carbon (OP)

Laser transmittance and reflectance signals are used to optically correct for pyrolytically-produced elemental carbon (or char or OP) formed from organic compounds during the initial non-oxidizing stage of the analysis. Formation of OP decreases the transmittance/reflectance of the laser beam through the system. During the second (oxidizing) stage of the analysis, all EC (including OP) 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, the EC that evolves after this point is quantitatively equal to the original EC of the sample. OP is defined as carbon evolved between the addition of oxygen and the OC/EC split point. It is assumed that the OP and the original EC have the same light absorption efficiency and that the OP evolves from the filter media earlier than the original EC. If the OC/EC split occurs before the addition of oxygen, OP is zero and peak of OC4 ends at the split time.

6.2 Carbonate Carbon

Carbonate carbon (from calcium carbonate) is thermally decomposed at around 840 °C and therefore can be included in the EC quantification. The FID response for the distinctive carbonate peak can be integrated manually and subtracted from the total area assigned to EC, which allows calculation of separate values for elemental and carbonate carbon. Alternatively, a separate filter punch can be exposed to hydrogen chloride (HCl) vapors (which react with carbonate to form gaseous CO_2 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.

7. PERSONNEL QUALIFICATIONS, DUTIES, AND TRAINING

Before performing carbon analysis, all laboratory personnel working in the Quartz Carbon Laboratory should read and understand the Standard Operating Procedures (SOP) and the accompanying Technical Information documents (TIs).

The TIs are stored under U:\IMPROVE_Lab\Carbon Analysis Lab\Daily Operation files\Documentation\SOP\TIs and include detailed instructions for A-sample receiving and inventorying, B-routine sample analysis, C-gas cylinder replacement, D-troubleshooting, E-startup and shutdown procedures, F-main oven temperature calibration, G-punch certification, H-sucrose generation, and I-gas flow calibration.

The responsibilities of the Quartz Carbon Laboratory Supervisor include:

- to ensure that the carbon analysis procedures are properly followed;
- to train new operators on handling the quartz filters and operating the analyzers;
- to review and examine thermograms and data for blanks, standards and samples;
- to designate samples for reanalysis;
- to arrange for routine maintenance and repair of instruments;
- to deliver the sample analysis results in database format to the data validators, within the specified time period,
- to prepare monthly QC reports, including presentation of findings and evaluation of data with recommendations.

The responsibilities of the laboratory technician include:

- to inventory received filters and archive analyzed filters;
- to monitor and order supplies and gases to ensure uninterrupted analysis;
- to perform daily and weekly QC checks;
- to analyze routine network samples;
- to notify the lab supervisor about any issues that may influence the data quality.

8. PROCEDURAL STEPS

8.1 Standard Preparation and Calibration

A set of external liquid calibration standards containing sucrose in DI 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.

8.1.1 Preparation of Standards

8.1.1.1 Labware Cleaning

Make sure all glassware is clean by thoroughly rinsing each piece with DI water and either allowing to air-dry or drying in the muffle furnace for 1 hour at 100 °C and allowing to cool to room temperature.

8.1.1.2 Sucrose Stock Solution

Prepare the sucrose stock solution by weighing 5.0250 g (99.5 % purity) of sucrose (verify balance accuracy using NIST-traceable Class 1 reference weights before weighing out sucrose) into a 100 mL volumetric flask and diluting to the mark with DI water.

NOTE: 5.0250 g of sucrose ($C_{12}H_{22}O_{11}$, MW 342.31) with 99.5 % purity in 100.00 mL of solution has a carbon (C, AW 12.01) concentration of 21.051 µg C/µL.

$$\left(\frac{5.0250\ g\ sucrose \times 0.995}{100\ mL\ soln}\right)\left(\frac{(12)(12.01gC)}{342.31g\ sucrose}\right)\left(\frac{1mL}{10^3\mu L}\right)\left(\frac{10^6\mu g}{1g}\right) = 21.051\ \mu g\ C$$

8.1.1.3 Calibration Standards

Table 2 lists the target concentrations of the six sucrose standards (QC|Sucorse|11-16) that are used in the calibration. Standards are prepared by diluting aliquots of the sucrose stock solution (Section 8.1.1.2) with DI water in a 10 ml or 100 ml volumetric flask. Refer to *UCD CSN TI402H: Sucrose Generation* for the complete procedure.

