Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon 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), and total carbon (TC) in particulate matter collected on quartz-fiber filters. This method can also be used to estimate the quantities of OC evolved from the filter during each of four non-oxidizing heat ramps (Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC) and the quantity of OC that was pyrolyzed (Pyrol C) during those heat ramps.

2.0   Summary of Method

This is a thermal/optical-transmittance (TOT) method that speciates carbon in particulate matter collected on a quartz-fiber filter into OC, EC, and CC. In the first (or non-oxidizing) heating stage, organic and carbonate carbon are thermally desorbed from the filter under a flow of helium with controlled temperature ramps. The oven is then partially cooled, and the original flow of helium is switched to an oxidizing carrier gas (He/O$_2$). In the second (or oxidizing) heating stage, the original elemental carbon component plus pyrolyzed organic carbon formed during the first heating stage are oxidized/desorbed from the filter with another series of controlled temperature ramps. 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 methanator oven before being measured with a flame ionization detector (FID).

NOTE: The FID response for organic carbon can be divided into five separate measurements. These measurements correspond to the carbon evolved during each of the four separate heating ramps in the first (or non-oxidizing) heating stage of the analysis (Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC) and to the carbon evolved during the second (or oxidizing) heating stage that is counted as organic carbon to correct for pyrolytically-produced elemental carbon (Pyrol C, see Section 3.1).

3.0   Interferences

3.1   Pyrolytically-Produced Elemental Carbon (Pyrol C)

Laser transmittance is used to optically correct for pyrolytically-produced elemental carbon (or char or Pyrol C) formed from organic compounds during the first (non-oxidizing) part of the analysis. Formation of Pyrol C decreases the transmittance of the laser beam through the system. During the second (oxidizing) part of the analysis, all EC (including Pyrol C) is burned off the filter. The 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 at the beginning of the analysis. Total FID response to the left of the split is assigned to OC, and total FID response to the right of the split (but before the internal standard peak) is assigned to EC. Pyrol C 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, Pyrol C is zero and Pk4 OC ends at the split time.

3.2 Carbonate Carbon

Carbonate carbon (from calcium carbonate) is volatilized near the end of the first (or non-oxidizing) heating cycle and is therefore initially included with organic carbon. The FID response for the distinctive carbonate peak can be integrated separately and subtracted from the total area assigned to organic carbon, which allows calculation of separate values for organic and carbonate carbon. Alternatively, a separate filter punch can be exposed to hydrogen chloride vapors (which reacts with carbonate 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. The first method is usually adequate for $PM_{2.5}$ samples and can be accomplished with a single analysis.

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

4.0 Apparatus

4.1 Thermal/Optical-Transmittance 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 220 (OCECInst220.exe) or higher

4.1.4 Sunset Laboratory calculation software version 130 (OCECCalc130.exe) or higher

4.2 Precision Punch (for removal of filter sample portion, nominal 1.5 cm^2; punch areas are calculated using inside width and depth measurements--made with a micrometer caliper--of the rectangular punch; measured areas of the punches currently used for each instrument are: Retrofit, 1.48 cm^2; Second, 1.49 cm^2; and third, 1.49 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.

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

4.4 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

Quartz fiber filters (Whatman Catalog No. 1851047, Grade QMA, or equivalent) 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 3 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 as detailed in Section 7.3. If any filter analyzed gives a measured blank value that exceeds 1 μg/cm^2 for total carbon, the filters from that batch will either be rejected or re-cleaned and tested again.

Batches of filters that pass the acceptance-testing criterion ($\leq$1 μg/cm^2 total carbon) are assigned a Batch Number, which is used to associate the history of the filters with the batch and to track the batch until the filters are assigned individual identification numbers in the Sample Handling and Archiving Laboratory. Batches of acceptance-tested filters are placed individually in petri dish 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°C until the filters are used.

4.6 Volumetric Flasks, Class A

4.7 Analytical Balance, capable of weighing to $\pm$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 weight(s) before using. Record all weights in the appropriate Lab Notebook.

4.8 Class 1 Weights

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

NOTE: CO_2 in helium is used to test methanator performance.

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

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

NOTE: During TOT analysis of sucrose, some OC (the only kind of carbon in sucrose) is volatilized and some OC is pyrolyzed during all four of the non-oxidizing heat ramps. As a result, all OC fractions (Pk1 OC, Pk2 OC, Pk3 OC, Pk4 OC, and Pyrol C) show up in the thermogram. KHP, which also contains only OC, does not form significant char (Pyrol C), and it volatilizes from the filter over a fairly narrow temperature range.

