Standard Operating Procedure for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a Sunset Laboratory Dual-Mode Analyzer

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1.0 Scope and Application

This method covers the determination of organic carbon (OC), elemental carbon (EC), carbonate carbon (CC, optional), and total carbon (TC) in particulate matter collected on quartz-fiber filters by the Interagency Monitoring of Protected Visual Environments Thermal-Optical Reflectance/Transmittance (TOR/TOT) temperature-calibrated method (IMPROVE_A). This method can also be used to measure the quantities of carbon evolved from the filter during each of four non-oxidizing heat ramps (OC1, OC2, OC3, and OC4) and during each of three oxidizing heat steps (EC1, EC2, and EC3). The OC/EC split is not considered in the calculation of measured values for the seven peaks. The defining calibrated temperature ranges for carbon peaks are given in the table below.

Sample Temperatures at Which Carbon Peaks Are Evolved

Peak	IMPROVE_A
Helium Atmosphere	
OC1	140°C
OC2	280°C
OC3	480°C
OC4	580°C
98% Helium/2% Oxygen Atmosphere	
EC1	580°C
EC2	740°C
EC3	840°C

The quantity of OC that was pyrolyzed (PC) during the non-oxidizing heat ramps is determined based on the time the reflectance or transmittance of the filter rises back up to its initial value. The measured value for PC is different for TOR and for TOT; therefore, OC and EC are different for TOR and TOT even though TC and the seven peaks are the same. Thus, the defining abbreviations are PCR, OCR, and ECR when reflectance is used to set the split; and the defining abbreviations are PCT, OCT, and ECT when transmittance is used to set the split.

The SOP for temperature calibration of the analyzer sample thermocouple is a separate document titled, "Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer."

2.0 Summary of Method

The IMPROVE_A carbon method separates carbon in particulate matter collected on a quartz-fiber filter into seven so-called carbon peaks (OC1, OC2, OC3, OC4, EC1, EC2,

and EC3). In the first (or non-oxidizing) heating stage, organic carbon is thermally desorbed from the filter under a flow of helium with controlled temperature ramps. The original flow of helium is then switched to an oxidizing carrier gas (oven concentration: 2% O_2 in He). In the second (or oxidizing) heating stage, the original elemental carbon component plus any remaining pyrolyzed organic carbon formed during the first heating stage are oxidized/desorbed from the filter, first at the same temperature as OC4 then with two additional controlled temperature ramps. The sample is held at the target temperature at each stage of the analysis until evolution of carbon at that temperature is complete. All carbon evolved from the sample is converted to CO_2 in an oxidizing oven immediately downstream from the sample oven, and the CO_2 is converted to methane (CH_4) by a reduction catalyst in a methanator oven before being measured with a flame ionization detector (FID).

NOTE: For IMPROVE_A analysis, the analyzer sample thermocouple must be calibrated according to RTI SOP: "Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer".

3.0 Interferences

3.1 Pyrolytically-Produced Elemental Carbon (Pyrol C)

Laser reflectance (R) and/or laser transmittance (T) is used to optically correct for pyrolyzed carbon (char or Pyrol C or PC or PCR and PCT) formed from organic compounds during the first (non-oxidizing) part of the analysis. Formation of PC decreases the reflectance of the laser beam from the surface of the filter and decreases the transmittance of the laser beam through the filter. During the second (oxidizing) part of the analysis, all EC (including PC) is burned off the filter. The reflectance-based split between OC and EC is assigned by the calculation software as the time during the analysis when the reflectance of the laser beam rises back to its initial value measured at the beginning of the analysis. The transmittance-based split between OC and EC is assigned by the calculation software as the time during the analysis when the transmittance of the laser beam rises back to its initial value measured at the beginning of the analysis. Total FID response to the left of the OC-EC split (based on reflectance or transmittance) is assigned to OC, and total FID response to the right of the split (but before the internal standard peak) is assigned to EC. PC is defined as carbon evolved between the addition of oxygen and the OC-EC split. If the OC-EC split occurs before the addition of oxygen, PC has a negative value; if the OC-EC split occurs after the addition of oxygen, PC has a positive value. The table below gives the abbreviations used in this SOP and in reports for OC, EC, and PC determined using reflectance and using transmittance.

Carbon Fraction Abbreviations		
Carbon Fraction	Split Determined By Reflectance	Split Determined By Transmittance
Organic carbon	OCR	OCT
Elemental Carbon	ECR	ECT
Pyrolyzed Carbon	PCR	PCT

PC forms within the filter as well as on the surface during the non-oxidizing part of the analysis, but PC burns off the surface of the filter first when oxygen is added for the oxidizing part of the analysis. As a result of additional PC remaining within the filter at the time of the reflectance split, PCR is almost always less than PCT, OCR is almost always less than OCT, and ECR is almost always greater than ECT.