Table 2. Target concentrations of sucrose standards 11-16 and dilution factors

	Sucrose Stock (µgC/10µL)	Volume of Stock (ml)	Volume Final (ml)	Dilution Factor	Final Concentration (µgC/10µL)
QC|Sucrose|11	210.51	NA	100 ml	NA	210.51
QC|Sucrose|12	210.51	5.0 ml	10 ml	2X	105.26
QC|Sucrose|13	210.51	2.0 ml	10 ml	5X	42.10
QC|Sucrose|14	210.51	1.0 ml	10 ml	10X	21.05
QC|Sucrose|15	210.51	0.5 ml	10 ml	20X	10.53
QC|Sucrose|16	210.51	1.0 ml	100 ml	100X	2.105

NOTE: Store sucrose stock solution and sucrose calibration standards in

a refrigerator at ≤ 4 °C. Prepare new stock solution and calibration standards every 6 months.

8.1.2 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:

- Punch out a new, clean section of a quartz filter and place the section on the quartz filter sample holder in the main oven.

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

- Run a **Clean Oven** cycle to completely clean the filter section.
- Open the quartz ball joint and pull out the quartz filter sample holder containing the cleaned filter punch.
- Use a calibrated pipettor to dispense 10.0 µL of a standard sucrose solution to the clean filter punch without removing the punch from the filter sample holder.

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

- Push the filter sample holder into the oven, close the quartz ball joint, run a **Dry Wet Filter** cycle.
- Choose **Sucrose** as the punch area and click the **Start Analysis** button.
- Repeat steps in Sections 8.3 until all five standards have been analyzed and the following criteria have been met:
- The 5-point calibration has an $R^2 \geq 0.995$ (linear least-squares fit forced through the origin of a plot of total FID area counts vs. mass of carbon spiked).
- Each of the five analyses gives an FID response to the internal standard within 90 % to110 % of the average FID response to the internal standard for the five calibration analyses.
- Calculate the new instrument-specific calibration constant by dividing the current constant by the slope (percent recovery) determined in 10.3.2.
- 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.

8.1.3 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, resulting in approximately 20 µg equivalent carbon mass. The exact value of carbon mass in an aliquot injected from the loop must be determined using the external standards described above. The response factor from the 5-point calibration is used to determine the mass of carbon in the internal standard loop.

8.1.4 Secondary Source Calibration Standard

To verify calibration results, a secondary source calibration standard, namely a sucrose solution at a fixed concentration acquired from the manufacturer (Sunset Laboratory Inc), is analyzed after the adjustment of any calibration constant. Result should meet acceptance criteria listed in Table 5 for single-point standard check.

8.2 Carbon Analysis of CSN Samples

8.2.1 Work Area Preparation

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 and cutting board with a layer of clean aluminum foil. Press down the edges so that the foil is secured.

8.2.2 Startup

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 supervisor.

From standby, press “Out-of-Standby” (if the program has been exited, double click the “OCECINST” icon to start the analyzer).

Wait 10-15 seconds for the gas flows to stabilize. The actual gas flows should be close to their preset values shown in Table 3.

Table 3. Gas flow chart at different stages of thermal/optical analysis.

	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. 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 0.55-0.7 psi. This oven pressure will change, depending upon flow rates and resistance of the MnO_2 oxidizer bed and methanator oven.

Ignite the FID flame by pushing the red button on methanator oven and run a "Clean Oven" cycle (detailed in *UCD CSN TI402B: Daily Operation*)

Select the "Improve a.par" Parameter file (or the most updated "Improve a.par" with a timestamp) 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\InstantData\.

Check laser reflectance and transmittance readings. Both should read ~32000 without a filter punch on the sample holder, and 5000 - 20000 with a blank filter loaded (the actual numbers vary from one analyzer to another).

8.2.3 Running a Sample

Quartz filter samples are stored long-term in a freezer at -15 °C or below. An individual batch containing up to 1,500 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 main oven while the computer is in the "Safe to put in a new sample" mode.

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

Open the quartz ball joint to the oven.

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

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

Close the quartz oven ball joint, making sure that the O-ring seals tightly by placing a clamp on the ball joint.

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

Check the Laser Transmittance signal to make sure the filter punch is in the laser pathway (Laser Transmittance signal should be less than 32,000). If not, open the oven ball joint and re-adjust the position of the sample holder.

