Standard Operating Procedure for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a DRI Model 2001 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 defining calibrated temperature ranges for carbon peaks are given in the table below.

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. 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 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 desorption 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 with either temperature-indicating liquids according to the procedure in Section 6.1 of this SOP or with a second thermocouple to measure actual sample temperature during analysis as described in a separate 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 (PC)

Laser reflectance (R) or laser transmittance (T) is used to optically correct for pyrolytically-produced elemental carbon (or char or PyrolC or PC) 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 absolute uncertainty of the method.

4.0 Apparatus

4.1 Dual Mode Thermal/Optical-Transmittance/Reflectance Carbon Aerosol Analyzer (DRI Model 2001, Atmoslytic, Inc.)

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

4.1.2 Color printer (for printing thermograms and other reports)

4.1.3 DRI Model 2001 instrument operation software (DriCarb.exe)

4.1.4 DRI Model 2001 Access database software application (CarbonNet.mdb)

4.2 Precision Punch (for removal of filter sample portion, nominal dimensions 5/16-in diameter circular punch)

NOTE: Each punch is inspected regularly for any unevenness around the sharp edges, and punches with one or more significant notches in the sharp edges are replaced 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, 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 at least 4 hours 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 ≤ -15°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 Custom Grooved Metal Plate, used to slice circular quartz filter punches into two circular punches each with one-half the thickness of the original filter punch. Used for Tempilaq° temperature calibration.

4.10 Microscope Slides, used to hold a circular filter punch in place against the custom grooved metal plate during the filter-slicing process.

4.11 Razor Blades, used to slice filters using the custom grooved metal plate and a microscope slide

4.12 Quartz Discs, 8mmOD x .5mm thick, polished

4.13 Glass Discs, 0.25inOD x 0.16mm to 0.19mm thick

5.0 Reagents

5.1 Helium, ultra-high purity (UHP)

NOTE: 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.

5.12 Tempilaq° Temperature Indicating Liquids, (manufactured by Tempil°, So. Plainfield, NJ 07080): 121°C, 184°C, 253°C, 510°C, 704°C, and 816°C.

6.0 Standards Preparation and Analysis

This section covers both temperature calibration of the sample oven thermocouple and calibration of the flame ionization detector (FID) used to measure evolved carbon.

Temperature calibration of the sample oven thermocouple may be accomplished in either of two ways: (1) by the use of a NIST-traceable calibrated thermocouple and data logger (described in "Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer") or (2) by the use of temperature-indicating liquids (described below). The external thermocouple approach is the preferred method because it is non-destructive to all components of the analysis system; whereas calibration with temperature-indicating liquids destroys all quartz surfaces and catalysts with which it comes into contact. The external thermocouple approach allows temperature calibration at the actual IMPROVE_A target temperatures using the same IMPROVE_A parameter command file, the same quartz components (i.e., sample oven, light pipes, and boat), and the same plumbing configuration that is used for analysis of samples. The two temperature calibration methods have been shown to give the same temperature calibration curve within the uncertainty (1%) claimed by the manufacturer of the temperature-indicating liquids.

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.

6.1 Temperature Calibration of Sample Oven Thermocouple

Two options are presented for temperature calibration of the sample oven thermocouple:

1. Calibration with six temperature-indicating liquids, which destroy all quartz components of the analysis system using the procedure below; or
2. Calibration with a second thermocouple (calibrated with its data logger to NIST traceable standards) positioned to just touch the center of the filter punch during an analysis run using a separate SOP, "Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer."

The procedure below requires the use of six temperature-indicating liquids that change phase at 121°C, 184°C, 253°C, 510°C, 704°C, and 816°C to calibrate the sample thermocouple in a quartz oven vented directly to a hood.

NOTE: Tempilaq° liquids destroy all quartz surfaces with which they come into contact during temperature calibration runs. It is important to have on hand a new or spare quartz oven and replacements for the quartz light pipes, and quartz boat before beginning the temperature calibration procedure. Only the non-quartz components (sample thermocouple, metal boat holder, and metal thermocouple push pipe) survive the temperature calibration in usable condition.

6.1.1 Use an old oven without the catalyst for this temperature calibration.

6.1.2 Disconnect the oven from the back of the instrument (methanator, FID, etc.).

6.1.3 Vent the back end of the oven to a fume hood using heat resistant tubing.

6.1.4 Align the upper and lower quartz rods to get the highest readings on the reflectance and transmittance photometers.

6.1.5 Prepare disc/filter Tempilaq° sandwiches for the temperature calibration.

NOTE: Either quartz or glass discs may be used for temperature calibrations at 121°C, 184°C, 253°C and 510°C, but only quartz discs may be used for 704°C and 816°C runs.

NOTE: Use 2 to 3 times more Tempilaq° solution when using the quartz disc.