3.2 Carbonate Carbon

Carbonate carbon (from thermal decomposition of calcium carbonate and any other carbonate- or bicarbonate-containing inorganic material present) is volatilized over several temperature ramps and therefore is spread over several of the seven carbon peaks, especially OC3, OC4, EC1, and EC2. A small sharp peak at the very beginning of the analysis (appearing as a leading shoulder on the OC1 peak) is probably due to the presence of a bicarbonate salt or mineral in the sample. A separate filter punch can be exposed to hydrogen chloride vapors (which react with carbonate and bicarbonate to form gaseous carbon dioxide and remove carbonate carbon from the filter) and organic and elemental carbon can be measured (in the absence of carbonate carbon) in a second analysis. Unfortunately, treatment with acid can cause a significant redistribution of organic and elemental carbon among the seven peaks. As expected, some peaks become smaller as carbonate is removed, but other peaks may become larger, apparently due to reaction of organic carbon species with the acid. As a result, the OC/EC split time for the analysis may be shifted by several minutes by the acid treatment.

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

4.0 Apparatus

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

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

4.1.2 Color printer (for printing thermograms)

4.1.3 Sunset Laboratory instrument operation software version 630 (OCEC2PD630.exe) or a more recent version

4.1.4 Sunset Laboratory calculation software version 183 (Calc2PD183.exe) or a more recent version

4.2 Precision Punch (for removal of filter sample portion, nominal dimensions 0.7 cm x 0.8 cm, nominal area 0.56 cm^2)

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 or resharpened.

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

4.3 Syringes or Automatic Pipettors, calibrated; capable of accurately pipetting standard solutions

4.3.1 Hamilton 700 Series Syringe, 25-µL (#80430), or equivalent, for aqueous standards

4.3.2 Hamilton Gas-Tight Syringes, 1-mL (#81330) and 2.5-mL (#81430), or equivalent, for gas standards

4.4 Forceps, silicone-coated forceps for manipulation of the quartz boat during sample loading; uncoated forceps for manipulation of quartz filter samples and punches.

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

4.5 Clean Quartz-Fiber Filters

NOTE: Quartz fiber filters are cleaned by placing a batch (typically 100) of the filters in a large crucible, placing the crucible in a muffle furnace (Lindberg/Blue M No. BF51732PBC Box Furnace, or equivalent), heating the filters at 900°C for 4 hours (for Pall Tissuquartz filters) or 3 hours (for Whatman QMA quartz filters) under a low flow of air, turning the furnace off, and allowing the filters to cool for at least 2 hours in the furnace under a low flow of nitrogen. Either 2% or a minimum of 2, whichever is more, of the filters are randomly selected from the cleaned batch and analyzed in the same fashion as regular samples. If any filter analyzed gives a measured blank value that exceeds 1.5 µg/cm^2 for total carbon, the filters from that batch will either be rejected or re-cleaned and tested again.

NOTE: Batches of filters that pass the acceptance-testing criterion ($\leq$1.5 µg/cm^2 total carbon) are assigned a Batch Number. Batches of acceptance-tested filters are placed individually in petri slide holders, which are placed in a resealable plastic bag labeled

with the Batch Number. The resealable plastic bag is stored in a freezer at $\leq -15\,^{\circ}C$ until the filters are used.

4.6 Volumetric Flasks, Class A

4.7 Analytical Balance, capable of weighing to ± 0.0001 g

Check the Balance Lab Notebook to make sure balance has been certified within the past one year. Check balance with Class 1 weights before using. Record all weights in the appropriate Lab Notebook.

4.8 Class 1a Weights

4.9 Sunset Laboratory Special Quartz Boat With Thermocouple

Standard procedures for temperature calibration are given in detail in a separate SOP titled, "Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer."

5.0 Reagents

5.1 Helium, ultra-high purity (UHP)

NOTE: Only copper and NO-OX™ tubing are used as transfer lines for helium. Helium gas is passed through both a non-indicating, high-capacity oxygen trap (Scott Specialty Gases, Catalog Number 53-43L, or equivalent) and an indicating, low-capacity oxygen trap (Scott Specialty Gases, Catalog Number 53-43T, or equivalent) before it reaches the carbon analyzer.

5.2 Hydrogen, ultra-high purity (UHP)

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

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

5.5 Carbon Dioxide (5%) in helium, premixed, certified

5.6 Air, Ultra Zero

5.7 Sucrose, 99.9% reagent grade

5.8 Potassium Hydrogen Phthalate, assay 99.95%-100.05%, Acidimetric Standard, EM Science PX1476-3 or equivalent.

5.9 Calcium Carbonate, 99.95% ACS Reagent Grade or equivalent

5.10 Hydrochloric Acid, 37%, ACS Reagent Grade or equivalent

5.11 Organic-Free Water, generated in-house by passage of tap water through a Millipore reverse-osmosis unit (Milli-RO Plus) with added filtration through a Milli-Q Plus unit.

6.0 Standards Preparation and Analysis

Two certified gas standards (CH_4 in helium and CO_2 in helium) and two liquid calibration standards (sucrose and potassium hydrogen phthalate) in organic-free water are 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.