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. Select the corresponding filter punch area. Check the Parameter file and Output Raw Data file name to make sure they are correct.

Enter the sample ID and operator's name in the lab notebook.

Press the **Start Analysis** button.

Apply proper flag and comment about filter deposit and/or analysis issue through the CSN Management Site.

8.2.4 Shutdown

If intending to return to the analyzer later in the day or at some time over the next several days, click on the STANDBY box.

NOTE: In STANDBY the back oven and methanator oven will be maintained at a lower than normal operating temperature to increase heating coil life. Additionally, the laser will be off and the pressure will be near zero since there is very little flow.

If not intending to use the instrument for an extended period, turn off the power to the methanator 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 on full shutdown, see *UCD CSN TI402E: Instrument Startup and Shutdown*).

8.3 Calculations

8.3.1 Blank Correction

Both blank corrected and uncorrected (raw) carbon values are reported for CSN. The blank correction represents the net influences from positive and negative sampling artifacts inherent in quartz filter measurements of carbon fractions. Blank correction consists of subtracting the median measurement value from at least 50 field blank filters from the sample measurement value. This median value is derived from field

blanks collected during the month of sample collection, unless there are fewer than 50. In that case, field blank values from the previous month are also used.

8.3.2 Concentrations of Carbon Fractions on the Filter

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. The text file containing raw carbon data is ingested into the CSN_1.0 SQL database qcarbon.RawData and qcarbon.SampleAnalysis tables using a Windows Service immediately after the analysis is completed. Upon ingestion, the areal densities of OC (transmittance and/or reflectance), EC (transmittance and/or reflectance), and TC, as well as OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP (in µg C/cm^2) are automatically calculated by qCarbon R package and are stored in the qcarbon.ProcessedData table in the CSN 1.0 database. The thermogram for each sample containing profiles of laser transmittance/reflectance signals, FID signal, temperature, and oven pressure during the analysis can be viewed via http://analysis.crocker.ucdavis.edu:3838/Thermograms/.

8.3.3 Mass Loadings of Carbon Fractions on the Filter

The mass loadings (in µg C) of OC, EC, TC, OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP on the filter are calculated by multiplying the areal density (d) of each type of carbon (µg C/cm^2) by the deposit area (A) of the filter in cm^2.

$$m = dA$$

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.

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

8.3.4 Concentrations of Carbon Fractions in Air

The concentrations (C_{air}) of each type of carbon in the air sampled are calculated by dividing the mass loadings (m, in µg C) of each type of carbon on a filter by the volume (V_{air}) of air sampled (in m^3). The blank correction value (B) is subtracted from the mass loadings for blank corrected samples. B is zero for uncorrected values.

$$C_{air} = \frac{m - B}{V_{air}}$$

8.3.5 Measurement Uncertainty

Uncertainties of measurements for OC, EC, and TC are calculated by the following equation, which contains both an additive uncertainty and a fractional uncertainty. The additive uncertainty term is the maximum of either the standard deviation of the field blank measurements for the given processing month (σ_{dfb}) or the analytical detection limit (t). The fractional uncertainty term (f) is estimated using the collocated precision of multiple years of data.

$$unc = \frac{\sqrt{\left(Max\left(\sigma_{dfb}, t\right)\right)^2 + (f * C_{air})^2}}{V_{air}}$$

For further information regarding data processing and calculations, please refer to *UCD CSN TI #801B: Data Processing*.

9. EQUIPMENT AND SUPPLIES

- Thermal-Optical Transmittance/Reflectance Carbon Aerosol Analyzer (Sunset Laboratory Inc.)
  - Computer system that meets Sunset Laboratory's specifications for running the analyzer, storing the analysis data, and performing calculations.
  - Sunset Laboratory instrument operation software version 1109 (OCECInst1109.exe) or higher.
  - Sunset Laboratory calculation software version 423(Calc423Refl.exe) or higher.
- Quartz filters
  - Pallflex® Tissuquartz, 2500 QAT-UP (Pall Life Sciences, Ann Arbor, MI) quartz-fiber filters or equivalent.
- Precision Punch
  - For removal of filter sample portion; nominal punch size of approximately 0.6 cm^2 (diameter of approximately 0.88 cm). Actual punch area varies with individual punch and is determined by comparing the weights between a 47 mm quartz filter and the same filter with 5-10 circular punch sections removed. Refer to *UCD CSN TI #402G: Punch Certification* for detailed instruction on punch area calibration. The calculated punch diameter is verified using inside diameter measurements, made with a micrometer caliper.