6.1 Preparation of Standards

6.1.1   Sucrose Stock Solution--Prepare a sucrose stock solution by weighing 10.000 ± 0.010 g sucrose (verify balance accuracy using NIST-traceable Class 1 10-g check weight before weighing out sucrose) into a 1000-mL volumetric flask and diluting to the mark with organic-free water.

NOTE: 10.000 g of sucrose ($C_{12}H_{22}O_{11}$, MW 342.31) in 1,000.00 mL of solution has a carbon (C, AW 12.01) concentration of 4.210 μgC/μL.

$$\left(\frac{10.000\,\text{g sucrose}}{1,000\,\text{mL soln}}\right)\left(\frac{(12)(12.01\,\text{g C})}{342.31\,\text{g sucrose}}\right)\left(\frac{1\,\text{mL}}{10^3\,\mu\text{L}}\right)\left(\frac{10^6\,\mu\text{g}}{1\,\text{g}}\right) = 4.210\,\frac{\mu\text{g C}}{\mu\text{L soln}}$$

6.1.2   Calibration Standards–Prepare at least three calibration standards that span the measurement range of the samples. Calibration standards are prepared either (1) by weighing appropriate masses of sucrose into a volumetric flasks and diluting to the mark with organic-free water, or (2) by diluting aliquots of the

sucrose stock solution (Section 6.1.1) with organic-free water in a volumetric flask.

NOTE: A typical set of calibration standards includes the sucrose stock solution (nominally 4.2 µgC/µL) and two dilutions of the sucrose stock solution (to 2.1 µgC/µL and to 0.42 µgC/µL). Normally, 10.0 µL of each standard is used in a calibration analysis, but a larger volume of the sucrose stock solution could be used to extend the measurement range.

6.1.3 KHP Verification Standard--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 0.5000 ± 0.010 g of KHP (verify balance accuracy using NIST-traceable Class 1 0.5-g check weight 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: 0.5000 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 2.352 ugC/uL.

$$\left(\frac{0.5000 \text{ g KHP}}{100.00 \text{ mL soln}}\right)\left(\frac{(8)(12.01 \text{ g C})}{204.23 \text{ g KHP}}\right)\left(\frac{1 \text{ mL}}{10^3 \text{ µL}}\right)\left(\frac{10^6 \text{ µg}}{1 \text{ g}}\right) = 2.352 \frac{\text{µgC}}{\text{µL soln}}$$

6.1.4 Store sucrose stock solution, KHP verification standard solution, and sucrose calibration standards in a refrigerator at ≤4°C.

6.1.5 Prepare new stock solution, verification standard, and calibration standards at least every 6 months.

6.2 Calibration with External Standards

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

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

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

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

6.2.3 Open the quartz door to the oven and pull the quartz filter boat containing the cleaned filter punch to the front of the analyzer oven.

6.2.4   Use a precision syringe or a calibrated Eppendorf pipettor (or equivalent) to deliver 10.0 μL (or other appropriate volume) of a standard sucrose solution (Section 6.1.2) to the clean filter punch without removing the punch from the filter boat.

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

6.2.5   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.

6.2.6   Analyze the filter punch as described in Section 7.2.

6.2.7   Repeat Sections 6.2.3 through 6.2.6 until all three standards have been analyzed and <u>all</u> of the following criteria have been met:

- The 3-point calibration has an R^2 $\geq$0.998 (linear least-squares fit forced through the origin of a plot of total FID area counts vs. mass of carbon spiked);

- Each of the three analyses shows a percent recovery of 93% to 107% of theoretical (μgC measured/μgC spiked);

- Each of the three analyses gives an FID response to the internal standard within 90% to110% of the average FID response to the internal standard for the three calibration analyses; and

- Each of the three analyses gives a response factor (counts/μgC) for the calibration standard that is within 90% to 110% of the average response factor for the three calibration analyses.

6.2.8   If necessary, change the calibration constant to a value that gives an average percent recovery of 99.95% to 100.05% when the new calibration constant is used to recalculate results from the 3-point calibration analyses.

6.3   Internal Standard

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

7.0   TOT 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.

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 scrub an area about 2 inches in diameter on the aluminum foil 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 as follows:

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 methanator oven.

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

7.2.4   Select the RTIQuartz.par Parameter file and either select the instrument and current date data file or enter the name of it into the Raw Data file text box.

NOTE: The temperature profile (RTIQuartz.par) used for all OC-EC Analyzers at RTI beginning March 15, 2001, is given below.