NOTE: Much of the organic carbon in sucrose is converted to char (or PC) during the non-oxidizing heat ramps. KHP, which also contains only OC, does not form significant char (PC), and it volatilizes from the filter over a fairly narrow temperature range.

6.1 Preparation of Liquid Standards

6.1.1 Sucrose Standard Solution--Prepare a sucrose standard solution by weighing 0.4300 ± 0.0100 g sucrose (verify balance accuracy using NIST-traceable Class 1 check weights before weighing out sucrose) into a 100-mL volumetric flask and diluting to the mark with organic-free water.

NOTE: 0.4300 g of sucrose ($C_{12}H_{22}O_{11}$, MW 342.31) in 100.00 mL of solution has a carbon (C, AW 12.01) concentration of 1.810 µgC/µL.

$$\left(\frac{0.4300\ \text{g sucrose}}{100.00\ \text{mL soln}}\right)\left(\frac{(12)(12.01\ \text{g C})}{342.31\ \text{g sucrose}}\right)\left(\frac{1\ \text{mL}}{10^3\ \mu\text{L}}\right)\left(\frac{10^6\ \mu\text{g}}{1\ \text{g}}\right)=1.810\ \frac{\mu\text{gC}}{\mu\text{L soln}}$$

6.1.2 KHP Standard Solution--Prepare a potassium hydrogen phthalate (KHP) standard solution by drying KHP at 110°C for two hours, allowing the dried KHP to equilibrate to room temperature, weighing out 0.3900 ± 0.0100 g of KHP (verify balance accuracy using NIST-traceable Class 1 check weights before weighing out KHP) , dissolving the KHP in reagent grade water with 0.4 mL concentrated HCl, and diluting the solution to volume in a 100-mL volumetric flask

NOTE: 0.3900 g of dry KHP ($KHC_8H_4O_4$, FW 204.22) in 100.00 mL of solution has a carbon (C, AW 12.01) concentration of 1.835 ugC/uL.

$$\left(\frac{0.3900\ \text{g KHP}}{100.00\ \text{mL soln}}\right)\left(\frac{(8)(12.01\ \text{g C})}{204.23\ \text{g KHP}}\right)\left(\frac{1\ \text{mL}}{10^3\ \mu\text{L}}\right)\left(\frac{10^6\ \mu\text{g}}{1\ \text{g}}\right)=1.835\ \frac{\mu\text{gC}}{\mu\text{L soln}}$$

6.1.3 Store sucrose and KHP standard solutions in a refrigerator at $\leq 4°C$.

6.1.4 Prepare new liquid calibration standards at least every 6 months.

6.2 Calibration with External Standards

Four different external standards are used to establish linearity of FID response and to

determine the mass of carbon held in the internal standard loop that is injected into the analysis system at the end of each analysis.

6.2.1 Calibration with standard gases (CH_4 in helium and CO_2 in helium, certified)

6.2.1.1 Replace the Swagelok union that attaches the helium supply line to the quartz oven cap on the analyzer with the Swagelok tee that has a septum port.

6.2.1.2 Run an oven clean on the analyzer.

6.2.1.3 Load the calibration gas injection parameter file (CalGasInj_*.par).

6.2.1.4 Using the gas name and injection volume as the Sample ID, run an analysis for each volume of gas in the table below for each of the two standard gases.

Volume of Gas Standard (µL)	Syringe
100	1.0-mL
200	1.0-mL
500	1.0-mL
1000	1.0-mL
1000	2.5-mL
1500	2.5-mL

NOTE: It is not necessary to open the oven between runs.

Step 1: Type in the Sample ID (for example, CH4 100uL)

Step 2: Start the analysis.

Step 3: Quickly purge and then load the syringe with the appropriate volume of calibration gas.

Step 4: Inject the calibration gas into the system through the septum approximately two minutes after data recording begins.

Step 5: Run the calculation software to obtain the total area and the calibration gas area for the injection.

6.2.1.5 Repeat Section 6.2.1.4 until all six volumes of both gas standards have been analyzed and <u>all</u> of the following criteria have been met:

- Each 6-point calibration has an $R^2 \geq 0.998$ (linear least-squares fit

forced through the origin) in a plot of mass of carbon injected (on the y-axis) vs. the ratio of sample total area counts to internal standard area counts (on the x-axis);

- Each of the six analyses shows a percent recovery of 95% to 105% of the average percent recovery across the six calibration analyses; and
- Each of the six analyses gives an FID response to the internal standard within 95% to105% of the average FID response to the internal standard across the six calibration analyses.

6.2.2 Calibration with standard aqueous solutions (sucrose and KHP)

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

6.2.2.2 Run an "Oven Clean " cycle to completely clean the filter section; then run an "Instrument Blank."

6.2.2.3 Repeat the steps in this section once for each of the following volumes of the sucrose and KHP aqueous standards: 5 µL, 10 µL, 15 µL, 15 µL, and 20 µL.