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

- Automatic Pipettes
  - Calibrated; capable of accurately pipetting standard solutions.

    NOTE: Pipettes used for sucrose generation and daily QC check are calibrated semi-annually through the UC Davis pipette calibration and maintenance service (https://supplychain.ucdavis.edu/procure-contract/buying-srvcs/pipette-calibration-maintenance)
- Forceps
  - Silicone-coated and uncoated wide tip forceps for manipulation of the quartz sample holder 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.
- Pre-fired Quartz-Fiber Filters
  - Quartz fiber filters (PALL Corporation, 25 mm) are pre-fired by placing a batch (typically 100) of the filters in a 100 ml porcelain evaporating dish (CoorsTek 60233, or equivalent) in a muffle furnace (Thermo Scientific Thermolyne FB1415M Muffle Furnace, or equivalent), heating the filters at 850 °C for at least 4 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. Pre-fired filters are wrapped in aluminum foil and stored in their original packaging in the refrigerator for later use.
- Volumetric Flasks
  - 100 ml, Class A.
- Analytical Balance
  - Capable of weighing to 0.0001 g.
- Porcelain Evaporating Dish
  - 100 ml.
- Reagents
  - Helium, ultra-high purity (UHP);
  - Hydrogen, ultra-high purity (UHP);

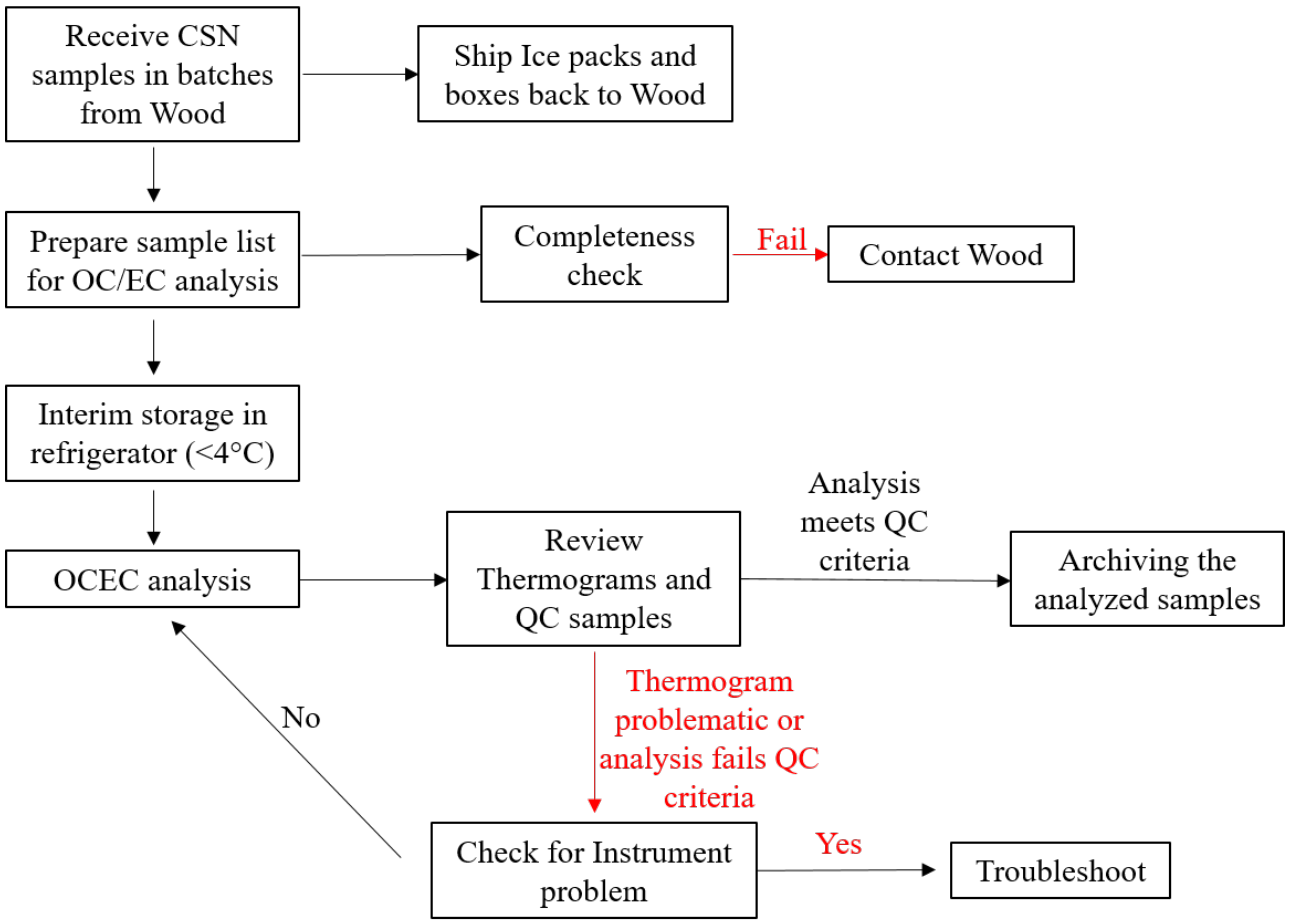
- Oxygen (10 %) in helium, premixed, purified;
- Methane (5 %) in helium, premixed, certified;
- Air, Ultra Zero;
- Sucrose, 99.5 % reagent grade;
- Organic-Free Water, generated in-house with a deionized water unit (DI water, MilliQ Academic).