NOTE: If a Tempilaq° solution gets too thick, dilute with Tempilaq° solvent or use a new bottle of Tempilaq°.

6.1.6 Analyze each disc/Tempilaq°/filter sandwich using a heating profile that increases the sample temperature at a rate of about 2°C/minute during the phase transition for that Tempilaq° sandwich.

6.1.7 Prepare plots of temperature (primary y-axis) versus time (x-axis) and the following on a secondary y-axis:

- Reflectance and transmittance counts
- Log or ln of reflectance and transmittance counts
- First derivative of reflectance and transmittance
- Second derivative of reflectance and transmittance

NOTE: Plots with the reciprocal of the reflectance and transmittance and with the reciprocal of the squared values may also be helpful.

6.1.8 For each plot, identify the times at which the reflectance and transmittance functions indicate the beginning of a phase change, and determine from the graph the temperature recorded for the sample oven thermocouple at the time of the beginning of the phase change.

6.1.9 Prepare a table containing the Tempilaq° phase-change temperature and the

sample oven thermocouple readings at the time of the phase change for each of the Tempilaq° runs.

6.1.10 Prepare a summary chart of thermocouple temperature reading versus Tempilaq° phase-change temperature for all acceptable runs.

6.1.11 Determine the slope and the intercept of the thermocouple temperature vs. Tempilaq° temperature plot; and use this slope and intercept to calculate sample thermocouple temperature readings that would indicate sample temperatures at the six different IMPROVE_A target temperatures. The table below gives an example.

Calibration Curve	
Slope	Intercept
0.9914	-17.0428
IMPROVE_A Temperature	Target DRI 2001 Thermocouple Reading
140°C	122°C
280°C	261°C
480°C	459°C
580°C	558°C
740°C	717°C
840°C	816°C

6.1.12 Make any necessary changes in the heating profile parameter table in CarbonNet.mdb and update the date portion of the parameter table name to reflect the effective date of the new temperature profile.

6.2 Preparation of Aqueous FID Standards

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.

6.2.1 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.

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

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.

6.2.2 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.

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

6.2.3 Store sucrose and KHP standard solutions in a refrigerator at ≤4°C.

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

6.3 FID Calibration with External Standards

NOTE: The analyzer sample thermocouple must be calibrated ("Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer" or "Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a DRI Model 2001 Carbon Aerosol Analyzer Using Temperature-Indicating Liquids") before the flame ionization detector (FID) is calibrated.

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.

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

6.3.1.1 Start the DriCarb.exe control software and select Analysis at the initial menu.

6.3.1.2 With no quartz filter punch in the boat, run an Oven Clean.

6.3.1.3 With no quartz filter punch in the boat, run a System Blank cycle to verify that the analysis system is clean (i.e., TC ≤ 0.2 µgC/cm^2)

6.3.1.4 In the Setup window, select:

- Type: Calib
- Cal Gas: Methane or CO_2 (as appropriate)
- Carrier Gas: HeOx or Helium
- Command table: cmdCalib-HeO2 or cmdCalib-He

6.3.1.5 Using the gas name (CO2 or CH4) 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: Do not open the oven between runs.

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

Step 2: Start the analysis and follow the recorded verbal instructions.

Step 3: When prompted, quickly purge and then load the syringe with the appropriate volume of calibration gas.

Step 4: When prompted, inject the calibration gas into the system through the septum.

At the end of the analysis, the software writes essential information to the CalTable and prints a report.

6.3.1.6 Repeat Section 6.3.1.4 until all six volumes of both gas standards have been analyzed and 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).

6.3.2 Calibration with standard aqueous solutions (sucrose and KHP)

6.3.2.1 Start the DriCarb.exe control software and select Analysis at the initial menu.

6.3.2.2 In the Setup window, select:

- Type: Sample
- Command table: cmdIMP_A_yyyymmdd (where yyyymmdd is the date of the current temperature-calibrated command file)

6.3.2.3 With a clean section of quartz filter on the quartz filter boat, run a "Filter Clean" cycle to clean the filter section; then run a "Filter Blank" cycle to verify that the filter section is clean.

6.3.2.3 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: With the quartz boat in the Load position, use a precision syringe to deliver a precise volume of aqueous solution to the center of the clean filter punch without removing the punch from the boat.

Step 2: Enter the standard name and volume in the Sample ID field.

Step 3: Enter a 1 in the Punch area and Deposit area fields.

Step 4: Click OK to start the analysis.

Step 5: In the time to delay analysis field, enter a number of secs corresponding to 1 min/µL of standard solution; i.e.,

300 sec for a 5-µL injection,

600 sec for a 10-µL injection,

900 sec for a 15-µL injection,

1200 sec for a 20-µL injection,

6.3.2.4 Repeat Section 6.3.2.3 until all five volumes of both aqueous standards have been analyzed and 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).