Step 1: Remove the quartz cap from the front of the oven and pull the quartz filter boat containing the cleaned filter punch to the front of the analyzer oven.

Step 2: Use a precision syringe to deliver a precise volume of aqueous solution to the clean filter punch without removing the punch from the filter boat.

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

Step 3: Push the filter boat into the oven, close the quartz door of the oven, and allow the filter to dry completely (20-30 minutes) inside the cool oven before clicking the Start Analysis button.

Step 4: Analyze the filter punch as described in Section 7.2.

6.2.2.4 Repeat Section 6.2.2.3 until all five volumes of both aqueous standards have been analyzed and <u>all</u> of the following criteria have been met:

- Each 5-point calibration has an $R^2 \geq 0.998$ (linear least-squares fit forced through the origin) in a plot of mass of carbon injected (on the y-axis) vs. the ratio of sample total area counts to internal

standard area counts (on the x-axis);

- Each of the five analyses shows a percent recovery of 95% to 105% of the average percent recovery across the five calibration analyses; and
- Each of the five analyses gives an FID response to the internal standard within 95% to105% of the average FID response to the internal standard across the five calibration analyses.

6.2.3 Use the slopes of the least squares plots for the four standards to calculate an average slope (or calibration factor) for the analyzer.

6.2.3.1 If each of the four slopes is within 95% to 105% of the average of the four slopes, the full calibration is valid.

6.2.3.2 If the slope for one or more of the standards falls outside the 95% to 105% window, repeat the calibration using that standard.

6.2.3.3 When the slopes of all four calibration standards are within 95% to 105% of the average slope, the full calibration is valid.

6.3 Internal Standard

6.3.1 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 full FID calibration is used to determine the mass of carbon in the internal standard loop.

6.3.2 The internal standard can also be used in a crude test of catalyst efficiency by injecting the internal standard through its loop in a non-oxidizing atmosphere (pure helium), then again in an oxidizing atmosphere (2% O_2 in helium), and finally as usual at the end of the analysis. Each of the three injections should give an FID area count that is within 95% to 105% of the average of the area counts for the three injections.

6.3.2.1 Use the AutoCalGas*.par file and a Sample ID of “AutoCal” to run this test.

6.3.2.2 Run the calculation software and paste the results into the AutoCal spreadsheet to quickly determine if the three injections meet the criterion.

6.3.2.3 If the AutoCal repeatedly fails the acceptance criterion, adjust the He-Ox flow rate up or down slightly until the acceptance criterion is met.

7.0 Carbon Analyzer Procedure

7.1 Work Area Preparation

7.1.1 In a designated area near the OC/EC instrument, clear an area which can be maintained free of clutter, dust and chemicals. Cover the area with 5-6 layers of clean aluminum foil. Tape the edges down so that the foil is secured.

NOTE: A glass plate may also be used to support the filter sample as a sample punch is removed for analysis. Be sure to clean the plate with a section of clean quartz filter before use. (Do not use a cloth wipe to clean the plate because of the increased possibility of contamination. Contamination of a sample with a fiber from the wipe could inflate the OC measurement.)

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

7.2 Startup

7.2.1 From standby press CONTINUE button (if program has been exited double clicking on the "OCECINST" icon will start the analyzer).

7.2.2 Set gas flow rates to the values given on the computer monitor for the analyzer. Typical ranges for gas flow rates are:

He-1 set to 54 - 58 cc/min

He-2 set to 12 - 15 cc/min

He-3 set to 67 - 70 cc/min

He/O2 set to 12 - 15 cc/min

Air set to 280 - 300 cc/min

Cal set to 10 - 14 cc/min

Hydrogen - when ready to ignite the flame in the FID, set the Hydrogen flow to 80-100 cc/min. Once the flame has been lit (usually signaled by a small pop), return the flow rate to 40-59 cc/min.

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 pressure (PSIG). In the off-line mode it should be in the range of 0.15-1 psi. While analyzing on-line it should increase by about 1-2 psi. This oven pressure will change, depending upon flow rates and resistance of the MnO_2 oxidizer bed and the reduction catalyst tube in the methanator

oven.

7.2.3 Fill in the Analyst field and the Punch Area field on the OCECInst form.

7.2.4 Select the most recent temperature-calibrated IMPROVE_A parameter file (Improve-A_yyyymmdd_*.par), as appropriate, and either select the instrument and current date data file or enter the name of the file (example for F analyzer: fmmddyy_imp_a.txt) into the Raw Data file text box.