' RTIQuartz.par

' Heating profile used on all RTI instruments beginning 15 March 2001

'

' modified quartz to run with true target temps

' added 28 July 1999 by David Smith

' sample carbon analyzer Parameter file for Sunset Lab;

' analyzes for organic and elemental carbon .

```
' by Robert A. Cary.
'  1995 Feb 15: added calibration O2 mode.
' mode <comma> time <comma> temperature
' @ regimen must end 'Offline' mode.
' .
' purge for 10 sec with blower off.
'
Helium, 10, 1
' start ramping the temperature
Helium, 60, 310
Helium, 60, 480
Helium, 60, 615
Helium, 90, 900
' let the oven cool before starting elemental
Helium, 30, 0
' elemental
Oxygen, 10, 0
Oxygen, 35, 600
Oxygen, 45, 675
Oxygen, 45, 750
Oxygen, 45, 825
Oxygen, 120, 920
CalibrationOx, 30, 1
CalibrationOx, 50, 0
CalibrationHe, 30, 0
' All done!
' this last mode persists until we start a new sample.
' The last entry *must* be "go offline and turn blower on".
Offline, 1, 0
' end.
```

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 Partially remove the quartz filter boat from the oven with 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 it is stopped by the tip of the oven thermocouple.

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 Enter the sample ID, the initial laser 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 transmittance of the filter punch in the lab notebook before opening the oven for the next sample.

7.4 Procedures for Estimating Carbonate Carbon

NOTE: The procedures for estimating carbonate carbon are performed only for clients who specifically request it and who authorize payment for it.

Carbon from calcium carbonate is volatilized near the end of the first (non-oxidizing) heating cycle of the analysis. Instrument FID response for carbonate carbon is included in the response for the organic fraction and must be accounted for either electronically (through integration of the FID response for the carbonate peak) or by performing a second analysis using a filter punch from which carbonate has been chemically removed (by exposure to gaseous hydrogen chloride).

7.4.1 Integration of Calcium Carbonate Peak.

Enter numeric values for the start and end points (which show up as vertical dashed lines on the on-screen thermogram) for manual integration of the calcium carbonate peak. Click the Integrate button to display the recalculated thermogram.

NOTE: Integration of the calcium carbonate peak in this fashion assigns the total peak area between and above the start and end points under the FID trace to carbonate carbon and subtracts this area from the organic carbon total area.

This approach can be used to account for than 60% of the carbonate in a PM10 sample. Fortunately, PM2.5 contains almost no carbonate carbon.

7.4.2 Chemical Removal of Carbonate from Filter Punch.

Expose a second 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. 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. Disappearance of the calcium carbonate peak confirms the presence of carbonate carbon. Report EC and TC from the first (untreated) analysis; report carbonate carbon (CC) as the difference between the two TC measurements (TC untreated – TC treated); and report OC as (OC untreated – CC).

NOTE: CC actually evolves over several of the OC peaks, and the treatment with HCl vapors can dramatically change the distribution of carbon among the OC Peaks and EC. Some OC peaks become smaller (as expected) and some become larger as a result of the treatment. The HCl apparently reacts with carbon-containing species in the sample and changes the distribution of carbon among the OC Peaks and even EC.

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 and the pressure will be near zero, since there is very little flow.

7.5.2 If not intending to use the instrument for several days 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 few days all gases should be turned off except for He1 and He3 (about 5-10 cc/min each).

8.0   Calculations

8.1   Blank Correction

In accordance with current EPA guidance, 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 (OCECCalcxxx.exe) provided by Sunset Laboratory. The data for each sample can be printed in graphic form (referred to as a thermogram) with temperature, laser transmittance and absorbance, and FID profiles. Text output on the thermogram includes calculated loadings of OC, EC, and TC, as well as Pk1 OC, Pk2 OC, Pk3 OC, Pk4 OC, and Pyrol C 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. Uncertainty is not estimated by the software for CC, Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC because the limits of integration for these are manually set by the analyst. Uncertainty is also not included with the Pyrol C measurement which has integration boundaries set by the software (time of addition of oxygen to the calculated OC-EC split time). Other text outputs include EC/TC ratio, date, time, calibration constant, punch area, FID1 and FID2 status, calibration area, split time, manual split time, initial absorbance, absorption coefficient of original elemental carbon, instrument name, analyst, laser correction factor, and transit time.