10. QUALITY ASSURANCE AND QUALITY CONTROL

10.1 Sample Handling and Analysis Work Flow

CSN quartz filter samples are received and analyzed at UCD in batches (typically one batch per month). Figure 1 illustrates the general work flow of the Quartz Carbon laboratory for CSN network sample handling and analysis.

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



10.2 Analysis Flags

Unusual conditions of the sample filters or analysis are noted by the laboratory technicians during sample analysis. Pre-Analysis flags and comments are applied to the sample analysis via the CSN Data Management Site (https://csn.aqrc.ucdavis.edu/CarbonSampleAnalysis/EditFlagsFind) and are reviewed during Level 0 validation for accuracy and clarity. Errors in data entry (e.g. in SampleID, punch size) are corrected directly in the CSN_1.0 production database within the qcarbon.SampleAnalysis table. Table 4 lists all carbon pre-analysis flags.

NOTE: Paste sample punches that remain a non-white color (e.g. orange or gray) after analysis onto the "Colored Punch Log" and apply ME-1 flag for Red/Orange sample punch and ME-2 flag for Gray/Black sample punch.

Table 4. Carbon pre-analysis flags.

Code	Type	Description	Invalid
LE-1	Lab Error	Interrupted analysis	1
LE-2	Lab Error	Sample dropped on counter/floor	0
LE-3	Lab Error	Scratches/wrinkles/dark deposit created during handling	0
LE-4	Lab Error	Other – specify in comment	0
ME-1	Matrix Effect	Red/Orange punch after analysis	0
ME-2	Matrix Effect	Gray/Black punch after analysis	0
FI-1	Filter Integrity	Filter damaged inside analysis area	1
FI-2	Filter Integrity	In-homogeneous deposit	0
FI-3	Filter Integrity	Filter wrinkled or damaged outside analysis area	0
FI-4	Filter Integrity	Foreign substance on sample	0
SA-1	Sampling Anomaly	Double filters loaded, top analyzed	0
QC-1	Data Validation	Original analysis failed QC criteria. Sample reanalyzed.	0
QC-2	Data Validation	Reflectance split point questionable	0
QC-3	Data Validation	Transmittance split point questionable	0

10.3 Summary of Quality Assurance/Quality Control Activities

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 5 summarizes the various QC checks performed. Detailed descriptions are provided in the following sub-sections.

Table 5. QC criteria for OC/EC analysis using the IMPROVE_A thermal/optical carbon analysis method.