NOTE: An example temperature parameter file for IMPROVE_A is given below.

```
' improve-A.par
' Temperature Calibrated on 11 Dec 2007
' mode <comma> time <comma> temperature
'n.b. regimen must end 'Offline' mode.
Helium, 10, 1,.001, 100, 8
' start ramping the temperature
Helium, -1, 195, .0275, 120, 6
Helium, -1, 341, .07, 95, 4
Helium, -1, 549, .165, 65, 0
Helium, -1, 653, .175, 50, 0
Oxygen, -1, 653, .175, 50, 0
Oxygen, -1, 820, .30, 35, 0
Oxygen, -1, 920, .32, 25, 0
CalibrationOx, 110, 1,.001, 100, 16
' All done!
Offline, 1, 0,.001, 100, 16
' end.
'******************
'format
'Mode; time; temperature; power constant; time constant; blower mode
'power constant - .0001 to 1; think of it as a percentage
'typical .01 to .4  must be positive
'time constant (seconds) - 1 to 200  must be positive
'typical - 10 to 120
'low temperature - long time constant; low power
'high temperature - high power; short time constant
'blower speed - 0 and 3 to 16; 0 = off; 16 = full
'do not run blower at settings of 1 or 2 - too slow
```

7.3 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 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 and the petri slide holder to the refrigerator 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 new sample" mode.

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

7.3.2 Open the quartz door to the oven.

7.3.3 Pull the quartz filter boat to the front of the oven with the silicone-coated forceps, and place the sample filter punch on the boat with uncoated forceps.

7.3.4 Use the silicone-coated forceps to gently slide the boat into the oven until the filter punch is properly aligned under the laser beam.

7.3.5 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.

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

7.3.7 At the computer, type in (or scan the bar code of) a sample identification name or number in the SAMPLE ID # field. Check the Parameter file, Output Raw Data file, and Instrument Name to make sure they are correct.

7.3.8 Write the sample ID, the initial laser reflectance and transmittance of the filter punch, and the instrument name or designator in the lab notebook, along with any notes about the appearance of the filter.

7.3.9 Press the Start Analysis button.

7.3.10 At the end of the analysis, record the final laser reflectance and transmittance of the filter punch in the lab notebook before opening the oven for the next sample.

7.4 Procedure for Estimating Carbonate Carbon

The procedures for estimating carbonate carbon (CC) are performed only for clients who specifically request it and who authorize payment for it. CC is estimated as the difference in TC between an HCl-treated and an untreated sample punch. Two analyses are required: (1) analysis of an untreated sample punch, and (2) analysis of a second punch from the same filter from which carbonate has been chemically removed (by exposure to gaseous hydrogen chloride).

7.4.1 Expose a punch from the sample filter to hydrogen chloride vapor in a dessicator, petri dish, or similar chamber containing a small amount of concentrated hydrochloric acid for 1 hr.

7.4.2 Remove the filter punch from the chamber and allow acid vapor to volatilize from it for at least 30 minutes before analyzing the punch according to Section 7.3.

7.4.3 While the acid vapors are volatilizing from the first punch, analyze a second punch from the filter as a regular sample.

7.4.4 Report CC ($\mu g/cm^2$) as the difference in TC between the treated and untreated punches; report OC ($\mu g/cm^2$) as OC from the analysis of the untreated punch minus CC; and report EC ($\mu g/cm^2$) as EC from the analysis of the untreated punch. If the amount of CC on the filter is large, consider the experimental results with pure calcium carbonate in the notes below.

NOTE: While treatment with HCl vapors provides a good estimate of CC, the HCl vapors cause a redistribution of carbon among the seven peaks, with some peaks becoming smaller (as expected) and some peaks becoming larger. The values for OC and EC can be dramatically different.

NOTE: Small amounts of pure calcium carbonate (100-200 µg $CaCO_3$, which contains 15 to 30 µg of CC) placed on a pre-cleaned quartz filter punch and analyzed by the IMPROVE_A method evolves primarily (74% to 94% of CC) as OC4, while larger amounts (~1000 µg) of pure calcium carbonate evolves as OC4 (~55%), EC1 (~30%), and EC2 (~15%). The higher loading evolves predominantly in a single large peak (initiated by the OC4 temperature ramp) that tails across OC4 and EC1 followed by a sharp peak initiated by the temperature ramp for EC2.

NOTE: While separate integration of a sharp CC peak appearing as a shoulder on Pk4C in the CSN/TOT timed analysis can be used to estimate CC, the portion of the CC peak appearing as part of OC4 for the IMPROVE_A event driven analysis is much broader, is poorly defined, and cannot be easily integrated.

7.5 Shutdown

7.5.1 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. 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, but the gases will continue to flow. Allowing the hydrogen to flow through the methanator will recharge the catalyst, and leaving the FID lit will reduce the amount of time required for the FID to equilibrate when the next working shift starts.

7.5.2 If not intending to use the instrument for an extended period (a week or more) choose EXIT from the file menu. This will turn off all power to the ovens,

causing them to cool down. Set gas flow rates as follows (or as recommended by the Sunset Laboratory instrument support technician):

H2 set to 4 - 7 cc/min.

Air set to off.

Cal set to off.