8.2.3   The calculation software application (OCECCalcxxx.exe) 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.

8.3   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). Concentration data for all species are calculated by SPIMS software routines, which divide 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, Pk1 OC, Pk2 OC, Pk3 OC, Pk4 OC, and Pyrol C on the filter are calculated by multiplying the concentration (c) of each type of carbon (µg C/cm^2) by the deposit area (A) of the filter in cm^2.

$$m = cA$$

NOTE: The filter deposit area is 11.76 cm^2 for a 47-mm quartz fiber filter used for sampling in a filter cassette with a 38.7-mm inside diameter, which defines the deposit area.

$$A = \pi r^2 = (3.14159)\left(\frac{38.7\text{mm}\left(\frac{1\text{cm}}{10\text{mm}}\right)}{2}\right)^2 = 11.76\text{cm}^2$$

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

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

$$\text{OC unc} = \pm\,[0.20\,\mu\text{gC/cm}^2 + 0.05*(\text{meas conc of EC in }\mu\text{gC/cm}^2)]$$

$$\text{EC unc} = \pm\,[0.20\,\mu\text{gC/cm}^2 + 0.05*(\text{meas conc of EC in }\mu\text{gC/cm}^2)]$$

$$\text{TC unc} = \pm\,[0.30\,\mu\text{gC/cm}^2 + 0.05*(\text{meas conc of TC in }\mu\text{gC/cm}^2)]$$

Uncertainties of measurements for the five OC Peaks have been empirically estimated based on analysis of 127 quartz filter samples from random sites, collected during different seasons, across a two-year period on three different analyzers.

$$\text{Pk1C unc} = \pm\,[0.20\,\mu\text{gC/cm}^2 + 0.05*(\text{meas conc of Pk1C in }\mu\text{gC/cm}^2)]$$

$$\text{Pk2C unc} = \pm\,[0.20\,\mu\text{gC/cm}^2 + 0.05*(\text{meas conc of Pk2C in }\mu\text{gC/cm}^2)]$$

$$\text{Pk3C unc} = \pm\,[0.30\,\mu\text{gC/cm}^2 + 0.05*(\text{meas conc of Pk3C in }\mu\text{gC/cm}^2)]$$

$$\text{Pk4C unc} = \pm\,[0.30\,\mu\text{gC/cm}^2 + 0.10*(\text{meas conc of Pk4C in }\mu\text{gC/cm}^2)]$$

$$\text{PyrolC unc} = \pm\,[0.20\,\mu\text{gC/cm}^2 + 1.40*(\text{meas conc of PyrolC in }\mu\text{gC/cm}^2)]$$

9.0   Quality Assurance and Quality Control

9.1   Instrument Blanks

Run an instrument blank, using a punch from a pre-cleaned quartz fiber filter, 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 <u>all</u> of the following criteria:

- TC for the blank must be ≤ 0.3 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 last (or current) 3-point calibration.

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

9.2   Calibrations

Run calibration check samples at the beginning of each day and a full three-point calibration at least once a week. Determine the minimum detection limit (MDL) for total carbon when the analyzer oven or methanator is changed or annually, which ever comes first.

9.2.1   Run a complete set of calibration standards (i.e., three different mass loadings) at least once a week. If the least-squares correlation coefficient (r^2) of area counts vs. total mass of carbon, force-fit through the origin (0,0), is <u>not</u> ≥ 0.998, determine the cause of the non-linearity, and initiate actions that will identify and solve any problem that may have arisen. Then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed. In addition, analysis of <u>each</u> of the three standards must meet <u>all</u> of the following criteria:

- The measured mass of total carbon for the calibration standard is within 93% to 107% of the true value.

- The FID response to the internal standard injected at the end of the calibration standard analysis is within 90% to 110% of the average FID response to the internal standard for all three calibration standards analyses.

- The response factor (counts/µgC) for the calibration standard is within 90% to 110% of the average response factor for all three calibration standards analyses.

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

NOTE: The calibration factor (mass of carbon in the fixed-volume internal standard gas loop) will be updated (1) when the calibration gas standard cylinder is replaced, (2) when measured mass of total carbon for standards differs from the true value by more than 7% on repeat analysis of standards, (3) when the day-to-day measured mass of sucrose standards is consistently higher or consistently lower than the true value by more than 7%, (4) or more frequently at the discretion of the laboratory manager.

9.2.2   Run a sucrose standard calibration check sample after the initial instrument blank each day. The calibration check sample analysis results are valid if <u>all</u> of the following criteria are met:

- The measured mass of total carbon for the calibration check sample within 93% to 107% of the true value.