Type	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Laboratory Blank Check	Beginning of analysis day	< 1.0 µg C/cm^2	Repeat analysis. If same result, check filter lots for possible contamination and perform pre-firing
Instrument Blank Check	Beginning of analysis day	between -0.3 and 0.3 µg C/cm^2	Repeat analysis. If same result, check instrument and gas lines for possible contamination
Single-point Sucrose Standard Check	Beginning of analysis day	Within ± 7 % of the calculated value	Repeat analysis. If same result, run a different sucrose solution to determine if the problem is with the solution or instrument. If former, make new sucrose solution. If latter, perform full 5-point calibration to determine new calibration constant.
Calibration Peak Area Check	Every analysis	Within ± 10 % of the daily average value for a specific instrument	Void analysis result; Repeat analysis with second filter punch
System Leak Check	Every analysis	Meet minimum oven pressure (criterion is instrument-specific)	Re-adjust the oven seal and check oven temperatures 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 20th network sample analyses	See Table 6	Investigate instrument and sample anomalies Analyze the third punch on a difference analyzer
Inter-instrument Comparison Check	Once per week	Measurement bias for a given analyzer should be ≤ 10 % for TC and OC and ≤ 20 % 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	NA	Calculate new calibration constant based on calibration slope and update in the parameter file

	calibration gas cylinder		
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 should not decrease overnight with tank valve closed	Correct for the leak in the gas line
Oven Temperature	Every analysis	Back Oven: 870 ± 10 °C Methanator Oven: 500 ± 5 °C	Check heating coils; replace the heating coils if needed

10.3.1 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 between -0.3 and 0.3 µg C/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 specific instrument on the same day.

If the instrument blank fails to meet any one of the criteria above, the operator must 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 samples.

10.3.2 Calibrations

Run a complete set of calibration standards (i.e., five different mass loadings) at least once every six months, 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* ≥ 0.995, determine the cause of the non-linearity and initiate actions that will identify and solve any problem that may have arisen. Then repeat the five-point calibration, which must yield satisfactory results before samples are analyzed. In addition, analysis of *each* of the five 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 the analyses on the same day on the same analyzer.

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 lower than the true value by more than 7 %, (4) or more frequently at the discretion of the laboratory supervisor.

Run a sucrose standard calibration check sample after the instrument blank at the beginning of 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 the analyses on the same day on the same analyzer.

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.

10.3.3 Inter-Instrument Comparison

10.3.3.1 CSN Network Sample Replication Analysis

A replicate analysis is performed on every twentieth CSN network sample on a randomly selected analyzer. Agreement between replicate and routine measurements depends upon filter loading, the uniformity of the deposit and the instrument inter-comparisons. Acceptance criteria for replicate measurements at higher filter loadings (> 10 μg/cm^2 for TC and > 2.5 μg/cm^2 for EC) are based on the relative percent difference (RPD) of the pair; the acceptance criteria for replicate measurements at low filter loadings (≤ 10 μg/cm^2 for TC and ≤ 2.5 μg/cm^2 for EC) are based on absolute error, which dominates the measurement uncertainty for filters with lower mass loadings. Acceptance criteria for the various areal density ranges for replication analysis are given in Table 6.

$$RPD = \frac{Routine - Replicate}{(Routine + Replicate)/2} \times 100$$

Table 6. Acceptance criterion for TC and EC replication analysis.

TC Areal Density Range	Acceptance Criterion
> 10 μg/cm^2	Less than 10 % RPD
≤ 10 μg/cm^2	Absolute difference within 1 μg/cm^2

EC Areal Density Range	Acceptance Criterion
> 2.5 μg/cm^2	Less than 20 % RPD
≤ 2.5 μg/cm^2	Absolute difference within 0.5 μg/cm^2

NOTE: Non-uniform filter deposit can cause a difference between replicate and routine measurements. If the replicate analysis fails the QC criteria and from visual inspection the sample deposit on a filter appears non-uniform, apply the appropriate lab flag to the analysis data.

10.3.3.2 Inter-Instrument Comparison Evaluation

To evaluate instrument performance in terms of instrument inter-comparison, one performance check (PC) sample with enough deposit area for five 0.6 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 network 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 ≤ 10 % for TC and OC and ≤ 20 % for EC.

10.3.4 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 90-110 % 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. See Sections 10.3.1 and 10.3.2 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.

10.3.5 Transit Time

During TOR analysis, the laser signal monitors the reflectance 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 reflectance 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 $\mu g/cm^2$ 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.

10.3.6 Laser Transmittance/Reflectance

Laser transmittance and reflectance readings (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 sample holder and for the upper and lower windows of the quartz oven.