He3 set to trickle flow at 6 - 8 cc/min

He2 set to trickle flow at 0 - 4 cc/min

He1 set to trickle flow at 6 - 8 cc/min

He/O2 set to trickle flow at 4 - 6 cc/min

7.5.3 When the program is being shut down for more than a week all gases should be turned off except for He1 and He3 (about 5-10 cc/min each).

8.0 Calculations

8.1 Blank Correction

Unless specifically told (and funded) to do so, speciated carbon measurements will not be blank-corrected by laboratory personnel.

8.2 Concentrations of Carbon Fractions on the Filter (in µg C/cm^2)

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

8.2.2 Results are calculated using a second software application (Calc2PDvxxx.exe) provided by Sunset Laboratory. The data for each sample can be printed in graphic form (referred to as a thermogram) with temperature, laser reflectance or transmittance and absorbance, and FID profiles. Text output on the thermogram includes calculated loadings of OC, EC, and TC, as well as Pk1 C (or OC1), Pk2 C (or OC2), Pk3 C (or OC3), Pk4 C (or OC4), EC1, EC2, EC3, and Pyrol C (or PC) on the filter (each in µg C/cm^2). The uncertainty associated with the OC, EC, and TC measurements are also given on the thermogram. 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.

8.2.3 The calculation software application (Calc2PDvxxx.ex) also creates a tab-delimited output file with additional data columns. In the output file, several header rows are followed by one row of data for each analysis. New rows are

added to the bottom of the output file each time the calculation software is run, so the most recent calculations are always at the bottom of the file.

8.2.4 The calculation software application (Calc2PDvxxx.ex) has several options that can be invoked by checking appropriate boxes with a mouse click. In this fashion, the OC/EC split can be determined using either reflectance or transmittance (run the software once each way to get results for both), and the peaks data can be calculated using either the IMPROVE approach (the seven peaks are determined separately without regard to the OC/EC split) or the Chemical Speciation Network (CSN) approach (the four OC peaks are calculated as their contributions to OC).

8.3 Masses of Carbon Fractions on the Filter (in µg C)

NOTE: Calculations beyond filter concentration are not typically done by the OC/EC Laboratory, which reports filter concentrations of each type of carbon (in µg/cm^2) to RTI's Speciation Program Information Management System (SPIMS). Filter loading and concentration data for all species are calculated by SPIMS software routines, which compute mass per filter for each analyte (reported by RTI laboratories) by the volume of air sampled (reported by field personnel).

The mass (in µgC) of OC, EC, TC, CC, OC1, OC2, OC3, OC4, EC1, EC2, EC3, and PC on the filter are calculated by multiplying the concentration (c) of each type of carbon (µg C/cm^2) by the deposit area (A) of the filter in cm^2.

$$m = cA$$

NOTE: The filter deposit area is taken to be 3.38 cm^2 for a Tissuquartz (Pall) filter used for sampling in a filter cassette with a 22-mm inside diameter.

8.4 Concentrations of Carbon Fractions in Air

Mass (m, in µg 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.

$$c_{air} = \frac{m}{V_{air}}$$

8.5 Measurement Uncertainty

8.5.1 Uncertainties Estimated by Sunset Lab Software: Uncertainties for laboratory measurements of OC, EC, and TC are estimated by the data analysis software according to the following equations, each of which contains both a constant and a proportional component of uncertainty.

OC uncertainty = ±[0.20 µgC/cm^2 + 0.05*(meas. Conc. Of OC in µgC/cm^2)]

EC uncertainty = ±[0.20 μgC/cm^2 + 0.05*(meas. Conc. Of EC in μgC/cm^2)]
TC uncertainty = ±[0.30 μgC/cm^2 + 0.05*(meas. Conc. Of TC in μgC/cm^2)]

Unfortunately, the constants in the current software assume a punch area of 1.5 cm^2. The following table gives experimentally determined constant and proportional components of uncertainty for each carbon fraction reported were derived from replicate analyses of 44 filters on a Sunset Laboratory Dual-Mode analyzer and a DRI Model 2001 analyzer taking into account their much smaller punch sizes.

Fraction	"Best Fit" Uncertainty
OCR	±(0.60 + 0.05*OCR)
OCT	±(0.60 + 0.05*OCT)
ECR	±(1.00 + 0.10*ECR)
ECT	±(1.50 + 0.10*ECT)
TC	±(0.90 + 0.05*TC)
OC1	±(0.90 + 0.05*OC1)
OC2	±(0.60 + 0.05*OC2)
OC3	±(0.90 + 0.05*OC3)
OC4	±(0.60 + 0.40*OC4)
EC1	±(2.50 + 0.05*EC1)
EC2	±(0.20 + 0.05*EC2)
EC3	±(0.05 + 0.75*EC3)
PCR	±(0.90 + 0.30*PCT)
PCT	±(0.90 + 0.30*PCT)

The constant components of uncertainty in the table above were derived empirically in a way that approximates the expanded concept of uncertainty used in situations where health or safety is a concern. Since diesel particulate, which is almost certainly a human carcinogen, is a major component of EC, the expanded concept of uncertainty is used for carbon fractions measured by OC/EC analysis. If health and safety are not concerns, then smaller constant components of uncertainty could be used, but the proportional components of uncertainty should remain unchanged.