- The FID response to the internal standard injected at the end of the calibration check sample analysis is within 90% to 110% of the average FID response to the internal standard for the last (or current) 3-point calibration.

- The response factor (counts/µgC) for the calibration check sample is within 90% to 110% of the average response factor for the last (or current) 3-point calibration.

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

9.2.3   Analysis results for a KHP verification standard must meet the same three criteria as results for a daily calibration (Section 9.2.2)

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 1.05 µg C/µL standard solution onto a nominal 1.50-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 is ≥0.5 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

Run a duplicate punch about every tenth filter sample (at least 10% of samples). Agreement between duplicate total carbon measurements depends upon filter loading and the uniformity of the deposit. Acceptance criteria for duplicate measurements at higher filter loadings ($\geq$5 μg/cm^2) are based on the relative percent difference (RPD) of the duplicate measurements; and the acceptance criterion for duplicate measurements at low filter loadings (<5 μg/cm^2) is based on absolute error ($\pm$0.75 μg/cm^2), which dominates the uncertainty of the total carbon measurement at low filter loadings. Acceptance criteria for the various concentration ranges are given in the following table.

Total Carbon Concentration Range	Acceptance Criterion
Values greater than 10 μg/cm^2	Less than 10% RPD
5 - 10 μg/cm^2	Less than 15% RPD
Values less than 5 μg/cm^2	Within 0.75 μg/cm^2

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

9.4 Carbonate Carbon

If carbonate carbon is to be measured and the manual integration method (Section 7.4.1) will be used to estimate its concentration, confirm that the suspected peak appears at the correct location for $CaCO_3$ in the thermogram. A qualitative $CaCO_3$ sample must be run (or must have been run since the oven or heating coils in the analyzer were replaced) to determine the exact location at which the calcium carbonate peak shows up in the thermogram whenever carbonate is to be estimated by manual integration. Otherwise, measure carbonate carbon according to Section 7.4.2.

9.5 FID Response to Internal Standard

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

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

NOTE: See Sections 9.1 and 9.2 for acceptance criteria regarding FID response to the internal standard for instrument blanks and calibration check samples, both of which are run at the beginning of each day.

9.6   Start Integration Times for OC Fractions

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

NOTE: Times at which FID minima occur during analysis of particulate samples can vary between samples by a few seconds because of differences in filter loading and in the composition of material on the filter. Average times at which FID minima occur are very similar for calibration standards and for particulate samples. Start integration times for Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC are determined from analysis of sucrose and KHP standards in order to provide comparability between analyzers, which heat at slightly different rates.

NOTE: For small studies, average FID minima times for actual samples can be used for start integration times if all samples to be compared are analyzed on the same analyzer.

9.7   Transit Time

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

Control charts are used to show instrument performance over time and to compare performance of two or more analyzers.

9.8.1   Plot measured TC for all instrument blanks on all analyzers by date.

9.8.2   Plot linearity (R^2) of 3-point calibrations on all analyzers by date.

9.8.3 Plot percent recovery for low, mid-level, and high calibration standards as well as average percent recovery for each 3-point calibration by date. Show ±10% bars for average percent recovery. Prepare separate plots for each analyzer.

9.8.4 Plot FID response factors for total carbon for each 3-point calibration by date. Plot response factors measured for each standard (to show range) and the average response factor for all three standards (to show mean). Prepare separate plots for each analyzer.

9.8.5 Plot percent recovery for all daily calibration checks on all analyzers by date.

9.8.6 Plot relative percent difference of duplicate measurements versus average measured TC for all duplicates. Prepare separate plots for each analyzer.

9.9 Laser Transmittance

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

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

9.9.2 An initial laser reading ≥3,000 for a clean filter punch and a series of final laser readings that drift slightly upward during the last seconds of an analysis (as the oven cools) generally indicate that the quartz optical flats (boat and oven windows) are adequately free of frosting for an accurate assignment of the OC/EC split. If the initial laser reading is <3,000 or if the laser reading drifts slightly downward during the last seconds of an analysis (as the oven cools), the quartz optical flats (boat and oven windows) should be inspected for frosting and the boat or oven or both replaced, if necessary.

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

9.10 Analyst Training and Validation

Analyst training and validation consists of the following steps:

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

• 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.

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

- 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.

- 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).

- 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).

- 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).

9.11 Instrument Validation

Instruments are validated using the same type of test as that used for analysts (Section 9.10).

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

- 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.

- 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.

- 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).

- 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.

- 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

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