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

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

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

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

6.4 Internal FID Standard

6.4.1 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.

6.4.2 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 during the run should give an FID area count that is within 95% to 105% of the average of the area counts for the three injections.

6.4.2.1 Select cmdAutoCalibCheck as the command table, type in "AutoCal" as the Sample ID, then click Run.

6.4.2.2 When the run has been completed, open CarbonNet.mdb, and run the "qry_autocal" query, which calculates the percent of average for each of the three internal standard injections to determine if the AutoCal passed (i.e., all three percent-of-average values are within 95% to 105% of the average value) or failed (the percent-of-average value for at least one injection was outside the range of 95% to 105% of the average value).

6.4.2.3 If the AutoCal still fails the criterion three times in succession, try adjusting the He-Ox flow slightly up or down until the AutoCal gives acceptable results.

7.0 Carbon Analyzer Procedure

7.1 Startup

7.1.1 Set gas flow rates to the markings on the rotameters on the front of the analyzer.

NOTE: Use the recommended gas flows supplied by the vendor unless specifically directed by the vendor to use a different value.

7.1.2 Leak check (performed at the beginning of each day)

7.1.2.1 Make sure the sample loading port at the front of the oven is sealed.

7.1.2.2 Close the Sample Oven Outlet toggle switch on the right end of the analyzer, and immediately begin monitoring the Sample Oven

Pressure display on the front of the analyzer.

7.1.2.3 When the Sample Oven Pressure just passes 5 psi, close the Sample Oven Inlet toggle switch on the front of the analyzer.

7.1.2.4 As the Sample Oven Pressure drifts downward, measure the number of seconds required for the pressure to drop from 5.00 psi to 4.70 psi.

7.1.2.5 If the time required is 30 sec or longer, the oven passes the leak test. If the time required is less than 30 sec, the oven fails the leak test.

7.1.2.6 To return the oven to the operating configuration, open the Sample Oven Outlet toggle first, then open the Sample Oven Inlet toggle.

7.1.2.7 In the sample oven fails the leak test, use a helium leak detector to check all accessible seals and fittings for leaks. Replace leaking seals or other fittings, and repeat the leak check.

7.1.2.8 If the system still fails the leak check, contact RTI Lab Support for assistance. Do not use the analyzer until it has been repaired and passed the leak check.

7.1.3 Open the DriCarb.exe software and choose "Analysis" at the opening screen.

7.1.4 The Setup window opens:

7.1.4.1 In the Type field, select Sample.

7.1.4.2 In the Project Name field, select Improve.

7.1.4.3 In the Batch # field, enter the batch number (if required).

7.1.4.4 In the Sub-batch # field, enter the sub-batch number (if required).

7.1.4.5 In the Command table field, select:

- cmdBakeOven to clean the oven; or
- cmdAutoCalibcheck to run an automated gas calibration check; or
- cmdIMP_A_yyyymmdd (where the last eight characters are the year month and day of the last temperature calibration) to run an instrument blank, a liquid standard, or a filter sample.

7.1.4.6 In the Sample ID field, enter the name of the QC sample (Instrument Blank, AutoCalCheck, Sucrose Std 15 µL, etc.) to be run or the filter ID (using the barcode scanner) of a quartz filter sample.

7.1.4.7 In the Run # field, enter the run number (1, 2, 3...)

7.1.4.8 In the Punch area field, enter a 1 for QC samples (Instrument Blanks, calibration runs, and AutoCalibcheck) and the area of the filter

punch for quartz filter samples.

7.1.4.9 In the Deposit area field, enter a 1 for QC samples (Instrument Blanks, calibration runs, and AutoCalibcheck) and the area of the filter deposit for quartz filter samples.

7.1.4.10 In the Tech initials field, enter the initials of the analyst performing the analysis.

7.1.4.11 In the FID box, make sure FID_8 is selected.

7.1.4.12 For filter samples, select any flags that are appropriate in the Flags field and type any relevant comments in the Comment field.

NOTE: Do not change the fields in the Graph box.

7.1.4.13 Click the OK button to begin the run.

7.2 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.

7.2.1 Write the sample ID and the instrument name or designator in the lab notebook, along with any notes about the appearance of the filter.

7.2.2 Clean the precision punch and then use it to remove a circular section from the quartz fiber filter sample for analysis.

7.2.3 Using clean uncoated forceps, place the circular quartz filter section in the well of the quartz sample boat (which must be in the Load position).

7.2.4 At the computer, scan the bar code of (or type in) a sample identification name or number in the Sample ID field. Check the other fields in the Setup window to make sure they are correct.