A transmittance laser reading < 500 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. For samples with saturated laser response, the split point is automatically assigned to be when the carrier gas shifts from pure helium to helium/oxygen mixture. QC-2 and/or QC-3 flags are applied to these samples because the OC/EC split is uncertain (see Section 10.2).

An initial transmittance reflectance laser reading ≥ 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 (sample holder and oven windows) are adequately free of frosting for an accurate assignment of the OC/EC split. If the initial transmittance or reflectance 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 laser-sample alignment should be

checked and the quartz optical flats (sample holder and oven windows) should be inspected for frosting and the sample holder or oven or both replaced, if necessary.

10.3.7 Quality Control Charts

Quality control charts are used to evaluate daily QC results and instrument performance over time. They are accessible via http://analysis.crocker.ucdavis.edu:3838/qCarbonTouchScreen/. QC charts are reviewed daily or as much as needed as part of the QC exercise.

- Blanks: Time-series of total carbon (TC) for daily laboratory blanks (QB) and instrument blanks (IB). All QB should be below 1.0 μgC/cm^2 criterion line and IB between ± 0.3 μgC/cm^2 criterion lines on the chart.
- Single-Point Sucrose: Time-series of percentage recovery (error) of daily sucrose analysis. Recovery (error) should be within ± 7 % criteria lines.
- Calibration Area: Time-series of calibration peak area (i.e. FID response to internal calibration standard) of all sample analysis (including blanks, sucrose, and filter samples). Solid line represents average value of all sample analysis during the past two weeks on a specific analyzer; dashed lines show - 10 %, - 5 %, + 5 % and + 10 % of the average, respectively. Calibration area of any sample should be within ± 10 % criteria lines. One exception is that, for extremely heavily loaded sample, readings from FID 2 channel are used for calibration, and the resulting calibration area is approximately ¼ of the normal value.
- Replicates: Relative percentage difference (RPD) of replicate/routine paired analyses (blue points) and weekly performance check analyses (red points) as a function of parameter areal densities. All replicate analyses should meet the criteria specified in Table 6 for ECR and TC. Performance check analyses should meet the criteria specified in Section 10.3.3.2 for ECR and TC.
- EC/OC Ratio: Time series of ECR/OCR ratio and ECT/OCT ratio for all network sample analyses. Check thermogram of sample with EC > OC for anomaly.
- Total Carbon Loading: Time series of total carbon (TC) for CSN samples (plotted on log scale). Check thermograms and filter details page on the CSN Management Site (https://csn.aqrc.ucdavis.edu/Filters/Details) for samples with TC < 1 μg C/cm^2 and field blanks (FBs) with TC > 10 μg C/cm^2.

10.3.8 Thermogram Review

In addition to QC chart review, analysis thermograms (http://analysis.crocker.ucdavis.edu:3838/Thermograms/) are reviewed daily to catch the following anomalies that may not be observable in the QC charts:

- Baseline drift

- Noise in laser, FID, and system pressure
- Atypical laser response
- Unreported typing error in Sample ID and punch area

10.4 Method Detection Limits (MDLS)

The Method Detection Limits (MDLs) of thermal/optical carbon analysis are based on the analyses of pre-fired laboratory blank quartz-fiber filters from previous year and are defined as three times the standard deviation of their measurement results (Table 7). The MDLs are updated annually. From 2020 onward, MDLs will be determined with filter media employed in the CSN.

NOTE: MDLs for CSN network samples are determined differently from the MDLs for carbon analysis discussed here and is specified in *UCD SOP #801B: CSN Data Processing*.

Table 7. Method Detection Limits (MDLs) of each carbon parameter, based on 1104 laboratory blank measurements in 2019.

Parameter	**Sample Count**	**MDL ($\mu g/cm^2$)**	**MDL (µg/filter)**
EC1	1104	0.18	0.63
EC2	1104	0.40	1.40
EC3	1104	0.20	0.69
ECTR	1104	0.06	0.23
ECTT	1104	0.01	0.04
OC1	1104	0.09	0.32
OC2	1104	0.14	0.50
OC3	1104	0.46	1.63
OC4	1104	0.14	0.48
OCTR	1104	1.05	3.71
OCTT	1104	1.05	3.72
OPTR	1104	0.63	2.24
OPTT	1104	0.63	2.24
TCTC	1104	1.05	3.71

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