9.0 Quality Assurance and Quality Control

A full temperature calibration and a full FID calibration are performed every six months, or as needed after significant analyzer repairs or maintenance, whichever comes first.

Each analysis day begins with:

1. An Oven Clean cycle (with a clean filter punch in the boat)

2. An Instrument Blank (with the same clean filter punch in the boat)
3. An AutoCal (internal standard injected in pure He, He/O_2, and at the end of the run)
4. A 15-µL sucrose standard (spiked onto the same clean filter punch in the boat)

A system blank may be run at any time to confirm that the analysis system is clean.

9.1 Laboratory Blanks

9.1.1 Run an instrument blank (using a punch from a pre-cleaned quartz fiber filter in the quartz boat) at the beginning of each day and after approximately every 30 samples run on the same instrument on the same day. An instrument blank must meet both of the following criteria:

- TC for the instrument blank must be $\leq$0.6 µgC/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 most recent (current) full FID calibration.

If the instrument blank fails to meet either 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.

9.1.2 Run a system blank (with no filter punch on the quartz boat) as needed to assess background carbon contamination levels in the analyzer. A system blank must meet <u>all</u> of the following criteria:

- TC for the system blank must be $\leq$0.2 µgC/cm^2.
- The FID response to the internal standard injected at the end of the system blank analysis must be within 90% to 110% of the average FID response to the internal standard for the most recent (or current) full FID calibration.

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

9.2 Calibrations

Run a full calibration after significant instrument maintenance or repairs or at least at least every six months, whichever comes first. Run a 15-µL sucrose standard at the beginning of each day. Determine the minimum detection limit (MDL) for total carbon when the analyzer oven or methanator is changed or annually, whichever comes first.

9.2.1 Run a complete set of calibration standards (i.e., sucrose and KHP standard solutions and CH_4/He and CO_2/He standard gases) at least once every six months. Calibration results for each standard must meet all of the following criteria:

- Each calibration curve has an $R^2 \geq 0.998$ (linear least-squares fit forced through the origin) in a plot of mass of carbon injected (on the y-axis) vs. the ratio of sample total area counts to internal standard area counts (on the x-axis);
- Each analysis shows a percent recovery of 95% to 105% of the average percent recovery across all calibration analyses with that standard; and
- Each analysis gives an FID response to the internal standard within 95% to105% of the average FID response to the internal standard across all calibration analyses with that standard.

9.2.2 Run an AutoCal after an acceptable initial instrument blank each day. The peak area of each of the three injections (He only, He/O_2, and Internal Cal) must be within 95% to 105% of the average of the three peak areas.

9.2.3 Run a 15-µL sucrose standard after an acceptable AutoCal run each day. The results of the daily calibration check are acceptable if all of the following criteria are met:

- The percent recovery is 90% to 110%.
- The FID response to the internal standard is within 90% to 110% of the average of the FID response to the internal standard for the most recent (i.e., current) full calibration.

9.2.4 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.

NOTE: A 15.0-µL spike of a 0.10 µg C/µL standard solution onto a nominal 0.56-cm^2 filter punch is a typical example.

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 for TC is $\geq$0.6 µg C/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 for TC must be obtained before samples can be analyzed.

9.3 Duplicates and Replicates

9.3.1 Definitions

Duplicate - a second punch from the same filter run on the same analyzer-- most useful for determining uniformity of the filter deposit.

Replicate - a second, third, etc. punch from the same filter run on a different analyzer− most useful for determining between-analyzer differences.

Duplicates and replicates also provide analysis data for determination of within- and between-analyzer variability.

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

9.3.2 Run a replicate or a duplicate punch about every tenth filter sample (at least 10% of samples). Agreement between organic, elemental, and/or total carbon measurements depends upon filter loading and the uniformity of the deposit. Acceptance criteria for duplicate measurements at higher filter loadings ($\geq$10 µg/cm^2) are based on the relative percent difference (RPD) of the duplicate measurements; and the acceptance criteria for duplicate measurements at low filter loadings (<10 µg/cm^2) are based on constant error, which dominates the uncertainty of the total carbon measurement at low filter loadings. Acceptance criteria for OC, EC, and TC in the various concentration ranges are given in the following table.

Carbon Fraction & Loading Range	Acceptance Criterion (Difference)
OC or TC ≥ 10 μg/cm^2	Less than 10% RPD
OC or TC < 10 μg/cm^2	Within 1.0 μg/cm^2
EC ≥ 10 μg/cm^2	Less than 20% RPD
EC < 10 μg/cm^2	Within 2.0 μg/cm^2

If any comparison of OC, EC, or TC fails the appropriate criterion, flag the analysis results reported for that filter as failing the acceptance criteria.