7.2.5 Click the OK button at the bottom of the Setup window to advance to the Analysis window.

7.2.6 Record the initial LaserT and LaserR values in the lab notebook.

7.2.7 Check the Oven Pressure reading.

7.2.8 Click the Run button to begin the analysis.

7.3 Procedures 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).

7.3.1 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.

7.3.2 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.

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

7.3.4 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 OC/EC split and the values for OC and EC can also be dramatically different. Spiking the sample punch with aqueous hydrochloric acid often has an even larger effect on the distribution of carbon among the peaks.

NOTE: Small amounts of pure calcium carbonate (100-200 µg $CaCO_3$, which contain 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: A single regular analysis with integration of the area of a calcium carbonate FID peak is not currently an option for the IMPROVE_A method on the DRI Model 2001.

7.4 Shutdown

Click Exit to close the analyzer operation software, but leave the analyzer running and all gases flowing.

8.0 Calculations

8.1 Blank Correction

Unless specifically told (and funded) to do so, speciated carbon measurements will not be blank-corrected by OC/EC 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 (DriCarb.exe) automatically stores raw data, carbon peak data, and run data acquired during an analysis or calculated at the end of the run in a Microsoft Access database (CarbonNet.mdb), which includes the data tables listed below.

- RawTable: One row of raw data is recorded per second of analysis time.
- PeaksTable: One row of data is recorded for each of the seven carbon peaks for each analysis.
- RunsTable: One row of data is recorded for each analysis.
- CalTable: One row of data is recorded for each manual injection of a calibration gas.

8.2.2 OC/EC analysis results are calculated and assembled into tabular form using Microsoft Access queries. The data reported to the RTI Speciation Program Information Management System (SPIMS) includes calculated loadings of OC (by reflectance and transmittance), EC (by reflectance and transmittance), and TC, as well as OC1, OC2, OC3, OC4, EC1, EC2, EC3, and PC (by reflectance and transmittance), each in µg C/cm^2.

NOTE: Calculations beyond filter loading concentration are not typically done in the OC/EC Laboratory, which reports filter concentrations of each type of carbon (in µgC/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 analytical laboratories) and air concentration by dividing mass per filter by the volume of air sampled (reported by field personnel).

8.3 Measurement Uncertainty

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. The table is updated periodically as more data are added.

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 (see Taylor and Kuyatt reference) 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 after significant analyzer repairs or maintenance or every six months, which ever 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 filter punch pre-cleaned with a BakeOven cycle or a full IMPROVE_A analysis) at the beginning of each day. An instrument blank must meet both of the following criteria:

- TC for the instrument blank must be ≤0.6 μgC/cm^2.
- The FID response to the internal standard injected at the end of the instrument blank analysis must be within 90% to 110% of the average FID response to the internal standard for the last (or current) full FID calibration.

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

9.1.2 A system blank as needed to assess background carbon contamination levels in the analyzer and after approximately every 30 samples run on the same instrument on the same day.

A system blank, which is run without a filter punch in the boat must meet all of the following criteria:

- TC for the system blank must be ≤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 last (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

A full set of calibration standards is run after significant instrument maintenance or repairs or every six months, whichever comes first. A 15-μL sucrose standard is run after an instrument blank at the beginning of each analysis day. The minimum detection limit (MDL) for total carbon is determined 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 ≥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 a successful initial instrument blank each day. The results of the daily calibration check are acceptable if all of the following criteria are met:

- The percent recovery is 95% to 105%.
- 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 or current full calibration.

9.2.4 Run at least seven replicates of a low-level sucrose 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 sucrose standard solution onto a nominal 0.50-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 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 or third 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 non-uniform 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 "non-uniform 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 a constant component of uncertainty, 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 $\geq$ 10 µg/cm^2	Less than 10% RPD
OC or TC < 10 µg/cm^2	Within 1.0 µg/cm^2
EC $\geq$ 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

Carbonate carbon may be estimated according to Section 7.3 as required by the client.

9.5 FID Response to the Internal Standard

If the FID response to the internal standard for any sample analysis run on a given day on a given analyzer is outside the range of 95-105% of the average response for all 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 Analyst Training and Validation

Analyst training and validation consists of the following steps:

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

9.6.2 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.

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

9.6.4 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.

9.6.5 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).

9.6.6 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).

9.6.7 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).

9.7 Instrument Validation

NOTE: Instruments are validated using the same type of test as that used for analysts (Section 9.6).

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

9.7.2 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.

9.7.3 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.

9.7.4 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).

9.7.5 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.

9.7.6 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).

Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer; Revised May 2008. OC/EC Laboratory, Environmental & Industrial Sciences Division, Research Triangle Institute, Research Triangle Park, NC 27709.

Taylor, B.N.; Kuyatt, C.E. NIST Technical Note 1297: Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, Section 6. See http://physics.nist.gov/Document/tn1297.pdf (accessed April 2008).