9.4 Carbonate Carbon

Estimate the loading of carbonate carbon (CC) according to Section 7.4 as required by the client.

9.5 FID Response to Internal Standard

If the FID response to the internal standard for any filter sample analysis run on a given day on a given analyzer is outside the range of 95-105% of the average response for all filter 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. If another punch is not available, flag the results as having failed the acceptance criterion for the internal standard.

NOTE: See Sections 9.1 and 9.2 for acceptance criteria regarding FID response to the internal standard for instrument blanks, AutoCal checks, and sucrose mid-level cal checks, which are run at the beginning of each day.

9.6 Start Integration Times for Carbon Peaks

The IMPROVE_A method is event-driven. The analyzer control software initiates the next temperature ramp or the gas change (He to 2% O_2/He) when the FID response indicates that carbon evolution under the current conditions is complete or when the maximum time (580 sec) allowed for a peak is reached. The integration of peak areas by the calculation software takes into account the transit time of the analyzer.

9.7 Transit Time

During analysis, a reflectance photometer and a transmittance photometer monitor the reflectance and transmittance of the filter in real time while the 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 is used by the calculation software to align FID response properly with laser reflectance and transmittance measurements for calculation of OC

and EC fractions (by integration of FID response) based on the OC/EC split time (which is determined solely from the laser reflectance or transmittance).

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.

9.8 Laser Reflectance and Transmittance

Photodetector readings are output to raw data files under the following headings:

Heading	Definition
PD2	Total reflectance when laser is on minus PD2Lo
PD2Lo	Reflectance when laser is off
laser	Total transmittance when laser is on minus laserlow
laserlow	Transmittance when laser is off

Measurement of the reflectance and transmittance when the laser is off as well as when it is on allows correction of the laser-on photometer readings for the enhancement of the signal due solely to the glow of the oven, which generally increases with increasing temperature.

9.9 Analyst Training and Validation

Analyst training and validation consists of the following steps:

9.9.1 The trainee begins by studying and becoming familiar with this SOP.

9.9.2 The trainee spends time observing and listening to a trained analyst as he/she demonstrates and describes the procedures required to perform OC/EC analysis.

9.9.3 The trainee learns to perform the procedures under the immediate attention of a trained analyst.

9.9.4 The trainee spends several days analyzing samples with a trained analyst monitoring the trainee's work, answering any questions the trainee may have, and correcting any mistakes the trainee might make.

9.9.5 To test the trainee's competence, the trainee, left completely on his/her own, analyzes a minimum of 20 filter samples analyzed earlier by the trained analyst on the same analyzer(s).

9.9.6 The analysis results for the 20+ filter samples run by both the trained analyst and the trainee are compared using the same criteria used for duplicate analyses (Section 9.3).

9.9.7 If no more than about 5% of the trainee's analyses fail the duplicate criteria test, the analyst is considered validated to perform the analysis without immediate supervision; otherwise, the trainee must repeat the test after carefully reviewing the procedures he/she used to determine what (if anything other than non-uniform samples) could have caused the high percentage of failures.

NOTE: About 3% to 5% of filters fail the duplicate criteria because of non-uniform deposit. An initial failure by a trainee could be caused by an unusually high percentage of non-uniform filters in the group of test filters, but the test must be repeated and passed successfully to make sure the analyst's technique is not the problem.

NOTE: Analysts who smoke must not be around exposed filter samples or blanks until their clothes and lungs are clear of residual smoke fumes (typically, 15-20 min after they finish a smoking break).

9.10 Instrument Validation

Instruments are validated using the same type of test as that used for analysts (Section 9.9).

9.10.1 The same experienced analyst operates both the new analyzer and a previously validated analyzer.

9.10.2 Instrument blanks and calibration standards are run on the new instrument and the previously validated instrument until all criteria for those QC samples are met on both analyzers.

9.10.3 Duplicate punches of at least 10 filter samples are run on the new analyzer at the same time the initial punches from the same filters are run on a validated analyzer.

9.10.4 The new analyzer is considered validated if measurement results from no more than 1 or 5%, whichever is more, of the filters used in the test fail the appropriate duplicate criterion (Section 9.3).

9.10.5 If the new analyzer fails the test, it is inspected to identify and correct any problems with the analytical system before the test is repeated.

9.10.6 The new analyzer must pass the validation test before it can be used to perform analyses that will be reported to clients.

NOTE: About 3% to 5% of filters fail the duplicate criteria because of non-uniform

deposit. An initial failure by an analyzer could be caused by an unusually high percentage of non-uniform filters in the test group, but the test is repeated to make sure the analyzer is not the problem.

10.0 References

DRI Standard Operating Procedure: DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples - Method IMPROVE_A. DRI SOP #2-216.1; Revised November 2005. Desert Research Institute, Division of Atmospheric Sciences, 2215 Raggio Parkway, Reno, NV 89506. Available at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/2-216r1_IMPROVEA_20051115.pdf (accessed 6 May 2008).

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